

An alternative approach to the Boltzmann distribution through the chemical potential

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Summary. — The Boltzmann distribution is one of the most significant results of classical physics. Despite its importance and its wide range of application, at high school level it is mostly presented without any derivation or link to some basic ideas. In this contribution we present an approach based on the chemical potential that allows to derive it directly from the basic idea of thermodynamical equilibrium.

1. – Introduction

The Boltzmann distribution, first derived by Maxwell for the velocities of gas molecules at a given temperature, is one of the most important results of the molecular-kinetic approach, which has since become a cornerstone of statistical physics. Despite its historical and cultural relevance, there are only a few attempts to introduce suitably this result in high school teaching. Textbooks generally introduce the Boltzmann distribution without deriving it from some basic ideas, stating only the final result with some pictures that illustrate the situation together with some details about probabilities and mean values. The reason of this situation may be that Boltzmann distribution is considered one of the main results of the theory of statistical physics, and therefore well beyond the reach of secondary school ambitions.

This contribution proposes an alternative approach, which can be traced back to an idea expressed by Einstein in a paper dated July 1914 (what a lucky coincidence for the symposium!) [Einstein, 1914], in which he considered an ideal gas consisting of molecules in different excitation states as an *equilibrium mixture of distinct substances*, each one characterized by its own excitation energy. Moreover, the description of elementary processes of statistical physics as reactions between particles of such substances allows

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the use of the *chemical potential* and its basic dependence on concentration and excitation energy. In this way, the condition for *thermodynamical equilibrium* makes it possible to derive the Boltzmann distribution.

In the second part we are going to sketch how it is possible to extend this approach to other issues. As an example we'll discuss the *contribution of the vibrations* to the specific heat of bi-atomic gases.

As a conclusion, we shall briefly outline the general validity of this approach, indicating how, introducing the idea of free and occupied states as well as the quantum rules of occupation of energy levels, the same approach will lead to the Fermi-Dirac as well as to the Bose-Einstein distribution.

2. – The basic idea: a gas as a mixture of several substances

The basic idea is expressed by A. Einstein in a paper he presented at the session of the German Physical Society, July 24th, 1914. Taking a gas into consideration, Einstein adopted the following point of view:

“I take the liberty to consider two molecules chemically distinct, i.e. in principle separable by means of semi-permeable walls, if their resonator energies ε_σ and ε_τ are different. By doing so I can view the gas that was originally seen as uniform as also a mixture of different gases whose constituents are characterized by different values ε_σ .”

We generalize this point of view taking into account even the *translational motion* of the molecules as a kind of excitation. For the sake of simplicity, let us consider a dilute monatomic gas, so that the “molecules” can be regarded as pointlike particles as in the Newtonian mechanical model and their *translational kinetic energy* as excitation energy.

To parameterize the velocity of the molecules, we divide the *velocity space* into “cubic cells of volume $[\Delta v]^3$ ”, where each cell centre is identified by a triple of integers (n_x, n_y, n_z) (fig. 1)

$$(1) \quad \varepsilon(\vec{v}) = \frac{1}{2}m [v_x^2 + v_y^2 + v_z^2] = \frac{1}{2}m [n_x^2 + n_y^2 + n_z^2] [\Delta v]^2 = \varepsilon_{\vec{n}}.$$

In what follows we will refer to the molecules that belong to such a cell as to the \vec{n} -*substance*. Generalizing Einstein's suggestion, we interpret the physical system “gas” as a mixture of those different gaseous \vec{n} -substances. The kinetic energy of such molecules can be seen as the *excitation energy* of such a partial gas.

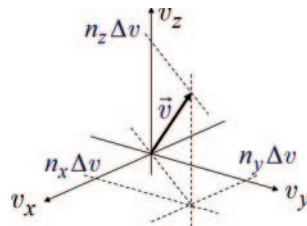


Fig. 1. – Individuating a cell centre in the velocity space.

