Journal of Mathematics and System Science 7 (2017) 278-288
doi: 10.17265/2159-5291/2017.10.002

Quantization of Particle Energy in the Analysis of the Boltzmann Distribution and Entropy

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Abstract. The Boltzmann equilibrium distribution is an important rigorous tool for determining entropy, since this function cannot be measured, but only calculated in accordance with Boltzmann's law.

On the basis of the commensuration coefficient of discrete and continuous similarly-named distributions developed by the authors, the article analyses the statistical sum in the Boltzmann distribution to the commensuration with the improper integral of the similarly-named function in the full range of the term of series of the statistical sum at the different combination of the temperature and the step of variation (quantum) of the particle energy. The convergence of series based on the Cauchy, Maclaurin criteria and the equal commensuration of series and improper integral of the similarly-named function in each unit interval of variation of series and similarly-named function were established.

The obtained formulas for the commensuration coefficient and statistical sum were analyzed, and a general expression for the total and residual statistical sums, which can be calculated with any given accuracy, is found. Given a direct calculation formula for the Boltzmann distribution, taking into account the values of the improper integral and commensuration coefficient.

To determine the entropy from the new expression for the Boltzmann distribution in the form of a series, the convergence of the similarly-named improper integral is established. However, the commensuration coefficient of integral and series in each unit interval turns out to be dependent on the number of the term of series and therefore cannot be used to determine the sum of series through the improper integral. In this case, the entropy can be calculated with a given accuracy with a corresponding quantity of the term of series n at a fixed value of the statistical sum.

The given accuracy of the statistical sum turns out to be mathematically identical to the fraction of particles with an energy exceeding a given level of the energy barrier equal to the activation energy in the Arrhenius equation.

The prospect of development of the proposed method for expressing the Boltzmann distribution and entropy is to establish the relationship between the magnitude of the energy quantum Δε and the properties of the system-forming particles.

Key words: distribution, entropy, sequence, commensuration, statistical sum, convergent series, analysis.

Introduction

The Boltzmann equilibrium distribution is the most important, if not the only, rigorous tool for determining entropy, since this function cannot be measured, but only calculated in accordance with Boltzmann's law [1, 2]:

$$P_i = \frac{N_i}{N} = e^{-\frac{\varepsilon_i}{kT}} \Big/ \sum_{i=1}^{m} e^{-\frac{\varepsilon_i}{kT}}\ , \qquad (1)$$

where P_i is the fraction of particles with energy ε_i; N_i is the number of particles possessing this energy; N is the total number of particles; m is the number of considered energy levels which can be infinite; k is the Boltzmann constant; T is the absolute temperature.

The fractional divisor in (1) is the sum of the states of particles or the statistical sum that is calculated for various objects in one way or another, including direct calculation by spectroscopic data, or as a continuous value with a transition from summation to integration [3]. However, the summation and integration are not identical procedures in either physical or mathematical terms, since in the first case it is necessary to take into account the actual quantization of energy, which is implied by the meaning of the Boltzmann constant, while in the second case the difference arises from inequality $\Delta x \neq dx$ in discrete and continuous distributions, even when the number of levels of energy m tends to infinity.

Thus, the calculation of the statistical sum is more or less approximate. However, for all non-identity of continuous and discrete distributions under certain conditions, their commensuration is ensured in the entire range of the function change, as we showed earlier [4], and this creates the possibility of a more rigorous direct calculation of the statistical sum and, together with it, entropy.

The method for determining the commensuration of the statistical sum in discrete and continuous epressions

As is known, the basis of differential and integral calculations is the reducibility of discrete dependencies to continuous ones while the argument variability interval Δx tends to infinitely small quantity dx. But the relationship between discrete and continuous distributions can turn out to be definite and productive at fixed variability intervals Δx.

This is most evident in the establishment of the convergence of series; i.e. the sum of discrete quantities, using the Cauchy, Maclaurin integral convergence criterion [5], according to which the series $\sum_{n=1}^{\infty} a_n$ converges if for a function *f(x)* that takes values of a_n at the points $x = n$, namely $f(n) = a_n$, and under the condition of a monotonic decrease of *f(x)* in the area $x \geq n_0$ observing inequality $f(x) \geq 0$, providing the convergence of the improper integral $\int_{n_0}^{\infty} f(x)\,dx$.

Thus, this sign establishes a certain equivalence of the discrete and continuous distributions of the variable value. Our paper [4] justifies the possibility of calculating the sum of series through the improper integral of the similarly-named function if for any unit interval of variation of series, $(n - 1) \div n$, the ratio of the integral of similarly-named function in this interval and hence of its mean value to the corresponding term of the series a_n is constant, independent of n:

$$K = \frac{\int_{n-1}^{n} f(x)dx}{a_n} = const \neq f(n). \quad (2)$$

In this case, all the improper integral also refers to the sum of series with the same coefficient of commensuration:

$$K = \frac{\int_{0}^{\infty} f(x)dx}{\sum_{n=1}^{\infty} a_n}. \quad (3)$$

From this the formula for calculating the sum of series follows

$$S = \sum_{n=1}^{\infty} a_n = \frac{1}{K}\int_{0}^{\infty} f(x)dx. \quad (4)$$

With respect to this expression, the statistical sum must be expressed through the general term of series, giving a certain energy variability interval (quantum) $\Delta\varepsilon$ and providing the first energy level equal to zero in the following form

$$a_n = e^{-(n-1)\Delta\varepsilon/kT}, \quad (5)$$

and the similarly-named function *f(x)* in the following form

$$f(x) = e^{-\frac{(x-1)\Delta\varepsilon}{kT}}, \quad (6)$$

Here it should be borne in mind that the fraction $\Delta\varepsilon/kT$ is a constant value for the undertaken analysis, i.e. as usual, the isothermal distribution of the function is considered at a some given value $\Delta\varepsilon$. This does not prevent to vary any further combinations of T and $\Delta\varepsilon$, including functionally related ones, for the solutions obtained. Therefore, in all calculations, this fraction can be designated as $b = \Delta\varepsilon/kT$.

