Perturbations and Statistical Distribution of the Thermal Energy [1,2]

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ABSTRACT. **T**he probability of finding the energy of a particle in the vicinity of a given energy is determined introducing the existence of perturbations. The thermal radiation already studied with this approach suggests that it is the origin of the perturbations. The introduction of these, leads to suppose that the maximum of the statistical weight is obtained in the vicinity of an M value slightly higher to the mean value U of the system. Several applications are proposed in particular new the velocity distribution in a gas first proposed by Maxwell is revisited.

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[1] The word perturbation is used with the meaning of anomaly, trouble, irregularity in the functioning of a system without reference to the mathematical method with the same name. It is interesting to underline that this word comes of the French perturber coming from Latin per for excess and turbare disturbed (troubler in French) from turba crowd (cohue in French) » having given tourbe that is peat a pejorative old word in French for crowd, multitude.

[2] English translation of "Les Perturbations et la Distribution Statistique de l'Energie Thermique", Ann. de la Fondation Louis de Broglie, 31, 53-74, (2006), http://www. ensmp.fr/aflb/AFLB-311/aflb311m388.htm, with an introduction modified to insist upon the hazard in statistics introduced by Boltzmann but the need of which is insufficiently underlined.

1   Introduction

In statistical thermodynamics the great number of particles responsible of the phenomena, leads to use the statistical methods to determine for example the number of particles in the vicinity of a given energy. The set of possible values leads to the notion of statistical distribution of the energy. Concerning the probabilities the coherency between theory and experiment justifies hypothesises. But the use of statistics supposes implicitly in some extend a part of hazard in the distribution, part introduced by Boltzmann [1] with the hypothesis of molecular disorder. It is possible to shed light on this hypothesis supposing that they are the thermal exchanges with the external space to the studied set which originate the molecular disorder. Indeed there is no system fully isolated and each experiment even the best isolated one is perturbed by a flux of thermal energy exchanged with the atoms of the gas or solid studied. In good experimental conditions this flux is constant in mean value and generally small before the mean thermal energy U. On the other hand for great accuracy it appears that the thermal radiation slightly modified the thermal equilibrium of the solids. It is that the study of the blackbody from the distribution $D(E,U)$ shown [2]. The purpose of this work is to determine how this flux introduces perturbations on the distribution of the energy of the atoms or electrons. In this view we will use the essential of our previous study simplifying it when it is possible and completing it to show the general character of the distribution $D(E,U)$ in the study of the physical phenomena.

2   Temperature and energy

The statistical thermodynamics is born from the works of a great number of researchers during the 19th century. Among those works we are more concerned with those of Maxwell [3] and Boltzmann [1] for the study of the distribution of the thermal energy among N particles of a given system. This branch of the physics in its beginning was built mostly from the study of the perfect gas which led to the notion of absolute temperature T. Quite naturally this new notion was used as statistical variable. Indeed it is natural to follow the variation of a property of a compound as a function of the temperature and at the beginning we can understand it use as statistical variable. But how much important the absolute temperature T may be, it is the mean thermal energy U per particle which play a fundamental role in statistics as we have already discussed [4], [5]. This point leads to determine $D(E,U)$ the density of probability per unit of energy for the energy E of the particles. To determine this function we have supposed that the most important number of exchanges of energy takes place around the mean value U. This hypothesis

gives good results for several applications [6], [7]. In the case of metallic conductivity of sodium just few conduction electrons appear to be really present in the metal [7]. This confirms that the properties of a metal do not need special quantum property as suppose in the Fermi-Dirac statistical approach. Further confirmation has been proposed with the study of the specific heat of the conduction electrons [8].

3 Notion of probability density

Consider a set of N identical particles, for example the atoms of a gas or a solid. Let U be the mean thermal energy per particle. The particles are supposed to exchange energy but without hypothesis about the way to do it. We suppose that there is no quantum property able to modify the distribution of the energy. Consider a segment i of energy $[E_i, \Delta E_i]$ defined by the energy E_i and its width ΔE_i. During the time there are numerous exchanges of energy. As a result the particles are continuously changing of segments of energy. But in mean value we can suppose that each particle leaving one segment is replaced by another one. This means that the number n_i of particles which occupy a segment is stable in the time that is at the scale of the time of the measures [3]. The statistical problem is to determine this number for all the possible values of E_i on a segment ΔE_i. This number is necessarily proportional to the total number N of the particles and to the width ΔE_i of the segment. This last aspect introduces the probability per unit of energy that is the notion of probability density for the thermal energy. This statistical aspect is important because even if we consider a total number N of particles endless, it is a countable number, which is not the case of the possible values of the energy. In other words the power of the infinity of the possible values of the energy is larger than that of the countable. Working like this we avoid the need of the partition function to determine the number of particles n_i. Thus, consider $D(E,U)$ the density of probability. If ΔE_i is small compared to U, n_i is also small compared to N. We can write:

