

Was Loschmidt correct in asserting that the entropy of a closed system can be decreased?

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Abstract: In 1868 J.C. Maxwell proved that a perpetual motion machine of the second kind would become possible, if the equilibrium temperature in a vertical column of gas subject to gravity were a function of height. However, Maxwell had claimed that the temperature had to be the same at all points of the column. So did Boltzmann. Their opponent was Loschmidt. He claimed that the equilibrium temperature declined with height, and that a perpetual motion machine of the second kind operating by means of such a column was compatible with his concept of the second law of thermodynamics. Thus he was convinced he had detected a never ending source of usable energy for mankind. At a later time, E. Mach, too, did not rate the invention of a perpetual motion machine of the second kind as being impossible, but did not mention Loschmidt's idea. In this article, new arguments (based on statistical mechanics) are provided for the hypothesis that an insulated column of gas subject to gravity does not take on a homogenous temperature: Since Boltzmann's distribution of energies leads to the general gas law even in case the molecules are supposed to be extended objects, it follows that Boltzmann's distribution cannot be strictly valid if experience requires to replace the general gas law $pV=NkT$ by $p(V-b)=NkT$. But such a modification of the general gas law is undoubtedly required. With a modification of the general gas law and hence a deviation from Boltzmann's distribution of energies thus being indispensable, it further follows that a homogeneous temperature cannot be achieved in an insulated column of gas subject to gravity.

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1) Introduction

When taking a look at any textbook on general physics, one finds the second law of thermodynamics formulated in two equivalent ways: "The total entropy of an isolated system can never decrease", and "A perpetual motion machine of the second kind is impossible". Today, doubting the impossibility of such a machine is just as inconceivable as is the assertion that a perpetual motion machine of the FIRST kind might exist, which creates energy from

nothing. A closer investigation, however, reveals that in the second half of the nineteenth century, a vivid debate was held among most reputable scientists on the possibility of a perpetual motion machine of the second kind. One of the most prominent propagators in favor of such a possibility was Josef Loschmidt, a name today well known even to school-kids through the celebrated Loschmidt's number. A perpetual motion machine of the second kind would be capable of permanently creating, in a cycle, mechanical energy from just one single reservoir of heat. Thus it would become possible, for instance, to convert the (dissipated) energy of heat contained in the air into mechanical energy without requiring a second, colder reservoir for the absorption of the refuse heat. Therefore mankind would have available a source of energy that practically cannot be exhausted.

Loschmidt and Maxwell asserted that, if there were a difference in equilibrium temperature in a column of gas subject to gravity, the construction of a perpetual motion machine of the second kind would be possible. Up to the present day, no one has ever challenged that assertion. Maxwell believed that the equilibrium temperature of the gas subject to gravity could not be stratified, but had to be the same at all points. He did not provide a special proof; rather, he intuitively extended his formula of velocities of molecules (which had been derived without regarding gravity) to a gas subject to gravity. Boltzmann sided with Maxwell; in contrast to Maxwell, he attempted to prove that the homogeneous temperature of a gas subject to gravity was ensured by the kinetic theory of gases and by statistical mechanics. Loschmidt, however, was convinced that a perpetual motion machine of the second kind was compatible with the second law of thermodynamics. In that point, he disagreed with Clausius, Thomson, Boltzmann, and Maxwell. In particular, he believed that a perpetual motion machine of the second kind could be operated by means of a vertical column of gas, the temperature of which he claimed to be stratified.

In the 20th century, Loschmidt's "revolutionary" assertion has hardly been paid any attention. After all, it was mentioned by Stephen G. Brush in his 1978 book: "The Temperature of History." However, Brush does not give more than a clue when telling his readers that the dispute over the stratification of temperature between Boltzmann and Loschmidt provided a contribution to the debate on the second law of thermodynamics. No further details are offered. In more recent times (1995), it was Claude Garrod ¹who tried to give a new proof of the uniformity of temperature. His arguments will be scrutinized further below.

It should be noted that the Second Law, when understood as the assertion that a perpetual motion machine of the second kind cannot be built, is not subject to possible falsification by observing *nature*, but by observing *inventors*. As a consequence, the "fruitlessness" of any efforts in building a perpetual motion machine of the second kind could *either* be due to the incompetence of inventors, *or* to nature itself not allowing the construction of such a machine. The "fruitlessness" alone does not provide any means for deciding which of these two alternatives is true. We will return to this point at the end of this essay.

2) On the history of the second law of thermodynamics

Though the expression "perpetual motion machine of the second kind" was only introduced by Ostwald towards the end of the 19th century, the impossibility of such machine had been

postulated as an axiom by Clausius already in 1849 and by Thomson in 1850. Both Clausius and Thomson are considered the discoverers of the second law of thermodynamics ^{1a)} .

One may wonder how Clausius and Thomson could obtain their firm belief in the truth of their axiom. The fact alone that such a machine had not been invented until those days is not capable of explaining this conviction. In addition, one has to take into account that already in the 18th century the opinion of the impossibility of a perpetual motion machine prevailed, long before the theorem of the conservation of energy or the distinction between the first and the second law of thermodynamics were advanced. The idea of a system of movable parts that, having come to rest once, would still be able to get into motion on its own, was simply inconceivable ²⁾ . Of course, the 18th century scientists were not yet familiar with the kinetic theory of heat and did not realize that apparent rest turns into motion in the microscopic perspective. Such knowledge would have impeded the formation of Clausius' and Thomson's axiom.

Picking up reflections previously published by Carnot, Thomson declared the impossibility of a perpetual motion machine the foundation of his further investigations in the field of thermodynamics: "It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest surrounding objects" ³⁾ (It is worth mentioning that the assertion applies to *cyclic* processes only, not to a non-cyclic process like an adiabatic expansion of a gas, in which the internal energy in the form of heat content is converted into mechanical work at a rate of 100%.) From the impossibility of such a perpetual motion machine one can easily infer the second law in a very general form (though different from the actual one), stating that a system will not depart from an attained state of equilibrium without interference from outside. Loschmidt accepted the second law in such a general form only (more precisely: he believed that this form of the second law could be derived from the mechanical principle of least action). However, as emphasized by Loschmidt several times, it is impossible to invert the order of inference, i.e. it is not permitted to infer the impossibility of a perpetual motion machine of the second kind from the second law in its very general form:

"From these reflections one can draw the conclusion that the second law of thermodynamics can be inferred from the axiom of Clausius 'It is impossible to transfer heat from a colder to a warmer body without compensation', or from the equivalent one of W. Thomson 'It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects', that the inversion of that inference, however, is not permissible, because the content of the second law is more general than that of those axioms." ⁴⁾

3) Maxwell's (hypothetical) perpetual motion machine of the second kind

In the 1860's and 70's scientists dealt with the question of whether a gas, which is subject to gravity in an insulated column, had the same temperature at all points, or whether its temperature was a function of height.

Maxwell was convinced that the temperature of a gas subject to gravity had to be uniform at all

heights. Moreover, like Thomson and Clausius, he regarded a perpetual motion machine of the second kind to be impossible. However, he was very sure that if there were a gradation of temperature and if that gradation were different for different substances, a perpetual motion machine would be possible:

"In fact, if the temperature of any substance, when in thermic equilibrium, is a function of the height, that of any other substance must be the same function of the height. For if not, let equal columns of the two substances be enclosed in cylinders impermeable to heat, and put in thermal communication at the bottom. If, when in thermal equilibrium, the tops of the two columns are at different temperatures, an engine might be worked by taking heat from the hotter and giving it up to the cooler, and the refuse heat would circulate round the system till it was all converted into mechanical energy, which is a contradiction to the second law of thermodynamics. The result as now given is, that temperature in gases, when in thermal equilibrium, is independent of height, and it follows from what has been said that temperature is independent of height in all other substances." ⁵⁾

Modifying the device introduced by Maxwell, we put up with one column (filled with gas) only, which is thermally insulated from its surroundings, with the exception of its floor and its ceiling. A metal block in thermal contact with the outer side of the floor has the temperature of the bottom part of the gas column (to start with). As a first step, the metal block is lifted upward until it finds itself on top of the ceiling of the column. Heat flows from the block into the upper part of the column, thereby passing a Stirling engine, where part of the heat flow is converted into mechanical work. As a next step, the metal block is lowered to its original position. As a third and last step, heat flows from the bottom part of the column into the block until the temperature of the bottom part of the column and the block are equal to each other. The mechanical work spent on lifting the block is just as large as is the mechanical work gained by lowering the block (the relativistic increase in weight brought about by the increase in thermal energy can be neglected).

One might be tempted to assume that the process of creating work has to come to a standstill as soon as the temperature of the column has reached uniformity (due to the extraction of heat at its bottom and the adding of refuse heat at its top). However, the starting point of our (and Maxwell's) reflections was the hypothetical assumption (which Maxwell did not believe to be true in reality) that a uniform temperature of a column of gas subject to gravity is NOT A STATE OF EQUILIBRIUM. Hence we have to conclude that the gas, left to itself during that break, will resume its state of temperature gradation. Then, the whole process can start over again. The internal energy of the gas as a whole will thus be diminished and turned into mechanical work without a second heat reservoir.

Strictly speaking, Maxwell's original device only demonstrates that DIFFERING temperature gradients of two substances enable the construction of a perpetual motion machine of the second kind, whereas the modification gives proof of the possibility of such machine already in case of a gradation of equilibrium temperature in one single substance (see W. Dreyer, W. Müller, W. Weiss, [Tales of Thermodynamics and Obscure Applications of the Second Law](#) , for a detailed report on the debate between Boltzmann and Loschmidt).

4) A statistical proof of the non-homogeneity of temperature in gases subject to gravity

I.

a) Abstract of proof

It shall be proved that Boltzmann's distribution of energies leads to the general gas law even in case we assume that the molecules are extended objects. As a consequence, it follows that Boltzmann's distribution cannot be strictly valid if experience requires to replace the general gas law $pV=NkT$ by $p(V-b)=NkT$. This condition is met in physical reality. But given Boltzmann's distribution of energies is not strictly valid, it can be easily shown that there cannot be a state of equilibrium in which the temperature of a gas subject to gravity is uniform.

b) Derivation of Boltzmann's distribution of energies

Before presenting the proof proper, Boltzmann's distribution of energies shall be derived (in doing so, I am following a thread laid out by L. Susskind in his [online-lectures on Statistical Mechanics](#) at Stanford University), on the basis of which, in turn, the general gas law of the ideal gas shall be derived as another (but last) pre-step ahead of the proof proper. This will provide an insight into the scope and the limits of the statistical foundation of the general gas law, which will be needed for the proof proper.

aa) We imagine a system of N boxes, in each of which energy can be stored. The energy stored in an individual box shall be capable of taking on different discrete values (energy levels). The numerous (discrete) energy states (energy levels) which any box is able to attain shall be given consecutive subscript numbers 1, 2, 3 etc.. The number of boxes that find themselves on a given level shall be named n . We thus have a succession of n_1, n_2, n_3 , and so on.

Moreover, we shall assume that a definite total amount of energy (that is subdivided into discrete portions) is being carried to the system of boxes and is being randomly distributed among the boxes. The process of distribution shall have no "memory". In other words: Even if a box is in possession of more than the average energy already, its chances of receiving the next energy portion that is to be distributed are as big as they are for a box that is almost empty yet.

For a better illustration, we imagine (as an example) that there are 15 boxes on the third energy level. Consequently, we have $n_3=15$. Different numbers may apply to the other levels.

At the end of the process of distribution of energy (in which, as an example, we assume there were 25 boxes and three energy levels whose occupation numbers are n_1, n_2 and n_3), we are interested in knowing how many variants exist for realizing the arbitrarily picked arrangement $n_1=10, n_2=11, n_3=4$ of occupation numbers. The result (number), which shall be labelled Lambda, is found by applying the following equation (a variant shall differ from a second variant if, with respect to one or more of the three occupations of energy levels whose numbers are n_1, n_2 and n_3 , the list of names given to the individual boxes that make up the occupation of an individual level n_1, n_2 or n_3 is not completely identical with the list of names that exist in the

compared variant):

(1)

$$\Lambda = \frac{N!}{\prod_{i=1}^{i=n} n_i!} = \frac{N!}{n_1! n_2! n_3!} = \frac{25!}{10! 11! 4!}$$

No proof shall be given for this well-known rule of combinatorics.

bb) We want to find the maximum of the Lambda function (for reasons that will become evident later on). The maximum of the Lambda function shall be subject to two constraints:

–The total sum of occupation numbers of any arrangement of occupations shall be **N**, that is, shall be equal to the total number of boxes,

– the total amount of energy distributed to the totality of boxes shall be the same no matter which arrangement of occupations is considered.

