

Is Loschmidt's greatest discovery still waiting for its discovery? (Or: Can we decrease the entropy of a closed system?)

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The previous version of this article including several figures (that differs substantially from the actual version you are looking at) was first published in [Physics Essays](#) , Vol. 12 No. 4, December 1999, pp. 614-628.

Last revised: March 14th, 2018.

Comments welcome !

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 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 proof (based on statistical mechanics) is given for the hypothesis that the equilibrium temperature is indeed a function of height: 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 given Boltzmann's distribution is not strictly valid, it can be shown that the temperature of a gas subject to gravity cannot be uniform in equilibrium. Finally, when dealing with liquids and their vapors (where the force of gravity is replaced by intermolecular forces effective at the surface of a liquid), even bigger differences in temperature can be achieved. Thereby an important law set up by [H. Le Chatelier](#) in 1897 is rediscovered.

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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 stratification of 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 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.

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. A vertical pipe is arranged in a way that it penetrates the entire column from its bottom to its top. The material of the pipe consists of small sections permeable to heat; each of such sections is followed by a section that is not permeable to heat. So the number of permeable sections equals the number of impermeable ones. In the interior of that vertical pipe, a piece of metal (of cylinder shape) suspended by a rope is allowed to move up and down. To start with, that metal piece has the temperature of the upper part of the column. Initially (before the device begins its operation), that temperature is also the temperature of the ambient. When being slowly lowered to the floor, the metal piece adopts the temperature of the gas surrounding it; by gathering tiny bits of heat at different heights where it is in thermal contact with the permeable sections. Thus it becomes hotter (without disturbing the phenomenon of a temperature gradation of the gas as such).

Finally it has reached the bottom (and the maximum temperature). Now it is towed back to the top in such a fast way that the temperature of the piece of metal has no chance of declining. In order to move the piece of metal up and down, no net work has to be spent: The expenditure of work when making it move upwards is completely compensated by the gain in work when it is lowered to the bottom. The hot metal piece, however, can make water boil, and by the steam thus created a steam engine can be run. The refuse heat of that engine flows into the upper part of the column (not into the ambient).

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 the event of a temperature gradation existent in one single substance, that is in case of a temperature gradation as such (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 proof of the stratification of temperature in gases subject to gravity

I.

a) Abstract of proof

It shall be proved that the temperature of a gas which is subject to a force field – especially a gravitational field – cannot be homogeneous, given the gas molecules are no point masses but are extended objects. Since Boltzmann's distribution of energies leads to the general gas law even in case we assume that the molecules are 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 given Boltzmann's distribution is not strictly valid, it can be shown that the temperature of a gas subject to gravity cannot be uniform in equilibrium.

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-lecture 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. The distances between two neighboring energy levels shall be the same for all levels.

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 \mathbf{n}_1 , \mathbf{n}_2 und \mathbf{n}_3), we are interested in knowing how many variants exist for realizing the arbitrarily picked arrangement $\mathbf{n}_1=10$, $\mathbf{n}_2=11$, $\mathbf{n}_3= 4$ 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 \mathbf{n}_1 , \mathbf{n}_2 and \mathbf{n}_3 , the list of names given to the individual boxes that make up the occupation of an individual level \mathbf{n}_1 , \mathbf{n}_2 or \mathbf{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) The Lambda function whose maximum we want to find shall be subject to two constraints:

–The total sum of occupation numbers of any arrangement of occupations shall be \mathbf{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 (\mathbf{E}_i denotes an energy level that a box may take on; \mathbf{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 $\mathbf{N}!$ 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)

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

When forming the logarithm of Lambda, we get:
(7)

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

For P_i , that is for the probability of finding a box on the i -th energy level, we have, by definition, $P_i = n_i/N$. In the last line of the equation, the sum of $P_i N \ln N$ was replaced by $N \ln N$, since the sum of 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 n_i by NP_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 **E** is the average energy of a single box (E_{total}/N).

With **F** being defined as a function that is equal to the logarithm of Lambda divided by N, we set:

(10)

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

Alpha and **beta** are two Lagrangian 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 probability **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:

(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)

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

The exponent 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.