$$n_i = ND(E_i, U) \, \Delta \, E_i \tag{3.1}$$

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[3] In a previous work [3,4] we have introduce intervals of time $[t-(\Delta t)_i, t]$ to discuss the exchanges of energy. The reason is that the exchanges of energy take place in the time. In addition these intervals of time are not equal when $[E_i, \Delta E_i]$ varies. But as finally the time does not appear, it is better to avoid it.

where the index *i* refer to a series of segments defined by the following energies:

$$\varepsilon_i = \varepsilon_{i-1} + \Delta E_i \quad \text{avec } \varepsilon_0 = 0 \text{ et } \Delta E_i \ll U \tag{3.2}$$

The segment *i* is the set of values E_i such as:

$$\varepsilon_{i-1} \leq E_i \ \triangle \varepsilon_i \tag{3.3}$$

The next point now is to determine the number ν_i of particles from which the n_i have been drawn.

4   The particules ν_i

To determine the number of particles ν_i from which the particles n_i have been drawn, people generally imagine the *N* particles at a given time *t*. By thinking to a given time it seems that the only possibility for the n_i is to suppose that they have been drawn among the whole number *N* of the particles of the set. In fact if the n_i belong to the set of the *N* particles, just looking at this aspect leads to ignore the exchanges which are at the basis of the statistical distribution. Indeed let us consider the exchanges of energy which have taken place a long time before the considered time *t*. As a result of the perturbations rapidly there is no correlation between the values of the energy of the same particle at two close times. It is thence reasonable to suppose that the exchanges distant in time do not have any influence upon the distribution at the time *t*. Furthermore, as a result of the mean time between two exchanges, one particle stays just a short interval of time on the segment $[E_i, \Delta E_i]$ in comparison of the experimental time measurement. These remarks lead to suppose that just a small number of exchanges and thus of particles ν_i, just before the considered time, determine the numbers n_i. By definition the n_i belong to the ν_i. It is interesting to remark that the expression "at a given time", from a physical point of view, is not sufficiently accurate since every event is produced in an interval of time. To be sufficiently accurate using this expression we mean a short interval of time, sufficiently short to can suppose that the particles n_i do not change of segment and that the ν_i remain the same.

5   The most probable distribution and the perturbations

Let us consider the particles n_i which occupy the segment *i* at the time *t*. We do not know which they are, so the particles are called undistinguishable. Nevertheless it is possible to limit the notion of undistinguishability to this aspect of the phenomena. On the other hand at the microscopic scale we

suppose that the particles between them have individuality. Consequently this means that in certain extent it is possible to distinguish them. For example we will assume that the particles have a volume and that two of them cannot occupy the same place at the same time.

As a result any exchanges of place between one particle n_i and one of the remaining particles $v_i - n_i$ should give the same distribution of the energy. Thus there are several exchanges or events able to produce the same distribution. The number W_i of these different events is the statistical weight to have n_i particles on the segment i.

To calculate W_i let us consider the thermal equilibrium of the set of particles. The exchanges of place can be produced by progressive transfer of energy between the particles of the set. In such a case it is a predictable mechanical variation, even if it is not really possible to describe it, such eventuality does not concern the statistics.

On the other hand the set of atoms or electrons continually exchanges with the outside, in particular it absorbs or emits photons which modify the distribution of the thermal energy. Thus there is absorbed or emitted energy which constitute positive or negative losses. In fact, one has to bring energy to work at stable temperature; indicating that the amount of energy emitted by the studied set is always higher to that received. That comes in particular from the thermal radiation the energy of which is taken from the studied set. It is that that shows the no turnal drop in temperature when the sky is clear, the thermal radiation of the earth makes cool down its temperature when the sun is not still there. The role of the thermal radiation as source of perturbations has already been underlined by Fer in his study of the irreversibility [9]. To balance the losses the set is in thermal contact with a heat bath, that is a large thermal mass at a temperature as close as possible from that of the studied set. Thus there is a continual flux of energy toward the set. The difficulty to work on an isolated system has been discussed in details by Fowler [3].

