

# A SIMPLE INTRODUCTION TO STATISTICAL THERMODYNAMICS DISREGARDING ENERGY QUANTATION

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## Summary

The exponential energy distribution is a general feature of many particles and does not necessitate the assumption of quantized energies or the case of the most probable distribution. The average energy is equal to  $\frac{3}{2} kT$  if it is a quadratic function of a variable over which the integration average is calculated and if it is distributed among three components. The expressions of entropy, distribution numbers belonging to the most probable state for solids and gases and Boltzmann's constant  $k$  can be interpreted solely on the basis of non-quantized energies. An application: Transmission coefficient occurring in the theory of absolute reaction rates can be calculated from the deduced formulae supposing that all normal vibrations of the activated complex can share the energy with equal probability.

## Introduction

The classical approach to statistical theory preceded its treatment taking quantized energies into consideration. It is generally said that "using the principle that an ensemble is described by the condition of maximum probability, it is possible to show that probability depends on energy  $u$  as the familiar exponential  $e^{-u/kT}$ " [1a]. On the other hand the average kinetic energy of a gas molecule can be determined using Liouville's Theorem which is based on Cartesian coordinates and conjugate momenta. Coordinates and momenta build the phase space suitable for the description of dynamical problems. The present paper approaches the problem of the exponential distribution of energy and energy averaging from a different angle.

## Energy distribution among particles

Non-quantized energy can be distributed among particles in infinitely many different ways so that the concept of the number of energy distributions has no meaning. One may however introduce, an arbitrarily small energy ( $\varepsilon_0$ )

and the energy is taken to be the integral multiple of this quantity:  $U = v\varepsilon_0$ . (The total energy  $U$  and the energies of particles should be expressed by the energy unit  $u$  multiplied by a rational number given with an accuracy of  $n$  arbitrary great number of decimals. In this case  $\varepsilon_0 = 10^{-n}u$ , and if  $U = ku$  where  $k$  is the rational number characterizing the total energy,  $v = 10^n k$ .) Let us take an example: energy is distributed among three particles so that the energy of the first particle would be  $5\varepsilon_0$ , that of the second  $3\varepsilon_0$  and the third would possess  $2\varepsilon_0$  energy.  $v = 10$ . This distribution can be schematically denoted as follows:

$N\varepsilon_0\varepsilon_0\varepsilon_0\varepsilon_0\varepsilon_0N\varepsilon_0\varepsilon_0\varepsilon_0N\varepsilon_0\varepsilon_0$ . The total number of distributions would be  $\frac{12!}{10!2!}$ .

(The scheme has to be initiated by a particle i.e. by the letter  $N$  whose position is therefore fixed.) In a general formula:

$$\Omega = \frac{(v + N - 1)!}{v!(N - 1)!} \quad (1)$$

As  $v$  is an arbitrary great number, irrespective of the number of particles,  $v \gg N$ , hence approximately:

$$\Omega = \frac{v^{N-1}}{(N-1)!} = \varepsilon_0^{1-N} \frac{U^{N-1}}{(N-1)!} \quad (2)$$

Let us examine what is the probability that the energy of the  $i$ -th particle falls between  $\varepsilon_i$  and  $\varepsilon_i + \varepsilon_0$ . In this case  $U - \varepsilon_i$  is shared among the other particles and the number of distributions is:

$$\Omega_i = \varepsilon_0^{2-N} \frac{(U - \varepsilon_i)^{N-2}}{(N-2)!} \quad (3)$$

The probability is the ratio of Eq. (3) and the number of all distributions i.e. Eq. (2):

$$\frac{1}{\varepsilon_0} \frac{\Omega_i}{\Omega} = \frac{1}{N} \frac{dN_i}{dU} = (N-1) \frac{(1 - \varepsilon_i/U)^{N-2}}{U} \quad (4)$$

