Maxwell–Boltzmann statistics

In statistical mechanics, **Maxwell–Boltzmann statistics** describes the statistical distribution of material particles over various energy states in thermal equilibrium, when the temperature is high enough and density is low enough to render quantum effects negligible.

The expected number of particles with energy ε_i for Maxwell–Boltzmann statistics is N_i where:

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/kT}} = \frac{N}{Z}\, g_i e^{-\varepsilon_i/kT}$$

where:

- N_i is the number of particles in state i
- ε_i is the energy of the i-th state
- g_i is the degeneracy of energy level i,
  the number of particle's states (excluding the "free particle" state) with energy ε_i
- μ is the chemical potential
- k is Boltzmann's constant
- T is absolute temperature
- N is the total number of particles

$$N = \sum_i N_i$$

- Z is the partition function

$$Z = \sum_i g_i e^{-\varepsilon_i/kT}$$

- $e^{(\dots)}$ is the exponential function

Distribution of particle speed for 10^6 oxygen particles at -100, 20 and 600 degrees Celsius. Speed distribution can be derived from Maxwell–Boltzmann distribution.

Equivalently, the distribution is sometimes expressed as

$$N_i = \frac{1}{e^{(\varepsilon_i - \mu)/kT}} = \frac{N}{Z}\, e^{-\varepsilon_i/kT}$$

where the index i now specifies a particular state rather than the set of all states with energy ε_i, and

$$Z = \sum_i e^{-\varepsilon_i/kT}$$

Fermi–Dirac and Bose–Einstein statistics apply when quantum effects are important and the particles are "indistinguishable". Quantum effects appear if the concentration of particles $(N/V) \geq n_q$. Here n_q is the quantum concentration, for which the interparticle distance is equal to the thermal de Broglie wavelength, so that the wavefunctions of the particles are touching but not overlapping. Fermi–Dirac statistics apply to fermions (particles that obey the Pauli exclusion principle), and Bose–Einstein statistics apply to bosons. As the quantum concentration depends on temperature; most systems at high temperatures obey the classical (Maxwell–Boltzmann) limit unless they have a very high density, as for a white dwarf. Both Fermi–Dirac and Bose–Einstein become Maxwell–Boltzmann statistics at high temperature or at low concentration.

Maxwell–Boltzmann statistics are often described as the statistics of "distinguishable" classical particles. In other words the configuration of particle A in state 1 and particle B in state 2 is different from the case where particle B is
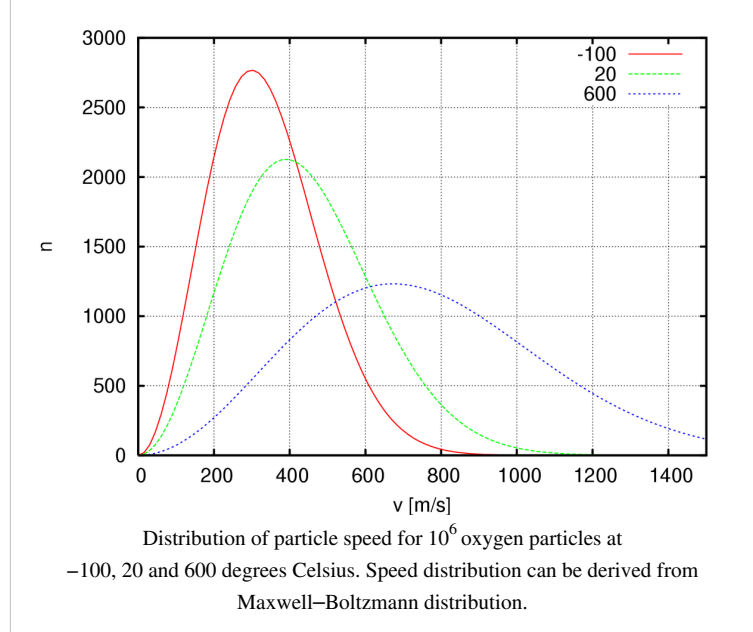
in state 1 and particle *A* is in state 2. This assumption leads to the proper (Boltzmann) distribution of particles in the energy states, but yields non-physical results for the entropy, as embodied in the Gibbs paradox. This problem is resolved if we treat all particles of a certain type (e.g., electrons, protons, etc.) as indistinguishable, and this assumption can be justified in the context of quantum mechanics. Both of these distributions approach the Maxwell−Boltzmann distribution in the limit of high temperature and low density, without the need for any ad hoc assumptions. Maxwell−Boltzmann statistics are particularly useful for studying gases. Fermi−Dirac statistics are most often used for the study of electrons in solids. As such, they form the basis of semiconductor device theory and electronics.