The perturbations in modifying in an aleatory way the energy of the particles corroborate the hypothesis of the molecular disorder [1] and make the different W_i probable. As a result at the scale of the particles, the evolution of the exchanges of energy is disordered. Thus it is not possible to describe the evolution of the energy of a particle. Therefore it is the most probable distribution corresponding to the means of n_i and of v_i that one has to determine.

Now at the scale of the particles the perturbations introduce a positive or negative energy. The stable temperature is the result of the balance between the perturbations with positive and negative energy. As a consequence at the scale of the exchanges, there is no conservation of the thermal energy between the particles.

With such disorder, during the interval of time of the order of magnitude of the mean time between two exchanges of energy, just one event among W_i is realized but all could be realized. As a result the numbers W_i play the role of statistical weight for the n_i's taken from the v_i's. In addition we make the hypothesis that all the events which belong to W_i, and whatever i may be, have the same probability of to be realized. This hypothesis allows a simple calculation using the method of the most probable distribution.

The particles v_i determine the W_i, consequently the numbers v_i must be chosen in such a way that they play their role of statistical weight between them. This leads to introduce a dependency between the probabilities on two different segments. We will get this result, if for $\Delta E_i = \Delta E_j$, the weights W_i and W_j are obtained from a same number of particles v_i and v_j whatever i and j may be. Thus let consider the same given width ΔE for all the ΔE_i, then whatever i may be, all the number v_i are equal to the same number v. Now we must keep in mind that if we have $v_i = v_j$, the particles themselves are not the same at least for a part of them.

6   The dependences

Let us now calculate the number W_i. The equality of the probability, assumes above, for the different events defining the W_i allows their calculation. It is the number of different ways to take n_i objects among v_i objects. The combinative analysis gives:

$$W_i = \frac{v_i !}{(v_i - n_i)!n_i !} \tag{6.1}$$

For a given width ΔE_i invariable with i, we have already imposed to all the v_i to be equal between them. In this manner the W_i compare as statistical weights. But we can still choose the number of particles v_i for a given width ΔE_i. This possibility allows choosing a physical property that the statistical weights have to respect.

In this view, let us consider the particles and the mean value U of their energy. As a result of the perturbations this mean value is not kept at each exchange but in average on a great number of exchanges. As a result there are necessary more particles with a low energy than particles with a high energy. Indeed as soon as there is one particle with an energy $E > 2U$ there are more than one particles with $E < U$ to balance the excess of energy of the first in

comparison to U. Thus the exchanges are correlated. Furthermore the events producing particles with high or low energy are less probable than those leaving particles in the vicinity of the mean value. Thus there is a maximum of W_i for a given constant width of ΔE_i. We suppose that this maximum corresponds to the segment which contains the value M of the energy close of the mean value U. As a result of looses this maximum M occurs for a value of energy a little higher to U. Thus we can write:

$$M = U(1 + \varepsilon) \qquad (6.2)$$

where the dimensionless number ε is positive but small, that is put in view in the study of the black body [2].

The determination of this maximum of the statistical weight replace the hypothesis of Boltzmann which links up the entropy to the maximum of the probability through it logarithm. We will show in the section 8.5 the validity and the limits of this hypothesis concerning the entropy.

To determine this maximum consider a given width ΔE_i, the ν_i are constant. It is an important point to determine the maximum. If W_i has a maximum its logarithm too and we can write $d(ln\ W_i) = 0$. Using the Stirling relation $P! = P(lnP - 1)$, it comes:

$$ln W_i = \nu_i ln(\nu_i) - n_i ln(n_i) - (\nu_i - n_i) ln(\nu_i - n_i) \qquad (6.3)$$

By differentiation keeping in mind that $d\nu_i = 0$ we have:

$$d(ln\ W_i) = -n_i ln(n_i)dn_i + ln(\nu_i - n_i)\ dn_i = 0 \qquad (6.4)$$

that is: $$d(ln\ W_i) = ln\frac{\nu_i - n_i}{n_i}dn_i = 0 \qquad (6.5)$$

Let us express that the maximum of W_i takes place on the segment containing M. Let ν and n be the values of ν_i and n_i for this segment and write:

$$\nu = \gamma n \qquad (6.6)$$

where γ is a dimension less number. The relation (6.5) allows calculating γ. This relation must be verified whatever dn_i may be. According to the relation (6.6) this gives:

$$ln(\gamma - 1) = 0 \quad \text{d'où} \quad \gamma = 2 \tag{6.7}$$

Now v_i is just a function of ΔE_i. For the segment containing M with a width ΔE_i from the relations(3.1), (6.6) and (6.7) its follows:

$$v_i = 2ND(M,U)\Delta E_i \quad \forall_i \tag{6.8}$$

$D(M,U)$ is the density of states for the value $E = M$. This term introduces the dependencies between the probabilities on two different segments. In different applications taking $M = U$ we have found theoretical values in good agreement with experimental results [6]. The physical meaning of the relation (6.7) is that around M, which in good experimental conditions is close to U, the exchanges happen mainly between two particles, a quite natural result. When M is close to U this means that the flux of energy brought with the perturbations is small in comparison of the value U. This can be used to verify the quality of the experiments.

