Wrong construing of the Boltzmann factor; $E = h\nu$ is wrong

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Abstract

As we know probability of finding a system in one of its accessible states is propertial to the Boltzmann factor. It is shown that contrary to what is thought at present in this proportion the energy appearing in the Boltzmann factor is not a variable but it is a constant and the variable is the state accessible for the system having this constant energy. So, what at present is accepted as Boltzmann factor is not real. Deduction of the Maxwell velocity distribution as an instance of the consequences of the real Boltzmann factor, and the first deduction of the relation $E = h\nu$ as an instance of the consequences of the wrong Boltzmann factor are presented. A logical review of some of the fundamental elements of the statistical mechanics, that also contains some new viewpoints, has been necessary. A factor is introduced in a general expression for molar specific heat which plays the role of partition (not equipartition) of energy and giving suitable amounts to it all the practical cases including ones related to ideal gases and crystalline solids are covered.

1   Introduction

The Boltzmann factor is a famous factor upon which several important relations have been obtained in physics. Unfortunately, carelessness about the essence of the parameters used in this factor has caused an untrue understanding of it. In other words the factor which at present is being used under the name of Boltzmann factor, because of using of some quantities other than what must be used in it, is a wrong factor.

In this paper the above material are proven in detail. In addition, some samples of the valid results obtained from the correct form of the Boltzmann factor and some samples of the current invalid results obtained

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from the wrong construing of this factor, including Planck's deduction of the famous relation $E = h\nu$, are shown.

2 Necessary elements of the statistical mechanics

State of a system of some particles, which don't have any influence on each other (except probably collision), will be specified by knowing the position and the momentum of each of these particles. We take into consideration a six-dimensional space named as phase space in which each point has six components x, y, z, p_x, p_y, and p_z. We divide the phase space into small cells volume of each being $\delta x \delta y \delta z \delta p_x \delta p_y \delta p_z$. If we prescribe $\delta x \delta p_x = h'$ and $\delta y \delta p_y = h'$ and $\delta z \delta p_z = h'$, then the volume of each of these cells will be h'^3. Each particle in its position and momentum is in fact placed in a point in the phase space and in fact is set in a cell of volume h'^3. We suppose that while a particle is being set in each point inside a cell, its energy change, ie its kinetic energy change, is negligible. Thus, in fact to each cell an energy is connected which is related to a particle inside this cell. It is obvious that f particles, forming an isolated system, are occupying f cells (being not necessarily different) in the phase space and their total energy will be conserved. It is certain that it is possible that the positions of the particles in the phase space will be changed, but this process will proceed in a definite path, namely in some path in which the total energy of the particles will be conserved. Therefore, for a definite total energy a definite path in the phase space will be distinguished in which the system can proceed. Attention to this fact is important that since a cell volume of the phase space doesn't have a differential magnitude, ie zero magnitude, although it is considered much small, it is possible that for a definite total energy, E, the path will remain the same and won't be changed in a much small energy interval about this energy, E. In fact since each cell volume in the phase space doesn't have a differential, ie in fact zero, magnitude, the path related to a definite energy in the phase space is not a continuous path, but it is in fact in the form of a successive series of various configurations of a definite set of points in the phase space. For example if we suppose that the energies connected to the cells of the phase space shown in the figure are proportional to the numbers written in the cells, then the path related to the energy 6 of two particles will be the same shown at subsequent figures. (Of course the displacement of these configurations by each other is completely unimportant, just like the unimportance of the displacement of the points of a curve by each other which will not at all change the essence of the curve.)

In an isolated system, with a total energy E, we call each of these configurations of the path related to E as an accessible state for the system. We call the number of the total of these configurations as $\Omega(E)$. On definition we say that an isolated system is in the equilibrium state when the probability of finding the system in each of its accessible states

is independent of time, ie when always a definite fraction of a numerous number of these systems is related to an accessible state.

Now we express here two important statistical postulates:
a) If an isolated system is in equilibrium state, then all of its accessible states will be equiprobable, and vice versa.
b) If an isolated system is not in equilibrium state, then it will transform during the time till it will reach the equilibrium state.