A derivation of the Maxwell−Boltzmann distribution

Suppose we have a container with a huge number of very small particles all with exactly the same physical characteristics (mass, charge, etc.). Let's refer to this as the *system*. We will assume that even though the particles have identical properties, they are nonetheless distinguishable. For example, we might identify each particle by continually observing their trajectories, or by placing a marking on each one, e.g., drawing a different number on each one as is done with lottery balls.

All of those tiny particles are moving inside that container in all directions with great speed. Because the particles are speeding around, they do possess some energy. The Maxwell−Boltzmann distribution is a mathematical function that speaks about how many particles in the container have a certain energy.

In general, there may be many particles with the same amount of energy ε. Let the number of particles with the same energy ε_1 be N_1, the number of particles possessing another energy ε_2 be N_2, and so forth for all the possible energies { ε_i | i=1,2,3,...}. To describe this situation, we say that N_i is the *occupation number* of the *energy level* i. If we know all the occupation numbers { N_i | i=1,2,3,...}, then we know the total energy of the system. However, because we can distinguish between *which* particles are occupying each energy level, the set of occupation numbers { N_i | i=1,2,3,...} does not completely describe the state of the system. To completely describe the state of the system, or the *microstate*, we must specify exactly which particles are in each energy level. Thus when we count the number of possible states of the system, we must count each and every microstate, and not just the possible sets of occupation numbers.

To begin with, let's ignore the degeneracy problem: assume that there is only one single way to put N_i particles into the energy level i. What follows next is a bit of combinatorial thinking which has little to do in accurately describing the reservoir of particles.

The number of different ways of performing an ordered selection of one single object from *N* objects is obviously *N*. The number of different ways of selecting two objects from *N* objects, in a particular order, is thus *N*(*N* − 1) and that of selecting *n* objects in a particular order is seen to be *N*!/(*N* − *n*)!. The number of ways of selecting 2 objects from *N* objects without regard to order is *N*(*N* − 1) divided by the number of ways 2 objects can be ordered, which is 2!. It can be seen that the number of ways of selecting *n* objects from N objects without regard to order is the binomial coefficient: *N*!/(*n*!(*N* − *n*)!). If we now have a set of boxes labelled *a, b, c, d, e, ..., k*, then the number of ways of selecting N_a objects from a total of *N* objects and placing them in box *a*, then selecting N_b objects from the remaining $N - N_a$ objects and placing them in box *b*, then selecting N_c objects from the remaining $N - N_a - N_b$ objects and placing them in box *c*, and continuing until no object is left outside is

$$W = \frac{N!}{N_a!(N-N_a)!} \times \frac{(N-N_a)!}{N_b!(N-N_a-N_b)!} \times \frac{(N-N_a-N_b)!}{N_c!(N-N_a-N_b-N_c)!} \times \ldots \times \frac{(N-\ldots-N_l)!}{N_k!(N-\ldots-N_l-N_k)!} =$$

$$= \frac{N!}{N_a!N_b!N_c!\ldots N_k!(N-\ldots-N_l-N_k)!}$$

and because not even a single object is to be left outside the boxes, implies that the sum made of the terms N_a, N_b, N_c, N_d, N_e, ..., N_k must equal *N*, thus the term *(N - N_a - N_b - N_c - ... - N_l - N_k)!* in the relation above evaluates to *0!*.

(0!=1) which makes possible to write down that relation as

$$W = N! \prod_{i=a,b,c,\dots}^{k} \frac{1}{N_i!}$$

Now going back to the degeneracy problem which characterize the reservoir of particles. If the *i*-th box has a "degeneracy" of g_i, that is, it has g_i "sub-boxes", such that any way of filling the *i*-th box where the number in the sub-boxes is changed is a distinct way of filling the box, then the number of ways of filling the *i*-th box must be increased by the number of ways of distributing the N_i objects in the g_i "sub-boxes". The number of ways of placing N_i distinguishable objects in g_i "sub-boxes" is $g_i^{N_i}$. Thus the number of ways W that a total of N particles can be classified into energy levels according to their energies, while each level i having g_i distinct states such that the *i*-th level accommodates N_i particles is:

$$W = N! \prod \frac{g_i^{N_i}}{N_i!}$$

This is the form for *W* first derived by Boltzmann. Boltzmann's fundamental equation $S = k \ln W$ relates the thermodynamic entropy *S* to the number of microstates *W*, where *k* is the Boltzmann constant. It was pointed out by Gibbs however, that the above expression for *W* does not yield an extensive entropy, and is therefore faulty. This problem is known as the Gibbs paradox The problem is that the particles considered by the above equation are not indistinguishable. In other words, for two particles (*A* and *B*) in two energy sublevels the population represented by [A,B] is considered distinct from the population [B,A] while for indistinguishable particles, they are not. If we carry out the argument for indistinguishable particles, we are led to the Bose-Einstein expression for *W*:

$$W = \prod_i \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$$

Both the Maxwell-Boltzmann distribution and the Bose-Einstein distribution are only valid for temperatures well above absolute zero, implying that $g_i \gg 1$. The Maxwell-Boltzmann distribution also requires low density, implying that $g_i \gg N_i$. Under these conditions, we may use Stirling's approximation for the factorial:

$$N! \approx N^N e^{-N},$$

to write:

$$W \approx \prod_i \frac{(N_i + g_i)^{N_i + g_i}}{N_i^{N_i} g_i^{g_i}} \approx \prod_i \frac{g_i^{N_i}(1 + N_i/g_i)^{g_i}}{N_i^{N_i}}$$

Using the fact that $(1 + N_i/g_i)^{g_i} \approx e^{N_i}$ for $g_i \gg N_i$ we can again use Stirlings approximation to write:

$$W \approx \prod_i \frac{g_i^{N_i}}{N_i!}$$

This is essentially a division by *N!* of Boltzmann's original expression for *W*, and this correction is referred to as **correct Boltzmann counting**.

We wish to find the N_i for which the function W is maximized, while considering the constraint that there is a fixed number of particles $(N = \sum N_i)$ and a fixed energy $(E = \sum N_i \varepsilon_i)$ in the container. The maxima of W and $\ln(W)$ are achieved by the same values of N_i and, since it is easier to accomplish mathematically, we will maximize the latter function instead. We constrain our solution using Lagrange multipliers forming the function:

$$f(N_1, N_2, \dots, N_n) = \ln(W) + \alpha(N - \sum N_i) + \beta(E - \sum N_i \varepsilon_i)$$

$$\ln W = \ln \left[\prod_{i=1}^{n} \frac{g_i^{N_i}}{N_i!} \right] \approx \sum_{i=1}^{n} (N_i \ln g_i - N_i \ln N_i + N_i)$$

Finally

$$f(N_1, N_2, \ldots, N_n) = \alpha N + \beta E + \sum_{i=1}^{n} \left(N_i \ln g_i - N_i \ln N_i + N_i - (\alpha + \beta \varepsilon_i) N_i \right)$$

In order to maximize the expression above we apply Fermat's theorem (stationary points), according to which local extrema, if exist, must be at critical points (partial derivatives vanish):

$$\frac{\partial f}{\partial N_i} = \ln g_i - \ln N_i - (\alpha + \beta \varepsilon_i) = 0$$

By solving the equations above ($i = 1 \ldots n$) we arrive to an expression for N_i:

$$N_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i}}$$

Substituting this expression for N_i into the equation for $\ln W$ and assuming that $N \gg 1$ yields:

$$\ln W = \alpha N + \beta E$$

or, differentiating and rearranging:

$$dE = \frac{1}{\beta} d \ln W - \frac{\alpha}{\beta} dN$$

Boltzmann realized that this is just an expression of the second law of thermodynamics. Identifying *dE* as the internal energy, the second law of thermodynamics states that for variation only in entropy (*S*) and particle number (*N*):

$$dE = T\, dS + \mu\, dN$$

where T is the temperature and μ is the chemical potential. Boltzmann's famous equation $S = k \ln W$ is the realization that the entropy is proportional to $\ln W$ with the constant of proportionality being Boltzmann's constant. It follows immediately that $\beta = 1/kT$ and $\alpha = -\mu/kT$ so that the populations may now be written:

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/kT}}$$

Note that the above formula is sometimes written:

$$N_i = \frac{g_i}{e^{\varepsilon_i/kT}/z}$$

where $z = \exp(\mu/kT)$ is the absolute activity.

Alternatively, we may use the fact that

$$\sum_i N_i = N$$

to obtain the population numbers as

$$N_i = N \frac{g_i e^{-\varepsilon_i/kT}}{Z}$$

where *Z* is the partition function defined by:

$$Z = \sum_i g_i e^{-\varepsilon_i/kT}$$

Another derivation (not as fundamental)

In the above discussion, the Boltzmann distribution function was obtained via directly analysing the multiplicities of a system. Alternatively, one can make use of the canonical ensemble. In a canonical ensemble, a system is in thermal contact with a reservoir. While energy is free to flow between the system and the reservoir, the reservoir is thought to have infinitely large heat capacity as to maintain constant temperature, T, for the combined system.

