

Chapter 6 - Boltzmann statistics

6.1 The Boltzmann factor

The Boltzmann factor is a formula the needs for the system to be in thermal eq with the reservoir that it touches. Further the ratio between two states S_1 and S_2 is

$$\frac{P(S_2)}{P(S_1)} = \frac{\Omega_R(S_2)}{\Omega_R(S_1)} = \frac{e^{-E(S_2)/kT}}{e^{-E(S_1)/kT}}$$

From this we get the Boltzmann factor

$$\text{Boltzmann factor} = e^{-E(s)/kT}$$

However to make this into a probability distribution we need to normalise it, so we use the partition function Z which is the sum over all states. This gives

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

where $Z = \sum_i e^{-E(s)/kT}$.

$P(s)$ is also often called the canonical distribution.

The partition function

The quantity Z is called the partition function, it is constant so it does not depend on the state, however it does depend on T ! For states with energy far larger than kT the states become very improbable, for states with energy smaller than kT the states become more probable.

At low T , $Z \approx 1$ since all excited states have very small boltzmann factors, at high T , Z will be much larger. Moreover an interesting fact is that if we shift all energies by a constant E_0 then so does the partition function so it gets cancelled in numerator and denominator.

Thermal excitations of atoms

More consiselly, the ratio of probabilities which we looked at earlier is the ratio of Boltzmann factors

$$\frac{P(S_2)}{P(S_1)} = \frac{e^{-E_2/kt}}{e^{-E_1/kt}} = e^{-(E_2-E_1)/kT}$$

6.2 Average values

Previously we have learned that the probability of the system in thermal eq with a reservoir at temp T is

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

where $\beta = 1/kT$. The exponential factor is called the boltzmann factor, while Z is the partition function

$$Z = \sum_i e^{-\beta E(s)}$$

If we have a system which can be described by the boltzmann factor and its partition function then we can calculate an average value for any value X with the formula

$$\langle X \rangle = \sum_i X(s)P(s) = \frac{1}{Z} \sum_i X(s)e^{-\beta E(s)}$$

And a nice feature of average values is that they are additive, so for example, the average total energies of two objects A and B is just $\langle E_A \rangle + \langle E_B \rangle$, or if you have a system of N identical particles that are also independent you only need to calculate on and multiply with N. $U = N\langle E \rangle$.

Paramagnets

For a paramagnet there are two possible states, up with energy $E = -\mu B$ and down with energy $E = \mu B$. The partition function then becomes

$$Z = \sum_s e^{-\beta E(s)} = e^{\beta \mu B} + e^{-\beta \mu B} = 2 \cosh(\beta \mu B)$$

$$P_{\uparrow} = \frac{e^{\beta \mu B}}{2 \cosh(\beta \mu B)} \quad , \quad P_{\downarrow} = \frac{e^{-\beta \mu B}}{2 \cosh(\beta \mu B)}$$

The average energies then becomes

$$\langle E \rangle = \sum_s E(s)P(s) = -\mu B P_{\uparrow} + \mu B P_{\downarrow} = \mu B \tanh(\beta \mu B)$$

However there is another way of calculating the average energies, we differentiate Z with respect to β and multiplying with $-\frac{1}{Z}$ we get

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

Moreover we can calculate the average value of the dipole's magnetic moment along the direction of B,

$$\langle \mu_z \rangle = \sum_s \mu_z(s)P(s) = \mu \tanh(\beta \mu B)$$

Thus the total magnetisation is

$$M = N\langle \mu_z \rangle = N\mu \tanh(\beta \mu B)$$

Relations of diatomic molecules

Lets apply Boltzmann statistics on the rotational motions of a diatomic molecule in isolation and in a low density gas. Rotational energies are quantized by $E(j) = j(j+1)\epsilon$, where $j \in 0, 1, 2, 3, \dots$ and ϵ is a constant inversely proportional to the molecules momentum of inertia. The partition function becomes a sum over j