This leads to the following two equations:

(2)

$$\sum_{i=1}^{i=n} n_i = N$$

and (**E_i** denotes an energy level that a box may take on; **E_{total}** denotes the total energy of the sum of boxes):

(3)

$$\sum_{i=1}^{i=n} n_i E_i = E_{total}$$

cc) Before consolidating (2) and (3) with (1), (1) shall be re-formulated with the help of Stirling's approximation. The logarithm of **N!** can be expressed as follows:

(4)

$$\ln N! = \ln 1 + \ln 2 + \dots + \ln N = \sum_1^N \ln x \approx \int_0^N \ln x \, dx = [(x \ln x) - x]_0^N = (N \ln N) - N$$

or

(5)

$$N! \approx e^{N \ln N} e^{-N} = N^N e^{-N}$$

This is Stirling's approximation for $N!$. Applying the approximation to (1), we get:
(6)

$$\Lambda = \frac{N!}{\prod_{i=1}^n n_i!} \approx \frac{N^N e^{-N}}{n_1^{n_1} n_2^{n_2} n_3^{n_3} \dots e^{-n_1-n_2-n_3-\dots}} = \frac{N^N}{n_1^{n_1} n_2^{n_2} n_3^{n_3} \dots}$$

When forming the logarithm of Lambda, we get (with the probability \mathbf{P}_i , that is the probability for a box to find itself on the i -th energy level, being defined as $\mathbf{n}_i / \mathbf{N}$):
(7)

$$\begin{aligned} \ln \Lambda &= N \ln N - \sum_i n_i \ln n_i = N \ln N - \sum_i P_i N \ln (P_i N) = N \ln N - \sum_i P_i N (\ln N + \ln P_i) \\ &= N \ln N - N \ln N - \sum_i (P_i N \ln P_i) = -N \sum_i (P_i \ln P_i) \end{aligned}$$

In the last line of the equation, the sum of $\mathbf{P}_i \mathbf{N} \ln \mathbf{N}$ was replaced by $\mathbf{N} \ln \mathbf{N}$, since the sum of \mathbf{P}_i is equal to unity.

dd) We now have to use the method of Lagrange multiplier for the purpose of giving consideration to the two constraints. When replacing \mathbf{n}_i by $\mathbf{N} \mathbf{P}_i$ (in accordance with the definition of \mathbf{P}_i) in the two equations for the constraints, we get:
(8)

$$G_1 = \left(\sum_i P_i \right) - 1 = 0$$

and
(9)

$$G_2 = \left(\sum_i P_i E_i \right) - \bar{E} = 0$$

Overlined \mathbf{E} is the average energy of a single box ($\mathbf{E}_{\text{total}}/\mathbf{N}$). The terms \mathbf{G}_1 and \mathbf{G}_2 are functions defined by the middle parts of the two equations.

With \mathbf{F} being defined as a function that is equal to the logarithm of Lambda divided by \mathbf{N} , we set:
(10)

$$F + \alpha G_1 + \beta G_2 = F + \alpha[(\sum_i P_i) - 1] + \beta[(\sum_i E_i P_i) - \overline{E}] = F'$$

Alpha and **beta** are two Langrangian multipliers, that is, fixed numbers whose value is unknown yet. **F'** is not the derivative of **F**, but is defined as an expression of the sum on the left side of the equation.

We shall now form the partial derivative of **F'** with respect to an arbitrarily picked probalidity **P_i**, say, **P₈**, that is the probability for the energy of a box to be on the 8th level. We will do this summand by summand. The first summand is **F**. For its derivative with respect to **P₈**, we get by using (7):

(11)

$$\frac{\delta F}{\delta P_8} = \frac{\delta \sum_i P_i \ln P_i}{\delta P_8} = P_8 \frac{\delta \ln P_8}{\delta P_8} + \frac{\delta P_8}{\delta P_8} \ln P_8 = \frac{P_8}{P_8} + \ln P_8 = \ln P_8 + 1$$

The derivative of the second summand (**alpha** term) with respect to **P₈** is **alpha**; the derivative of the third summand (**beta term**) with respect to **P₈** is beta times **E₈**, since both **E₈** and overlined **E** are constant with respect to a change in the value of **P₈**.

For the derivative of **F'** with respect to **P₈**, which we set equal to zero (since we are interested in the maximum), we hence get:

(12)

$$\frac{\delta F'}{\delta P_8} = \ln P_8 + 1 + \alpha + \beta E_{E_8} = 0$$

or

(13)

$$\ln P_8 = -(1 + \alpha) - \beta E_8$$

or

(14)

$$P_8 = e^{-(1+\alpha)} e^{-\beta E_8} = \frac{1}{z} e^{-\beta E_8}$$

Euler's number, raised to the power of **-(1+ alpha)**, has been replaced by a term **1/z** (by convention). The function **z** is called the partition function.

Since **P₈** can be replaced by any other energy level **P_i**, we may formulate in a general way:

(15)

$$P_i = \frac{n_i}{N} = \frac{1}{z} e^{-\beta E_i}$$

This is Boltzmann's distribution of energies: For every possible level of energy E_i of a box, a definite probability P_i (which is the occupation number of this energy level, divided by N , the total number of boxes) is given by the equation. The various probabilities of the many (possible) individual energy levels of a box yielded by (15) constitutes the special arrangement of occupation numbers of energy levels which, under the two constraints, comprises the maximum number of variants and is therefore the most likely one.

Equation (15) gives the special distribution of occupation numbers of energy levels (divided by N) whose number of variants is the biggest in comparison with other distributions one might think of. As stated above, an occupation number of a single energy level, divided by N , is called the probability for a single box to find itself on that level. Note that (15) does not give any clue as to HOW much bigger the number of variants is (in comparison with any other distribution of occupation numbers). One may criticize the reasoning for this lack of information, and assert that the proof of a usefulness of (15) is incomplete. One could, though, show that the number of variants drops sharply when considering any other distribution of occupation numbers.

As a consequence of Stirling's approximation that we used, the different energy levels are equidistant from each other.

ee) We may further write:
(16)

$$\sum_i P_i = \sum_i \frac{1}{z} e^{-\beta E_i} = 1$$

For the average energy of a box, we may write:
(17)

$$\bar{E} = \sum_i \frac{n_i}{N} E_i = \sum_i P_i E_i = \sum_i \frac{1}{z} E_i e^{-\beta E_i}$$

Since z is, by above definition, equal to Euler's number raised to the power of $(1 + \alpha)$, and since α does not depend on the possible energy level considered, z can be treated as a constant. In other words: $1/z$ can be factored out in (16). We may hence determine z as follows:
(19)

$$z = \sum_i e^{-\beta E_i}$$

This is the general expression of the z -function (partition function).

For the derivative of **z** with respect to **beta**, we get from (19):
(20)

$$\frac{\delta z}{\delta \beta} = -\sum_i E_i e^{-\beta E_i}$$

Multiplying both sides of the last equation by **1/z** gives:
(21)

$$\frac{1}{z} \frac{\delta z}{\delta \beta} = -\sum_i \frac{1}{z} E_i e^{-\beta E_i} = -\bar{E}$$

Since (because of **d ln z/dz=1/z**) the left side of (21) can be expressed by a logarithm of **z**, we may write:
(22)

$$\bar{E} = -\frac{\delta \ln z}{\delta \beta}$$

ff) We will now determine **beta**. For the average entropy **S** of a box, we may write (no proof shall be given for this famous equation of Boltzmann's):
(23)

$$\frac{S}{k} = -\sum_i P_i \ln P_i$$

The constant **k** is Boltzmann's constant. We may re-formulate this with the help of our equations for the average energy of a box (that is, Equation 21), for the probability **P_i**, and for the sum of the probabilities:
(24)

$$\begin{aligned} \frac{S}{k} &= -\sum_i P_i \ln P_i = -\sum_i \frac{1}{z} e^{-\beta E_i} (-\beta E_i - \ln z) = \sum_i \frac{1}{z} e^{-\beta E_i} (\beta E_i + \ln z) \\ &= \beta \bar{E} + \frac{1}{z} \ln z \sum_i e^{-\beta E_i} = \beta \bar{E} + \ln z \end{aligned}$$

When forming the differential of **dS**, we get (making use of Equation 22):
(25)

$$\frac{\delta S}{k} = \beta \delta \bar{E} + \bar{E} \delta \beta + \delta \ln z \frac{\delta \beta}{\delta \beta} = \beta \delta \bar{E} + \bar{E} \delta \beta - \bar{E} \delta \beta = \beta \delta \bar{E}$$

On the other hand, $dS=dE/T$ or $dS/k= dE/kT$. We thus obtain from (25):
(26)

$$\beta = \frac{1}{kT}$$

c) Derivation of the numerical value of the z-function; Liouville's theorem

aa) As a next step, we determine the numerical value of the z -function (appearing in the Boltzmann distribution) *for a gas*. That is to say: The role of a single “box” is, from now on, played by a single particle or molecule. In the previous sections, a box was defined as an entity having a discrete energy level that it had acquired as a result of a distribution process of energy bits. The number of “boxes” N was much bigger than the number of possible energy levels. Consequently, on all energy levels, one could find several boxes (and not just one single box). For instance, n_3 was the number of boxes that found themselves on the third energy level. Since we are now dealing with a gas, we replace the boxes by molecules: Each molecule (of which there are N all together) finds itself on one of the many discrete energy levels (of which there are much less than N).

We shall assume that the molecules (or particles) which make up the gas do not exert attractive forces on each other.

For the purpose of determining the numerical value of z , that is, for the purpose of finding another expression of the right side of (19), we will (as a first step) prove that the following equation is equivalent to (19) (the variable x denotes one of three spatial coordinates in a Cartesian system of coordinates; p_x , which can be numerically positive or negative, denotes the component of the momentum in the x -direction possessed by a single molecule; E_x is the possible magnitude of one direction component of the kinetic energy of a molecule; C is a constant):
(27)

$$z_x = C \int_0^h dx \int_{-\infty}^{\infty} dp_x e^{-\frac{E_x}{kT}} = C \int_0^h dx \int_{-\infty}^{\infty} dp_x e^{-\frac{p_x^2}{2mkT}}$$

For the time being, we are interested in the x -component of motion of particles only. This is why z has an index x , denoting that the partition function z_x is the partition function for the distribution of one single spatial component (the x -component) of kinetic energy only. We give ourselves permission to presume that the total kinetic energy of all particles in one spatial direction is constant, and is one third of the total kinetic energy of the gas.

All particles shall find themselves in a cube-shaped container. The term h shall be the length of one side of the cube. The integration of dx in (27) extends from zero to h . Since, for the time

being, we are interested in the **x**-direction of motion only (and not in the **y**- or **z**- direction), the first integral does not extend over the whole volume of the container, but only over its **x**-dimension, that is, over its height. The other directions will be given due consideration later on.

The possible energy E_x of a particle can be replaced by $\mathbf{p}_x^2/2\mathbf{m}$ (with **m** denoting the mass of a particle, and with \mathbf{p}_x denoting a possible a momentum of a particle in one direction).

(27) is equivalent to (19) because of:

(27a)

$$z_x = C \int_0^h dx \int_{-\infty}^{\infty} dp_x e^{-\frac{E_x}{kT}} = C \lim_{\Delta x \Delta p_x \rightarrow 0} \sum_i e^{-\frac{E_{x_i}}{kT}} \Delta x \Delta p_x$$

$$\approx C \sum_i e^{-\frac{E_{x_i}}{kT}} \Delta x \Delta p_x = \sum_i e^{-\frac{E_{x_i}}{kT}}$$

As in (19), the subscript **i** denotes any of many discrete energy levels of a single molecule (equidistant from each other in terms of energy, and not in momentum). We imagine that \mathbf{p}_x and **x** constitute the two horizontal axes in a three dimensional Cartesian system of coordinates, with the exponential term constituting the vertical axis. In the case of a double integral, the horizontal plane defined by the two horizontal axes forms a “chess board” with many squares $d\mathbf{x}d\mathbf{p}_x$ of identical shape, the area of each of which is vanishingly small. In the case of the sum (with the exponential term times **Delta x Delta p_x** as a summand) appearing in the second line (as an approximation to the double integral), the “chess board” does not present exact squares, but areas of equal size (magnitude) whose shapes may be squares or rectangles that may differ from each other (the variability of the shape being due to the fact that the steps considered within the sum are equidistant in energy and not in momentum). Different from the case of an integral, the size (magnitude) of an area does not vanish.

In both cases, the exponential term in (27a) yields the height of a “roof” above a given area (of rectangular or squared shape) which we imagine hovering above the “chess-board”. Moreover, both the double integral and the sum appearing in the second line give the volume that extends between the “chess-board” and the roof. The two volumes do not differ much from each other, if the number of summands that make up the sum is big enough. Different from the case of an integral, the size (magnitude) of an area does not vanish.

If both sides of (27) or (27a) are raised to the **3N**th power, we get:

(28)

$$z_x^{3N} = C^{3N} \int_0^h \int_0^h \int_0^h \dots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots d^{3N}x d^{3N}p_x e^{-\frac{3NE_x}{kT}}$$

$$\begin{aligned}
 &= C^{3N} \int_0^h \int_0^h \int_0^h \dots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots d^{3N}x \ d^{3N}p_x \ e^{-\frac{N(p_{x1}^2 + p_{x2}^2 + p_{x3}^2)}{2mkT}} \\
 &= [C \int_0^h \int_{-\infty}^{\infty} dx_1 \ dp_{x1} \ e^{-\frac{p_{x1}^2}{2mkT}}]^{3N} \\
 &\approx (C \sum_i e^{-\frac{E_{x_i}}{kT}} \Delta x \Delta p_x)^{3N} = (\sum_i e^{-\frac{E_{x_i}}{kT}})^{3N}
 \end{aligned}$$

When presuming that no direction is privileged, \mathbf{x} can be replaced by \mathbf{y} or \mathbf{z} . Instead of using $\mathbf{x}, \mathbf{y}, \mathbf{z}$ as coordinates or directions, the terms $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3$ are used for the same purposes. The term \mathbf{p}_x denotes the component of a momentum of a molecule in the \mathbf{x}_1 -, \mathbf{x}_2 - or \mathbf{x}_3 -direction (that is, in the \mathbf{x} -, \mathbf{y} - or \mathbf{z} -direction). Like before, \mathbf{E}_x denotes the magnitude of the component of the kinetic energy (in the direction $\mathbf{x}_1, \mathbf{x}_2$ or \mathbf{x}_3) that a molecule may be in possession of. \mathbf{E}_x thus ranges from 0 to (almost) infinity. The last two lines of (28) are accounted for by the fact that all members of a group of integrals (their number being $3N$ in each of the two groups) that appear in the first two lines are equal to each other.

bb) At first sight, however, (27a) or (28) do *not* seem to yield a useful value of \mathbf{z}_x , since the product **Delta x Delta p_x** may apparently take on an *arbitrarily small* (constant) value, thus entailing that the number of possible energy levels that have to be added up, and hence \mathbf{z}_x , is enormously large (exceeding all limits). (In case we applied the principles of quantum mechanics, we would, of course, know that Heisenberg's uncertainty principle guarantees that the product **Delta x Delta p** cannot vanish.)