But first we must verify the convergence of the statistical sum according to the Cauchy, Maclaurin criteria, taking the improper integral:

$$\int_{0}^{\infty} e^{-(x-1)\Delta\varepsilon/kT}\,dx = \int_{0}^{\infty} e^{-bx+b}\,dx = -\frac{1}{b}\left|e^{-bx+b}\right|_{0}^{\infty} = \frac{e^{b}}{b} = \frac{kT}{\Delta\varepsilon}e^{\frac{\Delta\varepsilon}{kT}}. \quad (7)$$

The integral converges for the constants T and $\Delta\varepsilon$, therefore, the statistical sum also converges $\sum_{n=1}^{\infty} e^{-(n-1)b} = \sum_{n=1}^{\infty} e^{-(n-1)\Delta\varepsilon/kT}$.

The commensuration coefficient of continuous and discrete distributions (4) in this case is expressed as

$$K = \frac{\int_{n-1}^{n} e^{-bx+b}\,dx}{e^{-(n-1)b}} = \frac{-\frac{1}{b}\left|e^{-bx+b}\right|_{n-1}^{n}}{e^{-(n-1)b}} = \frac{e^{b}-1}{b} = \frac{kT}{\Delta\varepsilon}\left(e^{\frac{\Delta\varepsilon}{kT}}-1\right). \quad (8)$$

This coefficient does not depend on n; hence it is applicable to the whole multitude $\sum_{n=1}^{\infty} a_n$, that has a limit

$$\sum_{n=1}^{\infty} e^{-bn+b} = \frac{1}{K}\int_{0}^{\infty} e^{-bx+b}\,dx = \frac{b}{e^{b}-1}\cdot\frac{e^{b}}{b} = \frac{e^{b}}{e^{b}-1} = \frac{e^{\frac{\Delta\varepsilon}{kT}}}{e^{\frac{\Delta\varepsilon}{kT}}-1}. \quad (9)$$

Thus, the statistical sum, and also the Boltzmann distribution, obtain a generalized mathematical certainty that in the familiar indexation of variables will take the following form

$$P_i = \frac{N_i}{N} = \frac{e^{-\frac{\varepsilon_i}{kT}}}{\sum_{i=1}^{\infty} e^{-\frac{\varepsilon_i}{kT}}} = \frac{e^{-\frac{(i-1)\Delta\varepsilon}{kT}}}{e^{\frac{\Delta\varepsilon}{kT}}}\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right) = e^{-\frac{i\Delta\varepsilon}{kT}}\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right). \qquad (10)$$

In the new form, this dependence, as well as the expressions for the commensuration coefficient (8) and statistical sum (9), and also for Boltzmann mathematical entropy,

$$H = -\sum_{i=1}^{\infty} P_i \ln P_i\,, \qquad (11)$$

are suitable not only for general, but also for numerical analysis, as well as for the direct calculation of all the characteristics discussed.

Analysis of the limits of change in the commensuration coefficient, the statistical sum and the Boltzmann entropy

The commensuration coefficient (8) is convenient for analyzing the limits of variation in the following form

$$K = \frac{e^{\frac{\Delta\varepsilon}{kT}} - 1}{\frac{\Delta\varepsilon}{kT}}. \qquad (12)$$

In the methodological respect it is important to verify the desire for complete commensuration of the discrete and continuous expressions of the statistical sum as the variability interval of the energy of particles tends to zero. In fact, the initially arising uncertainty

$$\lim_{\Delta\varepsilon\to 0} \frac{e^{\frac{\Delta\varepsilon}{kT}} - 1}{\frac{\Delta\varepsilon}{kT}} = \frac{0}{0}$$

is further disclosed according to L'Hospital's rule with the result

$$\lim_{\Delta\varepsilon\to 0} \frac{d\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right)}{d\left(\frac{\Delta\varepsilon}{kT}\right)} = e^{\frac{\Delta\varepsilon}{kT}} \Rightarrow 1, \qquad (13)$$

that indicates the identification of the compared distributions for $\Delta\varepsilon \to d\varepsilon$.

But with a very rough specification of intervals of the energy of particles, the opposite result is obtained, and the distributions under consideration become incommensurate:

$$\lim_{\Delta\varepsilon\to \infty} \frac{e^{\frac{\Delta\varepsilon}{kT}} - 1}{\frac{\Delta\varepsilon}{kT}} = \frac{\infty}{\infty} \Rightarrow \frac{d\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right)}{d\left(\frac{\Delta\varepsilon}{kT}\right)} = e^{\frac{\Delta\varepsilon}{kT}} = \infty. \qquad (14)$$

This determines the inevitability of errors in the direct replacement of a discrete sum by a continuous one.

As to the effect of temperature on the commensuration of discrete and integral expressions of the statistical sum, the very formula of the commensuration coefficient implies the opposite character of this effect in comparison with $\Delta\varepsilon$: when $T \to 0$ $K \to \infty$, and when $T \to \infty$ $K \to 1$. Such an effect is quite natural, since at an infinitely high temperature the relative role of any given energy variability intervals is reduced to zero, and at absolute zero temperature there is only a zero energy level, and any given energy variability interval with respect to the zero energy value becomes infinitely large, determining the impossibility of any distributions.