In the present context, our system is assumed to have the energy levels ε_i with degeneracies g_i. As before, we would like to calculate the probability that our system has energy ε_i.

If our system is in state s_1, then there would be a corresponding number of microstates available to the reservoir. Call this number $\Omega_R(s_1)$. By assumption, the combined system (of the system we are interested in and the reservoir) is isolated, so all microstates are equally probable. Therefore, for instance, if $\Omega_R(s_1) = 2\,\Omega_R(s_2)$, we can conclude that our system is twice as likely to be in state s_1 than s_2. In general, if $P(s_i)$ is the probability that our system is in state s_i,

$$\frac{P(s_1)}{P(s_2)} = \frac{\Omega_R(s_1)}{\Omega_R(s_2)}.$$

Since the entropy of the reservoir $S_R = k \ln \Omega_R$, the above becomes

$$\frac{P(s_1)}{P(s_2)} = \frac{e^{S_R(s_1)/k}}{e^{S_R(s_2)/k}} = e^{(S_R(s_1) - S_R(s_2))/k}.$$

Next we recall the thermodynamic identity (from the first law of thermodynamics):

$$dS_R = \frac{1}{T}(dU_R + P\,dV_R - \mu\,dN_R).$$

In a canonical ensemble, there is no exchange of particles, so the dN_R term is zero. Similarly, $dV_R = 0.$ This gives

$$S_R(s_1) - S_R(s_2) = \frac{1}{T}(U_R(s_1) - U_R(s_2)) = -\frac{1}{T}(E(s_1) - E(s_2)),$$

where $U_R(s_i)$ and $E(s_i)$ denote the energies of the reservoir and the system at s_i, respectively. For the second equality we have used the conservation of energy. Substituting into the first equation relating $P(s_1)$, $P(s_2)$:

$$\frac{P(s_1)}{P(s_2)} = \frac{e^{-E(s_1)/kT}}{e^{-E(s_2)/kT}},$$

which implies, for any state *s* of the system

$$P(s) = \frac{1}{Z}e^{-E(s)/kT},$$

where *Z* is an appropriately chosen "constant" to make total probability 1. (*Z* is constant provided that the temperature *T* is invariant.) It is obvious that

$$Z = \sum_s e^{-E(s)/kT},$$

where the index *s* runs through all microstates of the system. *Z* is sometimes called the Boltzmann **sum over states** (or "Zustandsumme" in the original German). If we index the summation via the energy eigenvalues instead of all possible states, degeneracy must be taken into account. The probability of our system having energy ε_i is simply the sum of the probabilities of all corresponding microstates:

$$P(\varepsilon_i) = \frac{1}{Z}g_i e^{-\varepsilon_i/kT}$$

where, with obvious modification,

$$Z = \sum_j g_j e^{-\varepsilon_j/kT},$$

this is the same result as before.

Comments

- Notice that in this formulation, the initial assumption "... *suppose the system has total* N *particles...*" is dispensed with. Indeed, the number of particles possessed by the system plays no role in arriving at the distribution. Rather, how many particles would occupy states with energy ε_i follows as an easy consequence.

- What has been presented above is essentially a derivation of the canonical partition function. As one can tell by comparing the definitions, the Boltzmann sum over states is really no different from the canonical partition function.

- Exactly the same approach can be used to derive Fermi–Dirac and Bose–Einstein statistics. However, there one would replace the canonical ensemble with the grand canonical ensemble, since there is exchange of particles between the system and the reservoir. Also, the system one considers in those cases is a single particle *state*, not a particle. (In the above discussion, we could have assumed our system to be a single atom.)

Limits of applicability

The Bose–Einstein and Fermi–Dirac distributions may be written:

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/kT} \mp 1}.$$

Assuming the minimum value of ε_i is small, it can be seen that the condition under which the Maxwell–Boltzmann distribution is valid is when

$$e^{-\mu/kT} \gg 1.$$

For an ideal gas, we can calculate the chemical potential using the development in the Sackur–Tetrode article to show that:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} = -kT \ln\left(\frac{V}{N\Lambda^3}\right)$$

where E is the total internal energy, S is the entropy, V is the volume, and Λ is the thermal de Broglie wavelength. The condition for the applicability of the Maxwell–Boltzmann distribution for an ideal gas is again shown to be

$$\frac{V}{N\Lambda^3} \gg 1.$$

References

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