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 equal to the exponent of **(1+ alpha)**, and since **alpha** 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

aa) As a next step, we determine the numerical value of the **z**-function (appearing in the Boltzmann distribution) *for a gas*. For a while, 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**, we start by setting up the following equation as a first “candidate” for **z** (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 one of the three direction components of a momentum possessed by a single molecule; **E_{ix}** is the possible magnitude of one direction component of the kinetic energy of a molecule; **C** is a constant):
(27)

$$z_x = C \int_1^{2\infty} \int_0^\infty dx dp_x e^{-\frac{E_{ix}}{kT}} = C \int_1^{2\infty} \int_0^\infty dx dp_x e^{-\frac{p_x^2}{2mkT}}$$

The possible energy **E_{ix}** of a particle can be replaced by **p_{ix}²/2m** (with **m** denoting the mass of a particle, and with **p_{ix}** denoting a possible a momentum of a particle in one direction). The index **i** shall indicate that one is dealing with possible values of a parameter, and not necessarily with actual ones.

This equation (in which the sum that appears in Equation 19 has been replaced by an integral) could be equivalent to the general equation for **z**, that is (19), if the product of the two differentials were a constant that is the reciprocal of **C** (note that there is no variable in Equation 19 other than in the exponential term). At first sight, however, this does not seem to be the case, since that product may apparently take on an *arbitrarily small* value and hence an *arbitrary* value.

bb) Things look different, though, if both sides of the equation are raised to the **3N**-th power. Then we get:
(28)

$$z_x^{3N} = C^{3N} \int_1^{2\infty} \int_1^{2\infty} \int_1^{2\infty} \dots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots d^{3N}x d^{3N}p_x e^{-\frac{3NE_{ix}}{kT}}$$

$$\begin{aligned}
 &= C^{3N} \int_1^2 \int_1^2 \int_1^2 \dots \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots d^{3N}x \ d^{3N}p_x \ e^{-\frac{N(p_{ix1}^2 + p_{ix2}^2 + p_{ix3}^2)}{2mkT}} \\
 &= [C \int_1^2 \int_{-\infty}^{\infty} dx_1 \ dp_{x1} \ e^{-\frac{p_{ix1}^2}{2mkT}}]^{3N}
 \end{aligned}$$

The x, y, z -coordinates have been replaced by x_1, x_2, x_3 . The term p_x denotes the component of a momentum of a molecule in the x_1 -, x_2 - or x_3 -direction (that is, in the x -, y - or z -direction). Like before, E_{ix} denotes the magnitude of the component of the kinetic energy (in the direction x_1, x_2 or x_3) that a molecule may be in possession of. E_{ix} thus ranges from 0 to (almost) infinity. The last line of (28) is accounted for by the fact that all members of each of the two groups of integrals (their number being $3N$ in each group) are equal to each other.

According to Liouville's theorem, the product $d^{3N}x \ d^{3N}p_x$ is independent of time, provided the energy of the system stays constant. (Setting the product $d^{3N}x \ d^{3N}p_x$ 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 $d^{3N}x \ d^{3N}p_x$ is also independent of the variant of an arrangement and also of the arrangement of occupation numbers itself. The number of boxes is replaced by the number of molecules.

Liouville's theorem shall be proved. Let us define a parameter H (called Hamiltonian) in the following way:

(28a)

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

Differentiating H with respect to a single p , that is, with respect to the momentum component in one direction of a single particle of mass m , gives:

(28b)

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

Differentiating H with respect to a single x , that is, with respect to the spatial position of a single particle, gives (F is force on a particle):

(28c)

$$\frac{\delta H}{\delta x_1} = \frac{\delta U_i}{\delta x} = -F_i = -\dot{p}_i$$

Note that (28b) and (28c) presume that the particles are subject to a force field, e.g., a gravity field, that may be vanishingly weak, but must not be exactly zero. If it were exactly zero, **delta p_i** would be exactly zero, and **delta H** over **delta p_i** would not be defined. One should also note that, even if **dH** is exactly zero (which is the case if the total energy of the system stays fixed), **delta H** may nevertheless be different from zero if one variable only, for instance **p₃₈** (the momentum of the 38th particle in one direction), is allowed to change while all the other variables, that is, the positions and velocities of all other particles, stay fixed.

