

Elements of Statistical Physics

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- In the study of thermodynamics, various relations between the properties of gases and temperature were obtained. In particular, the first and the second laws of thermodynamics were derived.
- These laws were first considered **empirical** laws, that is they are found to be true in all the cases that were studied.
- Can they be derived from a more fundamental point of view?
- Maxwell, Boltzmann and Gibbs derived thermodynamical properties of gases from a statistical point of view, assuming that the gas is made up of Avagadro's number of tiny molecules.

Statistical Physics

- Let us consider a set of six identical atoms. All of them have the same physical properties, in terms of mass, size etc.
- But we assume that the particles are **distinguishable**. That is, I can tell particle-1 from particle-2 from particle-3 etc somehow.
- Let us assume that there exist distinct energy levels with energies 0 , E , $2E$, ...
- The question we ask is: How to arrange these six particles in various energy states so that the total energy of the six particles is $8E$? How many different ways are there?
- For example we can put one particle in state $8E$ and all others in state 0 . Since we assumed that the particles are distinguishable, there are **six** ways of doing this.
- Suppose we put one particle in state $3E$, two in state $2E$, one in state E and two in state 0 . How many ways are there of doing this?

- If each particle is to be in a distinct state, then there are $6!$ ways of arranging the distinguishable particles (the number of permutations of six objects).
- But here two particles are in the same state $2E$ and two other particles are in the same state 0 . Permuting the two particles in the state $2E$, leads to the same state. Similarly permuting the two particles in the state 0 also leads to the same state.
- Hence the number of distinct states of six distinguishable particles, with one in $3E$, two in $2E$, one in E and two in 0 , is given by

$$\frac{6!}{(1!)(2!)(1!)(2!)} = 180.$$

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- There are 20 different ways of arranging six particles among the states 0, E, 2E, ... so that the total energy will be 8E. The number of distinct states in each case will be

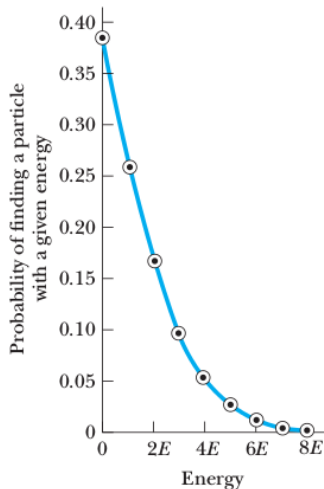
$$\frac{6!}{(n_0!)(n_1!)(n_2!)(n_3!)(n_4!)(n_5!)(n_6!)(n_7!)(n_8!)},$$

where n_0 is the number of particles in state 0, n_1 is the number of particles in state E, etc. Note $0! = 1$.

- For each of the 20 different arrangements of the particles, we can work out the number distinct **microstates**.
- Each of these microstates has six particles with total energy 8E. An important assumption Boltzmann made is that **each microstate occurs with the same probability**.
- With this assumption, we can ask the question: What is the probability of finding a particle in state nE ? It is equal to the number of microstates with a particle in state nE multiplied by the number of particles in state nE divided by the total number of microstates.

Statistical Physics

Thus we get $P(0)$, $P(E)$, $P(2E)$, etc. We plot $P(E)$ vs E . We find that the plot looks very similar to a decreasing exponential.



Maxwell-Boltzmann Distribution

- The above example can be extended to a system of very large number (Avagadro number) of particles.
- We say that the probability of finding a particle with energy E_i at temperature is given by

$$f_{\text{MB}} = A \exp(-E_i/kT),$$

where A is a normalization constant and k is the Boltzmann's constant.

- When we are dealing with Avagadro number of particles, the various different energy states are very close to each other. We treat the number of such states as a continuous function of energy E .
- We count the number of states per unit volume with energies between E and $E + dE$, label them as $g(E)dE$. The function $g(E)$ is called the **density of states**. Then the number of particles per unit volume with energies between E and $E + dE$ is

$$n(E)dE = g(E)f_{\text{MB}}(E)dE.$$

Maxwell-Boltzmann Distribution for Gas Molecules

- Let us apply this distribution law to an Avagadro number of gas molecules in equilibrium at temperature T .
- To keep the discussion simple, we assume that the gas consists of monatomic molecules and the only energy they have is the translational kinetic energy $p^2/2m$, where m is the mass of the molecule and p is its momentum.
- The momenta vary continuously from 0 to ∞ , so the energy distribution of the molecules may also assumed to be continuous.
- Before we apply Maxwell-Boltzmann distribution, we need to calculate the density of states $g(E)$ or equivalently the density of states with momentum p .