The effect of temperature on the statistical sum value (9) is expressed by the limits:

$$\lim_{T\to 0} \frac{\frac{\Delta\varepsilon}{kT}}{e^{\frac{\Delta\varepsilon}{kT}} - 1} = \frac{e^{\infty}}{e^{\infty} - 1} = 1, \qquad (15)$$

$$\lim_{T\to \infty} \frac{\frac{\Delta\varepsilon}{kT}}{e^{\frac{\Delta\varepsilon}{kT}} - 1} = \frac{1}{1 - 1} = \infty. \qquad (16)$$

Such limits are related to the fact that when $T = 0$ there exists only the first, zero energy level, which contribution to the statistical sum is always equal to one, which follows directly from the formula (5). At an infinitely high temperature, the improper integral (7) becomes divergent, and this according to the Cauchy, Maclaurin criterion determines the divergence of the similarly-named series. The physical picture of such a state is very conditional and reduces to a kind of uniform "smearing" of a finite number of particles over an infinite variety of energy levels [3] and even contradicts the information degeneration of the thermodynamic system at an infinitely high temperature, when the diversity of the system is determined only by the total number of particles and the corresponding limit of entropy [6-11]. However, this feature goes beyond the limits of the undertaken analysis of the statistical sum and is consistent with the existing formal approach to such an analysis [1-3]. As for the effect $\Delta\varepsilon$ on the statistical sum, it is also opposite to the effect of temperature: when $\Delta\varepsilon \to 0$ this sum tends to infinity for a given temperature, and when $\Delta\varepsilon \to \infty$ all the finite energy of the system formally refers to the first "interval" and also formally becomes zero with the first and only term of series equal to one.

It is theoretically and practically feasible to determine the sufficient number of terms of the statistical sum to calculate it with a certain accuracy. This is necessary to calculate the entropy by formula (11), which itself represents a new series requiring the determination of its sum, which includes the statistical sum (9). In the framework of the approach taken to consider such a sum as a convergent series, this problem has the following solution.

As shown in our paper [4], the commensuration coefficient of continuous and discrete distributions (2) can be used not only to express the total sum of the series (4), but also of any partial sum S_n through the improper integral of the similarly-named function with the upper limit n:

$$S_n = \frac{1}{K}\int_0^n f(x)dx. \tag{17}$$

This integral for the problem under consideration is defined as

$$S_n = \sum_{n=1}^{n} a_n = \frac{1}{K}\int_0^n e^{-(x-1)b}dx = -\frac{1}{Kb}\left|e^{-bx+b}\right|_0^n = \frac{e^b}{Kb}(1-e^{-bn}). \tag{18}$$

Substituting here the expressions for K (8) and $b = \Delta\varepsilon/kT$, we obtain a formula for calculating the partial sums

$$S_n = \sum_{n=1}^{n} a_n = \frac{e^{-\frac{n\Delta\varepsilon}{kT}}-1}{e^{-\frac{\Delta\varepsilon}{kT}}-1}. \tag{19}$$

With its help you can determine the amount of the residual sum

$$R_n = S - S_n = \frac{e^{\frac{\Delta\varepsilon}{kT}}}{e^{\frac{\Delta\varepsilon}{kT}}-1} - \frac{e^{-\frac{n\Delta\varepsilon}{kT}}-1}{e^{-\frac{\Delta\varepsilon}{kT}}-1} = \frac{e^{\frac{(1-n)\Delta\varepsilon}{kT}}}{e^{\frac{\Delta\varepsilon}{kT}}-1}. \tag{20}$$

The ratio of the residual sum to the total sum of the series can serve as a criterion for the accuracy of its calculation when the terms n are limited by the number. Using formulas (20) and (9), we find

$$\frac{R_n}{S} = e^{-\frac{n\Delta\varepsilon}{kT}}. \tag{21}$$

It is quite obvious that with an increase in the accounted terms of series, the contribution of the residual sum decreases and its fraction, as the calculation error, tends to zero. But the most important is that from here one can directly find the necessary number of terms of series to calculate the sum of series with a given accuracy equal to R_n/S in fractions of a unit:

$$n = -\frac{kT}{\Delta\varepsilon}\ln\frac{R_n}{S}. \tag{22}$$

All the calculations of this section of the Article, which were previously described in detail in our paper [12], are subject to numerical verification for a certain idea of the possibilities of the discussed approach to the analysis of the Boltzmann distribution.

However, expression (21) is even more informative, since the product $n\Delta\varepsilon$ has the meaning of an arbitrary value of energy ε_n, beginning from which all higher energy levels (i.e. residuals in the full range of the energy series) are related to the value of kT, which has a meaning of the store of thermal energy of the substance. This allows us to consider the value $\varepsilon_n = n\Delta\varepsilon$ as some energy barrier, which overcoming corresponds to a fraction of the particles equal to R_n/S. In turn, this fraction acquires the meaning of exponential factor in the expression for the rate constant in the Arrhenius equation (in terms of molar quantities)

$$k = A_0 e^{-\frac{E_a}{kT}} = A_0\frac{R_n}{S} = A_0 e^{-\frac{n\Delta\varepsilon}{kT}}. \tag{23}$$

The same result is obtained by using integral expressions for the residual fraction of the statistical sum

$$\frac{\int_{x=n}^{\infty} e^{-(x-1)b}dx}{\int_0^{\infty} e^{-(x-1)b}dx} = \frac{-\frac{1}{b}\left|e^{-bx+b}\right|_n^{\infty}}{\frac{1}{b}e^b} = \frac{\frac{1}{b}e^{-bn}e^b}{\frac{1}{b}e^b} = e^{-bn} = e^{-\frac{n\Delta\varepsilon}{kT}}. \tag{24}$$

Equality of expressions (23) and (24) is ensured by the commensuration of corresponding discrete and continuous distributions, so that the commensuration coefficients are reduced in their relative values.