Liouville's theorem comes to the rescue: Though **dx dp_x** may shrink to any arbitrarily small value, the product **Delta x Delta p_x** cannot. This shall be explained in greater detail:

According to Liouville's theorem, the product $\mathbf{d}^{3N}\mathbf{x} \mathbf{d}^{3N}\mathbf{p}_x$ (that is $\mathbf{dx}_1 \mathbf{dx}_2 \mathbf{dx}_3 \mathbf{dp}_{x1} \mathbf{dp}_{x2} \mathbf{dp}_{x3}$ for the first molecule, times $\mathbf{dx}_1 \mathbf{dx}_2 \mathbf{dx}_3 \mathbf{dp}_{x1} \mathbf{dp}_{x2} \mathbf{dp}_{x3}$ for the second molecule, etc) is independent of time, provided the energy of the system stays constant. Setting the product $\mathbf{d}^{3N}\mathbf{x} \mathbf{d}^{3N}\mathbf{p}_x$ equal to a constant is, as will be shown below, equivalent to saying that in six-dimensional phase space, the "swarm" of N mass-particles behaves like the flow of an incompressible liquid. Hence, the magnitude of the product $\mathbf{d}^{3N}\mathbf{x} \mathbf{d}^{3N}\mathbf{p}_x$ is also independent of the variant of an arrangement and also of the arrangement of occupation numbers itself.

Liouville's theorem shall be elaborated. Let us define a parameter \mathbf{H} (called Hamiltonian) in the following way:

(28a)

$$H = \sum_i \left(\frac{1}{2} m v_i^2 + U_i(x_i) \right) = \sum_i \left(\frac{1}{2} m \dot{x}_i^2 + U_i(x_i) \right) = \sum_i \left(\frac{p_i^2}{2m} + U_i(x_i) \right)$$

Partially differentiating \mathbf{H} with respect to a single \mathbf{p} , that is, with respect to the momentum component in one direction of a single particle of mass \mathbf{m} , gives:

(28b)

$$\frac{\delta H}{\delta p_i} = \frac{p_i}{m} = v_i = \dot{x}_i$$

Partially differentiating \mathbf{H} with respect to a single \mathbf{x} , that is, with respect to the spatial position of a single particle, gives (\mathbf{F} is force on a particle):

(28c)

$$\frac{\delta H}{\delta x_i} = \frac{\delta U_i}{\delta x_i} = -F_i = -\dot{p}_i$$

One should also note that, even if $d\mathbf{H}$ (the total differential of \mathbf{H}) is exactly zero (which is the case if the total energy of the system, kinetic and potential, stays fixed), **partial delta H** may nevertheless be different from zero, since we are considering the change brought about by the motion of one single particle only.

We shall now imagine that each of the many particles is moving in a six-dimensional phase space. That is to say: Each particle has, at any moment in time, six coordinates, which are $\mathbf{x}, \mathbf{y}, \mathbf{z}, \mathbf{p}_x, \mathbf{p}_y, \mathbf{p}_z$. (For a short while, we will use $\mathbf{x}, \mathbf{y}, \mathbf{z}$ instead of $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3$.)

At a later moment in time, the single point that represents that particle in six-dimensional phase space may have shifted. If there are many neighbouring points (in six-dimensional phase space) which each represent a particle, we are confronted with what we may call a “flow of stuff” in the six-dimensional phase space. We would like to find out whether or not the number of points in a stationary (six-dimensional) volume element (of constant volume, shape and position) stays constant over time. We presume that, at a given moment in time to start with, the density of points in phase space does not change abruptly near the volume element and is homogeneous in its interior. We further assume that this absence of any abrupt change will be the case during the whole interval of time in which we are watching it. We also assume that neither the position nor the momentum of a particle near or inside the volume element will change abruptly with time. That is to say: The density of points as well as positions and momenta of particles shall be differentiable with time. This assumption is by no means a daring one: It follows from the fact that the points would not be located at close distance from each other in phase space (as they are), if there were abrupt changes in position or velocity between them.

If, for a better illustration, we reduce the dimensions from six to merely two (this is for a short

while only), that is \mathbf{x} and \mathbf{p}_x , we would get for dZ/dt , that is, for the increase or decrease in the number Z of particles in the two-dimensional “volume” element over an interval of time (A is a factor that is an expression of the particle density in phase space; without any further knowledge, all parameters could depend on position in phase space and on time):

(28d)

$$\begin{aligned} -\frac{dZ}{dt}(x_2 p_x, t) &= A(x_2 p_x, t) \left[\frac{v_{horiz_2} - v_{horiz_1}}{x_2 - x_1} (x_2 p_x, t) + \frac{v_{vertic_2} - v_{vertic_1}}{p_{x_2} - p_{x_1}} (x_2 p_x, t) \right] \\ &= A(x_2 p_x, t) \left[\frac{\delta \dot{x}}{\delta x}(x_2 p_x, t) + \frac{\delta \dot{p}_x}{\delta p_x}(x_2 p_x, t) \right] \end{aligned}$$

The equation is based on the assumption that a large number of particles find themselves within the volume element and nearby. Horizontal velocities v_{horiz} and vertical velocities v_{vertic} refer to velocities of particle points in the two-dimensional diagram in which the horizontal axis stands for the direction \mathbf{x} , and the vertical axis stands for the \mathbf{x} -component of momentum \mathbf{p} . The subscript 1 refers to the location where particle-points enter the fixed volume element. The subscript 2 refers to the location where particle points-leave the volume element. We also assume that the changes in velocities from particle to particle at a frozen moment in time apply to a great number of particles which behave the same way.

When returning to six dimensions (instead of just two), we have:

(28e)

$$-\frac{dZ}{dt} = A \left(\frac{\delta \dot{x}}{\delta x} + \frac{\delta \dot{y}}{\delta y} + \frac{\delta \dot{z}}{\delta z} + \frac{\delta \dot{p}_x}{\delta p_x} + \frac{\delta \dot{p}_y}{\delta p_y} + \frac{\delta \dot{p}_z}{\delta p_z} \right)$$

Making use of (28b) and (28c), (28e) turns into:

(28f)

$$-\frac{dZ}{dt} = A \left(\frac{\delta}{\delta x} \frac{\delta H}{\delta p_x} + \frac{\delta}{\delta y} \frac{\delta H}{\delta p_y} + \frac{\delta}{\delta z} \frac{\delta H}{\delta p_z} - \frac{\delta}{\delta p_x} \frac{\delta H}{\delta x} - \frac{\delta}{\delta p_y} \frac{\delta H}{\delta y} - \frac{\delta}{\delta p_z} \frac{\delta H}{\delta z} \right)$$

or, after re-arranging the order of summands:

(28g)

$$-\frac{dZ}{dt} = A \left[\left(\frac{\delta}{\delta x} \frac{\delta H}{\delta p_x} - \frac{\delta}{\delta p_x} \frac{\delta H}{\delta x} \right) + \left(\frac{\delta}{\delta y} \frac{\delta H}{\delta p_y} - \frac{\delta}{\delta p_y} \frac{\delta H}{\delta y} \right) + \left(\frac{\delta}{\delta z} \frac{\delta H}{\delta p_z} - \frac{\delta}{\delta p_z} \frac{\delta H}{\delta z} \right) \right] = 0$$

Since the order of partial differentiations can be reversed without affecting the result, each of the

three brackets is zero, and so is the whole sum. Given the number of particle-points in a fixed six-dimensional volume element of phase space does not change with time, \mathbf{A} (which is an expression of particle density in phase space) does not depend on time.

With the density of particle-points in phase space being constant over time, the ensemble of points in six-dimensional phase space behaves like an incompressible liquid in real space that has a homogeneous density. Note that (28g) is valid in the interior of a “lump” of particle points only, and is not applicable right at the surface of the lump, where \mathbf{H} is not differentiable.

Also note that there may be different “lumps” of particle points at the same time that have different homogenous densities in phase space (similar to incompressible liquids in real space, which, too, come in different densities).

One can go a step further by replacing the six-dimensional phase space with a $6N$ -dimensional phase space. Then a whole lump of N particles is represented by a single point that has $6N$ coordinates. Other lumps (“colleagues”) of particles containing the same number of particles are represented by other points. The flow of those points, too, behaves like an incompressible liquid. Nevertheless, we confine ourselves to considering points that move in the six-dimensional phase space, each point thus representing a single particle. We then have (there are N particles; \mathbf{x} is the spatial coordinate, \mathbf{p} is the momentum, the subscript \mathbf{j} refers to the three directions in space, that is, the \mathbf{x} -, \mathbf{y} , and \mathbf{z} -direction) :

(28h)

$$-\frac{dZ}{dt} = C \left[\sum_{i=1}^{i=N} \sum_{j=1}^{j=3} \left(\frac{\delta}{\delta x_{ij}} \frac{\delta H}{\delta p_{ij}} - \frac{\delta}{\delta p_{ij}} \frac{\delta H}{\delta x_{ij}} \right) \right] = 0$$

dd) For a better illustration of (28h) and its consequence, we once more return (for a short while) to the two-dimensional phase space described by (28d). We imagine a diagram in which the horizontal axis is \mathbf{x} and the vertical axis is \mathbf{p}_x . Over time, all the points in the plane (defined by the two axes of the diagram) move. But since the divergence of the flow of points (in the stationary surface area considered) is zero, the density of points in the plane of the diagram stays fixed.

This is proof of the validity of Liouville’s theorem in two-dimensional phase space.

This being the case, each of the many points in the plane can be given its own little surface area (of squared or rectangular shape) in the plane, with all surface areas having the same non-vanishing size (magnitude), and with no area left over between the squares. Due to the “incompressibility of the two-dimensional liquid”, the size of the areas does not change when the points are moving with time.

In order to conclude our train of thoughts and to return to our gas, an additional assumption must be added: We have to presume that, at some point in the past or future, the density of the ideal gas we are considering is not infinite in phase space. This being the case, it cannot be infinite in phase space at any point in time, and can thus not be infinite at the point in time we

are scrutinizing it.

This is proof of z_x (appearing in Equation 27, 27a and 28) being finite.

ee) Let us now replace the two-dimensional phase space by $6N$ -dimensional phase space. The squares of constant size would then be replaced by $6N$ -dimensional “cubicles” $d^{3N}x d^{3N}p_x$ of uniform size (and of uniform shape) that cannot shrink indefinitely. Here, too, a point in its “cubicle” can be thought of as being smeared out to form a ($6N$ -dimensional) paste that fills the whole “cubicle”.

Equation (28) is thus equivalent to the general expression for z , namely (19).

ff) As a next step, the double integrals in (28) and (27) shall be solved. When solving the double integral in (28) (with V denoting the - external - volume of the gas the shape of which shall be cubic), we get for (28):

(29)

$$\left[C \int_1^\infty \int_{-\infty}^\infty dx_1 dp_{x1} e^{-\frac{p_{x1}^2}{2mkT}} \right]^{3N} = [CV^{1/3} \int_{-\infty}^\infty e^{-\frac{p_{x1}^2}{2mkT}} dp_{x1}]^{3N} = [CV^{1/3} \int_{-\infty}^\infty (2mkT)^{1/2} e^{-q^2} dq]^{3N}$$

The first integral, that is the integral of dx_1 , is equal to $V^{1/3}$ or to the length of an arbitrarily picked side of the cubic box. The variable q is an auxiliary variable that substitutes p_x by being defined as $q^2 = p_x^2 / 2mkT$.

Due to the fact that the integral of $e^{-q^2} dq$, taken from negative to positive infinity, is equal to the square root of π , we get for (28) and hence for (29):

(29a)

$$z_x^{3N} = [CV^{1/3} \int_{-\infty}^\infty (2mkT)^{1/2} e^{-q^2} dq]^{3N} = [CV^{1/3} (\pi mkT)^{1/2}]^{3N} = C^{3N} V^N (\pi mkT)^{3N/2}$$

or

(30)

$$z_x = C V^{1/3} (\pi mkT)^{1/2}$$

We have hence solved our task of determining the constant z_x . Since C is finite (as has been shown), the adding up of all possible, discrete energy levels does not yield an infinite sum (contrary to our first impression). Consequently, the number of possible energy levels is limited.

[It was U. Hoyer who pointed out that the principles of quantum theory could have been discovered even prior to the scrutiny of black body radiation, namely in connection with

Boltzmann's distribution of energies (see U. Hoyer, "Ludwig Boltzmann und das Grundlagenproblem der Quantentheorie", Zeitschrift für allgemeine Wissenschaftstheorie, Vol. XV, 1984, pp. 201-210). Nevertheless, Hoyer's view differs from the one presented here: In the face of our Equation 28, his train of thoughts would lead to the assertion that the product of the differentials in our Equation 28 must be given a non-vanishing value for purely statistical reasons, that is, in order to do statistics at all, with nothing in *nature* requiring that the phase space volume thereby described cannot be smaller (p. 210, my own translation from German): "*Heisenberg's uncertainty relations are not an expression of a general uncertainty of measurements, but are consequences of a necessity for partitioning phase space when it comes to treating atomism statistically.*" But it is Liouville's theorem and not our desire for doing statistics that requires us to consider the product of the differentials as non-vanishing. Liouville's theorem, in turn, is derived from Newton's mechanics.