3. – Chemical potential and equilibrium

With this image in mind, we ask how we can describe the *equilibrium condition* between all these substances. What we need is an *intensive quantity*, which can describe the tendency of one of the substances to transform into other ones. A suitable quantity for this purpose exists, and it is known under the name of *chemical potential* introduced 1876 by Josiah Willard Gibbs [Job, 2006], [Job, 2011].

This quantity accounts for the tendency of a given substance

- to react with other substances forming new ones;
- to transform into another state of aggregation, configuration, etc.;
- to migrate to another place.

Experimental data show that in general the value of the *chemical potential* depends on

- the *kind* and the *state of aggregation* of the substance;
- the physical “milieu” (*temperature, pressure, concentration*);
- the chemical “milieu” (in case of solutions or mixtures: on the kind and on the proportions of the components, on the acidity, etc.).

4. – Gas molecules velocity distribution

In order to go further we focus on two points: first, the concentration dependence of the chemical potential, and second the excitation energy that is characteristic for each of the different gaseous \vec{n} -substances. About the first point, we can assume that the gas maintains a constant temperature, so that a model that gives us a convenient description exhibits the usual logarithmic dependence on the concentration

$$(2) \quad \mu(c) = \mu_0 + RT \ln \left(\frac{c}{c^\circ} \right),$$

where

- c° is the reference concentration (1 mol/L);
- c is the actual concentration;
- μ_0 represents the value of the chemical potential at the temperature T by a gas concentration that equals the chosen reference concentration.

We will refer to this relation as to the *mass action equation*.

The second step allows us to express the excitation equation: the value of chemical potential of the molecules that belong to a particular “ \vec{n} -substance” is obtained by simply adding the molar kinetic energy to the ground value μ_0

$$(3) \quad \mu_{0,\vec{n}} = \mu_{0,\vec{0}} + N_A \varepsilon_{\vec{n}}.$$

Since our partial gases all belong to the same *chemical species*, it is *not* necessary to distinguish their μ_0 -values.

We can now express the chemical potential for the \vec{n} -substances by their actual concentration $c_{\vec{n}}$

$$(4) \quad \mu_{\vec{n}}(c_{\vec{n}}) = \mu_{0,\vec{0}} + N_A \varepsilon_{\vec{n}} + RT \ln \left(\frac{c_{\vec{n}}}{c^\circ} \right) = \mu_{0,\vec{0}} + \frac{1}{2} M v_{\vec{n}}^2 + RT \ln \left(\frac{c_{\vec{n}}}{c^\circ} \right),$$

where M represents the molar mass of the considered gas.

At *equilibrium* the chemical potential of the \vec{n} -substances all possess the same value. This can be expressed by the following relation:

$$(5) \quad \mu_{\vec{n}}(c_{\vec{n}}^{\text{eq}}) = \mu_{\vec{0}}(c_{\vec{0}}^{\text{eq}}),$$

so that we obtain

$$(6) \quad \mu_{0,\vec{0}} + \frac{1}{2} M v_{\vec{n}}^2 + RT \ln \left(\frac{c_{\vec{n}}^{\text{eq}}}{c^\circ} \right) = \mu_{0,\vec{0}} + RT \ln \left(\frac{c_{\vec{0}}^{\text{eq}}}{c^\circ} \right),$$

or

$$(7) \quad \ln \left(\frac{c_{\vec{n}}^{\text{eq}}}{c_{\vec{0}}^{\text{eq}}} \right) = - \frac{M v_{\vec{n}}^2}{2RT}.$$

Solving explicitly, we get the final result for *the rates* of the *equilibrium concentrations*:

$$(8) \quad \frac{c_{\vec{n}}^{\text{eq}}}{c_{\vec{0}}^{\text{eq}}} = \exp \left(- \frac{M v_{\vec{n}}^2}{2RT} \right) = \exp \left(- \frac{m v_{\vec{n}}^2}{2 k_B T} \right).$$

This is essentially the Boltzmann distribution of the gas molecules velocities.

