Analytical Proof of the Second Law of Thermodynamics from the Basis of the Conservation of Total Energy

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Suppose there existed an arbitrary body that was made up of r material points (atoms). We would write the rectangular coordinates of the atoms with $x_1, y_1, ...z_r$, the velocities with $v_1, v_2, ...v_r$, and the components in terms of $u_1, v_1, w_1, ...w_r$. Finally, let χ be the potential energy, also a function of x_1, y_2, z_r, whose negative differential quotient in relationship to the coordinates of some atom yields the effective force on the atom in the direction of the aforementioned coordinate axis.

Let the external properties (temperature, and that of the operating forces) found in the body, be unchanged for a very long time T, and in some fraction of T, where $x_1, y_1...z_r, u_1, v_1, w_r$ are in between the borders

$$x_1 \text{ and } x_1 + dx_1, y_1 \text{ and } y_1 + dy_1, ...w_r \text{ and } w_r + dw_r, \tag{1}$$

be denoted as τ.

The ratio τ/T, I designate as the time, which is the average state of the body in condition (1). I found in the previous paper under certain assumptions, this ratio (if the body is in contact with a resovoir of gas molecules) has the value

$$dt = \frac{e^{-h\phi}dx_1 dy_1...dx_r du_1 dv_1...dw_r}{\int \int e^{-h\phi}dx_1 dy_1...dw_r}, \tag{2}$$

where

$$\phi = \chi + \Sigma \frac{mv^2}{2}. \tag{3}$$

This formula is different from the last formula in the previous paper, because here the same probability of all velocity directions is expressed, and the constant λ'' has been determined. We can extract this through inference, and without complete speculation, from the findings in my paper "On Thermal Equilibrium in Polyatomic Gas Molecules." It should describe one of the gas molecules which surround the body which is made up of ρ atoms. The coordinates of the center of mass of this molecule should be x, y, z; the coordinates of its atoms in terms of three axes whose fixed coordinate axes are drawn parallel to the center of mass coordinates and are called $\xi_1, \eta_1, ...\zeta_\rho$ and the velocity components of the atoms parallel to the fixed axes are $\alpha_1, \beta_1, ...\gamma_\rho$. All the gas molecules with kinetic energy should be denoted ϕ^*. Finally, of the types of gas considered to

have molecules, there should be N molecules in a unit volume. I found in the paper "On Thermal Equilibrium in Polyatomic Gas Molecules." that the number of molecules of this gas in the unit volume which have coordinates $\xi_1, \eta_1, ...\zeta_{\rho-1}, \alpha_1, \beta_1, ...\gamma_\rho$ and lie between the boundaries

$$\xi_1 \ and \ \xi_1 + d\xi_1, \eta_1 \ and \ \eta_1 + d\eta_1, ...\gamma_\rho \ and \ \gamma_\rho + d\gamma_\rho, \tag{4}$$

so,

$$dN = ae^{-h\phi^*} d\xi_1 d\eta_1 ... d\gamma_\rho, \tag{5}$$

where a and h are introduced as contants. The onset of an interaction of one of these molecules with the body K, and collisions of the same type, should be characterised thusly that a known function of the relative position of all of the atoms of the body K and with the collided molecules F $(x_1, y_1, ...z_r, x, y, z, \xi_1, \eta_1...\zeta_{e-1})$ be set as a known constant b. The same equation should describe the end of all the collisions. We want to describe the change through an unknown time τ, in which during the course of a very long time T, the states of the body lie between the border (A), with $Tg dx_1 dy_1 ... dw_r$, so that also $g dx_1 dy_1 ... dw_r$ is the time, where on average the state of the body lies between the borders. Then g is a function of $x_1, y_1...z_r, u_1, v_1...w_r$. The state of the collisions of the body is completely known at the beginning of the collsions, if the value of $6r + 6\rho - 1$ (a function of $x_1, y_1...z_r, u_1, v_1...w_r, \xi_1, \eta_1...\zeta_{\rho-1}, \alpha_1, \beta_1...\gamma_\rho, x, y$) is known at this moment. z is known for the beginning of the collisions through the applicable equation $F = b$. Through a similar examination, which I talked about in my paper "On Thermal Equilibrium of Polyatomic Gas Molecules", you can satisfy yourself that the number of collisions which happen in the time T that in the moment the collisions began (C): the collisions of the body K has variables in range (A); the molecules are in range (B); x is between x and $x + dx$, y between $y and dy$ which is