We shall now imagine that each of the many particles is moving in a six-dimensional phase space. That means each particle has, at any moment in time, six coordinates, which are **x, y, z, p_x, p_y, p_z**. (For a short while, we will use **x,y,z** instead of **x₁, x₂, x₃**.) 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 stays constant over time. We assume that, at a given moment in time, the density of points does not change abruptly near and inside the volume element. We further assume that this 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 (the case of mutual collisions of particles will be given due consideration further below).

If, for a better illustration, we reduce the dimensions from six to merely two (this is for a short while only), that is **x** and **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 (**C** is a constant of proportionality):

(28d)

$$-\frac{dZ}{dt} = C \left(\frac{\delta x}{\delta x} + \frac{\delta p_x}{\delta p_x} \right)$$

The velocity in the **x**-direction appearing in the numerator on the right side of the equation is the velocity of a particle that finds itself very close to the volume element during the interval of time considered. According our our presuppositions, it has many “colleagues” in its immediate neighborhood whose velocities and whose changes in velocity with **x** are indistinguishably similar. The same shall be true for the partial derivative of the **p_x**-coordinate with respect to time, that is, for the force component acting on a particle in the **x**-direction, and its change with **p_x**.

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

(28e)

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

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

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

or, after re-arranging the order of summands:
(28g)

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

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.

As the divergence of the flow of points is zero in any situation (the zero result applies to any sort of motion of points, and makes no exceptions for special flows), the ensemble of points in six-dimensional phase space behaves like an incompressible liquid.

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, as we have (there are three \mathbf{x} and three \mathbf{p} for each of the N particles):
(28h)

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

Saying that the flow of those points is incompressible means that each of the many points (each of which represents N particles) can be attributed his own small $6N$ -dimensional volume $\mathbf{d}^{3N}\mathbf{x} \mathbf{d}^{3N}\mathbf{p}_x$ which can neither be enlarged nor reduced.

For a better illustration of (28h) and its consequence, we return (for a short while one) 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 . Our lump of N molecules has shrunken to a “lump” of one single molecule only, which is represented by a single point. Other points represent other

molecules. 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 is zero, the density of points in the plane of the diagram stays fixed. This being the case, each of the many points in the plane can be given its own little square in the plane, with all squares having the same size, and with no area left over between the squares. Due to the “incompressibility of the two-dimensional liquid”, the size of the squares does not change when the points are moving with time. The precise position of a point within a square may vary from square to square. Given that the points and squares are needed in connection with an integration in (27), we can drop our knowledge of the precise position of the points in phase space, and put up with the knowledge that each point sits *somewhere* within its square. This is because a double integral like the one in (27), when viewed geometrically, is equivalent to determining the total three-dimensional volume of an object by adding up the volumes of columns the base area of which is $dx dy$, and the height of which is either given by a function of x , or a by a function of y . Since the function of x or of y may vary within the confines of the base area of a column, the height of a column is not precisely determined. But this does not affect the result of integration: The function of *any* of the x - or y -values of the base area of a column will do. For the error is of higher order, and will hence vanish in an integration in which the number of columns gets very large, so that the base area of each column becomes very tiny. It does not even matter if the size of the base area does not vanish, but shrinks to a lower limit only, provided the lower limit is small enough.

Since the uncertainty of position within the square does not affect the integration, a point in its own square can even be imagined to be smeared out to form a (two-dimensional) paste that fills the whole square homogeneously.

Even more: Since the integral we would like to do in (27) is extended over areas of phase space, the phase point that represents the particle is wandering around in the plane of the \mathbf{p}_x, \mathbf{x} -diagram during the integration (the height z of the column mentioned above – whose base is the square occupied by the point – is determined by the exponential term that appears in the equation). More precisely: It is not the *point* that is wandering, but it is our attention that is hopping from point to point (during an integration), that is, from a possible position of a point to another possible position of a point, and hence from square to square. But different from a usual integration, the size of the squares cannot shrink indefinitely (due to the incompressibility of the “point liquid”).