If  $N$  is large that is  $U \gg \varepsilon_i$ :  $(1 - \varepsilon_i/U)^{N-2} \approx \exp \left[ -(N-2) \frac{\varepsilon_i}{U} \right] \approx \exp \left( -\frac{\varepsilon_i}{\bar{\varepsilon}} \right)$  where  $\bar{\varepsilon}$  is the average energy. Thus:

$$\frac{1}{N} \frac{dN_i}{dU} = (1/\bar{\varepsilon}) e^{-\varepsilon_i/\bar{\varepsilon}} \quad (5)$$

This mean energy is an average obtained by integrating over the energies:  $\int_0^\infty e^{-\varepsilon_i/\bar{\varepsilon}} d\varepsilon_i \equiv \bar{\varepsilon}$ . As it is seen the energy distribution has an exponential character and nothing was stated about the most probable distribution.

### Energy distribution among systems (Gibbs-statistics) [2]

Let us regard many uniform systems containing equal numbers of particles. What is the probability that the energy of the  $j$ -th system falls between  $U_j$  and  $U_j + dU$ . The energy  $U_j$  of a system is built from the energies  $\varepsilon_{ij}$  of particles and the probability is the product of those belonging to single particles:

$$\frac{1}{n} \cdot \frac{d n_j}{d U} = (1/\bar{\varepsilon}^{N_j}) e^{-\sum_i \varepsilon_{ij}/\bar{\varepsilon}} = (1/\bar{\varepsilon}^{N_j}) e^{-U_j/\bar{\varepsilon}} \quad (6)$$

Systems have, however, a structure, i.e. they consist of particles among which the energy can be distributed in different ways [3a] so that Eq. (6) has to be multiplied by the numbers of distributions within the systems (Eq. (2)):

$$\frac{1}{n} \cdot \frac{d n_j}{d U} = A \frac{U_j^{N_j-1}}{(N_j-1)!} (1/\bar{\varepsilon}^{N_j}) e^{-U_j/\bar{\varepsilon}} \quad (7)$$

where  $A$  is a normalizing factor. As the sum of probabilities equals 1:

$$\frac{A}{(N_j-1)!} (1/\bar{\varepsilon}^{N_j}) \int_0^{\infty} U_j^{N_j-1} e^{-U_j/\bar{\varepsilon}} d U_j = 1 \quad (8)$$

$\int_0^{\infty} U_j^{N_j-1} e^{-U_j/\bar{\varepsilon}} d U_j = \bar{\varepsilon}^{N_j} (N_j-1)!$  so that:

$$A = 1 \quad (9)$$

Hence the probability of a system having energy  $U_j$  is:

$$\frac{1}{n} \cdot \frac{d n_j}{d U} = \frac{U_j^{N_j-1}}{(N_j-1)!} (1/\bar{\varepsilon}^{N_j}) e^{-U_j/\bar{\varepsilon}} \quad (10)$$

$\int_0^{\infty} \frac{U_j^{N_j-1}}{(N_j-1)!} e^{-U_j/\bar{\varepsilon}} d U_j = \bar{\varepsilon}^{N_j}$  thus in the case of energy distribution among

systems the *partition function integrated over the energy* is given by  $\bar{\varepsilon}^N$ . Attention is called to the fact that partition functions in Eq. (5) and (10) are not dimensionless. On the other hand *partition function of systems is just the  $N$ -th power of that of particles.*

### Energy distribution among gaseous systems

Eq. (10) refers to systems in which the particles are distinguishable. E.g. the distribution  $N_{\varepsilon_0 \varepsilon_0 \varepsilon_0 \varepsilon_0} N_{\varepsilon_0 \varepsilon_0 \varepsilon_0} N_{\varepsilon_0 \varepsilon_0}$  is distinct from  $N_{\varepsilon_0 \varepsilon_0 \varepsilon_0 \varepsilon_0} N_{\varepsilon_0 \varepsilon_0} N_{\varepsilon_0 \varepsilon_0}$ . All distribution 5-3-2 were taken into con-