Now suppose that our isolated system consists only of a particle with the energy ϵ. We know that this particle has three degrees of freedom. Let's set at present this particle at freedom in only one of these degrees. It is clear that in a specified time interval this particle can pass through some paths the number of which is proportional to the speed of the particle. Then, if the particle (kinetic) energy becomes n fold, total number of its accessible states will become $\sqrt{n}$ fold, because in fact the speed will have become $\sqrt{n}$ fold. Therefore, in this case that the particle has only one degree of freedom, the total number of its accessible states is proportional to $\epsilon^{1/2}$; but since in practice the particle has three degrees of freedom, the total number of its accessible states is proportional to $\epsilon^{1/2}\epsilon^{1/2}\epsilon^{1/2}$, ie $\Omega(\epsilon)$ is proportional to $\epsilon^{3/2}$.

Now suppose that we have an f-particle isolated system with a total energy E. Mean energy of each particle is $\epsilon = E/f$. When $\Omega(E)$ is the total number of accessible states of the system with energy E, we say that $\omega(\epsilon)$ is the total number of accessible states of one particle of this system with energy ϵ. As we indicated we have $\omega(\epsilon)$ being proportional to $\epsilon^{3/2}$. For evaluating $\Omega(E)$ we know that on the average there are $\omega(\epsilon)$ accessible states for each particle and then in general there will be $\omega(\epsilon)^f$ accessible states for f particles. Thus $\Omega(E)$ is proportional to $\omega(\epsilon)^f$, and since $\omega(\epsilon)$ is proportional to $\epsilon^{3/2}$, we conclude that $\Omega(E)$ is proportional to $\epsilon^{3f/2}$.

Suppose that the two systems A and A' are in energetic contact with each other, but the set of these two systems is isolated. We name the set of these two systems as A^*. Since A^* is isolated, its total energy, E^*, must remain constant. We suppose that $\Omega^*(E^*)$ is the total number of accessible states of the isolated system A^*, and $\Omega^*(E^*)_E$ is the total number of accessible states of A^* in each of which the energy of the system A is E. Probability of finding the energy of A equal to E is $P(E) = \Omega^*(E^*)_E/\Omega^*(E^*) = c\Omega^*(E^*)_E$ in which $c = 1/\Omega^*(E^*)$ is a constant coefficient independent of E. $\Omega(E)$ is the number of accessible states for the system A with the energy E, and $\Omega'(E^* - E)$ is the number of accessible states for the system A' with the energy $E' = E^* - E$, and $\Omega(E)\Omega'(E^* - E)$ is the number of accessible states for the system A^* in each of which the energy of the system A is E, ie $\Omega^*(E^*)_E = \Omega(E)\Omega'(E^* - E)$, and therefore $P(E) = c\Omega(E)\Omega'(E^* - E)$.

Let's see under which conditions the curve of $P(E)$ in terms of E will have its maximum. Since $E \geq 0$ and then certainly $P(E) > 0$, for

extremum we have:

$$\frac{dP(E)}{dE} = 0 \Leftrightarrow (\frac{d}{dE}lnP(E) = \frac{1}{P(E)}\frac{dP(E)}{dE}) = 0$$

and in the point of extremum, ie when we have $dP(E)/dE = 0$, we shall also have:

$$\frac{d^2P(E)}{dE^2} \gtreqqless 0 \Leftrightarrow (\frac{d^2}{dE^2}lnP(E) = \frac{1}{P(E)}\frac{dP(E)}{dE}) \gtreqqless 0.$$

Therefore, the conditions that cause maximization of the curve $P(E)$ in terms of E are the same conditions that cause maximization of the curve $lnP(E)$ in terms of E, and we shall investigate this recent case. We have:

$$P(E) = c\Omega(E)\Omega'(E') \Rightarrow lnP(E) = lnc + ln\Omega(E) + ln\Omega'(E^* - E)$$

$$\Rightarrow \frac{dlnP(E)}{dE} = \frac{dln\Omega(E)}{dE} + \frac{dln\Omega'(E^* - E)}{dE} = \frac{dln\Omega(E)}{dE} - \frac{dln\Omega'(E^* - E)}{d(E^* - E)}$$