$dm = \tau dN \omega dx dy = Tg ae^{-h\psi^*})\omega dx_1 dy_1 ... dw_r d\xi_1 ... d\gamma_\rho$, where $\omega = \frac{i}{\frac{\delta F}{\delta x}}(\frac{\delta F}{\delta x_1}\frac{\delta x_1}{\delta t} + \frac{\delta y}{\delta y_1}\frac{\delta y_1}{\delta t} + ... \frac{\delta F}{\delta x}\frac{\delta x}{\delta t}$. The state of the colliding body should have known variables if in the moment of the the beginning of the collisions lies between borders (C) and the moment of end, the same lies between the border (D) $X_1 and X_1 + dX_1, Y_1 and Y_1 + dY_1...W_r and W_r + dW_r, \Xi_1 and \Xi_1 + d\Xi_1, H_1 and H_1 + dH_1...Y and Y + dY$.

Then you can reach the case just as I discussed in my paper through the equation $\omega D = \Omega$, where d is the functional determinant $\Sigma \pm \frac{\delta x_1}{\delta X_1}\frac{\delta y_1}{\delta Y_1}...\frac{\delta w_r}{\delta W_r}\frac{\delta \xi_1}{\delta \Xi_1}\frac{\delta \eta_1}{\delta H_1}...\frac{\delta y}{\delta Y}$.

With Ω, G, Φ^*, we want to express the terms in which $\omega, g\phi^*$ are passed over if you substitute X_1, Y_1 for x_1, y_1. The number of collisions, which happen in the time T where the variables lie between the specification (D) in the beginning are $dM = TGae^{-h\Phi^*}\Omega dX_1 dY_1 dW_r d\Xi_1 ... dY$. You can express $X_1, Y_1...$ as a function of $x_1, y_1...$ and vice versa. If you do that to the previous form, you obtain $dm = Tg ae^{-h\phi^*}\omega D dX_1 dY_1...dW_r d\Xi_1...dY$. This is the number of collisions that happen within the time T, when the end lies in range (D). You can also think of the variables $x_1 y_1...$ in g, ω and ϕ^* as being expressed in terms of $X_1 Y_1...$. We integrate dm over all possible values of the gas molecules, also over all the possible values of $\Xi_1, H_1...Z_{\rho-1}$, so that we wind up with the number of collisions happening in the time T, where the determining variables of state of the body

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lie in range (E) X_1 and $X_1 + dX_1, Y_1$ and $Y_1 + dY_1...W_r$ and $W_r + dW_r$, while the determining variables of the state of the molecules are not subject to any restrictions. This number will be denoted with $\int dm$ (where the integration is performed over the determining variables of the state of the gas molecules). We now first want to theoretically consider a special case not found in nature, that will make the examination of the general cases easier. Namely, we want to accept that the collisions happen so often that momentarily when a collision ceases, then next begins already, but that the molecule is never in two collisions at once. If at the end of the collisions, it lies between the border (E), the atomic motion of the body, when there is no collision, always withdraws from this border. There, when the body is withdrawing from a molecular collision, no second collision takes place, so we want to exclude this time from the entire time T, and using T we want to understand the essence of all moments when the body is not colliding with anything. With this condition, the number of collisions that occur where the variables at the end lie between the border (E) is the same as the number that happen when the variables at the beginning lie at this same border. Because the former is the number of how often the variables occur between these borders, and the second is how often this happens, then under this assumption, you can neglect the number of comings and goings as a result of atomic motion of hte body without collisions with other gas molecules. The first is $\int dm$; the second you can obtain when you integrate $dM = TGae^{-h\Phi^*}\Omega dX_1 dY_1 dW_r d\Xi_1...dY$ over all possible values for the state of the gas molecules. We want to refer to this as $\int dM$. It is also clear that this is a single condition for determining what the function g is. But this condition that $\int dm = \int dM$ is satisfied if you set $g = Ae^{-h\phi}$, which you can convince yourself of in the following manner. substitute this value for g into the condition $\int dm = \int dM$, and put in the values of dm and dM from the previous equations and divide through by $TaAdX_1 dY_1...dW_r$, giving $\int \int ...e^{-h(\phi+\phi^*)}\omega D d\Xi_1 dH_1...dY = \int \int ...e^{-h(\Phi+\Phi^*)}\Omega d\Xi_1 dH_1...dY$ and substitute Ω for ωD. Here ϕ and ϕ^* contain the total potential and kinetic energy in the body and molecule before the collision, Φ and Φ^* are the total after the collisions. You can express ϕ and ϕ^* with the values $x_1 y_1...$ as functions of $X_1 Y_1...$ and obtain Φ and Φ^* in terms of ϕ and ϕ^*. Now together all of the potential and kinetic energy in the body and the molecule is conserved, meaning that $\phi + \phi^* = \Phi$ and Φ^*; and when we integrate the function over all values of the variables, $\int dm$ and $\int dM$ are the same! This is performed to find the assumed value of g which requires the condition that $\int dm = \int dM$ and it follows also the time during which the body lies in range (A) gives equation (1). In this formula g has that value. (Assuming the constant A is appropriately determined). I've already done this in my paper "On Thermal Equilibrium in Polyatomic Gas Molecules" that through formula (1) the state distribution would not be changed through the atomic motion in the body without collisions; consequently, the probability of the different states fo the body can be found using formula (1), when the intial assumption that the collisions happen so often that the atomic motion without collisions has no impact on the state distribution are not true anymore. Formula (1) still remains valid if the collisions happen so infrequently that the body is in contact with more than one molecule at once, which we previously disallowed. Incidentally, this shows that in the complicated case,