Since nature thus requires us to treat a product of differences as a constant, it seems that nature does not only consist of tangible things, that is things which have mass and therefore energy, but also of mathematical abstractions as separate entities. For, given that the partitioning of phase space is a mathematical operation, and given that this partitioning is nevertheless part of nature and not just part of our pure imagination, the first part of Hoyer's discovery, that is the recognition that the product of differences in Equation 28 must have a non-vanishing value, is hence evidence of a mathematical universe postulated expressis verbis (although at a later time) by Tegmark and others. But it had been U. Hoyer who had paved the way for the "mathematical universe" by his under-rated discovery.]

d) The derivation of some other parameters of the gas

aa) Inserting (30) into (15) and making use of (26) gives the probability distribution for the **x**-component of kinetic energies:

(30a)

$$dP = \frac{dn}{N} = \frac{C_2}{z_x} e^{-\beta E_x} dE_x = \frac{C_2}{C_1 V^{1/3} (2\pi m k T)^{1/2}} e^{-\frac{E_x}{kT}} dE_x = \frac{C_3}{V^{1/3} (2\pi m k T)^{1/2}} e^{-\frac{E_x}{kT}} dE_x$$

The constant C_3 plays the role of a norming constant, since the integral of (30a) has to be equal to unity.

When forming the integral of (30a) from zero to positive infinity, and setting it equal to unity, the constant C_3 is found to be equal to $V^{1/3} (2 \pi m k T)^{1/2} (kT)^{-1}$. The integral cannot be taken from negative infinity to positive infinity, as it would then be divergent.

Hence, (30a) is turned into

(30b)

$$dP = \frac{dn}{N} = \frac{1}{kT} e^{-\frac{E_x}{kT}} dE_x$$

For the average kinetic energy of a particle in the positive \mathbf{x} -direction, we get from (22) [if **beta** is replaced by (26), that is by $(\mathbf{kT})^{-1}$, \mathbf{z}_x is replaced by (30), and if assuming that \mathbf{C} , \mathbf{V} , and \mathbf{m} do not depend on \mathbf{T} and hence on **beta**):

(30c)

$$\begin{aligned}\overline{E_x} &= -\frac{\delta \ln[CV^{1/3}(2\pi mkT)^{1/2}]}{\delta\beta} = -\frac{\delta[\ln(CV^{1/3}) + \frac{1}{2}\ln(2\pi m) + \frac{1}{2}\ln\beta^{-1}]}{\delta\beta} = -\frac{\delta(-\frac{1}{2}\ln\beta)}{\delta\beta} \\ &= \frac{1}{2} \frac{1}{\beta} = \frac{1}{2} kT\end{aligned}$$

But when determining the average energy E_x by taking the integral of the product of (30b) and E_x , we would get:

(30d)

$$\overline{E_x} = \int_0^N E_x(n) \frac{dn}{N} = \int_0^\infty \frac{1}{kT} E_x e^{-\frac{E_x}{kT}} dE_x = kT$$

The only way to prevent a contradiction is the following: in (30d), a factor of $1/2$ has to be placed in front of E_x . Without this correction, both kinetic energy of motion in the positive \mathbf{x} -direction and also kinetic energy of motion in the negative \mathbf{x} -direction are distributed among *all* particles (as a result of the integration from zero to infinity), just as if a single particle could carry both of these two energies. In other words: In (30d), E_x is treated as being equal to $E_{x+} + E_{x-}$. By introducing the factor $1/2$, (30d) turns into:

(30e)

$$\overline{E_x} = \int_0^N \frac{1}{2} E_x(n) \frac{dn}{N} = \int_0^\infty \frac{1}{2kT} E_x e^{-\frac{E_x}{kT}} dE_x = \frac{1}{2} kT$$

For the average “energetic velocity”, that is, for the square root of the average square of \mathbf{v} , we get from (30d) and (30e):

(30f)

$$\sqrt{\overline{v_x^2}} = \sqrt{\frac{2\overline{E_x}}{m}} = \sqrt{\frac{kT}{m}}$$

bb) In order to obtain the distribution of *velocities* (rather than kinetic energies) from (30b), dE

is replaced by $\mathbf{mv}_x d\mathbf{v}_x$ according to the rules of differential calculus, and \mathbf{E} in the exponent of (30b) is replaced by $\mathbf{1/2 mv}^2$. We then get from (30b):
(30g)

$$dP = \frac{dn}{N} = \frac{mv_x}{kT} e^{-\frac{mv_x^2}{2kT}} dv_x$$

The integral of (30g) amounts to unity when extended from zero to positive infinity.

For the average velocity in one direction, we get from (30g) (instead of the factor of $\mathbf{1/2}$ that was used in Equation 30e, a factor of $\mathbf{2^{-1/2}}$ is now used, given that *energies* and not *velocities* are counted twice if no correction is made):
(30h)

$$\overline{v_x} = \int_0^N \frac{1}{\sqrt{2}} v_x(n) \frac{dn}{N} = \int_0^\infty \frac{1}{\sqrt{2}} \frac{mv_x^2}{kT} e^{-\frac{mv_x^2}{2kT}} dv_x = \frac{\sqrt{\pi}}{2} \sqrt{\frac{kT}{m}} = 0.886 \sqrt{\frac{kT}{m}}$$

cc) If one is interested in determining the \mathbf{z} -function not only with respect to the Boltzmann distribution of a *single* direction-component of the kinetic energy, but with respect to the Boltzmann distribution of the *total* kinetic energy, we take the \mathbf{N} -th root (not the $\mathbf{3N}$ -th root) of (29a). We thus get:
(31)

$$z_x^3 = z = C^3 V (2\pi mkT)^{3/2}$$

This is the \mathbf{z} -function for any system of elements whose randomly distributed energy is kinetic energy that has three direction-components.

e) Deriving the general gas law

We will now derive the general gas equation (in doing so, I am still following a thread laid out by L. Susskind in his [online-lecture on Statistical Mechanics](#) at Stanford University). (24) can be re-written as (replacing $\mathbf{\beta}$ bei $\mathbf{1/kT}$):
(32)

$$\frac{S}{k} = \beta \overline{E} + \ln z = \frac{\overline{E}}{kT} + \ln z$$

or (multiplying by \mathbf{T}):

(32a)

$$\frac{TS}{k} = \frac{\bar{E}}{k} + T \ln z$$

or:

(33)

$$\bar{E} - TS = -kT \ln z$$

Next, we will consider an adiabatic change of state in which entropy **S** stays fixed. For the total differential of the energy **E** of the gas (which shall depend on **T** and **V**) we have:

(34)

$$(dE)_S = \left(\frac{\delta E}{\delta V} \right)_T dV + \left(\frac{\delta E}{\delta T} \right)_V dT = \left(\frac{\delta E}{\delta V} \right)_T dV + \left(\frac{\delta S}{\delta T} \frac{\delta E}{\delta S} \right)_V dT$$

Dividing by **dV** gives:

(35)

$$\left(\frac{dE}{dV} \right)_S = \left(\frac{\delta E}{\delta V} \right)_T + \left(\frac{\delta S}{\delta T} \frac{\delta E}{\delta S} \right)_V \frac{dT}{dV}$$

Since the change in state shall be adiabatic, we can formulate:

(36)

$$dS = \left(\frac{\delta S}{\delta V} \right)_T dV + \left(\frac{\delta S}{\delta T} \right)_V dT = 0$$

Dividing by **dV** gives:

(37)

$$\left(\frac{\delta S}{\delta V} \right)_T + \left(\frac{\delta S}{\delta T} \right)_V \frac{dT}{dV} = 0$$

Hence

(38)

$$\frac{dT}{dV} = -\left(\frac{\delta S}{\delta V}\right)_T \left[\left(\frac{\delta S}{\delta T}\right)_V\right]^{-1}$$

Inserting (38) into (35) gives:
(39)

$$\left(\frac{dE}{dV}\right)_S = \left(\frac{\delta E}{\delta V}\right)_T - \left(\frac{\delta S}{\delta V}\right)_T \left(\frac{\delta E}{\delta S}\right)_V = \left(\frac{\delta E}{\delta V}\right)_T - \left(\frac{\delta S}{\delta V}\right)_T T$$

The partial derivative dE/dS was replaced by T .

Moreover, for an adiabatic change of state, the principle of energy conservation requires:
(40)

$$dE = p dV$$

or (with p denoting external pressure and no longer momentum):
(41)

$$p = \left(\frac{\delta E}{\delta V}\right)_S$$

Inserting this into (39) yields:
(42)

$$-\left(\frac{dE}{dV}\right)_S = p = -\left(\frac{\delta E}{\delta V}\right)_T + \left(\frac{\delta S}{\delta V}\right)_T T = -\left(\frac{\delta(E - TS)}{\delta V}\right)_T = NkT \left(\frac{\delta \ln z}{\delta V}\right)_T = \frac{NkT}{V}$$

The substitution of $E-TS$ by $-NkT \ln z$ in (42) is in accordance with (33). Since (33) denotes the entropy of a single box, the factor N has to be introduced into (33) in order to apply (33) to the gas as a whole. The derivative of $\ln z$ with respect to V (appearing in Equation 42) is simply $1/V$. This is because z is given by (31), so that the derivative of $\ln z$ with respect to V is equal to the derivative (with respect to V) of
(42a)

$$\ln z = \ln C^3 + \ln V + \ln [(2\pi mkT)^{3/2}]$$

But of the three summands, it is only $\ln V$ that depends on V . Hence the derivative of the above sum (that is, the derivative of $\ln z$) with respect to V is $1/V$. This explains the equality of $d \ln z / dV$ and $1/V$ on the right hand side of (42).

(42) can be re-written as:

(43)

$$pV = NkT$$

This is the general gas law.

f) Replacing point masses by extended objekts (spheres)

aa) So far, it has been left undecided whether the molecules have a size different from zero, or whether they are just point molecules. If one assumes that their size is different from zero, the above equations are nevertheless fully applicable. This is because Liouville's theorem does not only pertain to a "swarm" of *point* particles, but to a "swarm" of *spatially extended* particles as well, since all positions occupied by the point-like centers of the spatially extended particles in phase-space may as well be occupied by pure point particles.

Even mutual collisions of molecules do not jeopardize the validity of Liouville's theorem: On our path to Liouville's theorem we formed partial derivatives of the Hamiltonian \mathbf{H} , with the spatial positions of all particles – except one particle – being fixed. This is why the partial derivative of \mathbf{H} with respect to the position of that particle (which boils down to the partial derivative of the potential energy of the particle with respect to its position) yields the correct – and finite – force the particle is subject to at any instant of time or spatial position considered. Moreover, since a collision with another particle is nothing but a situation in which the particle considered finds itself in the repulsive force-field of another particle, a collision occurs over a period of time and a length of a spatial path that are not vanishingly small. Consequently, the derivative of the momentum of a particle with respect to time (that was used above) does never yield an infinitely large numerical value.

Since the mutual repulsive forces of the molecules can be assumed to act over extremely short spatial distances only (much shorter than the distances over which the mutual attractive forces – if any – can be supposed to act), the neglect of potential energies they generate cannot affect the result of distribution of energies obtained above. Instead, at any moment in time picked, practically all molecules are so far apart from each other that practically all molecules are in possession of a potential energy of zero.

Moreover, the volume V appearing in (31) and in equations of higher number is not affected by the introduction of particles that have a spatial extension, provided the diameter of a single particle is very small compared to the length, width or height of the container. In other words: Though the center of a particle that is spatially extended cannot reach the wall of the container, and though this reduction in the spatial range of a molecule's motion leads to a reduction of the effective volume of the container, that reduction is minuscule if a particle is very small in diameter compared with the size of the container. In other words: From a statistical perspective, it is only the space volume

$$\int_{\text{inner surface } A \text{ of container}} r dA$$

that has to be subtracted from the available volume V of the container (with r being the radius of a spherical model particle), and not the proper volume of the molecules.

bb) However, when it comes to gases of higher densities, the general equation of the ideal gas yields results that deviate considerably from empirical reality. In those cases (in which the diameter of a single particle is still very small compared to the length, height, and width of the container, but in which the combined volume proper of all particles is not small compared to the volume of the container), reality is better described by
(44)

$$p (V-b) = NkT$$

with b denoting a positive term bigger than zero.

From this follows: When dealing with a real gas that is made up of spatially extended molecules, the real distribution of energies must differ considerably from Boltzmann's distribution!

In other words: When observing a gas (confined in a box) over a very long period of time, each spatially extended particle, that is, its center, has visited all cubicles the box is subdivided into in our imagination, and the number of visits is practically the same for every cubicle. At a given total energy of the gas, it cannot, for these numbers of visits and their durations, make a difference as to whether or not the particles are spatially extended.

cc) Consequently, the slightly higher pressure (compared to an ideal gas) at a fixed volume of the box and a fixed temperature of the gas cannot be blamed on the proper volume of the particles.