$$Z_{rot} = \sum_{j=0}^{\infty} (2j+1)e^{-E(j)/kT} = \sum_{j=0}^{\infty} (2j+1)e^{-j(j+1)\epsilon/kT}$$

where we have a $2j+1$ level of degeneracy per j. We further approximate the sum to an integral so

$$Z_{rot} \approx \int_0^{\infty} (2j+1)e^{-j(j+1)\epsilon/kT} dj = \frac{kT}{\epsilon} \quad (\text{when } kT \gg \epsilon)$$

with this we can calculate the average energy with

$$\langle E_{rot} \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -(\beta \epsilon) \frac{\partial}{\partial \beta} \frac{1}{\beta \epsilon} = \frac{1}{\beta} = kT$$

However we assumed that the two atoms in the diatomic molecule were different. If they are similar we loose half of our states since spinning the states by 180° does not change the molecule. This means that for example, the molecule O_2 the partition function becomes

$$Z_{rot} \approx \frac{kT}{2\epsilon}, \quad (\text{identical atoms, } kT \gg \epsilon)$$

6.3 The Equipartition Theorem

The equipartition theorem does not apply to all systems. It applies only to systems whose energy is in the form of quadratic "degrees of freedom", of the form

$$E(q) = cq^2$$

where c is a constant coefficient and q is any coordinate or momentum variable, like x or L_x . Now assuming our system has only one degree of freedom and assuming equilibrium with a reservoir at temperature T we calculate the average energy, $\langle E \rangle$. To count the number of states, we assume that they are separated by a constant interval Δq . As long as this interval is extremely small, we expect it to cancel out. The partition function for the system becomes

$$Z = \sum_q e^{-\beta E(q)} = \sum_q e^{-\beta cq^2}.$$

To evaluate the sum, we utilise the fact that the energy intervals are tiny compared to the energy and multiply with $\frac{\Delta q}{\Delta q}$.

$$Z = \frac{1}{\Delta q} \sum_q e^{-\beta cq^2} \Delta q$$

$$Z = \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta cq^2} dq$$

Before evaluating we change the integral variables so that we get

$$Z = \frac{1}{\Delta q} \frac{1}{\sqrt{\beta c}} \int_{-\infty}^{\infty} e^{-x^2} dx$$

This is a Gaussian integral, and the result becomes

$$Z = \frac{1}{Z} \sqrt{\frac{\pi}{\beta c}} = C \beta^{-1/2}$$

where $C = \sqrt{\pi/c}/\Delta q$.

Now that we have the partition function calculating the average energy becomes trivial

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{1}{c\beta^{-1/2}} \frac{\partial}{\partial \beta} C \beta^{-1/2} = \frac{1}{2} kT$$

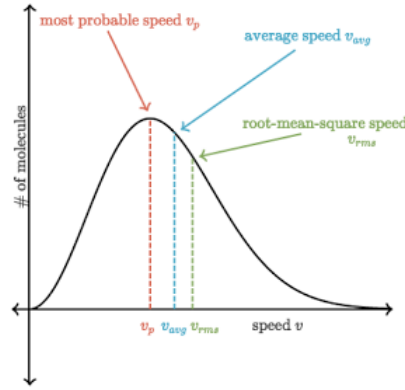
And this is the equipartition theorem. The most important thing about this proof is that it does not carry over to quantum mechanical systems. This is because in general, the equipartition theorem applies only when the spacing between energy levels is much less than kT .

6.4 The Maxwell Speed Distribution

This section inspects how the Boltzmann factors can describe the motion of molecules in an ideal gas. We know from the equipartition theorem that the RMS speed of the molecules is given by the formula

$$V_{rms} = \sqrt{\frac{3kT}{m}}$$

However this is just an average, what we wish to know is what percentage of the molecules that move with a certain velocity. Technically, the probability that a molecule is moving at a certain speed is approximately zero, this is because the speed at which the particles can move is continuous, so each speed has a minuscule probability approximately close to zero. However some speeds are less probable than others, so we can represent the relative probability of various speeds.