sideration  $3!$  times which can not be done if the particles are indistinguishable. Therefore the number of distributions of gaseous systems has to be divided by  $N!$ :

$$\Omega_g = \varepsilon_0^{1-N} \frac{U^{N-1}}{(N-1)! N!} \quad (11)$$

In the case of gaseous systems  $N!$  appears in the denominator of Eq. (7) so that the normalizing factor is instead of Eq. (9):

$$A_g = N_j!, \quad (12)$$

and instead of (10):

$$\frac{1}{n} \cdot \frac{d n_j}{d U} = \frac{U_j^{N_j-1}}{(N_j-1)! N_j!} (N_j! / \bar{\varepsilon}^{N_j}) e^{-U_j / \bar{\varepsilon}} \quad (13)$$

$\int_0^\infty \frac{U_j^{N_j-1}}{(N_j-1)! N_j!} e^{-U_j / \bar{\varepsilon}} d U_j = \bar{\varepsilon}^{N_j} / N_j!$  from which it follows that the *partition function of gaseous systems is the  $N$ -th power of the partition function belonging to particles, divided by  $N!$* . Let us denote the partition function of particles by  $q$  and that of systems by  $Q$ , then the corresponding expressions are:

$$Q_s = q^N \quad \text{and} \quad Q_g = \frac{q^N}{N!} \quad [3b] \quad (14)$$

### Energy fluctuation of systems

If, by means of a fixed temperature, the overall energy of very many systems is determined, the energy of an individual system may be different according to Eq. (10) and (13). Let us examine now the *most probable distribution* by differentiating Eqs (10) or (13). We obtain for the most probable energy:

$$U_{\max} = (N-1)\bar{\varepsilon} \quad (15)$$

that is if  $N$  is sufficiently high it is  $N$  times greater than the average energy.

The second derivative provides information about the width of the maximum curve. Hence the energy values at the inflexion points of the curve are equal to:

$$U_{\text{infl}} = \bar{\varepsilon}(N-1 \pm \sqrt{N-1}) \quad (16)$$

and the uncertainty of energy as measured by the distance between the inflexion points is:

$$\Delta U = 2\bar{\epsilon} \sqrt{N-1} \quad (17)$$

Figure 1 shows the energy distribution of a system in the case of different number of particles. If the quantity of the substance is one mole, the most probable energy amounts to  $6 \cdot 10^{23}\bar{\epsilon}$ , its uncertainty to  $1.5 \cdot 10^{12}\bar{\epsilon}$ , whose relative value is then  $2.5 \cdot 10^{-12}$ . *It is impossible to measure temperature with such an accuracy.*

An example: *The probability of breaking up a chemical bond or that of a transition of a libration into internal rotation.* If a molecule contains the dissociation energy necessary to break one of its bonds the event requires also that this energy should be concentrated in the degree of freedom of a stretching vibration of the corresponding bond. For the sake of simplicity let us assume that all normal vibrations could share this energy with equal probability. (Generally higher and lower normal frequencies equally occur in the molecule so that this assumption does not cause a significant error.)

In the present case energy is distributed not among particles but among normal vibrations. The probability of the presence of dissociation energy  $D$  can be calculated by integrating Eq. (10) from  $D$  to  $\infty$  and dividing it by the same integral from 0 to  $\infty$ :

$$P_1 = \frac{\int_D^{\infty} U^{s-1} e^{-U/\bar{\epsilon}} dU}{\int_0^{\infty} U^{s-1} e^{-U/\bar{\epsilon}} dU} \quad (18)$$

where  $s$  is the number of normal vibrations. The denominator equals  $\bar{\epsilon}^s (s-1)!$ . The numerator:

$$\int_D^{\infty} U^{s-1} e^{-U/\bar{\epsilon}} dU = \bar{\epsilon}^s (s-1)! e^{-D/\bar{\epsilon}} \left[ \frac{(D/\bar{\epsilon})^{s-1}}{(s-1)!} + \frac{(D/\bar{\epsilon})^{s-2}}{(s-2)!} + \dots + D/\bar{\epsilon} + 1 \right].$$