The obtained independent treatment of statistical meaning of the exponential factor in the Arrhenius equation, in addition to confirming all the computations undertaken, makes it even more definite to emphasize the necessity of using equilibrium distributions in the mapping of kinetic processes, as well as probabilistic representations under the influence of chemical, physical and mechanical factors.

But first we must verify the convergence of the new entropy expression (11) in terms of the found statistical sum (9) for the particle distribution according to the energy P_i (10):

$$H = -\sum_{i=1}^{\infty} e^{-\frac{i\Delta\varepsilon}{kT}}\left(e^{\frac{\Delta\varepsilon}{kT}}-1\right) ln\left[e^{-\frac{i\Delta\varepsilon}{kT}}\left(e^{\frac{\Delta\varepsilon}{kT}}-1.\right.\right. \quad (25)$$

This sum is a functional series, general term of which can be expressed by taking into account the designation of constants for a given series of quantities $b = \Delta\varepsilon/kT$ and $A = e^{\frac{\Delta\varepsilon}{kT}} - 1$ as

$$a_n = Ae^{-bn} ln(Ae^{-bn}). \quad (26)$$

A necessary condition for the convergence of series according to the Cauchy criterion is

$$\lim_{n\to\infty} a_n = 0.$$

Then

$$\lim_{n\to\infty}(Ae^{-bn})\, ln(Ae^{-bn}) = 0\cdot\infty.$$

This uncertainty is revealed according to L'Hospital's rule by differentiating the fractional expression a_n:

$$\lim_{n\to\infty}\frac{Aln(Ae^{-bn})}{e^{bn}} = \frac{\infty}{\infty} \Rightarrow \frac{Adln(Ae^{-bn})}{de^{bn}} = -\frac{A}{e^{2bn}} \Rightarrow 0.$$

The necessary condition is met, but sufficient can be established by the integral criterion of Cauchy, Maclaurin. Here the similarly-named function for the general term of series (26) will be

$$f(x) = Ae^{-bx} ln(Ae^{-bx}). \quad (27)$$

The improper integral of this function within the variation of a_n is expressed as

$$\int_0^\infty f(x)dx = \int_0^\infty Ae^{-bx} ln(Ae^{-bx})\, dx = \int_0^\infty (AlnA)\, e^{-bx} dx - \int_0^\infty Ab\, xe^{-bx} dx. \quad (28)$$

This allows us to use table integrals of the following form

$$\int e^{ax}\, dx = \frac{1}{a}e^{-ax} \text{ and } \int xe^{ax}\, dx = \frac{e^{ax}}{a^2}(ax-1).$$

The first integral in (28) is equal to

$$\int_0^\infty (AlnA)\, e^{-bx} dx = AlnA\left(-\frac{1}{b}\right)\left|e^{-bx}\right|_0^\infty = \frac{AlnA}{b}. \quad (29)$$

The second integral leads to the following uncertainty

$$\int_0^\infty Ab\, xe^{-bx} dx = \frac{A}{b}\left|-bxe^{-bx} - e^{-bx}\right|_0^\infty = \frac{A}{b}(-\infty\cdot 0 + 1),$$

which is disclosed according to L'Hospital's rule

$$\lim_{x\to\infty}(bxe^{-bx}) = \lim_{x\to\infty}\frac{bx}{e^{bx}} = \frac{dbx}{de^{bx}} = \frac{1}{e^{bx}} = 0.$$

Then

$$\int_0^\infty Ab\, xe^{-bx} dx = \frac{A}{b}. \quad (30)$$

Both integrals converge, and so does their difference

$$\int_0^\infty Ae^{-bx} ln(Ae^{-bx})\, dx = \frac{AlnA}{b} - \frac{A}{b} = \frac{A}{b}(lnA - 1) = \frac{kT}{\Delta\varepsilon}\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right)\left[ln\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right) - 1\right]. \quad (31)$$

Therefore, the similarly-named series converges, and the Boltzmann entropy (25) does the same. However, the discrete expression of this entropy, as well as of other similarly-named series and functions, can lead to the same limit only under certain boundary conditions. In the general case, as shown above, it is required to establish the independence of the commensuration coefficient of discrete and continuous distributions from the number of terms of series, $k \neq f(n)$.