if these simultaneous collisions take place so often, by formula (1), they still don't alter the state distribution. Bodies which are in contact with gas naturally have collisions that take place simultaneously; but the parts of the body that interact with different gas molecules don't interact in any distinct direction, therefore, the body must always be colliding with some gas molecule. We will now suppose that the state distribution in a thermal body, also if it is not in contact with a gas, would be the same. Under this assumption, formula (2) applies to every thermal body, and I will now show that in the same manner an analytical proof of the second law of thermodynamics can be derived.

Equation (2) can be used to determine the average value of some quantity X.

That is,

$$\overline{X} = \int X dt, \tag{6}$$

where the integration is over all values of the variable, dt contains the differential. With this method, we lookk for the average kinetic energy of some atom, so the integral (which contains χ) reduces and gives the following:

$$\frac{m\overline{v}^2}{2} = \int \frac{mv^2}{2} dt = \frac{3}{2}\frac{1}{h}. \tag{7}$$

This is true for all atoms and the constant h is inversely proportional; we can, therefore, view the average kinetic energy of the atom or the reciprocal value of the constant h as a measure of temperature. In any case, the temperature is the function of the average kinetic energy of an atom. We see that if we treat an ideal gas as a thermometric substance, and we begin counting the temperature from absolute zero, so the average kinetic energy must be directly proportional to the temperature T. Because the the average kinetic energy is the same among all r atoms, then the average value of the summation of the kinetic energy of all atoms is:

$$\overline{\Sigma \frac{mv^2}{2}} = \frac{3r}{2h}. \tag{8}$$

Integrating over dt in terms of $u_1, v_1, ... w_r$ over all possible values, as well as from $-\infty$ to ∞, yields the time dt' which on average lies in range:

$$x_1 \ and \ x_1 + dx_1, y_1 \ and \ y_1 + dy_1, ... z_1 \ and \ z_1 + dz_1, \tag{9}$$

without being subject to the restrictions of the value and direction of velocity. It follows that if the integrations are performed in the denominator, which so far was displayed as

$$dt' = \frac{\chi e^{-h\chi} dx_1 dy_1 ... dx_r du_1 dv_1 ... dw_r}{\int \int e^{-h\chi} dx_1 dy_1 ... dw_r}. \tag{10}$$

Picking X as a value which is the average, independent of coordinates, and, in the form of equation (6), performing the integral over the velocity gives

$$\overline{X} = \int X dt'. \tag{11}$$

So the average value of the potential energy is

$$\overline{\chi} = \int \chi dt' = \frac{\int \int ... \chi e^{-h\chi} dx_1 dy_1 ... dx_r du_1 dv_1 ... dw_r}{\int \int ... e^{-h\chi} dx_1 dy_1 ... dw_r}. \tag{12}$$

We now want to progress towards the proof, that the differential of the given heat δQ, divided through by the average kinetic energy of an atom

$$T = \frac{m}{2} \overline{v}^2 \tag{13}$$

is always a complete differential, and therefore the values can be found analytically. If the particles move in a closed path, I have already solved the differential $\frac{\delta Q}{T}$ in a paper published in 1866. If, however, the path of the atoms of the body is not closed, as long as the probability of the different positions of the atoms is left as a variable, it is possible to find special cases in which $\frac{\delta Q}{T}$ is not a complete differential. The potential energy function χ is completely known when all of the effective forces and positions of the points are given, and it also relates to probability. These can be combined into a single constant. As long as the nature of the function χ is not changed, these constants play no kind of role.

On the other hand, when the body transitions to a new energy state as a function of other coordinates, the function χ will change its form.