An impression of this distribution might be gained by imagining a small amount of gas, possibly about $1 \mu\text{m}^3$, whose particles are allowed to escape into a vacuum by suddenly removing the walls enclosing it. The positions the particles have reached after about $30 \mu\text{s}$ are then marked producing an image as in fig. 2. The position reached by a particle simultaneously characterizes the direction and absolute value of the particle's velocity vector \vec{v} .

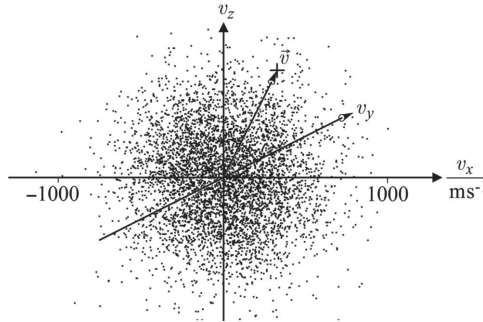


Fig. 2. – Velocity distribution for nitrogen molecules at 298 K.

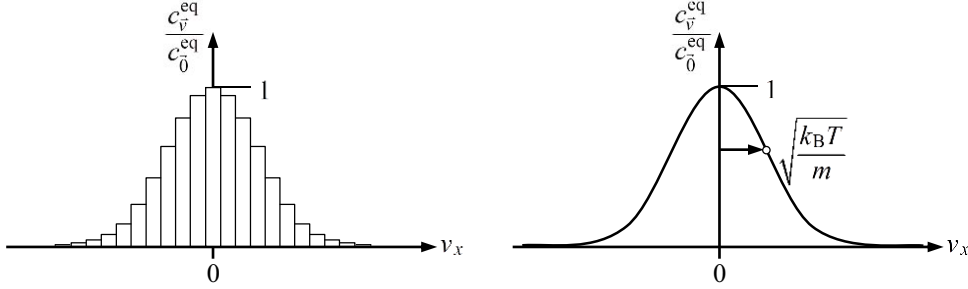


Fig. 3. – Velocity distribution along the v_x -axis: a) for finite velocity intervals; b) after performing the limit to infinitesimal intervals ($\Delta v \rightarrow 0$): the right inflection point of the bell-shaped curve is marked with a circle (o).

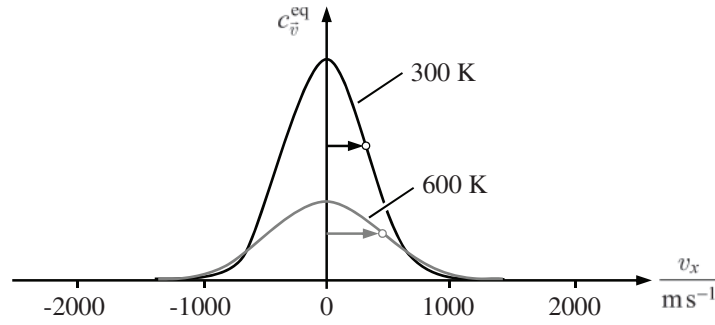


Fig. 4. – Velocity distribution for N_2 molecules at different temperatures. The point cloud (fig. 2) expands with rising temperature in all three spatial directions proportional to $T^{1/2}$ and the equilibrium concentration of particles with zero velocity decreases correspondingly as $T^{-3/2}$ (provided the velocity interval Δv is small but finite).

We can also plot the relative concentration distribution of the velocities along the v_x -axis: the graphs can be seen as the result of cutting the “cloud” in the velocity space along the v_x -axis for finite velocity intervals (fig. 3(a)) or after performing the limit to infinitesimal intervals (fig. 3(b)), so that we recover the well-known Gaussian distribution⁽¹⁾.

As a concrete example, fig. 4 illustrates the situation of nitrogen molecules in the same sample at two temperatures.