This coefficient can be determined by parts of the integral (28), correlating them with the corresponding general terms of series

$$k_1 = \frac{\int_{n-1}^{n}(AlnA)e^{-bx}dx}{(AlnA)e^{-bn}} = \frac{\int_{n-1}^{n} e^{-bx}dx}{e^{-bn}}, \quad (32)$$

$$k_2 = \frac{\int_{n-1}^{n} Abxe^{-bx}dx}{Abne^{-bn}} = \frac{\int_{n-1}^{n} xe^{-bx}dx}{ne^{-bn}}. \quad (33)$$

For k_1 we find the solution

$$k_1 = \frac{-\frac{1}{b}\left|e^{-bx}\right|_{n-1}^{n}}{e^{-bn}} = \frac{e^b - 1}{b} \neq f(n). \quad (34)$$

This part of the continuous and discrete dependences is commensurate, and the corresponding sum of the series is expressed as

$$\sum_{n=1}^{\infty}(AlnA)e^{-bn} = \frac{1}{k_1}\int_0^{\infty}(AlnA)e^{-bx}dx = \frac{b}{e^b - 1}\cdot\frac{AlnA}{b} = \frac{AlnA}{e^b - 1}. \quad (35)$$

For k_2 we obtain an expression depending on n

$$k_2 = \frac{\int_{n-1}^{n} xe^{-bx}dx}{ne^{-bn}} = \frac{\frac{1}{b^2}\left|e^{-bx}(-bx-1)\right|_{n-1}^{n}}{ne^{-bn}} = \frac{bn(e^b-1) + e^b(1-b) - 1}{b^2 n} = f(n). \quad (36)$$

These parts of integral and the sum of series change their ratio in each unit interval, and therefore it is difficult to determine the ratio of the improper integral to the sum of series both in this part and in the whole according to (31). In any case, a direct computation of entropy according to (25) with a certain accuracy will be simpler, and besides, it will be possible to find the commensuration coefficient

$$K = \frac{\int_0^{\infty} Ae^{-bx}\,ln(Ae^{-bx})\,dx}{\sum_{n=1}^{n'} Ae^{-bn}\,ln(Ae^{-bn})}, \quad (37)$$

where n' - the number of terms in series that ensure the calculation of the sum of series with a given accuracy.

Estimated part and examples of using the obtained formulas

Table 1 shows the results of calculating the commensuration coefficient K and the statistical sum $S = \sum_{n=1}^{\infty} a_n$ over a wide range of temperatures and the characteristic step of varying the energy of particles, rounded to four values of the figures. The first energy variability interval is given numerically equal to the Boltzmann constant, $\Delta\varepsilon = 1.3806505\cdot10^{-23} \approx 1.381\cdot10^{-23}$ J. The calculations were performed with an accuracy of up to 7 digit order numbers in the range of $10^{-99}\div10^{99}$.

From these tables it follows that at the smallest variation step $\Delta\varepsilon = 1{,}381\cdot10^{-23}$ J, starting from 10 K, with accurate up to 5% and better the statistical sum is comparable according to the commensuration coefficient with the corresponding integral value. With a coarser variability interval $\Delta\varepsilon$ such comparability shifts to higher temperatures: for $\Delta\varepsilon = 10^{-22}$ J – starting from 100 K, for $\Delta\varepsilon = 10^{-21}$ J – from 1000 K, for $\Delta\varepsilon = 10^{-20}$ J – from 10^4 K, $\Delta\varepsilon = 10^{-19}$ J – from 10^5. At lower temperatures, the identification of discrete and continuous summation is unacceptable.

As for the very value of the statistical sum, it indirectly indicates the need to take into account the increasing number of terms of their sequence, of course, with some given accuracy in the calculation of each term of series. Proceeding from the fact that any statistical sum begins with one and continues with decreasing terms, it can be argued that in this sum it is necessary to take into account at least the number of terms $n = S$. This number increases with an increase in temperature and with a decrease in the variability interval $\Delta\varepsilon$. So $\Delta\varepsilon = 1{,}381\cdot10^{-23}$ J and a temperature of 500 K will require accounting for more than 500 terms of the amount.

Table 1 – Dependence of the statistical sum $S = \sum_{n=1}^{\infty} a_n$ (9) and the commensuration coefficient K (8) on the temperature T and on the variability interval of the energy of particles $\Delta\varepsilon$

T, K	S and K at $\Delta\varepsilon$, J									
	$1.381{\cdot}10^{-23}$		10^{-22}		10^{-21}		10^{-20}		10^{-19}	
	S	K	S	K	S	K	S	K	S	K
0	1	∞	1	∞	1	∞	1	∞	1	∞
1	1.582	1.718	1.001	192.9	1.000	$3.94{\cdot}10^{29}$	1.000	$>10^{99}$	1.000	$>10^{99}$
10	10.51	1.052	1.940	1.468	1.001	192.9	1.000	$3.94{\cdot}10^{29}$	1.000	$>10^{99}$
50	50.50	1.010	7.415	1.076	1.307	2.248	1.000	$1.35{\cdot}10^{5}$	1.000	$5.53{\cdot}10^{60}$
100	100.5	1.005	14.31	1.037	1.940	1.468	1.000	192.9	1.000	$3.94{\cdot}10^{29}$
200	200.5	1.002	28.12	1.018	3.291	1.205	1.028	10.05	1.000	$1.48{\cdot}10^{14}$
300	300.5	1.002	41.92	1.012	4.662	1.131	1.098	4.217	1.000	$6.94{\cdot}10^{8}$
400	400.5	1.001	55.73	1.009	6.038	1.096	1.196	2.825	1.000	$4.04{\cdot}10^{6}$
500	500.5	1.001	69.53	1.007	7.415	1.076	1.307	2.248	1.000	$1.35{\cdot}10^{5}$
1000	1000	1.000	138.6	1.004	14.31	1.037	1.940	1.468	1.000	192.9
2000	2001	1.000	276.6	1.002	28.12	1.018	3.291	1.205	1.028	10.05
3000	3000	1.000	414.7	1.001	41.92	1.012	4.662	1.131	1.098	4.217
4000	4001	1.000	522.8	1.001	55.73	1.009	6.038	1.096	1.196	2.825
5000	5001	1.000	690.8	1.001	69.53	1.007	7.415	1.076	1.307	2.249
10^4	10^4	1.000	1381	1.000	138.6	1.004	14.31	1.037	1.940	1.468
10^5	10^5	1.000	$1.38{\cdot}10^{4}$	1.000	1381	1.004	138.6	1.004	14.31	1.037
10^6	10^6	1.000	$1.39{\cdot}10^{5}$	1.000	$1.38{\cdot}10^{4}$	1.000	1381	1.000	138.6	1.004

In fact, at low temperatures and large energy variability intervals characterized by a steep decline in the distribution of the terms of sum, their necessary number for calculating this sum with a given accuracy is much greater S.