$$= \frac{dln\Omega(E)}{dE} - \frac{dln\Omega'(E')}{dE'}.$$

Therefore, it is seen that the condition under which $P(E)$ is extremum is that the expression $dlnP(E)/dE = dln\Omega(E)/dE - dln\Omega'(E')/dE'$ to be equal to zero, ie this condition is establishment of the equality $dln\Omega(E)/dE = dln\Omega'(E')/dE'$ or $\beta(E) = \beta'(E')$ where $\beta(E) = dln\Omega(E)/dE$ and $\beta'(E') = dln\Omega'(E')/dE'$. We shall now prove that this condition for being extremum is the same condition for maximization. We have:

$$(E = f\epsilon \quad \& \quad \Omega(E) \propto \epsilon^{3f/2}) \Rightarrow \Omega(E) \propto E^{3f/2} \Rightarrow ln\Omega(E) = cte. + \frac{3f}{2}lnE$$

$$\Rightarrow (\beta(E) = \frac{dln\Omega(E)}{dE}) = \frac{3f}{2}.\frac{1}{E} \Rightarrow (\frac{d\beta(E)}{dE} = \frac{d^2ln\Omega(E)}{dE^2}) = \frac{-3f}{2}.\frac{1}{E^2} < 0,$$

and similarly

$$(E' = f'\epsilon' \quad \& \quad \Omega'(E') \propto \epsilon'^{3f'/2}) \Rightarrow \Omega'(E') \propto E'^{3f'/2}$$

$$\Rightarrow ln\Omega'(E') = cte'. + \frac{3f'}{2}lnE' \Rightarrow (\beta'(E') = \frac{dln\Omega'(E')}{dE'}) = \frac{3f'}{2} \cdot \frac{1}{E'}$$

$$\Rightarrow (\frac{d\beta'(E')}{dE'} = \frac{d^2ln\Omega'(E')}{dE'^2}) = \frac{-3f'}{2} \cdot \frac{1}{E'^2} < 0$$

Therefore, $P(E)$ will be maximum if and only if $\beta(E) = \beta'(E')$.

Temperature of a system of particles (solid, liquid or gas) is an expression proportional to the mean kinetic energy (excluding the potential one) of each molecule (or particle) of the system. Proportion constant should be selected properly one time for always. This act will be done soon. It should be emphasized that what the thermometers show as the temperature of a system is the mean kinetic energy of the molecules of the system (regardless of the kind of the system as solid, liquid or gas)

not also probably the (mean) potential energy of the molecules of the system. The reason of this statement is, in a quite intuitive manner, that it is only the motion of the molecules that can have practical effect on the thermometer, not probably their potential static states.

The system we have discussed so far in this article is a system which, as conditioned at first, its molecules don't have any influence on each other (except probably collision) (ie it is practically a set of the molecules of a perfect gas), and then all the energies indicated by E or ϵ are kinetic (not also potential which such an energy does not exist in such a system). Therefore, the mean kinetic energy of this set is $\epsilon = E/f$. We saw that $\beta(E) = 3f/(2E)$, and then $\epsilon = E/f = 3/(2\beta(E))$. Therefore, temperature is an expression proportional to the recent expression. We indicate the temperature by T and the proportion constant (which we want to be positive) by $2/(3k)$. In this manner we shall have:

$$T = \frac{2}{3k}\epsilon = \frac{2}{3k} \cdot \frac{3}{2\beta(E)} = \frac{1}{k\beta(E)}.$$

We see that the temperature of a system, which is proportional to the mean kinetic energy of its molecules, takes the form of $T = 1/(k\beta(E))$ in the case of the system under discussion. (k is named as Boltzmann constant.)

We saw that the condition of maximization of the curve $P(E)$ in terms of E was the establishment of the equality $\beta(E) = \beta'(E')$. This means, according to the definition of temperature, that the condition of maximization of $P(E)$ is that T and T', which are in turn the temperatures of the systems A and A', to become equal to each other. It is obvious that if E is such that T isn't equal to T', then the systems A and A' will be in states of little probability, and then will interchange so much energy that at last the result $T = T'$ will be obtained. Since $dT/dE = (-1/(k\beta^2))(d\beta/dE)$ and we saw $d\beta/dE < 0$, we have $dT/dE > 0$. (In a similar manner we can see that also $dT'/dE' > 0$.) This means that, as expected, the (kinetic) energy will flow toward that system which its temperature is less. (It can be seen from the relation $T = 1/(k\beta) = 1/(k(3f/(2E))) = 2E/(3kf)$ that if $E = 0$, we shall have $T = 0$, and if $E = \infty$, we shall have $T = \infty$.)

