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Some remarks on Boltzmann's thermodynamic systems and adiabatic invariants

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Abstract. – There exist two kinds of proof of adiabatic invariance, one of which is derived on the basis of mechanics, while the other is derived from thermodynamic theory and by using Boltzmann's formulas. The identity of the two methods, which is obviously necessary, is not always perfectly clear, and this paper intends to state precisely the physical hypotheses that are at the basis of both of them, and how they are related to one another.

The recent work of L. de Broglie [**1**] on the unification of the principle of the maximum of entropy and the principle of the minimum of the action integral has directed my attention to the mechanical theory of thermodynamics. In the course of the year 1961-1962, I was then led to reflect upon Boltzmann's formula and the theory of adiabatic invariants, and to attempt to present an article that I could, on the suggestion of L. de Broglie, submit for publication.

That attempt might surprise one, upon first glance. Indeed, it is generally assumed that the theory is perfectly well-founded, and it is, in fact, if one considers only the formalism. However, upon more careful reading, there remain several obscure points that I will examine in detail below, but which I will enumerate briefly here: Exactly what hypotheses were made regarding the constraint forces, and how does one combine them with the hypothesis of reversibility in order to fix the particular properties of reversible transformations? Why do the purely mechanical proofs of adiabatic invariance appeal to a hypothesis of phase incoherence between the constraint forces and the internal motions, although the thermodynamic proof omits that hypothesis? In a general manner, at what moment does the adiabatic hypothesis (in the proper sense of that term: zero heat exchange) intervene in the mechanical proof, since it is found in it implicitly, and it figures explicitly in the thermodynamic proof? How are the equations of analytical mechanics modified in the latter in order to make exchanges of heat appear, which are absent, in general?

This paper, which recalls the major ideas of Boltzmann's presentation [**2**] on mechanical thermodynamics and the proof of L. Brillouin [**3**], consists of a clarification of the physical hypotheses that permit one to answer these questions.

1. Analytical mechanics in the case of arbitrary forces. – As a preliminary, it is necessary to recall or establish some formulas of analytical mechanics in the case, which has generally been considered very little, in which the forces that are applied to the system separate into two groups that play different roles, and one of which is not required to depend upon a potential.

One considers a system *with perfect, bilateral, holonomic constraints*, and in order to avoid useless generality, ones that are *independent of time*. In Lagrange coordinates q^i (i = 1, to N), the kinetic energy T is a quadratic form in $\dot{q}^i = dq^i / dt$ whose coefficients depend upon only q^k. The applied forces are assumed to be divided into two groups: One of them depends upon a potential $V(q^i)$, which we assume is also independent of time; the other one can depend, partially depend, or not depend at all upon a potential. Leaving aside its physical origin, for the moment, we content ourselves by letting $F_i \, \delta q^i$ (with the summation convention) denote its virtual work.

For the moment, we make no hypothesis on the separation of the coordinates that would be parallel to that of the forces: The same coordinate q^i can be simultaneously subject to the two forces $-\partial V / \partial q^i$ or F_i. As one knows, the Lagrange equations are written as:

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}^i}\right) - \frac{\partial T}{\partial q^i} = -\frac{\partial V}{\partial q^i} + F_i \,. \tag{1}$$

We introduce the Lagrange function $L(q^i, \dot{q}^i)$ by the usual relation:

$$L = T - V.$$

Beyond its total kinetic energy, L is then defined by *only forces the first group*, and that will still be true even in the case where the forces of the second group depend upon a potential. As we will confirm later on, the obviously arbitrary character of this definition resides in the physical necessity of having to define an internal energy. Equations (1) can be written:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}^i}\right) - \frac{\partial L}{\partial q^i} = F_i \,. \tag{2}$$

As usual, one further introduces the moments p_i and the Hamilton function H:

$$p_i = \frac{\partial T}{\partial \dot{q}^i} = \frac{\partial L}{\partial \dot{q}^i} \rightarrow \dot{q}^i (q^k, p_k), \qquad H = p_i \, q^i - L = H(q, p).$$

Since T does not depend upon time explicitly, one will have:

$$H = T + V,$$

and we further give the sum $T + V$ the name of "energy of the system," and we also denote it by the letter E in order to conform to the usual notation.