Then let the alteration of the constants from the changing χ never separate. The difference of both values of χ for two different positions of the old, as well as for two new states can be specified. But the position of the old state corresponds to the position of the new state, so the difference in χ is a new unspecified variable. To bind this independent constant with χ in a known term, we want to consider the constant to always be certain, that is if χ is a known (the same in all states) position, this constant will disappear in all atoms. This position can be arbitrarily picked. To do this for forces occuring in nature, the work required to dispel the atoms to infinity is finite. It is therefore convenient to choose the constants so that χ disappears, when all of the atoms are within an infinite distance of each other. Then χ is totally specified. $\chi(x_1, y_1, z_1, x_2...z_r)$ is the work which must be done to pull the atoms from infinity to the positions where the first one has coordinates of x_1, y_1, z_1, the second with coordinates of x_2, y_2, z_2 and so on. I will now write the total energy of the body at some time t as the total work done to assemble the body in the case when atoms were at rest and at an infinite distance apart from each other. This workload is twofold: 1. The work needed to give every atom the velocity, which occurs in the time t is the same as

$$\Sigma \frac{mv^2}{2}; \tag{14}$$

2. the work needed to bring the atoms in the relative positions, held in the same time t, the energy of the body in the time t is also

$$E = \Sigma \frac{mv^2}{2} + \chi \tag{15}$$

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This is constant if the body is not in contact with anything else. We presume that the edges of the body are in contact with other things; and these undergo fluctuations. If the body is made up of many atoms, the ones next to each other have the same state, and each one moves through them in the course of time. When the atom gains kinetic energy, it loses potential, (and vice versa) so that the value of the energy in any time is no different from the average value of the energy over a long time. We can set

$$E = \overline{E} = \overline{\Sigma \frac{mv^2}{2} + \overline{\chi}}. \tag{16}$$

To alter the state of the body, we feed in a small amount of heat, but do so without changing the nature of the forces on the atoms or the form of the function χ. It is clear that the change in work of the body is the change in heat of the body, δQ which is the change in energy. We denote that as δE and, using (16),

$$\delta Q = \delta E = \overline{\delta \Sigma \frac{mv^2}{2}} + \delta \overline{\chi}. \tag{17}$$

As long as only the energy of the body is a variablethere is only a single independent variable; whether it is a complete or an incomplete differential expression cannot be taken into consideration at this point. To obtain another independent variable, we must accept that the nature of the function χ is a variable. We then want to begin to consider a special case. In this case, the action law of the effective force of the atoms never changes, but under a thermodynamic examination. But the second independent variable, except for what contributes to the energy state of the body, is due to a fixed temperature rise. And when the body is completely covered in a shell, and a constant pressure is exerted on the shell, some parts will give way and some will not. It is independent of the internal molecular forces and works on the outside of body, for example, the gravitational force on all atoms in the neighborhood of the surface of the body. Some of the surface elements under constant pressure have a small reduction from the equilibrium state. The work done is the pressure multiplied with the projection of the paths in the normal direction of the surface.

We want to try to analytically express this circumstance in the most general terms possible. All atoms have the same force working on them with the same potential energy χ_0. Additionally there should be forces with the following characteristic: for every atom there should exist a known, complete plane (Level 1). The distance of the atoms from this level is n. They should be parallel to a second plane, (Level 2), which is a distance ν from the first. n and ν should be counted in the opposing direction. The current effective force on the atom (except for the potential energy function χ_0) is parallel to both planes and is merely a function of the distance $n + \nu$ of the atoms in the second level. It has the same power function, the value

$$\chi_0 + \Sigma f(n + \nu), \tag{18}$$

where the sign Σ refers to a summation of all of the atoms and it should be noted that both the positions of the fixed levels, as well as the nature of the function f, for every

atom may be different. The function f for every atom that lies inside the region is zero. Changing the state of the body will only change the total energy by a small amount $\delta \overline{E}$. Also, the value of ν for every atom will grow by $\delta \nu$. $\delta \nu$ can also be different for different atoms. In the first level, it won't change its position (a rotation of it will give an infinitly small second order change); however the second level, where the effective forces on the atom originate from, should move $\delta \nu$. The question is now about the expression for the given heat δQ. If all ν were to remain constant, then the energy functions wouldn't have changed at all. Then the given heat would be

$$\delta \overline{E} = \delta \Sigma \overline{\frac{mv^2}{2}} + \delta \overline{\chi}. \tag{19}$$

But by simultaneously changing ν by $\delta \nu$, then some work must be used to displace the second level $\delta \nu$. We will write this work as δW, and so

$$\delta Q = \delta \Sigma \overline{\frac{mv^2}{2}} + \delta \overline{\chi} + \delta W. \tag{20}$$