Upon substitution into Eq. (18):

$$P_1 = e^{-D/\bar{\epsilon}} \left[ \frac{(D/\bar{\epsilon})^{s-1}}{(s-1)!} + \frac{(D/\bar{\epsilon})^{s-2}}{(s-2)!} + \dots + D/\bar{\epsilon} + 1 \right]. \quad (19)$$

(If the number of normal vibrations is very high e.g. in a crystal, the distribution curve is very sharp according to Eq. (16) and then, if  $D < \bar{\epsilon}$  the expression in brackets tends to  $e^{D/\bar{\epsilon}}$  thus  $P_1$  to 1. The result is trivial: if the dissociation energy

is smaller than the average energy of a normal vibration it is certainly possessed by the crystal. Figure 1 shows that the whole probability area which equals 1, lies at higher energies than  $D$  indicated by an arrow if the crystal possesses at least 1000 normal vibrations.)

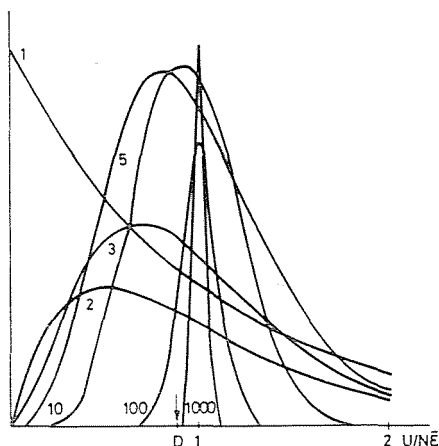


Fig. 1. Energy distribution of systems containing different number of particles. Ordinate values are arbitrary.  $\bar{\varepsilon}$  is the average energy of very many identical systems. For  $D$ , see text later

If the energy of one normal vibration falls between  $D$  and  $D + \varepsilon_0$  the other normal vibrations have to share the energy  $U - D$ . The ratio of the distribution numbers (see Eq. (2) and (3)):

$$\frac{1}{\varepsilon_0} \frac{\Omega_i}{\Omega} = (s-1) \frac{(U-D)^{s-2}}{U^{s-1}}$$

The condition of concentrating the dissociation energy is fulfilled, however, if the selected normal vibration has more than the dissociation energy and the other ones have correspondingly less. So that:

$$P_2 = \frac{1}{\varepsilon_0 \Omega} \int_D^U \Omega_i d\varepsilon = \frac{s-1}{U^{s-1}} \int_D^U (U-\varepsilon)^{s-2} d\varepsilon = \left( \frac{U-D}{U} \right)^{s-1} \quad (20)$$

(If  $D \ll U$ ,  $P_2 = e^{-(s-1)D/U} = e^{-D/\bar{\varepsilon}}$  that is if there are very many normal vibrations the probability  $P_2$  becomes independent of the distributions among the other normal vibrations.)

If we are not talking about the breaking of a bond but about the transition of a libration into internal rotation the height of the potential barrier

has to be inserted into the formulae instead of dissociation energy. The overall probability is then:

$$K = P_1 P_2 = \left( \frac{U-D}{U} \right)^{s-1} e^{-D/\bar{\epsilon}} \sum_{i=0}^{s-1} \frac{(D/\bar{\epsilon})^i}{i!} \quad (21)$$

( $K$  can be interpreted as the transmission coefficient in the theory of absolute reaction rates. [3c] Figure 2 denotes the dependence of  $K$  on different  $D/U$  ratios for different numbers of normal vibrations.