Considering the relation which we now have between the temperature and the mean kinetic energy of the molecules ($T = 2\epsilon/(3k)$), let's see what more we can say about the molecules of a perfect gas.

As performed in most of the preliminary textbooks, we can consider a molecule of the gas and calculate difference between its momentums before and after its hitting against a wall of the container, and consider the time of its travel between the walls and the number of the molecules of the gas. (For example see Physics by Halliday and Resnick, John Wiley & Sons, 1978.) In this manner we finally shall obtain $p = \rho\overline{v^2}/3$ in which p is the gas pressure, ρ is the (mass) density of the gas, and $\overline{v^2}$ is the mean value of the squares of the speeds of the molecules. Indicating the total mass of the gas molecules by M, the mass of each molecule by m, the

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volume occupied by the molecules by V, and the number of the molecules by N, we have

$$p = \frac{1}{3}\rho\overline{v^2} = \frac{1}{3}\frac{M}{V}\overline{v^2} \Rightarrow pV = \frac{2}{3}M\frac{\overline{v^2}}{2} = \frac{2}{3}Nm\frac{\overline{v^2}}{2} = \frac{2}{3}N(\frac{1}{2}m\overline{v^2}) = \frac{2}{3}N\epsilon$$

in which, as before, ϵ is the mean kinetic energy of each molecule ie is equal to $(1/2)m\overline{v^2}$. We saw, beforehand, that $T = 2\epsilon/(3k)$ or $\epsilon = (3/2)kT$, and then $pV = (2/3)N((3/2)kT) = NkT = nN_0kT$ in which n is the number of moles of the molecules and N_0 is Avogadro's number. Since both N_0 and k are constant, the factor N_0k is shown by a single constant, R (named as gas constant). Therefore, we have $pV = nRT$.

3   The real Boltzmann factor

Now we proceed to the more fundamental part of this paper. So far we have been discussing about $P(E)$, which was the probability of finding the energy of the system A equal to E. Now we want to know the probability of finding the system A with energy E in the quite special state r, ie we want to find the probability of finding the system A in a special one of its accessible states while the energy of A is the constant value E. This probability is obviously equal to $P_r = \Omega^*(E^*)_{rE}/\Omega^*(E^*) = c\Omega^*(E^*)_{rE}$ in which $\Omega^*(E^*)_{rE} = 1 \times \Omega'(E^* - E)$ and then $P_r = c\Omega'(E^* - E) = c\Omega'(E')$. (See Statistical Physics, Berkeley physics course, by Reif, McGraw-Hill, 1975.) We suppose that $E \ll E^*$. Let's expand $ln\Omega'(E')$ in the form of a Taylor series about the point $E' = E^*$:

$$ln\Omega'(E') = ln\Omega'(E')|_{E'=E^*} + \frac{dln\Omega'(E')}{dE'}|_{E'=E^*} \cdot (-E)$$

$$+\frac{1}{2!}\frac{d^2ln\Omega'(E')}{dE'^2}|_{E'=E^*} \cdot (-E)^2 + \frac{1}{3!}\frac{d^3ln\Omega'(E')}{dE'^3}|_{E'=E^*} \cdot (-E)^3 + \cdots.$$

We know that

$$ln\Omega'(E') = cte.' + \frac{3f'}{2}lnE'$$

because

$$(E' = f'\epsilon' \quad \& \quad \Omega'(E') \propto \epsilon'^{3f'/2}) \Rightarrow \Omega'(E') \propto E'^{3f'/2}.$$

Then

$$\frac{d^nln\Omega'(E')}{dE'^n} = \frac{3(-1)^{n+1}(n-1)!f'}{2E'^n}$$

in which $n = 1, 2, 3, \cdots$. Therefore, the general term of the above expansion is $-(3f'/(2n))(E/E^*)^n$ (of course for $n = 0$ we have the first term of the expansion, ie $ln\Omega'(E')|_{E'=E^*}$), and since $(E/E^*) \ll 1$, we can write with a very good approximation

$$ln\Omega'(E') = ln\Omega'(E')|_{E'=E^*} - (3f'/2)E/E^*.$$

Now we assert that we can write $(-3f'/2)E/E'$ instead of $(-3f'/2)E/E^*$ with a very good approximation if $(E/E^*) \ll 1$, because