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

cc) Equation (28) is thus equivalent to the general expression for z , namely (19). When solving the double integral (with V denoting the - external – volume of the gas the shape of which shall be cubic), we get for (28):

(29)

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

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)

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

or
(30)

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

The same equation, that is Equation 30, would have been obtained if one had solved Equation 27 immediately, which we had discarded because we erroneously believed that Equation 27 was not equivalent to the general equation of the z -function, that is, Equation 19.

From this (that is, from Liouville's theorem) follows: The product $dx dp_x$ appearing in Equation 27 is constant. To put it differently: It cannot shrink to an arbitrarily small value! Moreover, the number of possible energy levels of a molecule cannot be infinitely large; otherwise the sum appearing in the general equation of the z -function would be infinitely large, and could not take on the finite value which we have found. We have thus come across the basic recognitions of quantum theory.

[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 constant 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 a constant. Liouville's theorem, in turn, is derived from Newton's mechanics.

Since nature thus requires us to treat a product of differentials 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 differentials in Equation 28 must have a constant value which cannot vanish, is hence evidence of a mathematical universe postulated by Tegmark and others.]

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 x -direction, we get from (22) [if \mathbf{beta} is replaced by (26), that is by $(kT)^{-1}$, z_x is replaced by (30), and if assuming that C , V , and m do not depend on T and hence on \mathbf{beta}):

(30c)

$$\overline{E_x} = -\frac{\delta \ln[CV^{1/3}(2\pi m k T)^{1/2}]}{\delta \beta} = -\frac{\delta[\ln(CV^{1/3}) + \frac{1}{2}\ln(2\pi m) + \frac{1}{2}\ln\beta^{-1}]}{\delta \beta} = -\frac{\delta(-\frac{1}{2}\ln\beta)}{\delta \beta}$$

$$= \frac{1}{2} \frac{1}{\beta} = \frac{1}{2} kT$$

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

(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: A factor of $1/2$ has to be placed in front of E_x . Without this correction, as a result of the integration from zero to infinity, both kinetic energy of motion in the positive x -direction and also kinetic energy of motion in the negative x -direction are distributed among *all* particles, just as if a single particle could carry both of these two energies. In other words: E_x is treated as being equal to $E_{x+} + E_{x-}$. (30d) then turn 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” we get from (30d) and (30e):

(30f)

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

In order to obtain the distribution of *velocities* (rather than kinetic energies) from (30b), dE is replaced by $m\mathbf{v}_x d\mathbf{v}_x$ according to the rules of differential calculus, and E in the exponent is replaced by $1/2 m\mathbf{v}^2$. We then get from (30b):

(30g)

$$dP = \frac{dn}{N} = \frac{m\mathbf{v}_x}{kT} e^{-\frac{m\mathbf{v}_x^2}{2kT}} d\mathbf{v}_x$$

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 $1/2$ that was used in Equation 30e, a factor of $2^{-1/2}$ is now used, given that *energies* and not *velocities* are counted twice if no correction is made):

(30h)

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

If one is interested in determining the 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 N -th root (not the $3N$ -th root) of (29a). We thus get:

(31)

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

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

d) 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 β by $1/kT$):

(32)

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

or (multiplying by 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.

e) Proof of the stratification of temperature in a gas subject to gravity

aa) It is now time for presenting the proof of a stratification of temperature as a consequence of a force field (gravitational field).

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 – 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 – that will be given consideration further below – 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 \mathbf{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.

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 \mathbf{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!

More precisely: 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. 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 can be blamed on a deviation from the Boltzmann 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 $(0.88)^{-2} = 1.29$ in case the distribution of velocities were perfectly even, that is, in case all particles had the same velocity.

Of course, in case the density of particles gets so high that repulsive forces, then outweighing attractive forces, are not only relevant among the particles themselves, but also between the bulk of particles on the one hand and the walls of the container on the other hand, a new reason for the increase in external pressure arises.

bb) An explanation for the deviation from Boltzmann’s distribution (towards a more even one) might be the following: Chances for a molecule whose speed in the positive x -direction is above average to even increase its kinetic energy in the positive x -direction as a result of the next collision with another molecule are smaller than they are for a molecule that, as regards its positive x -direction of motion, is travelling at a speed much below average. The process of energy distribution (molecules have replaced the “boxes” which we first used for deriving the Boltzmann distribution) *does* have a “memory”, contrary to the basic assumption of the Boltzmann distribution!