More directly and strictly it is revealed with the help of the derived formula (22) (Table 2) with rounding up to integers to the higher side.

Table 2 – Dependence of the required number of terms n on the specified calculation accuracy R_n/S of the sum S with variation of the step $\Delta\varepsilon$ and temperature T

T, K	S and n at $\Delta\varepsilon = 10^{-22}$ J				S and n at $\Delta\varepsilon = 10^{-20}$ J			
		n at R_n/S				n at R_n/S		
	S	10^{-3}	10^{-4}	10^{-5}	S	10^{-3}	10^{-4}	10^{-5}
10	1.940	10	13	16	1.000	1	1	1
50	7.415	48	64	80	1.000	1	1	1
100	14.31	96	128	159	1.000	1	2	2
200	28.12	191	255	318	1.028	2	3	4
400	55.73	382	509	634	1.196	4	6	7
600	83.36	573	764	954	1.427	6	8	10
800	111.0	764	1018	1272	1.679	8	11	13
1000	138.6	954	1272	1590	1.940	10	13	16
2000	276.6	1908	2544	3180	3.291	20	26	32
3000	414.7	2862	3816	4770	4.662	29	39	48
4000	522.8	3816	5088	6360	6.038	39	51	64
5000	690.8	4770	6360	7950	7.415	48	64	80
10^4	1381	9540	12720	15900	14.31	96	128	159
10^5	$1.38{\cdot}10^{4}$	$9.54{\cdot}10^{4}$	$1.27{\cdot}10^{5}$	$1.59{\cdot}10^{5}$	138.6	954	1272	1590
10^6	$1.39{\cdot}10^{5}$	$9.54{\cdot}10^{5}$	$1.27{\cdot}10^{6}$	$1.59{\cdot}10^{6}$	1381	9540	12720	15900

Here, in addition to a more vivid expression of the increasing dependence of the required number of terms of sum on the given accuracy of calculating this sum and the apparent numerical superiority of n in comparison with the amount of the sum of S in all variations $\Delta\varepsilon$ and T there are given numerical values of n, which are subject to direct verification.

This can be illustrated by an example of calculating a_n by formula (5) at various temperatures, by setting an arbitrary value $\Delta\varepsilon = 10^{-20}$ J (Table 3). Here are given the values of the sum of series (denoted as S_n) calculated with rounding to the fourth decimal place, and hence with an accuracy of 10^{-4}, and the total values of the sum calculated according to formula (9) (denoted as S and given with greater accuracy, 10^{-5}), as well as the fractional values of the terms of sum calculated according to formula (10), with the aim of further determining the entropy by formula (11).

Table 3 – Distribution of the terms of statistical sum a_n and their fractional values P_n depending on temperature

n	200 K		400 K		600 K		800 K		1000 K	
	a_n	P_n	a_n	P_n	a_n	P_n	a_n	P_n	a_n	P_n
1	1	0.9732	1	0.8364	1	0.7009	1	0.5955	1	0.5152
2	0.0268	0.0260	0.1636	0.1368	0.2991	0.2096	0.4045	0.2409	0.4848	0.2498
3	0.0007	0.0007	0.0268	0.0224	0.0895	0.0627	0.1636	0.0974	0.2350	0.1211
4	0	0	0.0044	0.0037	0.0268	0.0188	0.0662	0.0394	0.1139	0.0587
5	0	0	0.0007	0.0006	0.0080	0.0056	0.0268	0.0159	0.0552	0.0284
6	0	0	0.0001	0.0001	0.0024	0.0017	0.0108	0.0064	0.0268	0.0138
7	0	0	0	0	0.0007	0.0005	0.0044	0.0026	0.0130	0.0067
8	0	0	0	0	0.0002	0.0002	0.0018	0.0011	0.0063	0.0032
9	0	0	0	0	0.0001	0	0.0007	0.0004	0.0030	0.0016
10	0	0	0	0	0	0	0.0003	0.0002	0.0015	0.0008
11	0	0	0	0	0	0	0.0001	0.0001	0.0007	0.0004
12	0	0	0	0	0	0	0	0	0.0004	0.0002
13	0	0	0	0	0	0	0	0	0.0002	0.0001
14	0	0	0	0	0	0	0	0	0.0001	0
15	0	0	0	0	0	0	0	0	0	0
S_n	1.0275	-	1.1956	-	1.4268	-	1.6792	-	1.9408	-
S	1.02750	-	1.19561	-	1.42681		1.67922	-	1.94082	-
ΣP_n	-	1.000	-	1.000	-	1.000	-	1.000	-	1.000

From this table it follows that with a given accuracy of calculation, taking into account seven significant digits and rounding up to 0.0001, the statistical sums coincide both at the term summing according to formula (5) and the direct calculation according to formula (9). Comparing with the data in Table 2 for $\Delta\varepsilon = 10^{-20}$ J with a specified accuracy of 10^{-4}, we make sure in practical coincidence of the necessary number of terms for calculating the partial sum in Table 3: at 200 K $n = 3$, at 400 K $n = 6$, at 600 K $n = 8$ and $n = 9$, at 800 K $n = 11$, at 1000 K $n = 13$ and $n = 14$. The same applies to the share distribution P_n.