$\delta(E/E^*)/\delta E^* = -E/E^{*2}$ and since here $\delta E^* = E' - E^* = -E$, we have $\delta(E/E^*) = (E/E^*)^2$, and since $(E/E^*) \ll 1$, we conclude that $\delta(E/E^*) = (E/E^*)^2 \simeq 0$ with a very good approximation. Namely with replacing E^* by E' in the second term of the above relation the produced change is negligible because of excessive smallness. Therefore, we can write

$$ln\Omega'(E') = ln\Omega'(E')|_{E'=E^*} - \frac{dln\Omega'(E')}{dE'} \cdot E = ln\Omega'(E')|_{E'=E^*} - \beta'(E') \cdot E$$

$$\Rightarrow \Omega'(E') = cte.e^{-\beta'(E').E}$$

in which $cte.$ is independent of E'. Therefore, $P_r = c\Omega'(E') = c \cdot cte.e^{-\beta'(E') \cdot E}$ or

$$P_r = c'e^{-\beta'(E')E} \tag{1}$$

in which $c' = c \cdot cte.$ is a constant independent of E and E'. It must be emphasized again that the expression (1) is the probability of finding the system A, with constant energy E, in the quite special accessible state r, under the condition that A is in contact with the source A' and $E \ll E + E' = E^*$ and E^* will remain constant because of the isolation of the set of A and A'.

Unfortunately, there is a wrong construing of this equation (ie (1)) in the current statistical physics books. This wrong construing is that after replacing E in Eq. (1) by E_r, this equation is interpreted as the probability of this matter that the system A, which is in contact with the much more energetic system A', has an energy between the special energy E_r and the energy $E_r + \delta E_r$, while the set of A and A' is isolated. It is obvious that this interpretation is not at all real.

Indeed, P_r in Eq. (1) is not a function of E, but E in this relation plays the role of a constant. P_r is a function of different states accessible for the system A which has the constant energy E. In the wrong interpretation, explained just now, P_r is taken as a function of E_r; then one can integrate it over some extent of energy. Such an integration will be done over (E_r in) the exponent of e in the equation (because wrongly E is replaced by E_r in this equation).

But truly the only integration which can be done on Eq. (1) is over the different states accessible for the system with the constant energy (E), ie in fact over the variable r which itself doesn't appear as a mathematical factor. In such an integration, E plays only the role of a constant.

But what is really the cause of this wrong construing of Eq. (1)? The existence reason of this wrong construing is that for obtaining Eq. (1), instead of the explicit method of this paper the implicit method of Lagrangian multipliers is used often, which eventually results in a relation like

$$n_i = g_i e^{-\alpha} e^{-\beta u_i}$$

in which n_i is the number of molecules each having the energy u_i, and g_i is the probability of that a molecule has the energy u_i $(g_i = n_i/n)$,

and β and α are the Lagrangian multipliers which must be determined (eg see Perspectives of Modern Physics by Beiser, McGraw-Hill, 1969). It is obvious that by dividing of each side of the recent relation by n (the number of all the molecules) we have $n_i/n = (g_i e^{-\alpha}/n)e^{-\beta u_i}$ the left side of which gives the probability of that the molecule has the energy u_i, and we can say that this probability has linear proportion to $e^{-\beta u_i}$ only when the coefficient $g_i e^{-\alpha}/n$ is constant (ie does not depend on the energy u_i), and it is quite obvious that this is not the case (because as in Eq. (1), β depends on E' and then on E, or in other words as in the recent relation β depends on u_i, α can also depend on u_i). But, unfortunately, to this fact is not paid attention, and it is assumed that this probability is proportional to $e^{-\beta u_i}$. This is just the same current wrong construing of Eq. (1). The correct is that we say that in the true relation $n_i = g_i e^{-\alpha} e^{-\beta u_i}$ the factor $e^{-\beta u_i}$ is what that in this paper appears in the form of Eq. (1).