The force which is exerted on every atom that is in the associated surface is the negative derivative of the related force function $-f'(n + \nu)$. in the opposite direction, it is the force which the atom exerts on the second plane. Even if the energy state does not change, the body will oscillate in time. The average value $-\overline{f'(n + \nu)}$ is the applied pressure on the second plane in the direction ν of the atoms in the body. An equal but opposite force must act on the outside, where pressure and anti-pressure are the same. The work that it is necessary to move the second level $\delta \nu$ is then $-\overline{f'(n + \nu)}\delta \nu$, where $\delta \nu$ for each and every state of the body is constant, can be written outside of or inside average. We form this expression for all level 2 and sum all for the formed expressions, and we obtain the entire work which is necessary to move all level 2 and which is denoted with δW. It can be written $\delta W = -\overline{\Sigma f'(n + \nu)\delta \nu}$ and therefore

$$\delta Q = \delta \Sigma \overline{\frac{mv^2}{2}} + \delta \overline{\chi} - \overline{\Sigma f'(n + \nu)\delta \nu} \tag{21}$$

We still need to consider that the transition of the body from the original to new state χ_0 has remained the exact same function of the position of the atoms and the term $\Sigma f(n + \nu)$ has only changed with respect to ν. So we find that if we denote $\delta \chi$ as the difference of the value of χ from the old and new state of the body for identical positions of all the atoms, for every arbitrary position of every atom, $\delta \chi = \Sigma f'(n + \nu)\delta \nu$. Multiplying both pieces of this equation by equation (10) which is the given probability of the given positions, and integrating over all positions, we arrive at the average value of all $\overline{\delta \chi}$, which I will denote

$$\overline{\delta \chi} = \frac{\int \int ...\delta \chi e^{-h\chi} dx_1 dy_1...dx_r du_1 dv_1...dw_r}{\int \int ...e^{-h\chi} dx_1 dy_1...dw_r}. \tag{22}$$

We obtain

$$\overline{\Sigma f'(n + \nu)\delta \nu} \tag{23}$$

This is also

$$\overline{\Sigma f'(n + \nu)\delta\nu} = \overline{\delta\chi} \tag{24}$$

Or,

$$\delta Q = \delta\Sigma\overline{\frac{mv^2}{2}} + \delta\overline{\chi} - \overline{\delta\chi}. \tag{25}$$

This expression, which we have actually found under a special assumption is true for the general case, since the nature of the function χ changes in an arbitrary way. We have proved that when the form of the function χ doesn't change at all,

$$\delta Q = \delta\Sigma\overline{\frac{mv^2}{2}} + \delta\overline{\chi}. \tag{26}$$

For identical atom positions, χ has the same values of $x_1, y_1...z_r$ for the old and the new states. The average value $\delta\overline{\chi}$ is therefore another, because every position in the new sate has a different probability, because the atoms in a new state on average appear to have shifted their positions from the old state. Th accrued heat now exists as two parts, the part used to increase the kinetic energy by

$$\delta\Sigma\overline{\frac{mv^2}{2}} \tag{27}$$

and the heat used to move the atom $\delta\overline{\chi}$.

It should only change the working principle of the forces and the form of the function χ in completely arbitrary way. Then $\overline{\chi}$ undergoes a twofold change 1. through the average position of the atoms appearing to shift from an old to new state, so that the probability of every position in the new state is different, 2. that for identical positions of all atoms, χ in the first state is completely different than the second. We will then denote the increase from the first reason as $\delta_1\overline{\chi}$ and the second with $\delta_2\overline{\chi}$ so that

$$\delta\overline{\chi} = \delta_1\overline{\chi} + \delta_2\overline{\chi}. \tag{28}$$

The heat input that contributes to the increase in kinetic energy is again

$$\delta\Sigma\overline{\frac{mv^2}{2}}; \tag{29}$$

likewise, the contribution to the average shift of the atom is $\delta_1\chi$. On the other hand, no heat supply is necessary to change χ for identical positions of all the atoms. Then it is clear that when the nature of the effective force on the body is changed, without changing the position and velocities of the atoms, such a process represents no heat supply at all. The entire heat increase therefore still

$$\delta Q = \delta\Sigma\overline{\frac{mv^2}{2}} + \delta_1\chi. \tag{30}$$

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We want to shorten the differential expression $dx_1, dy_x..dz_r$ from formula (10) as $\delta\sigma$ and integrate over all of the respective differentials with a single integral sign, again in the equation (10) multiplied with the expression $\delta\sigma$

$$\frac{e^{-h\chi}}{\int e^{-h\chi}\delta\sigma},\tag{31}$$

and denoting it f, so that $dt' = f\delta\sigma$. Again let δf and $\delta\chi$ be the change in the value of f and χ for identical positions of all atoms ($\delta\chi$ is also the work which is needed in a new state to bring the atoms an infintely close distance in every position with the coordinates $x_1, y_1...z_r$, which is less than the work that is needed for this process in the old state). Then

$$\delta_1\overline{\chi} = \int \chi\delta f\delta\sigma, \delta_2\chi = \int \delta\chi f\delta\sigma;\tag{32}$$

it is also

$$\delta Q = \delta\Sigma\overline{\frac{mv^2}{2}} + \int \chi\delta f\delta\sigma.\tag{33}$$