The dependence of the absolute and fractional distributions of the terms of statistical sum on temperature becomes more smoothed as the temperature increases, and requires a larger number of terms. Fig. 1 shows a more graphic picture of the change in the fractional content of the terms of the statistical sum, and hence the fractional distribution of particles from the temperature and energy level of the particles. These data are directly needed to calculate the entropy of the system.

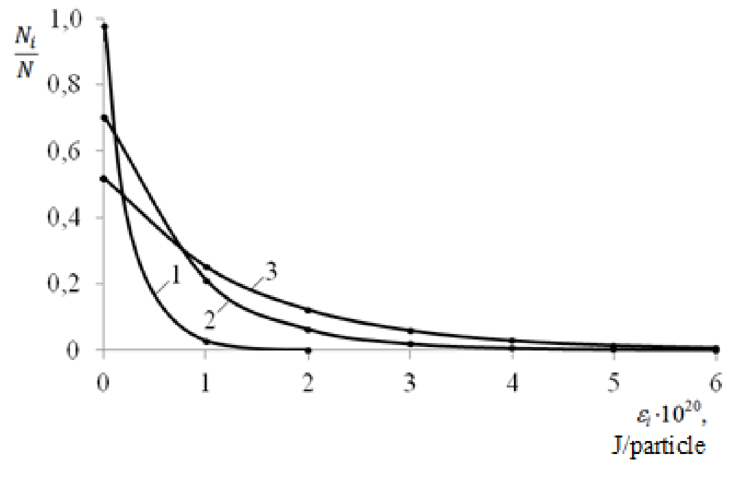

Figure 1 – Dependence of the energy distribution of particles on temperature: 1 – at 200 K, 2 – 600 K, 3 – 1000 K.
Points – a_n according to formula (5), lines – $f(x)$ according to formula (6)

Correspondingly, the mathematical entropy of the system according to the data in Table 3 and in accordance with formulas (10) and (11) is characterized by the following temperature dependence:

T, K	200	400	600	800	1000
N	0.1266	0.5326	0.8703	1.1328	1.3441

Relatively low values of entropy completely correlate with sharp distributions of statistical sums in the chosen example of a rather rough variation of energy levels with step of $\Delta\varepsilon = 10^{-20}$ J/particle. With a smaller value $\Delta\varepsilon$, as noted above, a much larger number of terms, hundreds and thousands, would have to be taken into account, and in this case an accurate knowledge of its limit according to the proposed formula (9) would make it possible to make informed decisions on limiting the number of terms in the sum according to formula (22) with the accuracy adopted for calculating the sum itself. In turn, this would determine the accuracy of calculating entropy.

In connection with the established possibility of direct calculation of the integral entropy of the Boltzmann distribution according to formula (31), it is expedient to compare it with formula (37) with the numerical definition of entropy as the sum of series, limited to the variation of temperature for $\Delta\varepsilon = 10^{-20}$ J/particle and a sufficient number of terms of series according to formula (22), applicable for calculating the statistical sum. In this case, we can determine the accuracy of calculating the entropy in comparison with the given accuracy in accordance with (22) by calculating the last term of series

$$a' = Ae^{-bn'}\ln\left(Ae^{-bn'}\right) \qquad (38)$$

with its ratio to the partial sum of series.

The corresponding expressions for the integral and total entropy have the following form

$$H_{int.} = -\int_0^{\infty} Ae^{-bx}\,ln(Ae^{-bx})\,dx = \frac{A}{b}(lnA - 1), \qquad (39)$$

$$H_{sum.} = -\sum_{n=1}^{n'} Ae^{-bn}\,ln(Ae^{-bn}). \qquad (40)$$

Calculation results with determination accuracy n' up to 0,0001 $-a_{n'}$ are given in Table 4.

Table 4 – Integral $N_{int.}$ and partially summarized $N_{sum.}$ Boltzmann entropy, their ratio $K = N_{int.}/N_{sum.}$ at different temperatures

T, K	$N_{int.}$	n'	$N_{sum.}$	K	$-a_{n'}$	$\frac{-a_{n'}}{H_{sum.}}$
400	1.1476	6	0.5324	2.1555	$9.03\cdot10^{-4}$	$1.70\cdot10^{-3}$
600	0.5762	8	0.8696	1.8126	$1.32\cdot10^{-3}$	$1.52\cdot10^{-3}$
800	0.7885	11	1.1324	1.5794	$6.67\cdot10^{-4}$	$5.89\cdot10^{-4}$
1000	0.9415	13	1.3492	1.4454	$8.10\cdot10^{-4}$	$6.03\cdot10^{-4}$
5000	3.1550	64	2.9317	1.0762	$1.63\cdot10^{-4}$	$5.57\cdot10^{-5}$
10^4	3.7596	128	3.6242	1.0374	$8.37\cdot10^{-5}$	$2.39\cdot10^{-5}$
10^5	5.9493	1272	5.9262	1.0039	$1.025\cdot10^{-5}$	$1.73\cdot10^{-6}$
10^6	8.2334	12720	8.2289	1.0006	$1.188\cdot10^{-6}$	$1.44\cdot10^{-7}$

From these data it follows that the commensuration coefficient K decreases with the temperature increase, tending to a one. This corresponds to the ratio of decreasing similarly-named dependencies for continuous and discrete distributions over the sum of the corresponding areas, as shown in [4]. This confirms the correctness of the analytically found and calculated values of $N_{int.}$ and $N_{sum.}$ entropy. At the same time, the accuracy of calculations, determined on the basis of the accuracy of calculation of the statistical sum, is also generally preserved for calculation of the entropy, becoming even more strict for high temperatures. No violations of established regularities and at the variation Δε - of value, most likely correlating with the properties of system-forming particles, are expected.