Similarly, L, H, or E are defined by starting with forces of only the first group.

The well-known differentiation of H and the utilization of equations (2) lead to the modified Hamilton equation:

$$\frac{dq^i}{dt} = \frac{\partial H}{\partial p_i}, \qquad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} + F_i ,$$

and since H does not depend upon time explicitly, an immediate consequence of these equations is that:

$$dH = dE = F_i\, dq^i . \tag{3}$$

We now pass on to the action integral. It will be:

$$S = \int_{t_1}^{t_2} L(q,\dot{q})\, dt ,$$

which is an integral that is taken along a real trajectory of the system. If Γ and Γ' are two infinitely close real trajectories (Γ goes from q_1^i, t_1 to q_2^i, t_2 , Γ' goes from $q_1^i + \delta q_1^i$, $t_1 + \delta t_1$ to $q_2^i + \delta q_2^i$, $t_2 + \delta t_2$) then the variation of the action integral between Γ and Γ' will be given by the equation, which generalizes the usual form:

$$\delta S = \delta \int_{t_1}^{t_2} L\, dt = \Big[p_i\, \delta q^i - H\, \delta t \Big]_1^2 - \int_{t_1}^{t_2} F_i\, \Delta q^i\, dt . \tag{4}$$

Δq^i is the variation in the course of motion of the coordinates q^i with t constant (δ denotes a variation that is taken in an arbitrary manner).

Subtract the variation $\delta \int_{t_1}^{t_2} 2T\, dt$ from both sides of (4); on the left-hand side, one will get:

$$\delta \int_{t_1}^{t_2} (L - 2T)\, dt = -\, \delta \int_{t_1}^{t_2} (T + V)\, dt = -\, \big[E\, \delta t \big]_1^2 - \int_{t_1}^{t_2} \delta E\, dt .$$

and since $E = H$, we arrive at:

$$\delta \int_{t_1}^{t_2} 2T\, dt = \Big[p_i\, \delta q^i \Big]_1^2 + \int_{t_1}^{t_2} (\delta E - F_i\, \Delta q^i)\, dt . \tag{5}$$

δE is the variation of energy with constant t. That equation generalizes the known variation of the Maupertius integral; however, one must note that, contrary to the usual custom, the system is not conservative by virtue of equation (3), and neither E, nor δE are constant along the unvaried trajectory Γ.

2. Definition of a Boltzmann system. – It is a system in which one distinguishes *two kinds of coordinates, three kinds of forces, and two possible modes of dynamical evolution.*

A. COORDINATES. – They are divided into two classes:

– Coordinates that pertain to rapid motions, which we denote by the symbols q^i (i = 1 to n); their motions can be vibratory or random.

– Coordinates that pertain to slow motions, which we denote by the symbols χ^ρ (ρ = n + 1 to N). These coordinates are restricted to either remain constant in the course of motion of the q^i or to vary, but in a very slow manner in comparison to the q^i. These are the constraint coordinates or the hidden coordinates.

There is no need to insist upon the illustrations of that classification. We remark only that the coordinates q^i do not appear in energetics, since they are all combined into the quantity of temperature, and one reasons solely with the constraint coordinates. The opposite (or almost the opposite) is true in mechanical thermodynamics, where the coordinates χ^ρ are often masked by their constancy.

For the moment, it is unimportant to know whether the coordinates q^i, on the one hand, and χ^ρ, on the other, refer to material points of different types: One may very well imagine that the same molecule possesses coordinates of both kinds. Boltzmann, to whom is due the essentials of the classification that is recalled here, effectively treated the problem in generalized coordinates, but he likewise defined systems that were more specialized, in which the material points that were represented by the coordinates q^i formed a material system that was distinct from the one that was represented by the χ^ρ, and that distinction, which appeared a bit too early in his exposition, can lead one to believe that certain results demand that specialization, although that is not true.

B. FORCES. – They are divided into three categories:

a) *Imposed forces.* – These are the forces whose existence and magnitude are independent of the will of the experimenter (for example, for a gas, the mutual interactions between the molecules and the forces of weight).