We have now the relation (3.1) and (6.8) giving n_i and v_i. The calculation of the function of E, $D(E,U)$ is then possible. This calculation is close to the classical one.

7 The calculation of $D(E,U)$

We have already expressed with the relation (6.1) the weight W_i which determines the number of particles n_i on the segment i. Let W be the product of all the W_i :

$$W = \prod_i W_i \tag{7.1}$$

Assume the hypothesis that the most probable density of states is that corresponding to the maximum of W, therefore we have:

$$d(lnW) = 0 \tag{7.2}$$

In this derivative, the deviations of the energy to consider are those from the most probable distribution. They come from the variation of the numbers

n_i, but not from the numbers v_i. Indeed for a given width ΔE_i, we have seen that the v_i are all equal in such a way that the W_i are statistical weight. Furthermore the v_i according to (6.7) also impose the constancy of the mean value of the energy. Working to find the most probable distribution, the mean energy must be a constant therefore the v_i too.

The way to find the conditions giving W maximum is similar to that used to find W_i, one has just to replace lnW_i by $lnW = \Sigma\ lnW_i$. Thus the relation (6.4) is replaced by:

$$lnW = \Sigma\ lnW_i = \Sigma_i ln\frac{v_i - n_i}{n_i}\,dn_i = 0 \qquad (7.3)$$

To satisfy this relation we must take into account the restrictive conditions:

$$\Sigma_i\ n_i = N = \text{constant}, \quad \text{leading}\ \ \Sigma\ dn_i = 0 \qquad (7.4)$$

$$\Sigma_i\ E_i\ n_i = NU = \text{constant}, \quad \text{leading}\ \ \Sigma\ E_i\ dn_i = 0 \qquad (7.5)$$

The differential aspect of these two relations is taken into account using the Lagrange method with the corresponding multipliers. It is also important to introduce in the determination of the function $ND(E,U)$ the fact that N and U are constant. Their exact values will be expressed through the two relations (7.11) and (7.12). Let us first take into account the differential aspects; whatever the dn_i may be, we must have:

$$\Sigma_i(-\alpha + \beta\ E_i)\,dn_i = \Sigma_i\ ln\frac{v_i - n_i}{n_i}\,dn_i \qquad (7.6)$$

Introducing $-\alpha$ and β as Lagrange's multipliers.

To have the equality (7.6) whatever dn_i may be we must have:

$$ln\frac{v_i - n_i}{n_i} = (-\alpha + \beta\ E_i) \qquad \forall\ i \qquad (7.7)$$

Introducing the relations (3.1) and (6.7) it comes:

$$\ln\left[\frac{2D(M,U)-D(E_i,U)}{D(E_i,U)}\right] = -\alpha + \beta E_i \qquad (7.8)$$

Now allowing the different ΔE to tend to zero, the sequence of $D(E_i, U)$ tends to a function of E :

$$D(E,U) = \frac{2D(M,U)}{1+\exp(\beta E - \alpha)} \qquad (7.9)$$

To determine the function $D(E,U)$ one has to calculate the parameters: α, β and $D(M,U)$ when $E = M$, which need three equations. The first one is obtained substituting E by M in the expression (7.9). This gives:

$$\alpha = \beta M \qquad (7.10)$$

By this way we impose to the function to have the correct value for $E = M$. It is interesting to note that they are the dependencies introduced by the constant $D(M,U)$ in the expression of the v_i, (7.8) which allow to get $\alpha = \beta M$, a new result in statistical thermodynamics.

The second relation is obtained by writing:

$$\int_0^\infty D(E,U)dE = 1 \qquad (7.11)$$

Such relation comes from the fact that $D(E,U)$ is a density of probability per unit of energy. It express that the probability of finding a particle in all the space of energies is always one.

The third relation is obtained writing:

$$\int_0^\infty ED(E,U)dE = U \qquad (7.12)$$

This relation imposes that the mean value of the energy of one particle among the all possible values is U.