It must be blamed on a deviation from Boltzmann's distribution of energies and velocities, instead. As was shown in (30h), the average velocity of a particle in one direction – under the rule of Boltzmann's distribution of energies and velocities – is only 88 percent of the average “energetic velocity” of a particle in that direction. In case the real distribution of velocities were somewhat more even than Boltzmann's, the average velocity of the particles in one direction and hence the pressure exerted on a wall would, at a fixed average energy of the particles and hence at a fixed temperature of the gas, be somewhat higher than it is under the rule of Boltzmann's distribution and hence under the rule of the general gas law. More precisely: Since the pressure on the walls of the box is proportional to the square of the average velocity in the direction of the normal of the wall, the pressure at a given density and a given temperature of the gas would increase by the factor of $(0.88)^{-2} = 1.29$ (even for a gas made up of extensionless point particles) in case the distribution of velocities were perfectly even, that is, in case all particles had the same velocity.

dd) A mechanical explanation for the obvious deviation from Boltzmann's distribution (towards a more even one) is the following: The mechanism of energy distribution has a memory of the

fact that in the recent past a very fast molecule has absorbed energy over average. This is because the fast molecule's chances of absorbing, by means of the next collision with another molecule, an energy quantum (that will increase its kinetic energy) are slimmer than those chances are for a molecule whose kinetic energy is very low (so that it is almost standing still). As a consequence, the precondition of our derivation of Boltzmann's distribution, that is, the principle of random distribution of bits of energy among molecules (under certain restrictions) regardless of what kinetic energy they are in possession of, is not strictly obeyed.

ee) This result is getting support from an argument forwarded by Sorin Cosofret ([About kinetic molecular theory, states of matter and nuclear reaction in stars, 2018, p.3](#)): If the velocities of molecules that constitute a gas were distributed in accordance with Boltzmann's distribution, there would be, at any time, a small fraction of molecules with extremely high velocities and hence with extremely high kinetic energies. This would inevitably lead to a destruction of the walls of the container that are housing the gas. No molecule of the wall material could stand the impact of those high energy gas particles, but would be forced to leave its position in the lattice. But such a destruction of the container walls has never been observed.

g) Proof of a stratification of temperature in a heavy gas if Boltzmann's law of distribution of energies is not observed

aa) The unrestricted validity of Boltzmann's distribution of energies, however, is a necessary condition for the temperature of a gas in an external force field to be the same at all heights. A proof of the sameness of temperature at all heights on the basis of Maxwell's-Boltzmann's distribution was provided by A.J. Walton (Alan J. Walton, Archimedes' principle in gases, Contemporary Physics, Vol. 10 – 1969 –, p. 185), by Claude Garrod (Statistical mechanics and thermodynamics, Oxford University Press, 1995), and also by K. Zhang / Y.-J. Zhang (Principle of detailed balance and a dilute gas in gravitational field, arXiv:1607.06692v3 [cond-mat. stat-mech] 30 Nov 2016).

Walton's train of thoughts shall be displayed in a somewhat modified form. Imagine a layer of gas right at the bottom of a container. Let the temperature of the gas in this layer be T_1 . The x -direction shall be the direction of the normal of the bottom. The average kinetic energy in the x -direction of motion in the fictive case that every particle had kinetic energy both in the positive and the negative x -direction (see above) amounts to kT_1 .

Now imagine a second horizontal layer of gas (of the same thickness) at some height h above the ground. All the particles in that layer are those whose kinetic energy in the x -direction, when finding themselves in the bottom layer, is bigger than the difference in potential energy between the two layers. This difference shall be labelled E_{pot} . For the average kinetic energy E of the particles (in the x -direction of motion) in the upper layer we then find from (30b) and (30d):

(45)

$$\overline{E_{2_x}} = \frac{\int_{n_0}^N E_x(n) \frac{dn}{N}}{\int_{n_0}^N \frac{dn}{N}} - E_{pot} = \frac{\int_{E_{pot}}^{\infty} \frac{E_x}{kT_1} e^{-\frac{E_x}{kT_1}} dE_x}{\int_{E_{pot}}^{\infty} \frac{1}{kT_1} e^{-\frac{E_x}{kT_1}} dE_x} - E_{pot} = E_{pot} + kT_1 - E_{pot} = kT_1$$

N is the total number of molecules; all molecules are given consecutive numbers in the order of their kinetic energies in the x-direction which they are in possession of at the bottom. The number n_0 is given to the molecule whose kinetic energy in the x-direction (at the bottom) is just big enough to reach the upper layer. The integral below the big fraction line gives rise to the fact that the total number of particles whose kinetic energies in the bottom layer are in the range between E_{pot} and infinity is not N, but is $N - n_0$.

In other words: Given Boltzmann's distribution of energies is applicable, the assumption of the uniformity of temperature in a column of gas (subject to gravity) at all heights is justified.

In case the real distribution of energies is *more even* than Boltzmann's distribution, the temperature of the gas in the column *declines* with height. In case the real distribution of energies is *less even* than Boltzmann's distribution, the temperature *increases* with height.

Since the real gas – that is made up of extended particles – does not strictly obey Boltzmann's distribution law for energies, but shows a more even distribution, it follows that there cannot be a homogeneous temperature of the gas as a state of equilibrium in an insulated column subject to gravity.

bb) A similar result, that is a result that defies Boltzmann's distribution of energies as a stationary state when gravity is at play, was obtained by L. Susskind. In his own words:

“Gravity has all kinds of problems with thermodynamics, even just Newtonian gravity. Newtonian gravity does not have a good thermal equilibrium. ... Gravity itself is a disastrous thing when you are thinking about thermal equilibrium.” It *“cannot correspond to a genuine equilibrium situation. ... Systems with negative specific heats cannot be in equilibrium with their environment. ... Thermodynamics breaks down eventually for systems with gravity.”*

III.

1) Attention shall be drawn to the experimental work done by Roderich Graeff¹⁶⁾ over many years concerning temperature differences in gases and liquids subject to gravity [see R.W. Graeff, [“Measuring Temperature Distribution in Gas Columns”](#) (2015), first version published in: D. Sheehan, editor, Quantum Limits to the Second Law, First International Conference on Quantum Limits to the Second Law, San Diego, California, 28-31 July 2002, AIP Conference Proceedings 643, pp. 225-230; see also R.W. Graeff, My path to Peaceful Energy, 2010]. Graeff's theory of a temperature gradient by which he explained his positive experimental

results could be quantitatively correct (only) in case the distribution of energies of the molecules were almost even.

2) A temperature gradient was also found experimentally by Chuanping Liao ¹⁷⁾ [[Temperature Gradient Caused by Gravitation](#)”, International Journal of Modern Physics B, Vol. 23, No. 22 (2009), pp. 4685-4696]. His *theoretical* proof of a temperature gradient can be contested, though:

Let us imagine that two long, horizontal pipes sitting at different levels of height are connected to each other by means of a vertical pipe. Let us further imagine that the volume of a unit mass of an ideal gas is big compared to the volume of the vertical pipe. That ideal gas shall be supposed to flow through the system of pipes, moving upward when it comes to flowing through the vertical section. Given no heat is added or withdrawn from the gas – neither from the ambient nor from other parts of the gas (adiabatic change of state) – , the principle of conservation of energy gives:

(55)

$$(U_1 - U_2) + (p_1 V_1 - p_2 V_2) = gh_2 - gh_1$$

U_1 is the internal energy of a unit mass of the gas in the lower horizontal pipe, U_2 is the internal energy of the unit mass of gas in the upper horizontal pipe. The work $p_1 V_1$ (with V being volume per unit mass, and p being pressure) is invested in the system when the unit mass of gas is isobarically pushed into the vertical section. The work $p_2 V_2$ is given off by the unit mass of gas when it, leaving the vertical section, isobarically shifts an imagined piston in the upper horizontal pipe. The right hand side of the equation denotes the gain in potential energy per unit mass (g is gravitational acceleration, h is height).

A re-arrangement of (55) leads to:

(56)

$$(U_2 + p_2 V_2) - (U_1 + p_1 V_1) = - (gh_2 - gh_1)$$

or

(57)

$$d(U+pV) = d(U+RT) = d(C_v T+RT) = -gdh$$

C_v is the heat capacity per unit mass at constant volume. The replacement of pV with RT follows from the general gas law (with R being the gas constant, and T being temperature).

In order to replace R , the following equation is used:

(58)

$$C_p - C_v = \frac{d(pV)}{dT} = R$$

C_p is the heat capacity per unit mass at constant pressure. The equality of the left hand side of (58) and its middle part follows from the principle of conservation of energy; the equality of the middle part and the right hand side of the equation follows from the general gas law when it is differentiated.

(57) hence turns into:

(58)

$$d(U+pV) = d(C_v T + RT) = d(C_v T + C_p T - C_v T) = C_p dT = -gdh$$

or

(59)

$$\frac{dT}{dh} = - \frac{g}{C_p}$$

This is the adiabatic lapse rate of temperature with height.

The equation does not change when all layers of gas in the vertical section are assumed to be in hydrostatic equilibrium, which means that their velocity of ascension is constant, and may be vanishingly small. But this does not entail that, in order for a layer to be thermally insulated (this was the starting point of the derivation), one could waive the two comoving, insulating bulkheads that separate the layer from its two neighbors. But this is what Liao (wrongly) regards as a consequence of a hydrostatic equilibrium.

Moreover, Liao's lapse rate is quantitatively wrong as he, in our Equation 57, that is, in his Equation 5, wrongly introduces another summand on the left side, namely the summand $-Vdp$. This error was carried into his Equation 5 by means of his Equation 2, in which he wrongly sets $dU=TdS-pdV-Mgdh$ instead of simply $dU=TdS-pdV$: A blob of gas ascending at constant velocity together with other blobs that share the same velocity of ascension does not "know" if or not it is moving in the vertical section or is standing still; in both cases, it will only "notice" a change in pressure and volume, and not a gain or loss in potential energy of height. On top of this, Liao wrongly adds a summand (of inconsistent dimensions), namely $(V-dTV)dp$, to $C_p dT$ appearing in our Equation 58, that is, in his Equation 6.

Nevertheless, Liao's experimental work produced impressive results: In a centrifuge he used, he could establish a permanent temperature difference in solid KI powder of almost 2 degrees Kelvin (the rotating arm had a length of no more than 15 cm, the maximum rotation speed was 4000 rpm). The difference in temperature was clearly proportional to the rotation speed squared (see his Fig. 2).

6) Temperature differences between a liquid and the vapor evolving from it

a) A solution and its vapor

Similar to molecules in a vertical column of gas that have a potential energy with respect to the bottom, molecules in a vapor that is in contact with the liquid phase have a potential energy relative to the surface of the liquid phase (from which they rose). The role of gravity is replaced by a different force field, namely the field of the attractive forces of the surface, whose reach is very short. As will be shown below, noticeable differences in temperature between the liquid and the vapor can occur (see also [A. Trupp, “Second Law Violations by Means of a Stratification of Temperature due to Force Fields”, in: Quantum Limits to the Second Law, American Institute of Physics – AIP – Conference Proceedings, Vol. 643, edited by D.P. Sheehan, 2002](#)):

aa) The proof consists in a “reductio ad absurdum”: It starts from the assumption that the vapor evolving from a liquid solution (e.g., salt in water) has the same temperature as the liquid. Two principles are applied to this assumption: The principle of conservation of energy, and Boltzmann’s law of distribution of potential energies among particles whose average kinetic energy does not depend on height. It is shown that this leads to contradictions.

In detail:

A saturated solution (salt in water) shall have a vapor pressure of 0.5 bar at a temperature of 100° Celsius. (It is well known that solving salt in water leads to a reduction in vapor pressure at a given temperature of the liquid phase.) We shall, for a short while, suppose that the vapor (0.5 bar) is as hot as the liquid (100°C), and is hence superheated. During a complete evaporation of the water (leaving behind the salt) at constant temperature as a first step of a cycle, the following amounts of heat **Q** and work **W** have been given off or have been added (amounts of work or heat added to the system are given a positive sign in front of the respective variable, whereas amounts of heat or work given off by the system have a negative sign in front of the respective variable; the numerical values of all variables **Q** and **W** are thus positive numbers):

(60)

$$\begin{aligned} Q_{W\text{-intern-1}} + Q_{W\text{-intern-extra-1}} + Q_{W\text{-extern-superheated-1}} - W_{\text{superheated-1}} + Q_{\text{solution}} \\ = Q_{W\text{-intern-1}} + Q_{W\text{-intern-extra-1}} + Q_{\text{solution}} \end{aligned}$$

$Q_{W\text{-intern-1}}$ is the amount of heat added from outside in order to compensate for the internal work done by the molecules when rising from the surface of the liquid in case the liquid is pure water at 100°C and 1 bar; $Q_{W\text{-intern-extra-1}}$ is the additional amount of heat added in order to compensate for the work done by extra intermolecular forces that are present in case the liquid is not pure water, but a saturated salt solution whose vapor pressure at 100°C is only 0.5 bar. The amount of heat $Q_{W\text{-intern-extra-1}}$ can be larger than zero, smaller than zero, or zero (we will have to find out which of the three alternatives is true). Compared to a saturated vapor of 1 bar at 100°C, the density ρ of that vapor (0,5 bar, 100°C) can be assumed to be about 1/2. $Q_{W\text{-extern-superheated-1}}$ is the amount of heat added from outside in order to compensate for the external work done by the

superheated vapor (100°C, 0.5 bar) when it is evolving from the surface of the liquid and is shifting a piston. $W_{\text{superheated-1}}$ is the amount of that work (of isobaric/isothermal expansion) done on a piston by the superheated vapor. $Q_{W\text{-extern-superheated-1}}$ and $W_{\text{superheated-1}}$ are equal in absolute amount. Q_{solution} is the solution heat that comes into play when the salt crystallizes. The right-hand-side of (60) is thus a short way of expressing all the amounts of heat and work involved during the first step.

As a next step (second step) of the cycle, the superheated vapor (100°C, 0.5 bar) shall be isothermally (but not isobarically) compressed until it is saturated (100°C, 1 bar). For the amounts of Q and W involved during this step, we get:

(61)

$$W_{\text{compr-2}} - Q_{\text{compr-2}} = W_{\text{compr-2}} - (Q_{W\text{-extern-2}} + Q_{W\text{-intern-2}}) = -Q_{W\text{-intern-2}}$$

W_{compr2} is the external work of (isothermal) compression. Q_{compr2} is the total heat that leaves the vapor during that (isothermal) compression. That heat consists of two parts. The first part, that is $Q_{W\text{-extern2}}$, is the heat leaving the vapor in order to compensate for the external compression work done on the vapor. The second part, that is $Q_{W\text{-intern2}}$, is the heat leaving the vapor in order to compensate for the internal work done by the mutual attraction of the vapor molecules. W_{compr2} and $Q_{W\text{-extern2}}$ are equal in absolute amount. The very right-hand side of (61) is thus a short way of expressing all the amounts of heat and work involved during the second step.