These must be exerted upon the coordinates q^i, as well as on the coordinates χ^ρ (for example, by introducing a cylinder and piston that compresses a gas into the physical system that is being treated). One can further subdivide them into forces that are internal to the system and external forces at a distance; that distinction is unimportant.

The only restrictive hypothesis that we will make upon this ensemble of forces is that it must depend upon a potential $V(q, \chi)$. We have thus constituted the first group of forces in paragraph 1.

b) *Control forces.* – These are forces that depend upon the experimenter, and which serve to vary the constraints as desired. By definition, they are attached to only the coordinates χ^ρ. We suppose nothing about their dependency upon a potential, and one knows that, at least macroscopically, they have non-zero rotation for the most of the time. We denote their virtual work by $A_\rho\,\delta\chi^\rho$; they are a subset of the second group of forces in paragraph 1. They are external forces of the reaction kind.

c) *Forces "of heat."* – These are forces that likewise depend upon the experimenter, but which, by definition, and contrary to the foregoing, *act upon only the coordinates* q^i. Their name says much about the phenomenon to which they are linked.

Along with the control forces, they define the second group of forces in paragraph 1, and we can affect them with symbols that belong to the category F_i and figure in the equation of analytical mechanics in that same paragraph. That notation is nonetheless useless, since the objective of the theory is to find the maximum number of results that are independent of the individual structures of these forces and arise only from the global transfer of energy that they cause.

We can now define the internal energy and the quantity of heat. By definition, the internal energy of a Boltzmann system is the sum:

$$E = T + V$$

of its *total* kinetic energy T and the potential V of the *imposed forces.* The quantity of heat dQ that is absorbed by the system during a real transformation is defined by the inequality:

$$\boxed{dE = A_\rho d\chi^\rho + dQ,} \tag{6}$$

where A_ρ are the control forces. It emerges from that definition and equation (3) that dQ will mechanically equal the work that is done by the forces of heat that we have named individually.

Before passing on to the following definition, we must make a remark about the control forces that will be very important for our future comprehension of the notion of reversibility. Since the coordinates q^i are rapidly-varying, it is clear that, in general, the potential V, and consequently, the force $-\partial V / \partial q^i$ that is derived from it, are themselves rapidly-varying. One can think, by a symmetry that is quickly adopted, that since the coordinates χ^ρ are slowly-varying, the forces A_ρ that they are attached to must be themselves slowly-varying. *That is not true, and as a general rule, the control forces A_ρ vary just as rapidly as the microscopic coordinates.* That is immediately obvious in the example of a pendulum, in which the control force is the reaction of the fixed point to the pendulum, and it is clear that it varies with the frequency of the latter. In the general case, one confirms that things are again the same as in paragraph *c*) above, after one establishes equation (7).

There can be no doubt that in certain cases the observer registers only the slowly-varying control forces (the pressure of the piston on a gas, for example); however, that will then be true because the observer is confined to a mean effect of the forces that act upon a large number of coordinates χ^ρ, or its temporal mean, moreover.

C. LAW OF DYNAMICAL EVOLUTION. – This is the essential distinction upon which all of the theory rests. We suppose that the Boltzmann system can have two sorts of real motions.

a) *Pure mechanical motions, which are further called adiabatic* (= with no exchange of heat).

By definition, these are motions that are ruled by imposed forces and control forces, while excluding the forces of heat, which are assumed to be zero. These motions thus obey the equations (2) of analytical mechanics, which we only need to transcribe here with a specialization:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}^i}\right) - \frac{\partial L}{\partial q^i} = 0 \qquad i = 1 \text{ to } n.$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\chi}^\rho}\right) - \frac{\partial L}{\partial \chi^\rho} = A_\rho \qquad \rho = n + 1 \text{ to } N. \tag{7}$$

L is defined as it was in paragraph 1: $L = T - V(q, \chi)$. From equation (3) in paragraph 1, one will then have:

$$dE = A_\rho \, d\chi^\rho \tag{8}$$

for a real motion, which, from definition (6), implies the vanishing of the exchange of heat.