Substituting the values of $\delta_1\overline{\chi}$ and $\delta_2\overline{\chi}$ into equation (28), this yields

$$\delta\overline{\chi} = \int \chi\delta f\delta\sigma + \int \delta\chi f\delta\sigma,\tag{34}$$

which incidentally follow from also through a direct variation of the equation

$$\overline{\chi} = \int \chi f\delta\sigma.\tag{35}$$

But now $\int \delta\chi f\delta\sigma$ is nothing different from what was already given in equation (22), the average values of $\overline{\delta\chi}$. Namely, it is $\delta\chi$ for all positions in various equilibrium. We multiply every position by the associated value of $\delta\chi$ with the probability $f\delta\sigma$ for the related positions and integrate over all possible positions, forming also the integral $\int f\delta\sigma$, and so we obtain the value $\overline{\delta\chi}$. It is also

$$\int \chi\delta f\delta\sigma = \delta\overline{\chi} - \overline{\delta\chi}\tag{36}$$

and [1]

$$+\delta\overline{\chi} - \overline{\delta\chi}.\tag{37}$$

This formula shows directly that $\frac{\delta Q}{T}$ is a complete differential. Now substituting equations (8), (12) and (22) in for $\Sigma\frac{mv^2}{2}, \overline{\chi}$, and $\overline{\delta\chi}$, and again writing $\delta\sigma$ in terms of $dx_1, dy_1...dz_r$,

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[1]I want to show in this note that formula (37) can be obtained from equation (22) in my paper published in the year 1866. Summing in terms of all atoms and bearing in mind that $\Sigma\epsilon = \delta Q$, this first gives $\delta Q = \delta\Sigma\frac{mv^2}{2} - \overline{X\delta x + Y\delta y + Z\delta z}$. But now $-\overline{X\delta x + Y\delta y + Z\delta z}$ is the average change in the power function following hte shift of hte atom, which is the same as $\delta_1\chi = \delta\overline{\chi} = \overline{\delta\chi}$, which is what needs to be substituted in to obtain equation (37).

$$\delta Q = -\frac{3r\delta h}{2h^2} + \delta\left[\frac{\int \chi e^{-h\chi}\delta\sigma}{\int e^{-h\chi}\delta\sigma}\right] - \frac{2h}{3}\frac{\int \delta\chi e^{-h\chi}\delta\sigma}{\int e^{-h\chi}\delta\sigma}. \tag{38}$$

where every integration runs over all values of the variables, there the differentials are contained in $\delta\sigma$ in terms of all coordinates from $-\infty$ to $+\infty$. Dividing through by

$$T = \frac{m}{2}\overline{v^2} = \frac{3}{2h}, \tag{39}$$

yields

$$\frac{\delta Q}{T} = -\frac{r\delta h}{h} + \frac{2h}{3}\delta\left[\frac{\int \chi e^{-h\chi}\delta\sigma}{\int e^{-h\chi}\delta\sigma}\right] - \frac{2h}{3}\frac{\int \delta\chi e^{-h\chi}\delta\sigma}{\int e^{-h\chi}\delta\sigma}. \tag{40}$$

This is also the complete differential of

$$-r\mathrm{log}h + \frac{2\mathrm{h}}{3}\frac{\int \chi \mathrm{e}^{-\mathrm{h}\chi}\delta\sigma}{\int \mathrm{e}^{-\mathrm{h}\chi}\delta\sigma} - \frac{2\mathrm{h}}{3}\frac{\int \delta\chi \mathrm{e}^{-\mathrm{h}\chi}\delta\sigma}{\int \mathrm{e}^{-\mathrm{h}\chi}\delta\sigma}. \tag{41}$$