5. – How could this approach be extended?

Let us now sketch how it is possible to extend this approach. Indeed the previous procedure can be applied to many other systems, provided that the *energy values* and the possible *occupation number* of each excited energy level are properly taken into account.

⁽¹⁾ Traditionally, for the Boltzmann distribution in books we find another formula than (8) and other pictures than those of figs. 3 and 4. In the appendix we will show how to link the two different presentations explicitly.

It is worthwhile pointing out that in 1914 Einstein, in connection with the Planck radiation distribution formula, used this approach in order to obtain the well-known *average energy* of the 1-dimensional resonator

$$(9) \quad \bar{\varepsilon} = \frac{h\nu}{e^{h\nu/k_B T} - 1}.$$

In what follows we try to make the above statement clearer by discussing the *contribution of the vibrations* to the specific heat of bi-atomic gases [Job, 2007].

Let us consider all the gas particles that are in the same vibrational state with the quantum number j to be molecules of the *substance* $B(j)$. As in the previous example, the entire gas is intended to be an *equilibrium mixture* of such j -substances.

On the basis of the *experimental results*, molecular vibrations can be considered to be approximately harmonic and independent of other kinds of movements of the molecule so that the *excited energy values* of the individual vibrational levels are assumed to form the well-known harmonic spectrum:

$$(10) \quad \varepsilon(j) = h\nu \cdot j,$$

where the quantity $h\nu$ represents the energy interval between two neighbourly excited energy levels. As long as this approximation is valid, the *excitation equation* gives us the chemical potential of the individual substance $B(j)$:

$$(11) \quad \mu_0(j) = \mu_0(0) + N_A h\nu \cdot j \quad \text{for } j = 0, 1, 2, 3 \dots$$

In this way, taking into account the concentration dependence, *i.e.* the *mass action equation*, we can express the chemical potential for the j -substance at the $c(j)$ concentration:

$$(12) \quad \mu(j) = \mu_0(0) + N_A h\nu \cdot j + RT \ln \left(\frac{c(j)}{c^\circ} \right) \quad \text{for } j = 0, 1, 2, 3 \dots$$

Again, *at equilibrium*, the value reached by all the chemical potentials of the j -substances is the same:

$$(13a) \quad \mu^{\text{eq}}(j) = \mu^{\text{eq}}(0) = \mu^{\text{eq}},$$

or explicitly:

$$(13b) \quad \mu_0(0) + N_A h\nu \cdot j + RT \ln \left(\frac{c^{\text{eq}}(j)}{c^\circ} \right) = \mu_0(0) + RT \ln \left(\frac{c^{\text{eq}}(0)}{c^\circ} \right),$$

so that, with a little algebra, the different j -concentrations can be calculated:

$$(14a) \quad c^{\text{eq}}(j) = c^{\text{eq}}(0) \left[\exp \left(-\frac{h\nu}{k_B T} \right) \right]^j = c^{\text{eq}}(0) q^j,$$

where

$$(14b) \quad c^{\text{eq}}(0) = c^\circ \exp \left(\frac{\mu^{\text{eq}} - \mu_0(0)}{RT} \right) \quad \text{and} \quad q = \exp \left(-\frac{h\nu}{k_B T} \right) < 1.$$

Since the sum of all these values must correspond to the *actual* concentration of the gas, we obtain a relation between the partial concentrations $c(j)$ and the actual gas concentration c .

$$(15) \quad c = \sum_j c^{\text{eq}}(j).$$

With the well-known property of the *geometrical series* we obtain in this way a relation between the actual gas concentration, the chemical potential and the temperature

$$(16) \quad c = \sum_j c^{\text{eq}}(j) \\ = c^{\text{eq}}(0) \sum_j q^j = c^{\text{eq}}(0) \frac{1}{1-q} = c^\circ \exp\left(\frac{\mu^{\text{eq}} - \mu_0(0)}{RT}\right) \cdot \frac{1}{1 - e^{-h\nu/k_B T}}.$$

Notice that the last term in the last equation is nothing else than the vibrational *partition function* of the 1-dimensional harmonic oscillator.