If the probability is normalised (or the graph per say) we can calculate the probability that a particle is between velocity 1 and velocity 2 by integrating the graph/distribution with the velocities as limits.

$$\text{Probability}(v_1 \dots v_2) = \int_{v_1}^{v_2} D(v) dv$$

where $D(v)$ is the height of the graph. If the integral between v_1 and v_2 is infinitesimal, then $D(v)$ does not change that much so it can be written as

$$\text{Probability}(v_1 \dots v_2) = D(v) dv$$

The function $D(v)$ is actually a distribution function, so it has no actual meaningful value at any point, instead $D(v)$ is a function whose purpose in life is to be integrated. $D(v)$ does not actually have the right units for a probability distribution (which are none) it actually has the units $(m/s)^{-1}$.

Another important fact is that the space we integrate over is in 3D, which implies that for a given speed there are multiple velocity vectors corresponding to it. $D(v)$ can even be written as

$$D(v) \propto \left(\frac{\text{probability of a molecule}}{\text{having velocity } \vec{v}} \right) \times \left(\frac{\text{number of vectors } \vec{v}}{\text{corresponding to speed } v} \right)$$

Where we for now have omitted the constant of proportionality. The first factor turns out to be the Boltzmann factor, for each state s the probability to be in it is $e^{-E(s)/kT}$. And in this case the energy is only kinetic, $\frac{1}{2}mv^2$ where $v = |\vec{v}|$. So

$$\left(\frac{\text{probability of a molecule}}{\text{having velocity } \vec{v}} \right) \propto e^{-mv^2/2kT}$$

This simplification is based on the ideal gas, so any variable besides velocity, like internal motion has been neglected. This equation says that the most probable state is one where the velocity is zero, and given what we have already stated about the Boltzmann distribution this is not surprising at all. Low-energy states are more probable than high energy ones. However the most likely velocity vector does not correspond to the most likely speed, because for some speeds there are more distinct velocity vectors than others.

When in 3D the set of velocity vectors corresponding to any given velocity lives on a surface with radius v . The larger the velocity the bigger the sphere and with that comes more possible velocity vectors. We then assume that the second term is a sphere in velocity space with the radius v .

$$\left(\frac{\text{number of vectors } \vec{v}}{\text{corresponding to speed } v} \right) \propto 4\pi v^2$$

This is the degeneracy factor and we put it with the other term we get

$$D(v) = C \cdot 4\pi v^2 e^{-mv^2/2kT}$$

Where C is the constant of proportionality we omitted earlier. To evaluate it we assume that the integral over the probability for all velocities must be equal to 1

$$1 = 4\pi C \int_0^\infty v^2 e^{-mv^2/2kT} dv$$

And from this integral we find that $C = (m/2\pi kT)^{3/2}$ and this gives

$$D(v) = (m/2\pi kT)^{3/2} 4\pi v^2 e^{-mv^2/2kT}$$

Where this result is called the Maxwell distribution and it holds for speeds of molecules in an ideal gas. It involves the Boltzmann factor as well as the geometrical factor of the surface area of the sphere in velocity space. If we wish to evaluate the mean velocity we simply evaluate

$$\langle v \rangle = \sum_{\text{all } v} v D(v) dv$$

where we assume that all velocities are separated by a value dv . Transforming it into an integral and evaluating it we get

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$$

An example of how to calculate the most probable speed of nitrogen can be found on page 245.

6.5 Partition Function and Free Energy

For an isolated system with fixed energy U , the most fundamental statistical quantity is the multiplicity, and the number of available microstates. We know that the entropy is the logarithm of the multiplicity and that it tends to increase. For a system at equilibrium with a reservoir at temperature T the quantity most analogous to Ω is the partition function $Z(T)$. Much like the multiplicity the partition function is more or less equal to the number of microstates available to the system however here with fixed temperature, not energy.

The Helmholtz free energy F tends to decrease under such conditions so the quantity that tends to increase should be $-F$, dimensionless this becomes $-F/kT$. Taking a massive fuckings intuitive leap(which is very trivial) we find that

$$F = -kT \ln(Z) \quad \text{or} \quad Z = e^{-F/kT}$$

Checking that the formula is true we recall that $F = U - TS$ and that $-S = \left(\frac{\partial F}{\partial T}\right)_{V,N}$.