The expression (41) is also the designated value of the entropy of a body from Clausius, the value which is the differential of $\frac{\delta Q}{T}$; this is, as you see, found by intergration, when you know the temperature determining the constant h and the forces, which are effective in all the positions of the atoms. The internal and exernal work done is

$$\delta L = \delta\overline{\chi} - \overline{\delta\chi}. \tag{42}$$

From Clausius, the disgregation of the given value $\frac{\int \delta L}{T}$ also has the value

$$S = \frac{2h}{3}\frac{\int \chi e^{-h\chi}\delta\sigma}{\int e^{-h\chi}\delta\sigma} + \frac{2}{3}\mathrm{log}\int \mathrm{e}^{-\mathrm{h}\chi}\delta\sigma + \mathrm{const.} \tag{43}$$

I want to show that $\frac{\delta Q}{T}$ is also a complete differential, when an endless number of atoms interact with each other, so when these move through they move through all possible states, where the equation of the kinetic energy is meets the conditions $\phi_n = a_n$.

λ is the number of standing material points in the interactions, so we can apply this to the equations (25) (26) and (27) from my earlier paper. It follow from (25) when the average kinetic energy is the same for all atoms,

$$\overline{\Sigma\frac{mv^2}{2}} = \lambda\frac{m_1}{2}\overline{v_1}^2 = \frac{\int\int ...(a_n - \chi)^{\frac{3\lambda}{2}}dx_1 dy_1...dx_\lambda}{\int\int ...(a_n - \chi)^{\frac{3\lambda}{2}-1}dx_1 dy_1...dx_\lambda} \tag{44}$$

The average energy is as follows

$$\overline{E} = \overline{\Sigma\frac{mv^2}{2}} + \overline{\chi} \tag{45}$$

the value a_n, which is self-evident, represents the sum of the potential energy and kinetic energy in the entire system which is absolutely constant for all times with an

unaltered state of the body, because it interacts with no other material points. As you substitute this value for the energy in formula (38) , it yields

$$\delta Q = \delta a_n - \overline{\delta \chi}. \tag{46}$$

We set $a_n - \chi$ equal to Ψ, so that Ψ is a function of $x_1, y_1...z_\lambda$ and the same as the total of some of the positions of the system in the form of velocity in the existing kinetic energy. We again show $\delta \Psi$ is the difference of the value of Ψ for identical positions of atoms in new and old sates. Then δQ is the average value of $\overline{\delta \Psi}$ of all $\delta \Psi$. This average value is in general a function of $x_1, y_1...z_\lambda$ after it is calculated with formula (26) in the previous paper. We write this using Ψ for all $(a_n - \chi)$ and $\delta \sigma$ for $dx_1, dy_1...dz_\lambda$, and obtain

$$\delta Q = \overline{\delta \Psi} = \int \delta \Psi dt_4 = \frac{\int \delta \Psi \Psi^{\frac{3\lambda}{2}-1} \delta \sigma}{\int \Psi^{\frac{3\lambda}{2}-1} \delta \sigma}. \tag{47}$$

For the average kinetic energy of an atom, formula (25) from my previous paper gives

$$T = \frac{m_1}{2}\overline{v}^2 = \frac{1}{\lambda} \frac{\int \Psi^{\frac{3\lambda}{2}} \delta \sigma}{\int \Psi^{\frac{3\lambda}{2}-1} \delta \sigma}. \tag{48}$$

When divided through by T,

$$\frac{\delta Q}{T} = \lambda \frac{\int \delta \Psi \Psi^{\frac{3\lambda}{2}-1} \delta \sigma}{\int \Psi^{\frac{3\lambda}{2}} \delta \sigma}. \tag{49}$$

But now, because the bounds of the integration must be chosen so that $\int \Psi^{\frac{3\lambda}{2}} \delta \sigma$ that the function under the integral term disappears completely:

$$\delta \int \Psi^{\frac{3\lambda}{2}} \delta \sigma = \frac{3\lambda}{2} \int \delta \Psi \Psi^{\frac{3\lambda}{2}-1} \delta \sigma, \tag{50}$$

the following is the expression of $\frac{\delta Q}{T}$ is a complete differential of

$$\frac{2}{3}\log \int \Psi^{\frac{3\lambda}{2}} \delta \sigma + \text{const.} \tag{51}$$

This expression gives us the entropy of the system. This can also be found by integration, if the forces for all positions and the total work contained in the system is given. For an ideal gas with atomic molecules, for example Ψ is muliplied by λ and the average kinetic energy of an atom, is $\Psi = \lambda T$. It is also the entropy if you substitue $\delta \sigma$ for its original value,

$$\frac{2}{3}\log \mathrm{T}^{\frac{3\lambda}{2}} \int \int ...\mathrm{dx_1 dy_1...dz_\lambda}. \tag{52}$$