(Under the condition $E \ll E^*$ we showed that $P_r(E) = c' e^{-\beta'(E')E}$. It is obvious that we must have $\sum_r P_r(E) = 1$, in which the summation is over all the accessible states in energy E. Therefore, $c' = (\sum_r e^{-\beta'(E')E})^{-1} = (\Omega(E)e^{-\beta'(E')E})^{-1}$ and then, as it is expected, we shall have $P_r(E) = 1/\Omega(E)$. If y is a quantity that assumes the amount y_r when the system A, with the constant energy E, is in the state r, then the mean value of y will be obtained from the relation $\overline{y} = \sum_r P_r(E)y_r = (\sum_r y_r)/\Omega(E)$ which could be written in the unsimplified form of

$$\overline{y} = \frac{\sum_r e^{-\beta'(E')E} y_r}{\sum_r e^{-\beta'(E')E}}.$$

4   Maxwell velocity distribution

Before more continuing the discussion it is necessary to say that the relation (1) can yield the fundamental relations of the statistical mechanics. For showing this, we shall obtain the Maxwell velocity distribution:

We saw that if $E \ll E^*$, then $P_r \propto e^{-\beta'(E')E}$. It is obvious that this probability (ie P_r) is also proportional to the volume of the cell in the phase space, $h'^3 = \delta x \delta y \delta z \delta p_x \delta p_y \delta p_z$. Thus $P_r \propto e^{-\beta'(E')E} \delta x \delta y \delta z \delta p_x \delta p_y \delta p_z$.

P_r/h'^3 is the density of the probability of finding the system A, with the energy E, in the special state r, and we indicate it by $\mathcal{P}_r$. Thus

$$\mathcal{P}_r h'^3 = c_1 e^{-\beta'(E')E} h'^3$$

in which c_1 is the proportion constant. We have $\sum_r \mathcal{P}_r \delta x \delta y \delta z \delta p_x \delta p_y \delta p_z = 1$, which in differential and integral form we can write it as $\int_r \mathcal{P}_r dx dy dz dp_x dp_y dp_z = 1$. (It is important to mind that the integration must be done over the different r-states not over any special volume in the phase space.) Therefore,
$c_1 = 1/(\sum_r e^{-\beta'(E')E} \delta x \delta y \delta z \delta p_x \delta p_y \delta p_z)$ or
$c_1 = 1/(\int_r e^{-\beta'(E')E} dx dy dz dp_x dp_y dp_z)$.

In the case of a particle of a monoatomic perfect gas we have $E = 1/2mv^2 = p^2/(2m)$; so the expression $e^{-\beta'(E')mv^2/2}d^3rd^3p$, in which we have $d^3r = dxdydz$ and $d^3p = dp_xdp_ydp_z$, is proportional to the probability of finding the location of the particle in the cubic range between $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$, and the momentum of the particle in the cubic range between $\mathbf{p}$ and $\mathbf{p} + d\mathbf{p}$. Now since $m\mathbf{v} = \mathbf{p}$ and so $md^3v = d^3p$, we conclude that $e^{-\beta'(E')mv^2/2}d^3rd^3p$ is proportional to the probability of finding the location of the particle in the cubic range between $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$ and the velocity of the particle in the cubic range between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$. If the proportion constant of this proportion is c_2, then this probability will be $c_2e^{-\beta'(E')mv^2/2}d^3rd^3v$. If we integrate this probability over the unit volume about a definite point, the result, ie $\int_V c_2e^{-\beta'(E')mv^2/2}d^3rd^3v = c_2e^{-\beta'(E')mv^2/2}d^3v$ in which V is the same unit volume about the point, will be the probability of this matter that in a unit volume about this point, the end of the velocity vector of a particle, which has the absolute speed v, is in the cubic range between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$ (ie its velocity components are between v_x and $v_x + dv_x, v_y$ and $v_y + dv_y$, and v_z and $v_z + dv_z$). If we show this probability as a percentage, eg in the form of $m\%$, this will mean that if, in the unit volume about the given point, we evaluate simultaneously a hundred particles, each of which having the absolute speed v, from the totality of the particles which are similar to and independent of each other, we shall see that on the average only m particles of these one hundred particles will have the velocity vectors the end of each being in the cubic range between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$. So, if we have n_v particles with absolute speed v in the unit volume about that definite point, and evaluate them simultaneously, we shall see that $n_v \times (m/100)$ particles of them will have the above characteristic. Therefore, since we said that $(m/100) = c_2e^{-\beta'(E')mv^2/2}d^3v$, the expression $n_v \times (m/100) = n_vc_2e^{-\beta'(E')mv^2/2}d^3v$ is in fact the volume density of those particles which the end of the velocity of each of them is in the cubic range between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$, in a definite point $\mathbf{r}$ (or in fact in a desirable point $\mathbf{r}$, because there isn't any dependence on $\mathbf{r}$ on the right side of the recent relation). Since the range of the velocity is a differential range (d^3v), this volume density is also in fact differential, and if we divide it by d^3v, the velocitical density of the volume density of those particles which the end of the velocity vector of each of them is in the cubic range between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$ will be obtained that we show it by $f(\mathbf{v})$. Therefore, we reach the Maxwell velocity distribution: $f(\mathbf{v})d^3v = c_3e^{-\beta'(E')mv^2/2}d^3v$ in which $c_3 = n_vc_2$.