To make this evident, we assume that the molecules are spheres. In order for a molecule with a great kinetic energy in the positive x -direction to have the same chance of increasing its kinetic energy in the positive x -direction (as a result of the next collision with another molecule) as has a molecule with a low kinetic energy in the positive x -direction, the numbers of molecules that are expected to hit the trailing hemisphere of a molecule (that is the hemisphere that faces the negative x -direction) during a short interval of time must be the same for the two molecules that are compared with each other. So must be the numbers of molecules that are expected to hit the *leading* hemispheres. But this is not the case. Instead, *less* molecules are expected to hit the trailing hemisphere over a given interval of time if the molecule is fast, and *more* molecules are expected to hit the *leading* hemisphere. Consequently, a fast molecule (i.e., fast in the positive x -direction) is more likely to *diminish* its kinetic energy in the positive x -direction as a result of the next encounter with another molecule than it is to *increase* its energy in the positive x -

direction. The faster the molecule, the greater that likeliness.

Imagine the molecules were little cubes that are unable to rotate, and hence keep their common orientations in space. Consider the cube whose kinetic energy in the positive x -direction is the greatest of all cubes. Its chances of increasing its kinetic energy as a result of the next collision with another molecule are zero! Compare it to a cube whose kinetic energy is zero. Its chances of gathering speed in the positive x -direction as a result of the next collision are much bigger.

cc) 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 this was provided by A.J. Walton (Alan J. Walton, Archimedes' principle in gases, Contemporary Physics, Vol. 10 – 1969 –, S. 185; see also Claude Garrod, Statistical mechanics and thermodynamics, Oxford University Press, 1995).

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 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 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 of the particles (in the x -direction of motion) in the upper layer we then find:

(45)

$$\overline{E_{2x}} = \frac{\int_{E_{pot}}^{\infty} \frac{E_x}{kT_1} e^{-\frac{E_x}{kT_1}} dE_x}{\int_{E_{pot}}^{\infty} e^{-\frac{E_x}{kT_1}} dE_x} - E_{pot} = E_{pot} + kT_1 - E_{pot} = kT_1$$

The integral below the big fraction line gives rise to the fact that the total number particles whose kinetic energy in the bottom layer lies between E_{pot} and infinity is not N , but is less than N . Hence, without a correcting factor, the result for the average kinetic energy yielded by the integral above the big fraction line would be too low.

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.

f) Mutual attractions of particles

One might raise the question of whether or not the discrepancy between the consequences of Boltzmann's distribution and empirical reality vanishes as soon as attractive (or repulsive) forces between the molecules are incorporated into the picture. The answer is in the negative.

When giving consideration to the mutual attraction of the molecules, the z -function (31) turns into:

(49)

$$z = C \int_{111}^{222} \int_{-\infty-\infty-\infty}^{\infty \infty \infty} d^3x d^3p_x e^{-3\beta \frac{p_x^2}{2m}} e^{-\beta U_i(x)} = \int_{-\infty-\infty-\infty}^{\infty \infty \infty} V d^3p_x e^{-3\beta \frac{p_x^2}{2m}} \int_{111}^{222} \frac{1}{V} d^3x e^{-\beta U_i(x)}$$

$$= z_0 \int_{111}^{222} \frac{1}{V} d^3x e^{-\beta U_i(x)} \approx z_0 \int_{111}^{222} \frac{1}{V} d^3x [1 - \beta U_i(x)] = z_0 [1 - \beta \int_{111}^{222} \frac{1}{V} d^3x U_i(x)]$$

U_i is a possible level of potential energy which a single molecule may be in possession of. V is the volume of the container. The triple integral of d^3p_x on the right side of the first line can be replaced by z_0 , that is by the z -function of the ideal gas (31). The exponential term on the left side of the second line can be approximated by the bracket, if the Taylor series is applied, by which the exponential term is replaced with a sum. Terms of quadratic and higher order are left out in the sum. This is justified as long as the possible level of potential energy of a molecule is low compared with its kinetic energy. Integrating d^3x gives V .