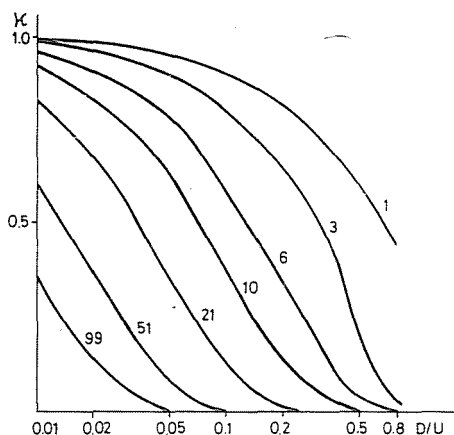


Fig. 2. Probability of bond breaking or of transition from libration into internal rotation.  $D$  is the energy of bond breaking or the height of the potential barrier,  $U$  is the energy of the molecule or crystal. Different curves refer to different numbers of normal vibrations

### Average kinetic energy of gaseous molecules

As it was formerly mentioned  $\bar{\epsilon}$  is a mean energy integrated over energy. According to Liouville's Theorem [1b], however, kinetic energy of gas molecules has to be averaged by momenta. Kinetic energy:  $T = p^2/(2m)$  where the momentum  $p$  of every molecule has three components and the kinetic energy can be distributed among these components. Using quantum theory,  $T = n^2 h^2 / (8ma^2)$  [3d] for one component. Applying a uniform treatment, the kinetic energy is a quadratic function of a variable and is distributed among three components. Let us denote this variable by  $r$ , then:

$$T = br^2. \quad (22)$$

The number of distributions among the three components according to Eq. (2) is:

$$\Omega = \alpha_r \frac{r^2}{2} \quad (23)$$

( $\alpha_r$  stands for  $\varepsilon_0^{-1}$ ) and the probability of particles belonging to variable  $r$ :

$$\frac{1}{N} \frac{d N_r}{d r} = \frac{A \alpha_r}{\bar{\varepsilon}} \frac{r^2}{2} e^{-br^2/\bar{\varepsilon}} \quad (24)$$

where  $A$  is again a normalizing factor. (If  $r$  is the velocity  $c$  and  $b$  equals  $m/2$ , then following the determination of the normalizing factor one obtains the well known Maxwell velocity distribution where  $kT$  stands for  $\bar{\varepsilon}$  [3c].) The average energy integrated over the variable  $r$ :

$$\bar{\varepsilon}_r = \frac{b \int_0^{\infty} r^4 e^{-br^2/\bar{\varepsilon}} d r}{\int_0^{\infty} r^2 e^{-br^2/\bar{\varepsilon}} d r} \quad (25)$$

The numerator equals  $(3\bar{\varepsilon}/2) \int_0^{\infty} r^2 e^{-br^2/\bar{\varepsilon}} d r$ , hence:

$$\bar{\varepsilon}_r = \frac{3}{2} \bar{\varepsilon} \quad (26)$$

This expression holds not only for the translational kinetic energy of molecules but also for the rotational energy which is equally a quadratic function of a variable (quantum number). Maxwell's classical theory yields the same average kinetic energy expression as the later quantum theory because the momenta of the phase space are linear functions of the quantum number.

### Entropy

In the case of many particles  $N-1$  in the expression of  $\Omega$  can be substituted by  $N$ :

$$\Omega = \varepsilon_0^{-N} \frac{U^N}{N!} \quad (27)$$

In logarithmic form:

$$\ln \Omega = -N \ln \{\varepsilon_0\} + N \ln \{U\} - N \ln N + N \quad (28)$$



If the energy of the system is increased by  $dU$ :

$$\frac{d \ln \Omega}{dU} = \frac{N}{U} = \bar{\varepsilon}^{-1} \quad (29)$$

Hence the differential of the entropy:

$$dS = \frac{dU}{T} = (\bar{\varepsilon}/T) d \ln \Omega \quad (30)$$

We may suppose that the average energy integrated over energy is proportional to the temperature:  
 $\bar{\varepsilon} = kT$  and:

$$dS = k d \ln \Omega \quad (31)$$

Let us integrate this equation from  $T=0$ . At  $0\text{ K}$  there is no thermal energy so that Eq. (2) does not hold. Instead of this one can use Eq. (1) taking  $v$  as equal to 0. It means that at  $0\text{ K}$ ,  $\Omega = 1$ . The thermal entropy:

$$S_{\text{th}} = k \ln \Omega \quad (32)$$

Let us write now the partition function of systems defined by the integral following Eq. (10) but supposing very many particles when the distribution curve (Fig. 1) is very sharp and the sum of states can be substituted by only one term belonging to the maximum:

$$Q = \Omega_m e^{-U_m/\bar{\varepsilon}} \quad (33)$$

where  $U_m$  is by far the most probable energy and  $\Omega_m$  is its distribution number. From Eq. (32):

$$Q = e^{S/k} \cdot e^{-U/(kT)} = e^{-A/(kT)} = e^{-N\mu/(kT)} \equiv \lambda^{-N} \quad (34)$$

where  $A$  is the free energy,  $\mu$  the chemical potential of a particle,  $\lambda$  is the absolute activity of a homogeneous system. [5]

From Eq. (33) the distribution number belonging to the most probable state:

$$\ln \Omega = \ln Q + \frac{U}{kT} \quad \text{and} \quad S_{\text{th}} = k \ln Q + \frac{U}{T} \quad (35)$$

Introducing the partition function of particles, according to Eq. (14) for solids:

$$\ln \Omega = N \ln q + \frac{U}{kT} \quad \text{and} \quad S_{\text{th}} = Nk \ln q + \frac{U}{T} \quad (36)$$

and for gases:

$$\ln \Omega = N \ln q - N \ln N + N + \frac{U}{kT} = N \left( \ln \frac{q}{N} + 1 \right) + \frac{U}{kT}$$

$$\text{and } S_{\text{th}} = Nk \left( \ln \frac{q}{N} + 1 \right) + \frac{U}{T} \quad (37)$$

The same expressions can be derived starting from quantized energies and using the Maxwell-Boltzmann and Bose-Einstein statistics, respectively, similarly supposing the most probable state. [6]

*What is the meaning of  $\varepsilon_0$  and  $k$ ?* If only energies which are multiples of  $\varepsilon_0$  can occur in a system the partition function may be composed as a sum:

$$q = \sum_{i=0}^{\infty} e^{-i\varepsilon_0/kT} = 1/(1 - e^{-\varepsilon_0/kT}) \approx kT/\varepsilon_0 \quad (38)$$

For a gas system:  $Q = (kT/\varepsilon_0)^N/N!$ . According to Eq. (34) the free energy:

$$A = -NkT \ln \frac{kT}{\varepsilon_0} - \ln N! \quad (39)$$

At constant temperature:

$$d A_T = -p dV = NkT d \ln \varepsilon_0 \quad \text{and} \quad (40)$$

$$p = -NkT \left( \frac{\partial \ln \varepsilon_0}{\partial V} \right)_T \quad (41)$$

If  $\varepsilon_0$  is an arbitrarily chosen small energy Eq. (41) cannot have any sense. In this case, namely, not only  $\varepsilon_0$  is an arbitrary quantity but also partition function  $q$ . If, however,  $q$  can be fixed by a physical model, for example by the molecular partition function of a perfect gas, belonging to physically quantized energies,  $\varepsilon_0$  would be arbitrary neither. In this case:

$$\frac{kT}{\varepsilon_0} = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V, \quad \text{hence:} \quad (42)$$

$$\varepsilon_0 = \frac{h^3}{(2\pi m)^{3/2} (kT)^{1/2} V} \quad (43)$$

The system where all energies occur which are multiples of  $\varepsilon_0$  is still a mathematical model. But if its partition function is equal to the expression in Eq. (42)  $\varepsilon_0$  is inversely proportional to the volume.

In this case  $d \ln \varepsilon_0 = -d \ln V$  and substituting it into Eq. (41):

$$p = \frac{NkT}{V} = n \frac{N_A kT}{V} \quad (44)$$

Comparing Eq. (44) to the law of perfect gases ( $p = nRT/V$ ) we obtain that  $k \equiv R/N_A$ .

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