Solving the first equation and applying it to the other we get

$$\left(\frac{\partial F}{\partial T}\right) = \frac{F - U}{T}$$

We can check if this is also true if we take the derivative of $-kT \ln(Z)$ with regards to T which turns out to be

$$\frac{\partial}{\partial T}(-k \ln(Z)) = \frac{F}{T} - \frac{U}{T}$$

where we see that these two terms are the same (sorry if this is messy, the book does this too).

What is important to understand is that with the equation $F = -kT \ln(Z)$ we can calculate the entropy, pressure and the chemical potential in the following ways.

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

In this way we can actually compute all the thermodynamic properties of a system, once we know its partition function.

6.6 Partition Function for Composite Systems

Before trying to figure out the partition function for an ideal gas, it is useful to ask in general how the partition function of a system with several particles is related to the partition function for each individual particle. Consider a system with 2 independent non-interacting particles 1 and 2. The partition function becomes

$$Z_{total} = \sum_s e^{-\beta(E_1(s) + E_2(s))} = \sum_s e^{-\beta E_1(s)} e^{-\beta E_2(s)}$$

If the particles are distinguishable then the set of states for the composite system is equal to the sum over all states s_1 and s_2 . We get

$$Z_{total} = \sum_{s_1} \sum_{s_2} e^{-\beta E_1(s_1)} e^{-\beta E_2(s_2)}$$

where s_i represents the state of particle i. This can further be reduced to the multiplication of the partition function for state particle number one and particle number 2 (since the sum over s_2 does not affect the exponential with s_1). This gives

$$Z_{total} = Z_1 Z_2$$

So we see a clear pattern here, if the particles are distinguishable particles we simply multiply all the respective partition functions.

$$Z_{total} = Z_1 Z_2 Z_3 \dots Z_N \quad (\text{noninteracting, distinguishable particles})$$

However if they are indistinguishable we can not tell the particles apart, this means that we can not know if one of the particles is in one state and the other in another. All we know is that two particles exist, and in what state they exist. This

means that we have to add a term which takes into account the over counting when multiplying. For N indistinguishable particles we then get that the total partition function becomes

$$Z_{total} = \frac{1}{N!} Z_1^N \quad (\text{noninteracting, indistinguishable particles})$$

When we deal with multi particle systems, one point of terminology can be rather confusing. It is important that we separate the "state" of an individual particle from the "state" of the entire system, so remember to always be certain of what state we refer to.

6.7 Ideal Gas Revised

So now, armed with the knowledge of how to calculate the partition function for an ideal gas we can calculate the thermal quantities of it too! An ideal gas as stated before, is a gas where we can assume that the particles are so far apart that we can neglect any energy due to the force between them. If we have an ideal gas of N particles the partition function becomes

$$Z = \frac{1}{N!} Z_1^N$$

where Z_1 is the partition function for one individual molecule (but since all molecules are the same it is essentially the partition function of each individual one). Moreover to calculate the partition function we need all the possible microstates of a single molecule. Each Boltzmann factor has the form

$$e^{-E(s)/kT} = e^{-E_{tr}(s)/kT} e^{-E_{int}(s)/kT}$$

where E_{tr} is the molecule's translational kinetic energy and E_{int} is its internal energy (rotational, etc), for the state s . This can further be simplified to

$$Z_1 = Z_{tr} Z_{int},$$

where

$$Z_{tr} = \sum_{\text{translational states}} e^{-E_{tr}/kT} \quad \text{and} \quad Z_{int} = \sum_{\text{internal states}} e^{-E_{int}/kT}$$

Now to compute Z_{tr} , we need to add up the Boltzmann factors for all possible translational states of a molecule. There are multiple ways of doing this, however we will do it by counting all the independent definite-energy wavefunctions. We start with the case where the molecules are confined to 1D box, and later look at it in 3D.