Integrating all possible levels of potential energy over the volume of the container gives a parameter \mathbf{Na} . That parameter can be assumed to be the same for every molecule in the container. Moreover, it can be assumed to be proportional to \mathbf{N} , the number of molecules in the container. The factor "a" is neither a function of V (if V doubles, \mathbf{N} doubles, too, and so does \mathbf{Na} , with no need to change \mathbf{a}), nor of \mathbf{N} . It can be left open whether or not there is only one possible level of potential energy in the interior of the box, or whether the potential energy of a molecule may be subject to change with position. (There would be only one possible level of potential energy for a molecule inside the container, if the attractive forces exerted by the other molecules would cancel inside the container; then the attractive forces of the other molecules would be noticeable for the molecule only when it finds itself near the surface.). If the potential energy is defined to be negative, the factor "a" is numerically negative. We hence get:

(50)

$$z \approx z_0 \left[1 - \frac{\beta \mathbf{Na}}{V} \right]$$

or [making use of the Taylor series once more, according to which $\ln(1-x)$ is approximately equal to $-x$]:

(51)

$$\ln z = \ln z_0 + \ln \left[1 - \frac{\beta Na}{V}\right] \approx \ln z_0 - \frac{\beta Na}{V}$$

Using (42), we get for the pressure p :

(52)

$$p = NkT \frac{\delta \ln z}{\delta V} = NkT \frac{\delta(\ln z_0 - \frac{\beta Na}{V})}{\delta V} = \frac{NkT}{V} + \frac{N^2 a}{V^2}$$

When re-arranging the equation, we get:

(53)

$$\left(p - \frac{N^2 a}{V^2}\right) V = NkT$$

Recall that “ a ”, which is material-dependent, is numerically negative if potential energy is negative. If we re-define “ a ” to have a positive sign, we get (if there were repulsive forces between the molecules, the re-defined “ a ” would be numerically negative):

(54)

$$\left(p + \frac{N^2 a}{V^2}\right) V = NkT$$

But this, though looking a lot like Van-der-Waals’ equation of a real gas, is still in mismatch with empirical reality, as V has not been replaced by $V-b$.

II.

It is hence important to recognize that the role of mutual collisions of the molecules is crucial for the phenomenon of temperature gradation. Without these collisions, the gas is an ideal gas, and the temperature of the model gas would indeed be uniform, as has been shown above. With no mutual collisions of molecules taking place, Boltzmann’s distribution of energies is not in jeopardy. See also, for a similar “proof” on the basis of an absence of collisions, *F.L. Roman, J.A. White, S. Velasco*, Microcanonical single-particle distributions for an ideal gas in a gravitational field, *Eur. J. Phys.*, vol. 16 -1995-, pp. 83-90, additional remarks in *Eur.J. Phys.*, vol. 17 -1996-, pp. 43-44; *Charles A. Coombes, Hans Laue*, A paradox concerning the temperature distribution of a gas in a gravitational field, *Am. J. Phys.*, vol. 53 -1985-, pp. 272-273.

III.

1) Attention shall be drawn to the experimental work done by Roderich Graeff ¹⁶⁾ 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. Graeff does not discuss the special behaviour of surface layers of a gas or a liquid in which, due to the fact that molecules in those layers are pulled backward by attractive forces, the average kinetic energies of the molecules hitting the thermometer may be different from those in the bulk of the material (see next chapter).

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)

$$(U_1 - U_2) + (p_1V_1 - p_2V_2) = gh_2 - gh_1$$

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_1V_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_2V_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)

$$(U_2 + p_2V_2) - (U_1 + p_1V_1) = - (gh_2 - gh_1)$$

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).

3) See also the short video by Charles Xie ("[A temperature gradient in saturated saltwater](#)") on Youtube.