5 Consequences of the wrong construing of the Boltzmann factor

In this section we want to see how the first deduction of the relation $E = h\nu$ has been based on the wrong construing of the Boltzmann factor.

So we accept the relation (1) in the form of $P_{E_r} = c'e^{-\beta'(E')E_r}$ deliberately temporarily and then we shall evaluate its consequences: Since $\sum_r P_{E_r} = 1$, we have $c' = 1/(\sum_r e^{-\beta'(E')E_r})$ and so

$$P_{E_r} = e^{-\beta'(E')E_r}/(\sum_r e^{-\beta'(E')E_r}).$$

Now we divide each side of the recent relation by δE_r:

$$\frac{P_{E_r}}{\delta E_r} = \frac{e^{-\beta'E_r}}{(\sum_r e^{-\beta'E_r})\delta E_r}$$

in which the expression on the left side is the density of probability, and in limit will result in the relation $\mathcal{P}_{E_r} = e^{-\beta'E_r}/\int_0^\infty e^{-\beta'(E')E_r}dE_r$, and since $\int_0^\infty e^{-\beta'E_r}dE_r = 1/\beta'$, we shall have $\mathcal{P}_{E_r} = \beta'e^{-\beta'E_r}$ which is the density of probability of finding the system A with some energy between E_r and $E_r + \delta E_r$. If we have a big system consisting of some numerous number of smaller systems (eg each similar to A) such that all of them are in contact with a thermal source which is much more energetic than each of them, then the mean value of the energy of each of these small systems will be $\overline{E} = \int_0^\infty E_r\mathcal{P}_{E_r}dE_r$ or $\overline{E} = \int_0^\infty \beta'e^{-\beta'E_r}E_rdE_r = 1/\beta' = kT'$ in which T' is the source temperature and k is the Boltzmann constant. (Just here we see another contradiction, because while it is claimed that $\overline{E} = kT'$ is the mean energy of the small systems which are in contact with a thermal source which its temperature is T', the limit of the smallness of these systems is not at all distinct, and so if we suppose that the source is the whole universe for example, we can suppose that the big system, mentioned above, to be a set of some separate molecules in a turn, and in another turn to be a set of some separate blocks of stone for example, while in each turn we shall obtain the same result $\overline{E} = kT'$ for the mean value of the energy of each molecule or each block! It is obvious that this is quite irrational.) Since according to the current equipartition theorem the mean value of the energy of each particle of a system of particles having both kinetic and elastic potential energies, is equal to $1/2kT' + 1/2kT' = kT'$, the obtained $\overline{E} = kT'$ can be interpreted as the mean value of the energy of these particles.