Given that the molecule is confined to a box its wavefunction must go to zero at each end, therefore the allowed standing-wave patterns are limited to wavelengths of

$$\lambda_n = \frac{2L}{n}, \quad n = 1, 2, \dots$$

Where L is the length of the box and n is the number of bumps. Each of the standing waves can be thought of as a superposition of left and right moving travelling waves with equal and opposite momenta. The magnitude of the momenta is given by the de Broglie relation $p = h/\lambda$. This gives

$$p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}$$

And the allowed energies are then

$$E_n = \frac{p_n^2}{2m} = \frac{h^2 n^2}{8mL^2}$$

now armed with the energies we can write down the translational partition wavefunction in one dimension

$$Z_{1d} = \sum_n e^{-E_n/kT} = \sum_n e^{-h^2 n^2 / 8mL^2 kT}$$

now unless L and/or T is extremely small the energy levels are so close that it can be thought of as an integral. Once evaluated we find that

$$Z_{1d} = \frac{L}{\ell_Q}$$

where $\ell_Q = \frac{h}{\sqrt{2\pi mkT}}$ and is called the quantum length. Aside from the factor of π , it is the de Broglie wavelength of a particle of mass m whose kinetic energy is kT . The ratio L/ℓ_Q is quite large for any realistic box, which points to that many translational states are available to the molecule under such conditions. For molecules existing in 3D we have that

$$E_{tr} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

We take the same integral with three independent factors in three dimensions and this gives

$$Z_{tr} = \frac{L_x}{\ell_Q} \frac{L_y}{\ell_Q} \frac{L_z}{\ell_Q} = \frac{V}{v_Q}$$

where V is the volume of the box and v_Q is the quantum volume $v_Q = \ell_Q^3 = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3$.

This then gives us the single particle partition function

$$Z_1 = \frac{V}{v_Q} Z_{int}$$

where Z_{int} is the sum over all relevant internal states. The partition function for the gas of N molecules is

$$Z = \frac{1}{N!} \left(\frac{V Z_{int}}{v_Q} \right)^N$$

and its logarithm is $\ln(Z) = N[\ln(V) + \ln(Z_{int}) - \ln(N) - \ln(v_Q) + 1]$.

Predictions

Now that we have the actual this partition function we can compute all the thermal properties of an ideal gas. Starting with the total average energy we have

$$U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln(Z)$$

taking the derivative with regards to β we get

$$U = N \langle E_{int} \rangle + N \cdot \frac{3}{2} \frac{1}{\beta} = U_{int} + \frac{3}{2} N kT.$$

where $\langle E_{int} \rangle$ is the average internal energy of a molecule. The average translational term is also hidden in this equation, as we know from the equipartition theorem it is $3kT/2$. Taking another derivative grants us the heat capacity C_V

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial U_{int}}{\partial T} + \frac{3}{2}Nk$$

For a diatomic gas, the internal contributions to the heat capacity comes from rotation and vibration. Each of these contributions adds approximately Nk to the heat capacity as sufficiently high temperatures, yet goes to zero for low temperatures. The translational contribution could also freeze out in theory, but only in temperatures where ℓ_Q is in orders of L , such that the sum replacement as an integral becomes invalid.

We compute the remaining thermal properties, P , S and μ with Helmholtz free energy.

$$F = -NkT[\ln(V) - \ln(N) - \ln(v_Q) + 1] + F_{int}$$

where F_{int} is the internal contribution to F , being $-NkT \ln(Z_{int})$. From this we get that

$$P = -\left(\frac{\partial F}{\partial V}\right) = \frac{NkT}{V} \quad , \quad S = -\left(\frac{\partial F}{\partial T}\right) = Nk \left[\ln\left(\frac{V}{Nv_Q}\right) + \frac{5}{2} \right] - \frac{\partial F_{int}}{\partial T}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right) = -kT \ln\left(\frac{VZ_{int}}{Nv_Q}\right)$$

And as we observe if we neglect the internal contributions these terms reduce to our earlier results from the mono-atomic gas!