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

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:

1) 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), 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, whereas amounts of heat or work given off by the system have a negative sign):
(60)

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

$Q_{W-intern}$ is the amount of heat added from outside in order to compensate 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; $Q_{W-intern-extra}$ is the additional amount of heat added in order to compensate 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. $Q_{W-extern-superheated}$ is the amount of heat added from outside in order to compensate the external work done by the superheated vapor (100°C, 0.5 bar) when it evolves from the surface of the liquid and shifts a piston. $W_{superheated}$ is the amount of that work (of isobaric expansion) done on a piston by the superheated vapor. $Q_{solution}$ is the solution heat that comes into play when the salt crystallizes. The solution shall be assumed to show the tendency of getting colder when the salt crystallizes.

This is why heat has been added from outside in order to keep the temperature fixed (100°C).

As a next step, 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)

$$W_{comp} - Q_{comp} = W_{compr} - (Q_{W2-extern} + Q_{W2-intern}) = -Q_{W2-intern}$$

W_{comp} is the external work of (isothermal) compression. Q_{comp} is the total heat that leaves the vapor during that (isothermal) compression. That heat consists of two parts. The first part, that is $Q_{W2-extern}$, is the heat leaving the vapor in order to compensate the external compression work done on the vapor. The second part, that is $Q_{W2-intern}$, is the heat leaving the vapor in order to compensate the internal work done by the mutual attraction of the vapor molecules.

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)

$$-Q_{W-intern} - Q_{W-extern-satur} + W_{satur} - Q_{solution} = -Q_{W-intern} - Q_{solution}$$

$Q_{W-extern-satur}$ is the heat leaving the system in order to compensate the external (isobaric) compression work done on the saturated vapor, W_{satur} is the amount of that external work (of isobaric compression) done on the saturated vapor.

The overall-sum of the three sub-sums should add up to zero. In other words:

(63)

$$Q_{W-intern} + Q_{W-intern-extra} + Q_{solution} - Q_{W2-intern} - Q_{W-intern} - Q_{solution} = 0$$

or

(64)

$$Q_{W-intern-extra} = Q_{W2-intern}$$

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

a) In order to determine the value of $Q_{W-intern-extra}$, we use the barometric formula of height. Presuming that the distribution of kinetic energies of the molecules of the liquid is the Boltzmann distribution, there would be a perfect analogy between an isothermal gas in a vertical

column subject to gravity. As was shown above, Boltzmann's distribution of kinetic energies of the molecules at the bottom of the gas column leads to the barometric formula, so that the potential gravitational energies of the molecules, too (and not just the kinetic energies), obey Boltzmann's distribution (that is what the barometric formula says). Presuming that the kinetic energies of molecules in the surface layer of the liquid, too, are distributed in accordance with Boltzmann's formula, we hence find: As regards the potential energy of the molecules 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 at height h above the bottom and the potential energy of molecules right above the bottom of a vertical column at height $h=0$ (see for this equality: *R.P. Feynman, Lectures on Physics I*, chapters 40-2 and 42-1).

The pressure at the bottom of the column of gas is p_0 . We hence get (with p being the pressure of the gas in the vertical column at height h ; 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 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)

$$p = \frac{1}{2}p_0 = p_0 e^{-\frac{mgh}{kT}}$$

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

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

b) Let us now determine the value of $Q_{W2-intern}$. What we get is:
(66)

$$Q_{W2-intern} = \int_{V_1=V_{saturated-vapor}}^{V=\infty} \frac{a}{V^2} dV = \left[-\frac{a}{V} \right]_{V_1}^{\infty}$$

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)

$$Q_{W2-extern} = 18.40 \frac{\text{kJ}}{\text{kmol}} = 1.02 \frac{\text{kJ}}{\text{kg}}$$

We realize that $Q_{W-intern-extra}$ is more than 100 times larger than $Q_{W2-intern}$, 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 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.

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. Prechtl*, “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 –.](#))

3) a) 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.

b)aa) 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. Pfaunder*, 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 –, though the compressed 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, beendigt haben werde, gedenke ich hierauf zurückzukommen. Ich erwähne nur die Zunahme des Dampfdruckes einer Flüssigkeit [by compression], welche man abkühlt, ohne ihren Dampf abzukühlen, ...*”).

bb) 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)

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

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 (*rho* 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. It can, however, also be derived by imagining that the evaporation of a compressed liquid (be it compressed 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 (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 surface of the liquid from which the vapor is evolving.