The full determination is given in [4], [5] and in the appendix, we obtain:

$$D(E,U) = \frac{1}{AM} \frac{1}{1+\exp\alpha\left(\dfrac{E}{M}-1\right)} \tag{7.13}$$

with $\alpha = 1.5049$ and $A = 1.7054$ when M can be taken equal to U.

In the general case we have a function of M and U in place of just U. The fact that $\alpha = 1.5049$ is close to 1.5 supposing M and U equal is a good indication that M is close to U. Indeed for the perfect gas $U = 1.5kT$ and in (7.13) the exponential is the Boltzmann factor $\exp\dfrac{E}{kT}$ multiplied by $e^{-\alpha}$. In fact the application in paramagnetism with $M = U$ gives good results, it shows thus equally that M is close to U [6]. As a result in many cases we can use the function $D(E,U)$ defined by (7.13) replacing M by U. That is:

$$D(E,U) = \frac{1}{AM} \frac{1}{1+\exp\alpha\left(\dfrac{E}{U}-1\right)} \tag{7.14}$$

Its representative curve is given figure 1.

When $U \rightarrow 0$; $D(E,U) \rightarrow 0$ for $E > U$ and $D(E,U) \rightarrow \infty$ for $E < U$, (7.15)

The function $D(E,U)$ which satisfies the relations (7.11) and (7.12) tends to that of Dirac. In several application of $D(E,U)$ it is the number $P(E_g,U)$ of particles having an energy higher than a given value E_g that one has to know. We have:

$$P(E_g,U) = A^{-1}ln[1+\exp{-\alpha(E_g/U-1)}] \tag{7.16}$$

The function $D(E,U)$ is a density of probability therefore $P(E_g,U)$ is a probability function:

When $U \rightarrow 0$, $P(E_g,U) \rightarrow 0$ and when $U \rightarrow \infty$, $P(E_g,U) \rightarrow 1$ (7.17)

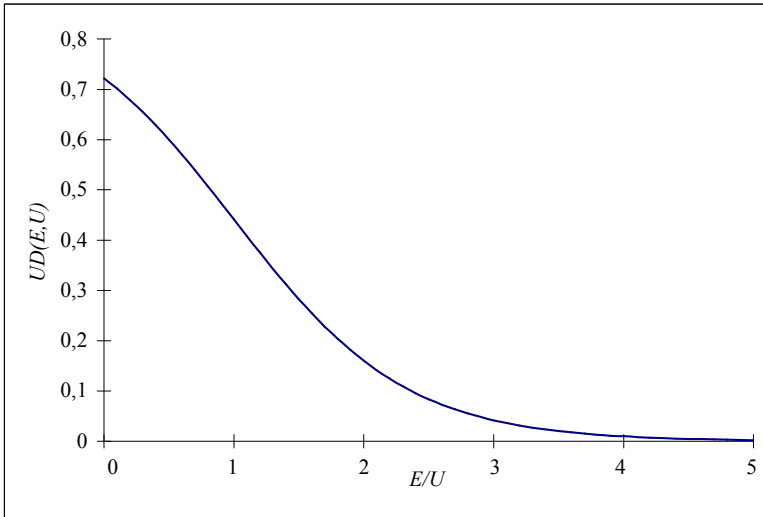The representative curve of this function is given figure 2.

Figure 1. The probability density $D(E,U)$ multiplied by the mean energy U as a func-
tion of the variable E/U.

8   Implications and comparison to the previous works

This study has allows us to find, for the statistical distribution of the ther-
mal energy of the atoms, a more satisfying solution than those proposed up to
now. Several implications of the distribution $D(E,U)$ have already proposed
[4]-[8]. To more completely work out the problem it is equally important to
undestand the difficulties that have been obstacles to this determin ation. It is
the purpose of this section.

8.1 *The condensation.*

Let us consider the condensation of a gas. When the temperature T of a gas
decreases the density of probability around zero Kelvin tends to infinity
(7.15). The corresponding probability tends to one. Let then E_g be the heat of
vaporization or sublimation. To belong to the gas the atoms must have energy
higher than E_g. The kinetic energy E of the atoms of the gas is the amount of
their energy above E_g. When the corresponding mean value U tends to zero,
the gas will tends to condense in a liquid or a solid. This result is natural and
can be considered as a necessary condition to which $D(E,U)$ must satisfy.