Recalling further that the value of the chemical potential $\mu(c)$ of the *gas* must obviously coincide with the one assumed at *equilibrium* by each of the individual j -substances:

$$(17) \quad \mu(c) = \mu^{\text{eq}},$$

relation (16) then shows us how to get the *chemical potential* of the gas at this concentration c . Solving for $\mu(c)$, we obtain

$$(18) \quad \mu(c) = \mu_0(0) + RT \ln\left(\frac{c}{c^\circ}\right) + \underbrace{RT \ln\left(1 - e^{-h\nu/k_B T}\right)}_{\mu_{\text{vib}}},$$

where the last term μ_{vib} represents the contribution of vibrations to the chemical potential: it is interesting to note that this term depends on temperature T but is independent of both concentration c and pressure p .

This result provides us with the answer to our initial question: indeed, from the thermodynamics we know that the *first derivative* of the chemical potential with respect to the temperature at constant pressure yields the *molar entropy* S_m

$$(19) \quad S_m = - \left(\frac{\partial \mu}{\partial T} \right)_p,$$

while the *second derivative* of the chemical potential with respect to the temperature, again at constant pressure, yields *molar heat capacity* $C_{p,m}$

$$(20) \quad C_{p,m} = - T \left(\frac{\partial^2 \mu}{\partial T^2} \right)_p.$$

Without discussing the details of the calculation, we just indicate here the final result for the contribution of vibrations to the molar heat capacity of bi-atomic gases:

$$(21) \quad C_{\text{vib}} = - T \frac{\partial^2 \mu_{\text{vib}}}{\partial T^2} = R \frac{[h\nu/k_B T]^2 e^{h\nu/k_B T}}{[e^{h\nu/k_B T} - 1]^2}.$$

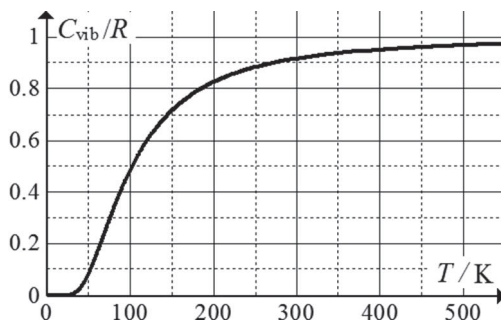


Fig. 5. – The contribution of molecular vibrations to the molar heat capacity of I₂-vapour.

The example in fig. 5 refers to the I₂-vapour. The *characteristic temperature of vibration* can be determined from spectroscopic measurements:

$$(22) \quad T_{\text{vib}} = h\nu/k_{\text{B}} = 305 \text{ K.}$$

6. – Conclusion and outlook

In this paper we have proposed an alternative approach to introduce the *Boltzmann distribution* based on general ideas that students meet in other contexts of science. Starting from:

- the concept of the *chemical potential*,
- the *mass action equation*,
- the *excitation equation*,
- the *equilibrium condition*

students are indeed no longer just faced, as is usually the case in textbooks, with the final result and some typical pictures based on probabilities and mean values, but they can deduce the Boltzmann distribution, extending to statistical physics problems the same kind of modeling they used for hydraulic, mechanical, electrical, thermal or chemical processes. Moreover, they could test the theoretical results experimentally, as we show, calculating the vibrational contribution to the *heat capacity* for bi-atomic gases.

The *same approach* can be applied in order to discuss quantitatively many other issues, such as the Planck radiation formula, the barometric formula, the sedimentation in a centrifuge, the contribution to heat capacity for poly-atomic molecules (vibrational and rotational), some simple nuclear reactions, redox and acid-base reactions, etc. [Job, 2007].