In a third and last step of the cycle, the saturated vapor (100°C, 1 bar) is made to condensate on the surface of the pure liquid (100°C, 1 bar). After this has been done, the salt is added to the liquid (100°C). For the amounts of Q and W involved during this step, we get:

(62)

$$-Q_{W\text{-intern3}} - Q_{W\text{-extern-satur3}} + W_{\text{satur3}} - Q_{\text{solution}} = -Q_{W\text{-intern3}} - Q_{\text{solution}}$$

$Q_{W\text{-intern3}}$ is the amount of heat leaving the substance in order to compensate for the internal work given off by the molecules when being absorbed by the surface of the liquid (at 100°C and 1 bar). $Q_{W\text{-extern-satur3}}$ is the heat leaving the system in order to compensate for the external (isobaric) compression work done on the saturated vapor, W_{satur3} is the amount of that external work (of isobaric compression) done on the saturated vapor. $Q_{W\text{-extern-satur3}}$ and W_{satur3} are equal in absolute amount. Q_{solution} is the heat involved when salt is eventually dissolved in the pure liquid. The right-hand side of (62) is thus a short way of expressing all the amounts of heat and work involved during the third step.

The overall-sum of the right-hand sides of (60=, (61), and (62) should add up to zero as a consequence of the principle of conservation of energy. In other words:

(63)

$$Q_{W\text{-intern-1}} + Q_{W\text{-intern-extra-1}} + Q_{\text{solution}} - Q_{W\text{-intern-2}} - Q_{W\text{-intern-3}} - Q_{\text{solution}} = 0$$

Since $Q_{W-intern1}$ and $Q_{W-intern3}$ are equal in numerical value, (63) reduces to:
(64)

$$Q_{W-intern-extra-1} = Q_{W-intern-2}$$

bb) Let us now determine the values of those two remaining parameters in (64)(that should be equal to each other).

aaa) In order to determine the value of $Q_{W-intern-extra-1}$ (that is the additional amount of heat added from outside during the first step – isothermal/isobaric evaporation -- needed to compensate for the extra intermolecular forces that are present in case the liquid is not pure water, but a saturated salt solution whose vapor pressure at 100°C is only 0.5 bar), we use the general principle that the number of atoms per unit volume in two different regions is $n_2/n_1 = e^{-(E_2-E_1)/kT}$, presuming Boltzmann's distribution is applicable. With this presumption, there would be a perfect analogy between an isothermal gas in a vertical column subject to gravity, and the vapor rising from the surface of a liquid. We would hence find: As regards the potential energy of the molecules (into which heat has been converted) that rose from the surface of the saturated salt solution, the difference between that potential energy and the potential energy of vapor molecules that rose from the surface of pure liquid water at the same temperature (100°C) would be the same as the difference between the gravitational potential energy of molecules in a column of gas at height h above the bottom and the potential energy of molecules right above the bottom of that column of gas at height $h=0$, given the ratios of the densities and the densities themselves are the same for the two compared cases (see for this equality: *R.P. Feynman, Lectures on Physics I*, chapters 40-2 and 42-1, especially chapter 42-1, page 42-1: “There is a certain difference, W , in the energy of a molecule in the liquid from what it would have if it were in the vapor, because we have to pull it away from the other molecules which attract it. Now we use the general principle that the number of atoms per unit volume in two different regions is $n_2/n_1 = e^{-(E_2-E_1)/kT}$. So the number n per unit volume in the vapor, divided by the number ... per unit volume in the liquid, is equal to ... $e^{-W/kT}$, because that is the general rule. It is like the atmosphere in equilibrium under gravity, where the gas at the bottom is denser than that at the top because of the work mgh needed to lift the gas molecules to the height h . In the liquid, the molecules are denser than in the vapor because we have to pull them out through the energy ‘hill’ W , and the ratio of the densities is $e^{-W/kT}$.”).

The density at the bottom of the column of gas – and also the density of the vapor rising from pure liquid water at 100°C and 1 bar – is q_0 . We hence get (with q being the density of the gas in the vertical column at height h and also the density of the vapor rising from the salty solution, with m being the mass of a single molecule; with T being the temperature; with k being Boltzmann's constant; with E_{potMol} being the numerically positive potential energy of a single vapor molecule with respect to the surface of the liquid, where the potential energy is defined to be zero; with R being equal to Nk ; with N being equal to the number of molecules per kmol; with M being equal to Nm ; and with E_{pot} being the potential energy per kmol of the vapor):
(65)

$$q = \frac{1}{2}q_0 = q_0 e^{-\frac{mgh}{kT}} = q_0 e^{-\frac{E_{potMol}}{kT}}$$

$$mgh = E_{potMol} = -kT \ln \frac{1}{2}$$

$$Mgh = E_{pot} = -RT \ln \frac{1}{2} = 2170 \text{ kJ/kmol} = 120 \text{ kJ/kg} = Q_{W-intern-extra-1}$$

bbb) Let us now determine the value of $Q_{W-intern2}$ (that is the heat leaving the vapor during step 2 – isothermal, but not isobaric compression of the vapor – in order to compensate for the internal work done by the mutual attraction of the vapor molecules). What we get from Van-der Waals' equation is:

(66)

$$Q_{W-intern-2} = \int_{V_1=V_{saturated-vapor}}^{V=\infty} \frac{a}{V^2} dV = \left[-\frac{a}{V} \right]_{V_1}^{\infty}$$

With $a=555000 \text{ Nm}^4/\text{kmol}^2$, and with a specific volume of the saturated vapor (100° C, 1 bar) of **30,157 m³/kmol** (with **1 kmol** corresponding to **18,015 kg**), we obtain:

(67)

$$Q_{W-intern-2} = 18.40 \frac{\text{kJ}}{\text{kmol}} = 1.02 \frac{\text{kJ}}{\text{kg}}$$

We realize that $Q_{W-intern-extra-1}$ is more than 100 times larger than $Q_{W-intern2}$, though the two parameters should be equal to each other (based on the assumption of a sameness of temperatures of the liquid solution and the vapor evolving from it).

The hypothesis of the sameness of temperature of a salty solution and its vapor has thus been subject to a “reductio ad absurdum”.

From this follows: The vapor evolving from a salt solution cannot have the same temperature as the liquid salt solution.

cc) Conversely, the temperature of the vapor and of the liquid from which it evolves could only be the same if the inner evaporation/condensation heat $Q_{W-intern-1}$ at a given temperature of the liquid were the same regardless of whether or not the liquid contains a solute (salt). Then $Q_{W-intern-extra-1}$ would vanish, and no inner contradiction would exist.

But experiments show that the inner evaporation/condensation heat $Q_{W-intern-1}$ at a given temperature *is* increased by the presence of a solute. E.T. Whittaker, Proceedings of the Royal Society A, Vol. 81 (1908), p. 21, cited in Bakker, Handbuch der Experimentalphysik, edited by

W. Wien und F. Harms, Vol. 6: Kapillarität und Oberflächenspannung, Leipzig 1928, § 4 b, p. 211, set up the following equation for $Q_{W-intern}$:

$$Q_{W-intern-1} = \frac{H-T \frac{dH}{dT}}{kT}$$

H denotes the surface tension of the liquid, **T** its temperature, **k** is Boltzmann's constant. The specific evaporation/condensation heat at a given temperature is thus increasing in case the surface tension does.

As regards the effect on the surface tension of a liquid when adding a solute, we find (Bakker, op. cit., § 5 a, p. 238):

“When adding a dissolving substance to a liquid, for instance NaCl in water, the surface tension is modified. The surface tension of the solution is larger than that of the pure liquid and increases roughly proportionally with concentration.”

We thus find: The non-zerosness of $Q_{W-intern-extra-1}$ is not only arrived at by an application of Boltzmann's law (of distribution of energy) to a column of gas of presumably homogeneous temperature under gravity (as was done in Equation 65 in accordance with a proposal by R.P. Feynman), but also by experiment.

dd) As Edwin Edser puts it ([*Heat for advanced students*, Macmillan & Co, London 1923, pp. 188, 189](#)):

“The actual temperature of the vapour above a boiling solution is generally slightly lower than the temperature of the solution. Thus above a salt solution, the temperature of which is 110°C, the steam may reach a temperature, say, of 105°C. A thermometer placed in the steam will, however, indicate a temperature of 100°C. ... As pointed out above, a thermometer when placed in the steam given off from a boiling aqueous solution of salt, will indicate the boiling point of the water, and not that of the solution. A similar law applies to solutions in general”.

(See also *F. Rudberg*, “Über die Dampfbildung”, *Annalen der Physik*, Vol. 110, 2nd series, Vol. 34, - 1835 -, pp. 257; *J.J. Precht*, “Über die Dampfbildung– Aus einem Brief an den Herausgeber”, *Annalen der Physik*, Vol. 111, 2nd series, Vol. 35 – 1835 –, pp. 198; *Ch. Drion/E. Fernet*, *Traite de Physique Elementaire*, 3rd edition, Paris 1869, pp. 275/276; *M.V. Regnault*, “Relation des experiences...”, *Memoires de l'Academie des Sciences de l'Institut Imperiale de France*, Vol. XXVI – 1862 –, pp. 665; *P.A. Daguin*, *Traite Elementaire de Physique Theorique et Experimentale*, Toulouse/Paris 1861, § 962, p. 349/350; *J. Gill*, “On the temperature of the vapours of boiling saline solutions”, *The London, Edinburgh, and Dublin Philosophical Magazine*, 4th series, Vol. 32 – 1866 –, pp. 481; *G. Magnus*, “Über die Temperatur der aus kochenden Salzlösungen und gemischten Flüssigkeiten entweichenden Dämpfe”, *Annalen der Physik*, Band 188, 2nd series, Vol. 112 – 1861 –, pp. 408; see also the [result of an experiment with a saturated salt solution and its vapor in a closed container](#),

compared to pure water and its vapor in the same container, performed at the Fachhochschule Münster – University of Applied Science – on behalf of the author .; see also the result of another experiment.)

b) Difference in temperature between a pure liquid and its vapor; Henry Le Chatelier's law

aa) Any reduction of vapor pressure at a given temperature of the *pure* liquid, brought about by making the surface of the pure liquid concave or by simply making the pure liquid superheated, leads, for energetic reasons analogous to those displayed in (60) - (67), to a noticeable difference in temperature between the liquid and the vapor evolving from it, similar to the case of the salty solution and its vapor.

bb) An *augmentation* of vapor pressure at a given temperature of the pure liquid, brought about by making the surface of the pure liquid convex or by exerting pressure on the flat surface of the pure liquid by means of a second gas, leads, for energetic reasons analogous to those displayed in (60)-(67), to the phenomenon that the vapor evolving from the surface of the liquid is warmer than the liquid (see, as regards an increase in vapor pressure by exerting an external pressure on the flat surface of the liquid, "Müller-Pouillet's Lehrbuch der Physik und Meteorologie", Vol. 3, edited by L. Pfaundler, Viertes Buch: Wärmelehre, Chemische Physik, Thermodynamik und Meteorologie, Braunschweig 1907, 4th chapter, § 103, pp. 344/345; see especially N. Schiller, "Einige Versuche über Verdampfung von Flüssigkeiten durch einen hohen Gasdruck", Annalen der Physik, Vol. 296 – 1897–, pp. 755-759, where an increase in the vapor density of ether in contact with its liquid phase by the factor 2.9 was achieved at a given temperature of the liquid phase by applying a pressure of more than 100 bar; see finally H. Le Chatelier regarding the co-existence of a compressed liquid and its uncompressed vapor – whose saturation pressure was higher than that of the vapor evolving from an uncompressed liquid of the same temperature –, when the pressed liquid was kept at a lower temperature than the vapor, "Über das Gleichgewicht chemischer Systeme bei ungleichförmigem Druck", Zeitschrift für physikalische Chemie, Vol. 9 – 1892 –, pp. 335, 338: "*Ich lasse hier den nicht weniger interessanten Fall bei Seite, wo die verschiedenen Teile des Gebildes nicht die gleiche Temperatur haben. Wenn ich meine Versuche über den Gegenstand, die augenblicklich im Gange sind, beendet haben werde, gedenke ich hierauf zurückzukommen. Ich erwähne nur die Zunahme des Dampfdruckes einer Flüssigkeit [by pressing the liquid], welche man abkühlt, ohne ihren Dampf abzukühlen, ...*").

cc) In his printed publication "Notice sur les travaux scientifiques de M. Henry Le Chatelier, Paris 1897, p. 16/17 (cinquieme loi)", the author H. Le Chatelier postulates (as a new law of equilibrium states in which the liquid and its vapor find themselves at different pressures and at different temperatures):

(67)

$$425 \quad L \frac{dT}{T} + pV \frac{dp}{p} = 0$$

With L denoting the thermal energy of the liquid (see his page 15, bottom), and with the factor 425 giving consideration to the fact that L is expressed in units of calories, the term $425 L/T$ can be replaced by the specific heat capacity C_v times the mass M of the liquid. When dropping the pressure p out of the equation, (67) can hence be re-written as (ρ is the density of the liquid):

(68)

$$dT = -\frac{V}{MC_v} dp = -\frac{1}{\rho C_v} dp$$

Historically, Le Chatelier's equation (68) – in the form of (67) – was derived by modifying the law of chemical equilibrium (see also H. Le Chatelier, “Lecons sur le carbone, la combustion, les lois chimiques”, nouvelle edition, Paris 1926, 14ieme lecon: “Resume des lois de la mecanique chimique”, p 355/356). It can, however, also be derived by imagining that the evaporation of a pressed liquid (be it pressed by means of the surface tension of a convex surface, or by a gas exerting pressure on the flat surface) is characterized as follows: It is as if – on top of a regular evaporation of a liquid from a flat surface (taking place at uniform pressure and at uniform temperature of the liquid and its vapor) – a [Joule-Thomson throttling process](#) were being performed (in combination with a regular evaporation). In a throttling process, the liquid is pressed through a thermally insulated, porous plug or a membrane at constant high pressure, so that it leaves the plug as vapor (at a much lower pressure), and is no longer a liquid. The role of the porous plug is played by the pressed surface of the liquid from which the vapor is evolving.