A motion of this kind corresponds to two kinds of energetic phenomena:

– Either a *state* that is characterized by the constancy of the constraint coordinates χ^ρ, and in which one abstracts from the motion of q^i.

– Or an *adiabatic transformation*, where the χ^ρ evolve the same way, but in such a manner as to respect condition (8), or furthermore $dQ = 0$.

One can remark, in passing, that instead of considering q^i and χ^ρ to be unknown for given A_ρ in equations (7), one can takes the q^i and the A_ρ to be unknown when one is given the functions $\chi^\rho(t)$: The first equation of (7) then provides the motion of the q^i , while the second one gives the values of the A_ρ; in that way, one can calculate the control forces that must be exerted in order to obtain a desired evolution of the constraint coordinates.

b) *Thermodynamic, non-adiabatic, motions.* – These are the motions in which the three kinds of forces that were defined above enter into play simultaneously; i.e., the forces of heat, as well.

Equations (7) are no longer valid for these motions. In order for them to be valid again, one must make the forces of heat enter into right-hand side of their first line of forces. One refrains from writing that new representation, for the reason that was given in paragraph B, *c*) above. However, there is no need for that notation in order to confirm that the equations of analytical mechanics will be different from the preceding case under a non-adiabatic transformation, since only the usual forces of rational mechanics will figure in the preceding case.

Furthermore, equation (8) is not valid; it must be replaced with the definition (6), in which dQ globally subsumes part of the right-hand side of the equality (3).

Now, return for an instant to the variability of the forces A_ρ . The second of equations (7) shows clearly that the velocity of variation of the microscopic coordinates q^i is recovered in A_ρ by the intermediary of L and its derivatives, as we saw above.

Finally, we can answer one of the questions that was posed in the introduction: viz., the intervention of the adiabatic hypothesis in the purely mechanical proof of the adiabatic invariance. For better clarity, reason with the special case of the pendulum, for which one can refer, for example, to the proof that was given by Sommerfeld [**4**]. That proof begins by calculating the work that is done by the reaction of the fixed point to the elongation of the suspension filament (upon supposing that the elongation is infinitely slow, but the slowness is not in effect for the moment). In order to obtain the desired relation (T / ν = const.), it is then sufficient to write that the work that is done by the reaction is equal to the variation of the energy of the oscillating mass. However, in that equality (which is nothing but the equality (8) above), one implicitly supposes that the sliding of the filament that permits the elongation is performed with no liberation of heat.

That fact is general; in all of the purely mechanical proofs of the adiabatic invariance of a phenomenon, there is a moment when one writes down an equality between work and energy that does not arise from the hypotheses that were made about the model, but which supposes that, in addition, one has some information of physical origin at one's disposal about the nullity of the exchange of heat (one also sometimes makes the hypothesis that equations (7) continue to be valid under the variation of the coordinates χ^ρ, which amounts to the same thing, from what we just saw).

3. Reversible transformations. – The term *reversible transformation* of a Boltzmann system refers to a *real* motion in the system for which one arranges that the application of the control forces should be such that:

– The velocities $d\chi^\rho / dt$ are infinitely small.

– They are constant, or even better, the accelerations $d^2\chi^\rho / dt^2$ are infinitely small.

– The q^i evolve with no other conditions than the ones that are imposed by the laws of the system.

These conditions are perfectly clear from the mathematical viewpoint, so the expression "infinitely small" means as small as is necessary in order for one to say that it is valid. However, the physical significance of that smallness is less obvious, and we can grasp it only from the proof that follows.

The expression for the quantity of heat takes a particular expression under a reversible transformation.