We then have (**U_{liq_compr}** denotes the internal energy of the compressed liquid; **U_{liq_uncompr}** denotes

the internal energy of the uncompressed liquid, provided that, by arrangement, both states of the liquid generate the same vapor, i.e., vapor of the same temperature; the term p_{liq_compr} denotes the pressure of the compressed liquid; the term p_{vapor} denotes the pressure of the uncompressed liquid and hence also the pressure of the vapor, no matter if the liquid is being compressed or uncompressed; V_{liq} denotes the volume of the liquid before evaporation; 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):

(69)

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

To elucidate:

– In order to describe the special throttling energetically, the internal energy of the compressed liquid and of the uncompressed liquid have to be considered (by arrangement, both states of the liquid give off the same vapor). According to the principle of energy conservation, the (numerically negative) difference in internal energy of the compressed and the uncompressed 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 compressed liquid, 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.

– 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.

Re-arranging (69) leads to (68).

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).

cc) 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.

(The increase in vapor pressure by exerting external pressure on the flat surface of the pure liquid is evidence of the fact that it is not the reduction in the attractive net force – exerted by a convex surface on molecules risen from the surface – that is responsible for the increase in equilibrium vapor pressure, but the compression of the liquid, either brought about by a piston effect of a second gas, or by the surface tension of a convex surface of the liquid.)

c) 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 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 compressed liquid (and its uncompressed vapor), Le Chatelier's equation (68) and also (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)

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

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

II.

A difference in temperature between the solution (liquid) and the vapor evolving from it enables the construction of a perpetual motion machine of the second kind (see [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](#)):

In a first step of a cycle, vapor evolves from a saturated salt solution whose temperature is that of the ambient.

In a second step, heat flows from the ambient into the vapor in case the vapor is colder than the ambient. The flow stops when the vapor has reached the temperature of the ambient. The pressure is kept fixed during this step, and is as high as it was during the first step. On its way from the ambient into the vapor, the heat flow traverses a Stirling-engine or a Carnot-cycle, where part of the heat flow is converted into mechanical work.

In a third step, the vapor is isobarically compressed, and condenses on the surface of the saturated solution. During this step, the pressure is the same as it was during the first and the second step. The condensation heat leaves the solution (that stays at ambient temperature during the condensation of the vapor) and flows into the ambient. The mechanical work spent on an isobaric compression during the third step is exactly equal in amount to the isobaric work given off by the vapor when it expanded during steps one and two.

(In case the vapor is warmer than the ambient, heat flows from the vapor into the ambient – via the Stirling engine or the Carnot cycle – during the second step.)

As a net result of the cycle, ambient heat has been converted into usable work.

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

a) 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.

b) aa) 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. 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 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 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.

bb) Why is it that one direction of development 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 if 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.

cc) 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.

c) It is hardly known that Ernst Mach ²⁰⁾, too, was restrictive as regards the reach of the Second Law. He objected to the generalization of the original, technical concept of entropy, that is the amount of heat received or given off by a body divided by its temperature, and was skeptical that an increase in technical entropy could be paralleled with an increase in disordered motions of particles. In chapter 102 of his "Principles of the Theory of Heat", he wrote (my own translation from German):

"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 the increase in entropy 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."

Loschmidt, on his part, 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⁾ .

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. Hasenöhr, 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.
- 16) R. Graeff, "Measuring Temperature Distribution in Gas Columns", 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.
- 17) R.W. Graeff, *My path to Peaceful Energy*, 2010.
- 18) Chuanping Liao, "Temperature Gradient Caused by Gravitation", *International Journal of Modern Physics B*, Vol. 23, No. 22 (2009), pp. 4685-4696.
- 19) U. Hoyer, "Ludwig Boltzmann und das Grundlagenproblem der Quantentheorie", *Zeitschrift für allgemeine Wissenschaftstheorie*, Bd XV, 1984, S. 201-210.
- 20) E. Mach, *Principles of the Theory of Heat*, 1900.