Let $U_{liq_pressed}$ denote the internal energy of the pressed liquid. $U_{liq_unpressed}$ denotes the internal energy of the unpressed liquid, provided that, by arrangement, both states of the liquid generate vapor of the same temperature. The term $p_{liq_pressed}$ denotes the pressure of the pressed liquid. The term p_{vapor} denotes the pressure of the vapor evolving from the unpressed liquid at given temperature. V_{liq} denotes the volume of the liquid before evaporation. The density of the liquid shall be unaffected by the use of external pressure. The term C_{v_liq} denotes the specific heat constant at constant volume of the liquid. M_{liq} denotes the mass of the liquid before evaporation.

The pressure p_{vapor} may not be exactly equal to the pressure of the vapor (of same temperature) that evolves from the pressed liquid. Nevertheless, both the internal energies of the two compared vapors, and also the products pV of the two compared vapors – i.e., the amounts of external work of isobaric expansion done – must be very similar to each other. This is because the potential energy of the vapor molecules generated by the Van-der-Waals-forces is small compared to their kinetic (thermal) energy. This results in a behaviour of the vapor that resembles that of an ideal gas at a fixed temperature. While the difference between the two states of the vapor can only be small (if exists at all), the difference between $p_{liq_pressed}$ and p_{vapor} can be chosen at will, and can hence be huge.

We thus have (according to the principle of energy conservation):

(69)

$$(U_{liq_pressed} - U_{liq_unpressed}) + (p_{liq_pressed} - p_{vapor})V_{liq} = C_{v_liq}M_{liq}\Delta T_{liq} + V_{liq}\Delta p = 0$$

This equation (69) is equivalent to Le Chatelier's equation (68).

To elucidate:

– In order to describe the special throttling energetically, the internal energy of the pressed liquid and of the unpressed liquid have to be considered (by arrangement, both states of the liquid give off vapor of same temperature). According to the principle of energy conservation, the (numerically negative) difference in internal energy of the pressed and the unpressed liquid (first bracket) must equal the extra mechanical work spent on pressing the liquid through the plug (second bracket times V_{liq}). The extra work is the work done on the pressed liquid at constant pressure, minus the mechanical work done on the liquid during a regular evaporation, when the surface is kept at a fixed position and the bottom of the box – which then acts as a piston – is being lifted. During this regular evaporation, the pressure on the liquid is identical in magnitude with the vapor pressure p_{vapor} .

– On the other side of the plug, it is as if no work is done by the vapor, since the mechanical work actually done by the vapor is considered to be the result of the regular evaporation, and is not given consideration in the analysis of the special throttling process.

Note that – different from a common throttling process – the special throttling is reversible!

Re-arranging (69) leads to (68), that is, to Le Chatelier's equation.

For Tetralin as an arbitrarily picked liquid, (68) gives a temperature difference of 0.11 degree Kelvin (between the warmer vapor and the colder liquid) per 1 bar of pressure difference (between the compressed liquid and the uncompressed vapor).

dd) The augmentation of vapor pressure can be explained by repulsive forces of the molecules: If the molecules are densely packed (as is the case in a liquid), a potential energy of the molecules is created that requires the constant “ a ” in the modified gas law (see above) to be numerically negative. When a molecule is traversing the convex surface of the pure liquid from below, thus traveling from a region of higher pressure (below the surface) to a region of lower pressure (above the surface), its potential energy due to repulsive forces is converted into kinetic energy, provided the neighboring substance does not exert its own repulsive force on the molecules. This potential energy (that is converted into kinetic energy) does not depend on the velocity of a molecule, but on its position. This is why it is evenly distributed among the molecules, and does not obey Boltzmann's rule of distribution of energies.

The situation may thus be compared to a gas that, flowing through a horizontal pipeline, passes through a downward vertical section of the pipeline, in order to pick up its horizontal path on a lower level. On the lower level, it is warmer than on the upper level, as potential energy – shared by all molecules regardless of their individual velocities – was converted into unordered kinetic energy. Likewise, the temperature of the pure liquid is lower than that of the vapor in contact with the convex surface of the liquid.

ee) In case the surface of the pure liquid is concave, the pressure below the surface is lower than above the surface. This is why molecules from the vapor space, when managing to enter the bulk of the liquid, are subject to a an acceleration that is stronger than it is in case of a flat surface. It is as if there were a repulsive force on the molecules that acted from the interior the vapor space in the direction of the interior of the liquid.

Because of this inverse analogy with a pressed liquid (and its uncompressed vapor), Le Chatelier's equations (68) and (69) can also be applied to a dilated liquid, i.e., to a liquid whose pressure is lower (and whose temperature is higher) than that of the vapor in contact with it. We then have (as an equation of state):

(70)

$$(U_{liq_{dilated}} - U_{liq_{undilated}}) + (p_{liq} - p_{vapor})V_{liq} = C_{v-liq}M_{liq}\Delta T_{liq} + V_{liq}\Delta p = 0$$

or:

(71)

$$dT = -\frac{V}{MC_v} dp = -\frac{1}{\rho C_v} dp$$

ff) Though H. Le Chatelier played an important role in physical chemistry (the [Chatelier-principle](#) was named after him), the importance of his Equation (67) or (68) has never been recognized so far.

7) A late completion of Boltzmann's homage paid to Loschmidt; consequences for the Second Law and for the nature of time

a) Loschmidt's conception of the Second Law of Thermodynamics

aa) When Josef Loschmidt died in 1895, Boltzmann held a memorial speech addressed to the Chemical-Physical Society of Vienna on the 29th of October, 1895. On this occasion, he rated the computation of the number of molecules contained in a unit volume to be Loschmidt's greatest discovery ¹²⁾. Such a rating must be contradicted. A discovery at least equivalent to the one mentioned by Boltzmann is the compatibility of the (re-formulated) second law of thermodynamics and the perpetual motion machine of the second kind. If Loschmidt's discovery of that compatibility had been widely accepted in those days, the evolution of energy technology might have been a different one. Unfortunately, Loschmidt's arguments in favor of the stratification of temperature in a gas subject to gravity do not provide a strict proof. With a strict proof at hand, he could have spread his thesis with a greater psychological effect.

bb) Loschmidt surmised that the second law could be derived from the principle of least action. To put it differently: he replaced the original foundation of the second law (that is the axiom of the impossibility of a perpetual motion machine of the second kind) by a different one. Doing so he referred to Boltzmann, who had already displayed such foundation in his article "*Über die mechanische Bedeutung des 2. Hauptsatzes der Wärmetheorie*".

It can be left undecided whether or not the derivation of the second law from the principle of least action is strictly convincing. In a more recent article, G. Bierhalter, who has published several articles on the history of the second law, doubted the strictness of such reasoning.¹³⁾ This doubt is justified as soon as one realizes that the principle of least action can be derived from the Euler-Lagrange equation (see L. Susskind/G. Hrabovsky, *The Theoretical Minimum: Classical Mechanics*, 2013, pp. 111-114, where the Euler-Lagrange equation is derived from the principle of least action by a reversible succession of steps), which, in turn, can be derived from Newton's principle of force and counterforce. Given the reversibility of motions brought about by forces, one can hardly see how the Second Law could be derived from this principle.

cc) Loschmidt had the following vision for the future:

*"Thereby the terroristic nimbus of the second law is destroyed, a nimbus which makes that second law appear as the annihilating principle of all life in the universe, and at the same time we are confronted with the comforting perspective that, as far as the conversion of heat into work is concerned, mankind will not solely be dependent on the intervention of coal or of the sun, but will have available an inexhaustable resource of convertible heat at all times."*¹⁵⁾

b) The formulation of the Second Law, reconsidered

In any case, the second law and a perpetual motion machine of the second kind are compatible, as soon as we no longer define the second law as it has been usual. Given the possibility of running a perpetual motion machine of the second kind, the second law should rather be formulated as follows (different from the modification of the Second Law suggested by Loschmidt, the modification suggested in the following avoids an unnecessarily wide scope of the Second Law):

"In an overwhelmingly large majority of all processes, entropy (of a closed system) increases or stays fixed, whereas it decreases only in small number of processes."

An equivalent formulation is the following:

"In an overwhelmingly large majority of processes, entropy (of any single, homogeneous substance) is a variable of state, whereas it is not a variable of state in a small number of processes."

Another equivalent formulation is the following:

"In an overwhelmingly large majority of processes, the coarse-grained volume of a system of **N** particles in phase space increases with time or stays fixed, whereas it decreases only in a small number of processes."

The last formulation is the most illustrative: As was shown above, the volume in phase space of a number **N** of particles does NOT change with time, but stays fixed (Liouville's theorem). However, it may happen that the volume started as a (more-than-three-dimensional) compact

sphere, and turned into a more complicated structure as time passed. The complicated structure is made up of many filaments, so that with a limited “sharpness of vision”, the new structure appears as if its volume in phase space had increased. This happens in the majority of all cases. Nevertheless, in a minority of cases, a lump of an “incompressible liquid” in phase space may start as a complex structure with many filaments, and may end up as a simple structure. In those cases, the apparent volume of the structure has decreased. So has entropy.

c) The Second Law and the Arrow of Time

aa) Why is it that one direction of development, that is from a simple structure in phase space to a complex one, is more likely than the other? It has to do with the arrow of time. If both directions had the same likelihood, there would be no direction of time in the universe. Since we do observe a direction of time in the visible universe, one direction of time prevails over the other.

But what is the reason for our universe to have a prevailing time direction? The fact that (most) differences in density and temperature will vanish “after” a while (and do thereby constitute a time direction) has to be ascribed to the *original state of matter* (in the visible universe), to which our present state is causally linked. In that respect, there is a resemblance between temperature nivellation and gravity: The fact that water in a cup, when stirred, will climb the walls of the cup as a result of the centrifugal “force” at work, is -as General Relativity tells us- a result of the special way the distant stellar masses of the universe are distributed. In much the same way, the fact that cold water, when added to a cup containing hot coffee, will mix with the coffee to form a liquid of uniform temperature, is a result of the state of matter in the universe billions of years ago. Or as S.M. Carroll (“The Cosmic Origins of Time’s Arrow”, Scientific American, June 2008, page 26) puts it:

“The universe started off orderly and has been getting increasingly disorderly ever since. The asymmetry of time ... plays an unmistakable role in our everyday lives: it accounts for why we cannot turn an omelet into an egg... And the origin of the asymmetry we experience can be traced all the way back to the orderliness of the universe near the big bang. Every time you break an egg, you are doing observational cosmology.”

The often discussed paradox, that is the question why temperature differences within an ideal gas will always vanish though all motions of the molecules are reversible (so that increases in temperature differences should be as frequent as reductions of these differences) is thereby resolved: The “initial” state of the gas to start with (which itself is causally dependent on prior states of things) isn't of the right kind for generating temperature differences.

bb) Moreover, this recognition gives rise to revisit Boltzmann's famous dispute with Zermelo. In a universe endless both in time and in space, he argues, there must exist “islands” in which, by random processes, matter is organized, whereas the universe is barren and at uniform temperature elsewhere. Living beings (including intelligent machines) on such an island will *define* the arrow of time by saying that the future is the *less* organized state, while the past is the *more* organized state of their island (there is no physical definition of the arrow of time other than this one, since the laws of physics are time-symmetric). Later on, this concept of time was

consolidated by Hans Reichenbach ("The Direction of Time"), who stressed that in those ordered states, the system is not free to find itself (as a result of random processes) in a much different state soon after or slightly prior to the moment in time considered (when the system is highly ordered), as laws of nature allow only slight changes within short periods of time. Different from dice or roulette balls, every bulk of gas has a memory.

The universe is hence in possession of different states, but is lacking of an intrinsic ordering of these states by the category earlier / later. Instead, such an ordering is *ex trinsic*. It seems that Boltzmann's view of the arrow of time is quite correct despite the fact that cosmology, by assuming the Big-Bang at the "origin" of the universe, may be dismissing the assumption of a universe endless both in space and time. Different from Boltzmann's view, though, an arrow of time whose direction is opposite to ours is not a phenomenon whose occurrence is restricted to regions billions of light years away. Given the possibility of running a perpetual motion machine of the second kind here on earth, that opposite arrow of time on the one hand, and our familiar arrow of time on the other hand penetrate each other, with one arrow being the BIG arrow and the other being the LITTLE arrow of time.

d) E. Mach and M. Planck on the Second Law

It is hardly known that Ernst Mach ²⁰⁾, too, was skeptical about the impossibility of a perpetual motion machine of the second kind (should the molecular theory of matter be correct). was restrictive as regards the reach of the Second Law. In his "Principles of the Theory of Heat" (Die Principien der Wärmelehre, 2nd edition 1900, p. 364) he wrote:

"The mechanical view of the Second Law, which distinguishes ordered and disordered motions by paralleling the increase in entropy with the increase in disordered motions at the expense of ordered motions, appears to be quite artificial. Taking into account that a real analogue of entropy increase does not exist in a purely mechanical system made up of perfectly elastic atoms, one can hardly reject the idea that an infringement of the Second Law should be quite possible -even without any help from demons- , given such a mechanical system is indeed the basis of heat phenomena. I agree completely with F. Wald, when he says: 'In my judgment the root of this [entropy] principle lies much deeper, and if it is possible to bring the molecular hypothesis and the entropy principle into harmony, then it is lucky for the hypothesis but not for the entropy theorem.' "

M. Planck's remarks on the Second Law are as follows (Treatise on Thermodynamics, Dover Publ 1945, translated from the 7th German edition 1922, § 116, p. 89):

"We, therefore, put forward the following proposition as given directly by experience: It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and the cooling of a heat-reservoir."