In any case, the possibility of freely combining the conditions affecting the calculation of the statistical sum, Boltzmann distribution and entropy, expands the limits of the use of these fundamental physical and chemical values and regularities.

Conclusion

1. On the basis of the commensuration coefficient of discrete and continuous similarly-named distributions developed by the authors, we analyzed the statistical sum in the Boltzmann distribution to the commensuration with the improper integral of the similarly-named function in the full range of the term of series of the statistical sum at the arbitrary combination of the temperature and interval (step) of the energy variation of particles. The convergence of series based on the Cauchy, Maclaurin criteria and the equal commensuration of series and improper integral of the similarly-named function in each unit interval of variation of series and similarly-named function were established.

2. Independence of the commensuration coefficient from the number of terms of series

$$K = \frac{\int_{x=n-1}^{x=n} e^{-(x-1)\Delta\varepsilon/kT}\,dx}{e^{-(n-1)\Delta\varepsilon/kT}} = \frac{kT}{\Delta\varepsilon}\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right)$$

allows us to express the total statistical sum through this coefficient and certain value of the improper integral

$$\int_0^\infty e^{-(x-1)\Delta\varepsilon/kT}\,dx = \frac{kT}{\Delta\varepsilon}e^{\frac{\Delta\varepsilon}{kT}}$$

in the form of calculated formula

$$\sum_{n=1}^{\infty} e^{-(n-1)\Delta\varepsilon/kT} = \frac{1}{K}\int_0^\infty e^{-(x-1)\Delta\varepsilon/kT}\,dx = \frac{e^{\frac{\Delta\varepsilon}{kT}}}{e^{\frac{\Delta\varepsilon}{kT}} - 1}.$$

Accordingly, the Boltzmann distribution, which is necessary for calculating entropy according to formula $H = -\sum_{i=1}^{\infty} P_i \ln P_i$, gets a more direct expression

$$P_i = e^{-\frac{i\Delta\varepsilon}{kT}}\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right).$$

Within the framework of this same commensuration, we determined the possibility to calculate the necessary number of terms of sum to calculate it with a given accuracy equal to the ratio of the residual and total sum of the series R_n/S in the form of formula

$$n = -\frac{kT}{\Delta\varepsilon}\ln\frac{R_n}{S}.$$

3. An analysis of the expressions obtained for the commensuration coefficient and the statistical sum establishes its identity with the similarly-named improper integral only in the area of $\Delta\varepsilon \to 0$ and $T \to \infty$. In other combinations $\Delta\varepsilon$ and T a direct replacement of the statistical sum by an improper integral is accompanied by an error reaching $K \to \infty$ at $\Delta\varepsilon \to \infty$ and $T \to 0$. Therefore, the general expression for the total statistical sum is analytically correct and can be calculated with any given accuracy.

4. This amount for various combinations $\Delta\varepsilon$ and T may vary from one (at $T \to 0$ or $\Delta\varepsilon \to \infty$) to infinity (at $T \to \infty$ or $\Delta\varepsilon \to 0$), respectively, determining either a steep decline or a complete uniformity in the distribution of the terms of sum, and thus close to zero or infinitely large entropy of the system. In any case, direct calculation of the statistical sum, as well as the particle's energy distribution in accordance with the Boltzmann law, makes it possible to apply this law more rigorously to various problems of statistical physics and physical chemistry.

5. To determine the entropy from the new expression for the Boltzmann distribution in the form of a series,

$$H = -\sum_{i=1}^{\infty} e^{-\frac{i\Delta\varepsilon}{kT}}\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right) ln\left[e^{-\frac{i\Delta\varepsilon}{kT}}\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right)\right]$$

the convergence of the similarly-named improper integral is established.

$$\int_0^\infty e^{-\frac{\Delta\varepsilon x}{kT}}\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right) ln\left[e^{-\frac{\Delta\varepsilon x}{kT}}\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right)\right]dx = \frac{kT}{\Delta\varepsilon}\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right)\left[ln\left(e^{\frac{\Delta\varepsilon}{kT}} - 1\right) - 1\right].$$

However, the commensuration coefficient of integral and series in each unit interval turns out to be dependent on the number of the term of series and therefore cannot be used to determine the sum of series through the improper integral. In this case, the entropy can be calculated with a given accuracy with a corresponding quantity of the term of series n.

6. Given accuracy of the statistical sum of series R_n/S reveals the meaning of the exponential factor in the Arrhenius equation as the fraction of particles with energy above the energy level (the activation barrier) ε_n:

$$\frac{R_n}{S} = e^{-\frac{n\Delta\varepsilon}{kT}} = e^{-\frac{\varepsilon_n}{kT}} = e^{-\frac{E_a}{RT}}.$$

7. The prospect of development of the proposed method for expressing the Boltzmann distribution and entropy is to establish the relationship between the magnitude of the energy quantum

$\Delta\varepsilon$ and the properties of the system-forming particles.

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