Let such a transformation start at a point q_1^i, t_1 and stop at a point q_2^i, t_2. The variation of internal energy is ΔE, the absorbed heat is Q, and from the definition (6), one has:

$$Q = \Delta E - \int_{t_1}^{t_2} A_\rho \, d\chi^\rho .$$

Now, the χ^ρ are constant, and consequently:

$$\int_{t_1}^{t_2} A_\rho \, d\chi^\rho = \dot{\chi}^\rho \int_{t_1}^{t_2} A_\rho \, dt = \dot{\chi}^\rho (t_2 - t_1) \bar{A}_\rho .$$

$\bar{A}_\rho$ is the *temporal* mean of A^ρ. In addition, one has $(t_2 - t_1)\dot{\chi}^\rho = \Delta\chi^\rho$, and consequently:

$$\boxed{Q = \Delta E - \bar{A}_\rho \Delta\chi^\rho .} \tag{10}$$

This equation deserves several remarks.

In the first place, it seems trivial, and in fact, it will be trivial if $\bar{A}_\rho$ is a mean that is obtained by integrating over the coordinates χ^ρ. Equation (10) will then be valid even for an irreversible motion, but the mean $\bar{A}_\rho$ will depend essentially upon the path that was traversed by the χ^ρ. The temporal mean $\bar{A}_\rho$ avoids that indeterminacy, but at the expense of the reversibility condition; i.e., upon imposing a particular path to the χ^ρ that is linear and infinitely slow. $\bar{A}_\rho$ must be considered to be a limit that is attained by "a continuous sequence of equilibrium states." One confirms below that it is the particular form thus-chosen for the mean that permits one to prove the Boltzmann formula.

We shall see what the constancy of the velocity χ^ρ signifies physically. For that, one can write down the first equality (9), and it suffices for the χ^ρ to vary weakly, while the A_ρ vary considerably. If, to fix ideas, one considers a vibratory motion of the q^i then that will signify that the fluctuation of the χ^ρ must have a frequency that is much less than the frequency of vibration of the q^i; one recovers the physical hypothesis of phase incoherence from a purely mechanical proof. In other words, one can say that the infinite smallness of the $d^2\chi^\rho / dt^2$ that one supposed at the beginning of this paragraph does not need to be realized mathematically; it suffices that $\ddot{\chi}^\rho / \dot{\chi}^\rho$ should be small in comparison to the frequencies of vibration of the q^i.

Finally, let us make a remark about terminology. One is often in the habit of calling a transformation "adiabatic" when it is both adiabatic (in the proper sense) and reversible in a context that is distinct from energetics, where the term "adiabatic" signifies only "with no exchange of heat". Now, in the purely mechanical proofs of "adiabatic" invariance, it is, in reality, the reversibility that is important; as I remarked above, the hypothesis of zero heat is introduced at a point when one does not even speak of it, and the entire proof revolves around the slowness of the variation of the constraint coordinates. As long as one remains in the domain of pure mechanics, the best terminology will then be "reversibility invariants"; however, in order to embrace the general thermodynamic case, it would be preferable to utilize the expression "Ehrenfest invariants" exclusively, as one does quite often, moreover, and to which one can give the meaning of "adiabatico-reversible" invariants.

4. Variation of the Maupertuisian action under a virtual transformation between thermodynamic states. – Consider two real, neighboring trajectories of a Boltzmann system that are defined as follows:

– One of them Γ goes from the point q_1^i, t_1 to the point q_2^i, t_2 while keeping the constraint coordinates χ^ρ *constant.*

– The other one, Γ' goes from the point $q_1^i + \delta q_1^i$, $t_1 + \delta t_1$ to the point $q_2^i + \delta q_2^i$, $t_2 + \delta t_2$ while $\chi^\rho + \delta\chi^\rho$ is likewise *constant.*

– The two motions are purely mechanical (i.e., adiabatic).

In the thermodynamic sense of the term, these two motions thus represent states (neither motion of the χ^ρ nor exchange of heat).

One can pass from the first motion to the second one by a continuous *virtual* transformation δq^i, δt, $\delta\chi^\rho$ with $\delta\chi^\rho$ = const. From equation (8), E is a constant for each motion, and δE is a constant. Now, apply the general equation (5), upon specializing it in order to make the two kinds of coordinates q^i and χ^ρ appear. One will get:

$$\delta\int_{t_1}^{t_2} 2T\,dt = \left[p_i\,\delta q^i + \pi_\rho \delta\chi^\rho \right]_1^2 + \int_{t_1}^{t_2} (\delta E - A_\rho \delta\chi^\rho)\,dt\,.$$

π_ρ is the moment $\partial T / \partial\dot{\chi}^\rho$. Since the $\delta\chi^\rho$ and δE are constant, that equation can also be written:

$$\delta\int_{t_1}^{t_2} 2T\,dt = \left[p_i\,\delta q^i + \pi_\rho \delta\chi^\rho \right]_1^2 + (t_2 - t_1)(\delta E - \overline{A}_\rho \delta\chi^\rho)\,, \tag{11}$$

and one sees the temporal mean of A^ρ appear.