But the validity of a law of nature cannot depend on the capability or incapability of mankind to build certain machines. Planck agreed with this objection (though he then should better have chosen a different formulation of the second law), as he wrote (op cit, § 136, pp. 105, 106):

"In conclusion, we shall briefly discuss the question of possible limitations to the second law. If there exist any such limitations -- a view held by many scientists and philosophers -- this much may be asserted, that their existence presupposes an error in our starting point, viz the impossibility of perpetual motion of the second kind, or a fault in our method of proof. From the beginning we have recognized the legitimacy of the first of these objections, and it cannot be removed by any line of argument. The second objection generally amounts to the following. The impracticability of perpetual motion of the second kind is granted, yet its absolute impossibility is contested, since our limited experimental appliances, supposing it were possible, would be insufficient for the realization of the ideal processes which the line of proof presupposes. This position, however, proves untenable. It would be absurd to assume that the validity of the second law depends in any way on the skill of the physicist or chemist in observing or experimenting. ... the law asserts briefly that there exists a quantity which changes always in the same sense in all natural processes. The proposition in this form may be correct or incorrect; but whichever it may be, it will remain so, irrespective of whether thinking and measuring beings exist on earth or not, and whether or not, assuming they do exist, they are able to measure the details of physical or chemical processes"

But given Boltzmann's view on reversibility is correct, there is no such quantity (entropy) which changes always in the same direction (increase); instead, it also changes in the opposite direction (decrease) if one waits long enough. Hence, the Second Law in the form of "there exists a quantity which changes always in the same sense in all natural processes" is not a true description of nature if Boltzmann is correct. It seems that Planck himself realized this objection, as he added a footnote to the first sentence of § 136 in which he stated:

"The following discussion, of course, deals with the meaning of the second law only in so far as it can be surveyed from the points of view contained in this work avoiding all atomic hypotheses." (The original German text is: "Die folgenden Betrachtungen erörtern die Bedeutung des zweiten Hauptsatzes selbstverständlich nur so weit, als sie sich von dem in diesem Werk eingehaltenen, alle atomistischen Hypothesen vermeidenden Standpunkte aus übersehen läßt.")

This has an effect on Planck's initial formulation of the second law as well ("We, therefore, put forward the following proposition as given directly by experience: It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and the cooling of a heat-reservoir."). Given it is only improbable but not impossible that entropy decreases, nothing can be said on the improbability or probability of finding a way to build a perpetual motion machine of the second kind, since Boltzmann's reflections on probability do not apply to engineers, but only to gas particles.

e) The Second Law expressed in equations in which the parameters "entropy" (of which there are two different variants S and S_{exp}) appear

aa) In textbooks, the following expression of the Second Law can be found:
(72)

$$\oint dS = \oint \frac{dQ_{rev}}{T} = 0$$

S is the entropy of a single, homogeneous substance of finite mass (not the entropy of a closed system!), dQ_{rev} is the heat added to the substance or taken from it during a reversible process. A reversible process, in turn, is a process that can be conceived of as a succession of quasi-equilibrium states.

By setting the numerical value of the loop-integral of dS to zero, the textbook equation postulates that entropy is a variable of state. As a consequence, it follows that any perpetual motion machine of the second kind is impossible. This is because of the following: in order for such a machine to work, there would have to exist cases in which entropy is not a variable of state, so that the loop- integral is not always zero, but different from zero in some cases (dependent on the path chosen).

But this textbook-equation is empirically wrong. It has to be replaced by the following set of statements, which contain an altered formulation of the Second Law (with $dS = dQ_{rev}/T$ – and not Boltzmann’s equation $S = k \ln W + C$ – being a definition of entropy):
(73)

$$dS := \frac{dQ_{rev}}{T}$$

$$S = k \ln W + C$$

$$\begin{aligned} \Rightarrow \oint k d[\ln W] &= 0 \quad \wedge \quad \left[\oint dS = \oint \frac{dQ_{rev}}{T} = \oint dC = 0 \quad \vee \quad \oint dS \right. \\ &= \oint \frac{dQ_{rev}}{T} = \oint dC < 0 \quad \vee \quad \left. \oint dS = \oint dC = \oint \frac{dQ_{rev}}{T} > 0 \right] \quad \wedge \quad dQ_{rev} = dQ \end{aligned}$$

The sign $:=$ stands for a definition. S again denotes the entropy of a single substance (e.g., a quantity of gas). C is a summand that may or may not be a constant. W is an expression of the number of microstates each of which is a realization of a given macrostate of the substance. The loop-integral of $d[\ln W]$ is zero in any case (W is a variable of state, its value being independent of the history of the current state to which W is ascribed). Any given macrostate with a given W may be succeeded by a different macrostate with a different W , either by adding or removing heat, or by an adiabatic process. In the latter case, with no interference from outside, we might need to wait very long for such process to happen, but this is of no importance here. What counts is Boltzmann’s presumption of all microstates (of any macrostate) being equally likely to materialize (under certain constraints). *And this entails that reversible processes can either be unadiabatic or adiabatic.*

In other words: Given all microstates have the same change of realization (it would even suffice to state that no microstate has a zero probability of realization), all transitions from a given

microstate to a different microstate are reversible, no matter if the new microstate belongs to the old macrostate or to a new one. Hence, strictly speaking, the subscript “rev” (for: “reversible”) in the definition of entropy ($dS = dQ_{\text{rev}}/T$) is obsolete once Boltzmann’s statement on entropy (expressed in his famous equation $S = k \ln W + C$) has been adopted.

To give an example, imagine that a closed path consists of two legs: On the first leg, the gas in a container gathers in one corner of the container within several minutes or hours without any interference from outside, thus constituting an adiabatic, reversible change of states that occurs whenever you wait long enough for it to happen. Therefore the integral of dQ_{rev}/T along this leg is zero. The second leg consists of a usual isothermal and thus reversible expansion of the gas performed by means of a piston that is thereby giving off work while the gas is absorbing thermal energy from the ambient. As a result of the closed loop, the entropy of the substance (defined as $dS = dQ_{\text{rev}}/T$) is not unchanged, but has increased, although pressure, temperature and density are the same as they were at the beginning of the cycle.

Conversely, let us imagine that the closed path consists, as a first leg, of a slow, adiabatic expansion into the vacuum, which is performed in a way that the piston does not feel any pressure. In order for that to happen, one would again have to wait for a very, very long time. This unusual expansion shall be followed by a slow (but usual) isothermal compression which leads back to the starting point. Then the loop-integral of $dS = dQ_{\text{rev}}/T$ results in a decrease in entropy of the substance. However, the same result is obtained if the adiabatic expansion (first leg) is such that the piston moves out so fast that the molecules have hardly time to be reflected by it (expansion of the gas into the vacuum). This leg shall again be followed by a slow (but usual) isothermal compression which leads back to the starting point. Since the distinction between a reversible and an irreversible change of state is obsolete (given any change of microstate is a reversible one), this loop-integral of $dS = dQ_{\text{rev}}/T = dQ/T$ results in the same decrease in the entropy of the work substance as did the previous one (although textbooks would wrongly assert that the loop-integral of dS is zero in the latter case).

We thus realize: The summand C has to be adapted to the path that has been chosen, and is thus not the same at any point along any path chosen (nor is the entropy S of the substance). Or: Entropy S of the substance is not a variable of state.

No probability judgement can be made with regard to each of the three alternatives (“or”) in our mathematical statement (73), if we do not leave the gas in the container to its own devices, but are free in interfering with it by any means engineers could possibly invent. In other words: Boltzmann’s probability reflections do not allow us to make judgements on how probable the invention of a perpetual motion machine of the second kind might be.

bb) This leads to consequences for the entropy of a closed system:

If we have $dQ_{\text{rev}} = dQ$, the entropy of a closed system (work substance and the substance that functions as a heat reservoir) can stay constant during all the processes considered. This is because the amount of heat dQ absorbed or given off by the work substance at a temperature T can be given off or absorbed by the heat reservoir at the same temperature T .

If such an outcome (of an invariance of entropy) is to be avoided, the definition of entropy S has

to be expanded in the following way (the term S_{exp} then stands for the entropy whose definition is expanded, C_{exp} then is the summand in Boltzmann's equation if his equation is that of the expanded entropy S_{exp}):
(74)

$$dS_{\text{exp}} := \frac{dQ_{\text{rev}}}{T} \quad \wedge \quad \oint dS_{\text{exp}} := 0$$

$$S_{\text{exp}} = k \ln W + C_{\text{exp}}$$

$$\Rightarrow \oint k d[\ln W] = 0 \quad \wedge \quad \oint dC_{\text{exp}} = 0 \quad \wedge \quad \left[\sum_{k=1}^{k=n} \int_{t=0}^{t=t} dS_{\text{exp}_k} = \sum_{k=1}^{k=n} \int_{t=0}^t \frac{dQ_{\text{rev}_k}}{T_k(t)} = 0 \right]$$

$$\vee \quad \sum_{k=1}^{k=n} \int_{t=0}^{t=t} dS_{\text{exp}_k} = \sum_{k=1}^{k=n} \int_{t=0}^t \frac{dQ_{\text{rev}_k}}{T_k(t)} > 0 \quad \vee \quad \sum_{k=1}^{k=n} \int dS_{\text{exp}_k} = \sum_1^n \int_{t=0}^t \frac{dQ_{\text{rev}_k}}{T_k(t)} < 0 \quad]$$

To each substance that belongs to the closed system, a number k (ranging from 1 to n) is ascribed. The parameter n denotes the total number of substances (each of homogeneous temperature) in the closed system. The integrals are taken over a period of time from $t=0$ to $t=t$.

Now the entropy S_{exp} of a single substance is a variable of state by definition. That is to say: Whenever the closed-loop integral of dS_{exp} should not be zero at first sight, it then follows as a logical necessity that not all steps have been those that could be labelled “reversible”, that is, not all have been manifestations of dQ_{rev} .

Even without Boltzmann's statistical reasoning, the physical validity of the square bracket (that contains a formulation of the Second Law of Thermodynamics that uses S_{exp} rather than S) follows from the general theorem that all processes in nature are reversible in principle. In other words: The temporal limits of the integral can be interchanged. Hence, if an increase in expanded entropy of a closed system is possible, a decrease, too, must be possible.

Of course, when following Boltzmann's reasoning, a decrease in entropy of an almost closed system can only be observed from outside. Within the closed system, any observer whose body is part of the closed system will define his or her ordering of “earlier-later”, that is, his or her direction of time, in a way so that the entropy of the closed system (he or she is part of) is increasing and not decreasing.

Thus the question raised in the title of this article can be answered in the positive.

NOTES

1) Claude Garrod: Statistical mechanics and thermodynamics, Oxford University Press, 1995

- 1a) See also: R. Baierlein, "How Entropy got its Name", American Journal of Physics, 60, 1151.
- 2) See E. Pertigen: Der Teufel in der Physik - Eine Kulturgeschichte des Perpetuum Mobile, Berlin 1988 (Verlag für Reisen und Wissenschaft).
- 3) Transactions of the Royal Society of Edinburgh 20 (1851), 265.
- 4) J. Loschmidt, "Über den Zustand des Wärmegleichgewichts eines Systems von Körpern mit Rücksicht auf die Schwerkraft I", Sitzungsberichte der mathematisch - naturwissenschaftlichen Classe der Kaiserlichen Akademie der Wissenschaften zu Wien 73.2 (1876), 135.
- 5) J.C. Maxwell, "On the Dynamical Theory of Gases", The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science 35 (1868), 215/216. Some years later, Maxwell repeated his argument. In his book "Theory of heat", published in London in 1877, he writes (p. 320): *"...if two vertical columns of different substances stand on the same perfectly conducting horizontal plate, the temperature of the bottom of each column will be the same; and if each column is in thermal equilibrium of itself, the temperatures at all equal heights must be the same. In fact, if the temperatures of the tops of the two columns were different, we might drive an engine with this difference of temperature, and the refuse heat would pass down the colder column, through the conducting plate, and up the warmer column; and this would go on till all the heat was converted into work, contrary to the second law of thermodynamics. But we know that if one of the columns is gaseous, its temperature is uniform. Hence that of the other must be uniform, whatever its material."* Thus Maxwell did not modify his assertion that if there were a temperature gradation in a column of gas subject to gravity, a perpetual motion machine of the second kind would become possible.
- 6) A.J. Walton, "Archimedes' Principle in Gases", in: Contemp. Phys., 1969, Vol. 10, No. 2
- 6) Loschmidt, "Über den Zustand des Wärmegleichgewichts...I ", p. 133.
- 7) See L. Boltzmann, "Über die Aufstellung und Integration von Gleichungen, welche die Molekularbewegung von Gasen bestimmen" in L. Boltzmann, Wissenschaftliche Abhandlungen, edited by F. Hasenöhl, vol. 2 (Leipzig: Barth 1909), p. 56ff.
- 8) J. Loschmidt, "Über den Zustand des Wärmegleichgewichts eines Systems von Körpern mit Rücksicht auf die Schwerkraft IV", Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften zu Wien 76.2 (1877), 225.
- 9) An argument similar to Boltzmann's can be found with S.H. Burbury, "Equilibrium of Temperature in a Vertical Column of Gas", Nature, Vol. 12 -1875-, p. 107.
- 10) L. Boltzmann: Lectures on Gas Theory, Dover Publ. 1964, par. 19, p.141
- 11) L. Boltzmann: Lectures on Gas Theory, Dover Publ., par. 15
- 12) See L. Boltzmann, "Zur Erinnerung an Josef Loschmidt", in L. Boltzmann, Populäre Schriften (Leipzig: Barth 1905).

- 13) G. Bierhalter, "Von L. Boltzmann bis J.J. Thomson: die Versuche einer mechanischen Grundlegung der Thermodynamik", Archive for the History of Exact Science 44 (1992), 25-72.
- 14) See Loschmidt, "Über den Zustand des Wärmegleichgewichts... I", p. 141.
- 15) Loschmidt, "Über den Zustand des Wärmegleichgewichts... I", p. 135.
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