Again, every one of the integrals

$$\int \int \int dx_1 dy_1 dz_2, \int \int \int dx_2 dy_2 dz_2... \tag{53}$$

is the same as the total volume v of the gases; it is also the same as the entropy

$$\log(\mathrm{T}^\lambda \mathrm{v}^{\frac{2\lambda}{2}}) + \text{const.} \tag{54}$$

This naturally proves the equation (41) which applies in this case that the gas interacts with other atoms which would take place in nature. To apply this formula to a gas with monatomic molecules, we must always accept χ as a constant as long as all of the gases are filling the space, as soon as the atoms are outside the space, which is assumed infinitely large. It can also be set as χ and h outside the integral, but the integrations are only carried out over the entire volume of the gas. Therefore, formula (41) gives

$$-r\mathrm{log}h + \frac{2\mathrm{h}\chi}{2} + \frac{2}{3}\log(\mathrm{e}^{-\mathrm{h}\chi}\int \delta\sigma) \tag{55}$$

$$= -r\mathrm{log}h + \frac{2}{3}\log\int \delta\sigma + \text{const.} \tag{56}$$

There $\int \delta\sigma$ is again the same as v^r and $\frac{3}{2h} = T$, which we obtain when we count the atoms again with λ instead of with r, from the previous expression

$$\log(\mathrm{T}^\lambda \mathrm{v}^{\frac{2\lambda}{3}}) + \text{const.} \tag{57}$$

This value can be verified through a direct calculation of entropy. For monatomic gases, it is the same, when p is the pressure related to the unit area, T the average kinetic energy of the atoms or molecules, and λ previously is the count of the molecule of the gases

$$pv = \frac{2\lambda T}{3}. \tag{58}$$

Again when, as I always do, supposing that the measure of work and heat are the same (mechanically)

$$\delta Q = \lambda\delta T + p\delta v, \tag{59}$$

hence

$$\frac{\delta Q}{T} = \lambda\frac{\delta T}{T} + \frac{p\delta v}{T} = \lambda\frac{\delta T}{T} + \frac{2\lambda}{3}\frac{\delta v}{v} \tag{60}$$

yielding

$$\int \frac{\delta Q}{T} = \log(\mathrm{T}^\lambda \mathrm{v}^{\frac{2\lambda}{3}}) + \text{const.} \tag{61}$$

I will finally consider two consequences of formula (38). This is the same as considering the change in heat in three parts. The first, $\delta\overline{\Sigma\frac{mv^2}{2}}$, should increase the kinetic energy or temperature, the second, $\delta\overline{\chi}$, from the interior work and the third $\overline{\delta\chi}$ which disappears, as soon as the action principle of all the effective forces of the atoms in the

body does not change. The amount of heat expended to cause a temperature change is called the quotient of the termperature raise for one unit of weight of the heat change is the same as what Rankine called the true specific heat, and what Clausius called the heat capacity of a body. Now the temperature of the average kinetic energy of a body is proportional to the value of $\overline{\Sigma\frac{mv^2}{2}}$ after equation (8) is the r-times is the kinetic energy of the atoms, so the true heat capacity is the same as a constant multiplied with the number of atoms in the unit weight. It is also constant for a body in all transitions and inversely proportional to the atomic weight (which is the number of atoms in the molecule divided by the molecular mass). For a fixed body, the force which works on some atom in the first approach is truly proportional to the distance of the atoms from the rest position, the energy function in the first case

$$\chi = \Sigma(Ax^2 + By^2 + Cz^2 + Dyz + Exz + Fxy + Gx + Hy + Jz). \qquad (62)$$

We substitute this value into formula (12) so we can perform the integral which turns the polynomial into a second degree by transforming the variables to $x^2 + y^2 + z^2$. We then obtain

$$\overline{\chi} = \overline{\Sigma\frac{mv^2}{2}}. \qquad (63)$$

(I noted that the formula (27) for the case that the atoms of the body are not in contact with everything also yields equation (63))

For a fixed body that is in the first approach,

$$\delta\overline{\chi} = \delta\overline{\Sigma\frac{mv^2}{2}}, \qquad (64)$$

that is, the heat used to increase the work is the same as the heat used to raise the temperature, and with a fixed body, the external work can be neglected, so the supplied heat doubles as what is used to increase temperature. The actual specific heat, which we find experimentally, is therefore doubled with the heat capacity; and there the latter is proportional to the atomic weight, so much as the former. With these solid bodies, which follows the law of Dulong and Petit or Neumann's laws, it seems that the effective force on the atom in the first approximation of the distance is indeed proportional to the distance from the rest position. With the fixed bodies that do not follow Dulong's law, this doesn't have to be the case anymore.