Now we suppose that these particles are the contents of a blackbody cavity in the temperature T'. Experience shows that the mean energy of the cavity radiation is about kT' for the frequencies approaching zero, but is about zero for the frequencies approaching infinity. As an attempt to justify this matter, we can draw the curve of $E_r\mathcal{P}_{E_r}$ in terms of E_r (see Quantum Physics of atoms, molecules, solids, nuclei and particles by Eisberg and Resnick, John Wiley & Sons, 1974). Since $\mathcal{P}_{E_r} = (1/(kT'))e^{-E_r/(kT')}$, the maximum of the curve will occur in $E_r = \overline{E} = kT'$, also we have

$$\overline{E} = \int_0^\infty E_r\mathcal{P}_{E_r}dE_r = kT'$$

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which is equal to the area under the curve. If we suppose that E_r can exist in discontinuous forms of 0, ΔE_r, $2\Delta E_r$, $3\Delta E_r$, $\cdots$, then we shall see that $\overline{E} \approx kT'$ when $\Delta E_r \approx 0$, and $\overline{E} \approx 0$ when $\Delta E_r \approx \infty$. Comparison of these results with the previous results obtained by the experience indicates that we must have $\Delta E_r \propto \nu$.

Above reasoning is Planck's reasoning in obtaining the relation $\Delta E_r \propto \nu$ or $E = h\nu$; but as we said, this reasoning is on the basis of a quite wrong construing of Eq. (1). Therefore, the equation $\Delta E = h\nu$ or simply $E = h\nu$ may be valid only if it can be derived uniquely from the results obtained from the photoelectric effect (which is not of course the case as shown in the paper "Classical justification of the photoelectric effect").

The Langevin formula for orientational polarizability has also been obtained in a similar manner by using the above mentioned wrong construing of Eq. (1), and then can not be valid unless it can be obtained through another way.

6 Specific heat of solids and gases

Maybe it is said that but the equipartition theorem has been obtained by using the very current construing of the Boltzmann factor which according to this paper is wrong. (To prove this theorem, in fact, integration is done over different energies not over different forms of a constant energy.) And important is that the result of this theorem can predict the empirical relation $c_V = 3R$ valid for hot crystalline metals. Thus, let's see what the actuality is:

As we said, temperature of a set of molecules is an expression proportional to the mean kinetic energy of them. Indicating this mean kinetic energy by ϵ, the total kinetic energy (not including the potential one) of the molecules of the set by E, and the number of the molecules of the set by f, we saw that for the temperature of the system (or set), T, we have

$$T = \frac{2}{3k}\epsilon = \frac{2}{3k}\frac{E}{f} = \frac{2}{3R/N_0}\frac{E}{f} = \frac{2E}{3(f/N_0)R} = \frac{2}{3nR}E \tag{2}$$

in which R is the gas constant, k is the Boltzmann constant, N_0 is Avogadro's number and n is the number of moles of the molecules of the set.

Notice a point again. Temperature is the mean "kinetic" energy of each molecule, not its mean total energy regardless of its kind (including probably its potential energy). Therefore, if we should calculate the expression

$$c_V = \frac{1}{n}\frac{dU}{dT} \tag{3}$$

for the molar specific heat of a crystalline solid by giving it the energy dU and measuring its increment of dT in temperature, we must be attentive that U in this relation (ie in Eq. (3)) is other than the term E in Eq. (2).

In other words all the energy given to the set won't necessarily be conserved as the kinetic energy of the molecules of the set, but a part of the given energy may be conserved, eg, in the form of potential energy of the molecules of the set if possible.

Then, we suppose that the conditions of the molecules of the set are such that only $1/z$ of the energy given to the set conserves in the form of kinetic energy of the molecules of the set and the rest of it conserves as the potential energy of these molecules. Then, we must write $E = U/z$ which considering Eq. (2) results in $T = 2U/(3nRz)$ which leads to $U/n = 3/2RzT$ whereby we shall have $n^{-1}dU/dT = 3/2Rz$. Therefore, we have

$$c_V = \frac{3Rz}{2} \qquad (4)$$

for Eq. (3).

For ideal gases that all the energy given to the gas molecules are conserved as their kinetic energy and z is equal to one for them, we have $c_V = 3/2R$. But for a crystalline solid which, on average, half of the energy of each of its molecules, like an oscillating spring, is in the form of kinetic energy and the other half is in the form of potential energy, z is equal to 2. In this case we shall have $c_V = 3R$ for Eq. (4). As we see the empirical equation $c_V = 3R$ for hot crystalline metals has been obtained without any necessity to use the current wrong construing of the Boltzmann factor.

The mechanism presented above by introducing the factor z merits the name of partition of energy instead of equipartition of energy.

1	2	3
4	5	6
7	0	3