8.2 *The black body.*

With the condensation, characteristic property of the distribution $D(E,U)$, we do not need to introduce special quantum properties as in the Bose Einstein approach to determine the distribution of the black body. A first approach was initially proposed by Planck to describe the spectral density of the black body. To understand the difficulties of this approach one has to look at the historical context. It is Planck the first who has introduced the quantification of the light associated to *the harmonic oscillator*. In this way he was able to use the statistical approach of Boltzmann and to avoid the difficulties of the classical model which diverges for the high energies. In 1900 there was not yet quantum model to explain the emission of the light. One has to wait Einstein in 1905 for the hypothesis of the photon and Bohr in 1913 for the first atomic model. With the lack of a clear understanding of the emission of the photons Planck was supposing the existence of harmonic oscillators that we can easily identify with the quantum transitions of the electrons of the atoms of the solids building the black body. He was supposing that the oscillator emitted all a series of quanta of energy $nh\nu$. Now we know that the atoms emit photons of variable energy as a result of the thermal energy. Thus the remarkable approach of Planck is perfectible. Furthermore at this time it was difficult to suppose that the quanta of energy $nh\nu$ do not exchange directly energy between them, as their constant velocity allows supposing it. Yet without exchange of energy it cannot have statistical distribution in the same meaning than that of the energy of the atoms. Since the photons are emitted by the electrons of the atoms their statistical properties must be the reflection of that of the atoms of the solids emitting them as it appears in our study of the black body [2].

8.3 *The heat capacity of the conduction electrons to low temperature*

It is interesting to recall how the conduction electrons are come to disturb the understanding of the statistical distribution of the energy of a set. Disposing of the model of the perfect gas, all the possible conduction electrons of a metal were supposed free and able to contribute to the electrical current flow. Their heat capacity tends to zero with the temperature instead of staying constant as in the case of the gas. As a result it special quantum properties were supposed able to play a role in their statistical distribution and explain this property. With a wrong starting departure the chain of hypothesises complicates inevitably the future understanding. The mistake was that of the free electron. Just a small number of free electrons are needed to understand the

current flow [7], the most important number being localized each one on one atom. This is exhibited with the mean free path which can be as high as one centimetre or more [11]. Thus the heat capacity of the metals is no longer a particular problem [8].

8.4 Velocity-distribution of the kinetic energy.

"The challenge of Maxwell in establishing the velocity distribution was to show that numerous collisions between molecules in a gas, instead of tending to equalize the velocities of all molecules, as some scientists expected, would produce a statistical distribution of the velocities in which all velocities might occur, with a known probability" [3], [12], [13]. This hypothesis belongs now to the classical approach of the statistical description of the gas. Nevertheless one has to keep in mind that this distribution results from perturbations, because they allow the different probabilities to be realized.

The role of the thermal radiations as source of perturbations shed light equally of the origin of the high energies. Indeed by supposing with Maxwell that the atoms of a gas can have all the possible energies between zero and infinity, one supposes implicitly a fact but without understanding the origin of the high values. The extension of our knowledge since Maxwell allows attributing to perturbations, as for example the high energy in thermal radiation, the origin of high velocity of the atoms in a gas. Here I wish to underline that I have discussed of this statistical aspect with Dembno-Tchaikowsky concerned as me with this difficulty. His different approach results of experiences of gaseous expansions exhibiting a difficulty in the statistical approach [14].

Maxwell also believed that the probability distribution for each component of the velocity is independent of the values of the other components. This assumption leads to a different function from $D(E,U)$ and it is important to understand why. Regarding the continuous perturbations giving the most probable distribution of the thermal energy at the atomic scale, there is no conservation of the energy and the second assumption at this scale is not correct. The conservation of the energy at the macroscopic scale is the result of a mean value of the perturbations, keeping in the mean time, the mean value of the thermal energy.

Let v be a positive number representing the velocity. The distribution of the thermal energy is a function of v since $E = \frac{1}{2}mv^2$. Thus the probability to

have a molecule with a velocity v on a segment of velocity dv is directly function of $D(E,U)\ dE$. We have $dE = mdv$, thus:

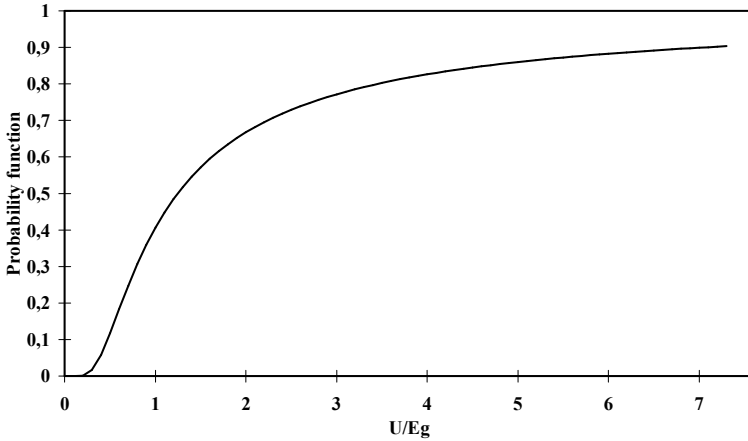$$D(E,U)\ dE = mvD(\tfrac{1}{2}mv^2,U)dv \tag{8.1}$$

Figure 2. The probability function.

Thus the relation (8.1) gives access to the probability to have a molecule with a velocity v on the segment of width dv containing v. Writing $U = \tfrac{1}{2}m\,\overline{v}^2$ where $\overline{v}$ is the velocity corresponding to the mean energy U. Taking $M = U$, the relation (8.1) becomes:

$$D(E,U)dE = \frac{2}{A\overline{v}}\ \frac{1}{1+\exp\alpha\left(\dfrac{v^2}{\overline{v}^2}-1\right)}\,dv = D(v,\ \overline{v}\,)dv \tag{8.2}$$

The function $D(v,\overline{v})$ is the density of probability to have the velocity v on the segment dv in the vicinity of v. In fact in supposing a strictly exponential form for the velocity distribution, Maxwell obtained the equipartition of the energy in the three directions of the space. Thus he introduced a sufficient but not necessary condition. It seems reasonable to say that the equipartition of the velocities results of that the perturbations.

8.5 *The Boltzmann relation*.

The determination of $D(E,U)$ having been obtained without using the Boltzmann relation: $dS = kdlnW$ it is interesting to show its validity. Consider an increase of entropy there is a corresponding increase of the amount of the energy:

$$dU = \Sigma i\ Ei\ dni \qquad (8.3)$$

The Boltzmann relation is used mainly to finalize the determination of the distribution of the energy which is generally thought as a function of E and T that is $D(E,T)$. We are just concern with the maximum of W therefore of lnW. In a first step let us consider that the increase is obtained by a variation of the most probable distribution of the n_i. From the relation (7.6) we can write:

$$\Sigma i\ ln\frac{v_i - n_i}{n_i}\ dn_i = \Sigma i\ (-\ \alpha + \beta\ E_i)\ dn_i \qquad (8.4)$$

But from (7.4) we have $\Sigma_i\ dn_i = 0$ and from (7.10) taking $M = U$ we have $\alpha = \beta U$. Thus from (8.4) it comes:

$$\Sigma i\ ln\frac{v_i - n_i}{n_i}\ dn_i = \alpha\ \frac{dQ}{U} \qquad (8.5)$$

Let us then consider the maximum of the statistical weight W. From (7.3) and (8.4) we have:

$$dlnW = \Sigma_i\ \sum_i ln\frac{v_i - n_i}{n_i}\ dn_i = \alpha\ \frac{dQ}{U} \qquad (8.6)$$

For the perfect gas we have $U = 3/2kT$. As $\alpha = 1{,}5049$ approximating α to 1.5 then (8.6) becomes:

$$dlnW = \alpha\, \frac{dQ}{kT} \quad \text{soit} \quad dS = k\, dlnW \tag{8.7}$$

When the Boltzmann' relation is used to find the maximum of the statistical weight the relation (8.7) is a good approximation in the case of the perfect gas. For the solids in the temperature region of the Dulong and Petit law, in place of k one has to use $2k$. But the correct method is that giving $D(E,U)$. Now as soon as we have to take into account a small increase dU of U the mean thermal energy, the Boltzmann relation is not sufficient.

Now if in place to take $M = U$ we keep its value using (6.2) and (7.10) giving $\alpha = \beta U$, the differential entropy dS of the relation (8.7) becomes:

$$dS = k(1 + \varepsilon)\, dlnW \tag{8.8}$$

The epsilon term is characteristic of the perturbations. This relation shows the influence of the perturbations on Boltzmann relation. In all measurements taking place with exchanges of thermal energy there are always an influence of the perturbations lead by the thermal radiation.

9 Conclusion

The most probable distribution is the result of ceaseless perturbations. They are the result of positive or negative losses of thermal energy in the set of particles and of a positive or negative flux of heat mainly from the heat bath to compensate the losses. This means that the bath is not at a very different temperature from that of the set of particles. As a result the maximum of the statistical weight is obtained for a value M of the energy not very different from U. It seems possible that the perturbations play a role in different experiments for example the paradoxical results involving the second law of thermodynamics [15] as we have already underlined in a previous work [16]. We hope that this aspect of the thermodynamics statistic will appear as a source of new progress in a near future.