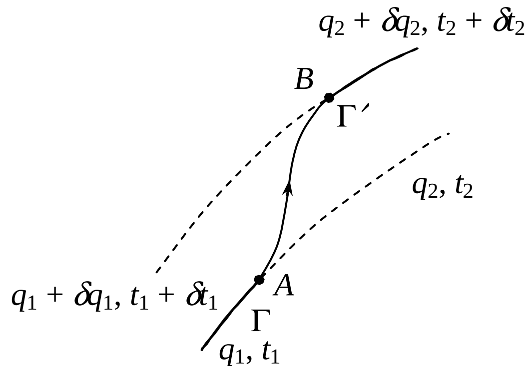

Figure 1.

5. Boltzmann's formula and Ehrenfest invariants. – The last term in equation (11) acquires a physical significance in the case where the two real motions, which were varied with respect to each other by a *virtual* transformation up to now, can be coupled by a *real, reversible* transformation. The figure represents what happens. The moving body (in the extension-in-phase) follows the trajectory Γ from the instant t_1 to the instant t_A ; from t_A to t_B, and under the impulse of supplementary forces, it follows the real transitional trajectory γ; finally, upon starting from t_B, the supplementary forces disappear, and the trajectory that is followed will be Γ′.

The variations that figure in the two sides of (11) are not calculated, in general, along the trajectories that are actually followed, but between the real trajectory and the prolonged one: Γ forwards, Γ′ backwards. In the particular case in which Γ and Γ′ are closed trajectories, the variations can be taken between the real points of passage on the trajectories.

If the transformation γ is reversible, and $\overline{A}_\rho$ is a temporal mean then equation (10) will show that $(\delta E - A_\rho\, d\chi^\rho)$ is the heat that is absorbed by the system under the real transformation γ. Hence, one will have the Boltzmann formula:

$$\frac{1}{t_2 - t_1}\delta\int_{t_1}^{t_2} 2T\,dt = \frac{1}{t_2 - t_1}\left[p_i\,\delta q^i + \pi_\rho \delta\chi^\rho \right]_1^2 + \delta Q. \tag{12}$$

As a special case of great important, we place ourselves in the case where the total kinetic energy has the form:

$$T = T_q(q, \dot{q}) + T_\chi(\chi, \dot{\chi}).$$

T_q and T_χ are two quadratic forms, in which the rectangular terms are absent. One will arrive at that, in particular, when the coordinates q and χ are attached to two systems of different material points.

T_χ is zero under the motions Γ and Γ' with constant constraints, just like $\pi_\rho = \partial T / \partial \dot{\chi}^\rho$, since the $\dot{\chi}^\rho$ are zero. (12) then becomes:

$$\boxed{\frac{1}{t_2 - t_1}\delta\int_{t_1}^{t_2} 2T_q\, dt = \frac{1}{t_2 - t_1}\Big[\, p_i\, \delta q^i \,\Big]_1^2 + \delta Q,} \tag{13}$$

in which the kinetic energy and the sum $p_i\, \delta q^i$ refer to *only the microscopic coordinates.*

Now, define an Ehrenfest (i.e., "adiabatic") invariant to be a quantity that is defined along a certain class of *purely mechanical motions with constant constraints* (thermodynamic states), and which remain constant when one passes from one motion to another of the same class by a reversible and adiabatic transformation.

If one starts with equation (13) then the proof of the existence of an adiabatic invariant for periodic motions will be immediate: It suffices for one to know how to make $dQ = 0$, and to consider the integral $\oint T\, dt$, taken over the period.

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