Furthermore, if we look at states of a system as *sites* that can be free or occupied, this approach allows us to discuss also the Debye T^3 -law, the single or multi-layer adsorption, the electron gas in metals and semi-conductors, the Fermi-Dirac and Bose-Einstein distribution and gas degeneration, and many, many other questions.

Appendix

Equation (A.1) shows us a typical formulation of the Maxwell-Boltzmann distribution of the *speed* v of the molecules:

$$(A.1) \quad df(v) = 4\pi \left[\frac{m}{2\pi k_B T} \right]^{3/2} \exp\left(-\frac{m v^2}{2k_B T}\right) v^2 dv,$$

where $f(v)$ is the fraction of all molecules with a speed smaller than v . Figure 6 reports typical illustrations we generally find in books: on the left we see the temperature dependence, while on the right we have the result for different molecular masses.

They look very different from those we have discussed and perhaps it is worthwhile to link the previous formulation to these ones. This is achieved when we look for the fraction of particles $df(v)$ having the absolute value of the velocity within a spherical shell of radius v and thickness dv (fig. 7).

$df(v)$ is proportional to both the “volume” $4\pi v^2 dv$ of the shell *and* to the concentrations $c(v)$ of the partial gases that belong to this shell. $c(v)$ is the same function for all our \vec{n} -substances. Indicating with γ the proportionality factor, we get

$$(A.2) \quad df(v) = \gamma c(v) 4\pi v^2 dv.$$

Inserting the result of eq. (8) we then find

$$(A.3) \quad df(v) = \gamma c(0) \exp\left(-\frac{m v^2}{2k_B T}\right) 4\pi v^2 dv.$$

Obviously, the integration of all the contributions $df(v)$ from $v = 0$ to ∞ gives 1, so that

$$(A.4) \quad 1 = \int_0^{\infty} df(v) = \gamma 4\pi c(0) \int_0^{\infty} \exp\left(-\frac{m v^2}{2k_B T}\right) v^2 dv = \gamma c(0) \left[\frac{2\pi k_B T}{m} \right]^{3/2},$$

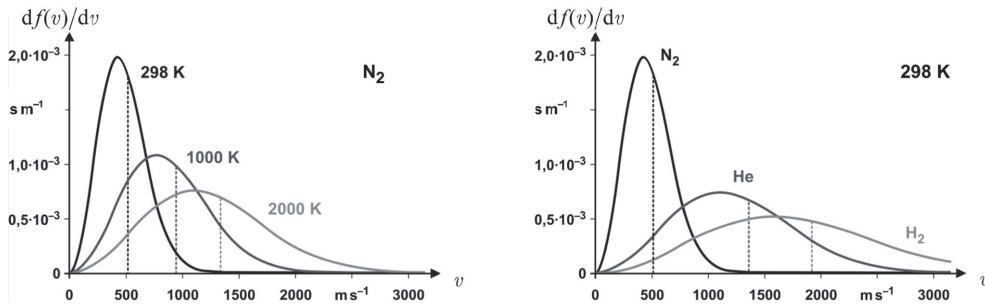


Fig. 6. – Usual illustration to the Maxwell-Boltzmann distribution of the *speed* of the gas molecules.

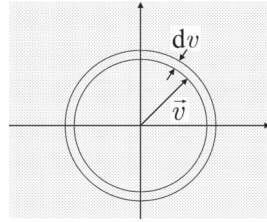


Fig. 7. – Spherical shell in the velocity space (2-dimensional representation).

while for the last equality we used the well-known result

$$(A.5) \quad \int_0^{\infty} x^2 \exp(-ax^2) dx = \frac{\sqrt{\pi}}{4} a^{-3/2}.$$

After getting $\gamma c(0)$ as

$$(A.6) \quad \gamma c(0) = \left[\frac{m}{2\pi k_B T} \right]^{3/2},$$

we then find the relation (A.1) we are looking for.

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