To finish let us take again our conclusion in the study of the black body [2]. We know that the temperature is a macroscopic variable which in accurate experiments stays well defined. We can put $M = 3kT_{eff}$, the measured or effective temperature is T_{eff}. This measured temperature includes the flux of energy need to balance the losses. It is always higher than the temperature

defined from $PV = RT$ the law of perfect gas allowing to define the mean energy of a monatomic gas as $U = 3k/2$ or that of a solid as $U = 3kT$ values used to determine the statistical distribution of the energy of the corresponding sets. In particular if we refer to the definition of the temperature standards: the triple point of water 273.15K that is 0.01°C and the gallium melting point 29.7646°C [17]-[19], there is, it seems to me, a contribution of the perturbations due to the thermal radiation to take into account to improve the fundamental measurements.

Annexe

The callculation of $D(E,U)$ given by (7.9).
We have already got:

$$D(E,U) = \frac{2D(M,U)}{1+\exp(\beta E - \alpha)} \tag{7.9}$$

Using the variable substitution $x = \beta(E - M)$, the relation (6.10) $\alpha = \beta M$ gives $x = -\alpha$ for $E = 0$. Then the relations (7.9), and (7.11) leads to:

$$2\,D(M,U) = \frac{\beta}{A} \quad \text{avec} \quad A = \int_{-\alpha}^{\infty} \frac{x\,dx}{1+e^x} \tag{A.1}$$

The equation (7.12) can be written:

$$\int_0^{\infty} \beta E D(E,U)\,dE = \beta U \tag{A.2}$$

Using (7.11) the equation (A.2) can be written:

$$\int_0^{\infty} \beta E D(E,U)\,dE = \beta U \int_0^{\infty} D(E,U)\,dE \tag{A.3}$$

It comes:

$$\int_0^\infty \beta(E-U)D(E,U)dE = 0 \tag{A.4}$$

The total amount of energy M is close to U. To use the same substitution x = $\beta(E-M)$ using (6.2) giving $M = (1 +\varepsilon)U$ and the relations (7.9), (7.10) and (7.12) it comes:

$$\beta(E-U) = \beta(E-M) + \beta(M-U) = x + \alpha\frac{\varepsilon}{1+\varepsilon} \tag{A.5}$$

For $E = 0$ the corresponding integration limit in A4 takes the vlue α. The equation A4 taking into account A1 and A5 becomes:

$$\int_{-\alpha}^\infty \frac{xdx}{1+e^x} = -\alpha A\frac{\varepsilon}{1+\varepsilon} \tag{A.6}$$

This relation is an equation that determines α. It gives:

$$\int_0^{-\alpha} \frac{xdx}{1+e^x} = \frac{\pi^2}{12} - \alpha A\frac{\varepsilon}{1+\varepsilon} \tag{A.7}$$

Developing $x(1+e^x)^{-1}$ into series with $x < 0$, we get:

$$\int_0^{-\alpha} \frac{xdx}{1+e^x} = \frac{\alpha^2}{2} + \sum_{n=1}^\infty \left[(-1)^n \frac{e^{nx}}{n^2}(nx-1)\right]_0^\alpha \tag{A.8}$$

From the relation: $\qquad \sum_{n=1}^\infty \frac{(-1)^n}{n^2} = \frac{\pi^2}{12}$ $\tag{A.9}$

and
$$\sum_{n=1}^{\infty} (-1)^{n+1} \alpha \frac{e^{-n\alpha}}{n} = \alpha \ln(1 + e^{-\alpha})$$ (A.10)

it follows :

$$\frac{\alpha^2}{2} + \alpha \ln(1 + e^{-\alpha}) + \sum_{n=1}^{\infty} \left[(-1)^{n+1} \frac{e^{-n\alpha}}{n^2} \right]_0^{\alpha} = \frac{\pi}{6} - \alpha A \frac{\varepsilon}{1 + \varepsilon}$$ (A.11)

If one can take $\varepsilon = 0$ then α is very close to 1.5. A more accurate calculation gives $\alpha = 1.5049$. With this value of α we get A = 1.7054. The study of the case with $\varepsilon \neq 0$ is a little longer and is not often need; we will not do it here. The relation (7.13) gives the expression of $D(E,M)$.

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