Maxwell-Boltzmann Distribution for Gas Molecules

- Consider a gas molecule with momentum $\vec{p} = p_x\hat{i} + p_y\hat{j} + p_z\hat{k}$. The magnitude of momentum is given by $p = \sqrt{p_x^2 + p_y^2 + p_z^2}$.
- Consider a three dimensional space whose axes are p_x , p_y and p_z . We **assume** there are a constant number of microstates per unit volume in this space.
- This assumption can be justified by the following argument. Consider that the molecules are in an impenetrable cubical box of size L .
- For such a box, the momenta are quantized as $p_x = n_x\pi\hbar/L$, $p_y = n_y\pi\hbar/L$ and $p_z = n_z\pi\hbar/L$. So a momentum is specified by a set of three integers n_x , n_y and n_z . And the density of points in three dimensional space with integer coordinates is constant.
- Since \hbar is extremely small, we can treat these discrete points as being nearly continuous.

Maxwell-Boltzmann Distribution for Gas Molecules

- Within this space defined by p_x , p_y and p_z , consider a spherical shell with inner radius p and the outer radius p' .
- The volume of the spherical shell is $(4\pi/3)(p'^3 - p^3)$.
- For $p' = p + dp$, this volume is $4\pi p^2 dp$, where we have neglected terms of order $(dp)^2$ and $(dp)^3$.
- Hence the number of microstates with magnitude of momentum between p and $p + dp$ is given by

$$f(p)dp = C4\pi p^2 dp,$$

where C is some constant.

- Because $E = p^2/2m$, each given p (defined to be positive) corresponds to a single energy E . Therefore the number of energy states $g(E)dE$ with energies between E and $E + dE$ is the same as the number of states with momenta between p and $p + dp$.

$$g(E)dE = f(p)dp = C4\pi p^2 dp.$$

Maxwell-Boltzmann Distribution for Gas Molecules

- Thus the number of molecules per unit volume with energies between E and $E + dE$ is the product of the number of energy states between E and $E + dE$ and the probability of the molecule having energy E ,

$$n(E)dE = A4\pi p^2 \exp(-p^2/2mkT)dp,$$

where the constant C is absorbed into the normalization constant A .

- The LHS is written in terms of E and the RHS is written in terms of p . This need not worry us because there is a one-to-one relation between E and p in the form $E = p^2/2m$ and $dE = pdp/m$.
- We fix the constant A by the condition

$$\int_0^\infty n(E)dE = \frac{N}{V},$$

where N is the total number of molecules and V is the volume of the box holding the molecules.

- This condition becomes

$$\frac{N}{V} = A4\pi \int_0^\infty p^2 \exp(-p^2/2mkT)dp.$$

Maxwell-Boltzmann Distribution for Gas Molecules

- This integral is called a Gaussian integral (because the integrand contains a Gaussian function) and there is a standard method to do it. Here we need

$$\int_0^{\infty} x^2 \exp(-\alpha x^2) dx = \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}}.$$

- Using the above result, we get

$$\frac{N}{V} = \frac{4\pi A}{2^2(1/2mkT)} \sqrt{\pi 2mkT} = A(2\pi mkT)^{3/2},$$

leading to

$$A = \frac{N}{V} \left(\frac{1}{2\pi mkT} \right)^{3/2}.$$

- We obtain the Maxwell-Boltzmann distribution to be

$$n(p)dp = \frac{4\pi N}{V} \left(\frac{1}{2\pi mkT} \right)^{3/2} p^2 \exp(-p^2/2mkT) dp.$$

Maxwell-Boltzmann Distribution for Gas Molecules

- The above distribution vanishes as $p \rightarrow 0$ and vanishes as $p \rightarrow \infty$. By setting $dn(p)/dp = 0$, one can calculate the most probable value of the momentum and hence the most probable speed v_{mp} .

- The average momentum is given by

$$\bar{p} = \frac{\int_0^\infty pn(p)dp}{N/V} = \sqrt{\frac{8mkT}{\pi}}.$$

- That is average speed of the molecules is proportional to the square root of the temperature and inversely proportional to the square root of the molecular mass.
- The root mean square of the momentum is given by the average value of $p^2 = 3mkT$.
- Thus the rms speed v_{rms} is equal to

$$v_{\text{rms}} = \sqrt{\frac{\bar{p}^2}{m^2}} = \sqrt{\frac{3kT}{m}}.$$

- Note that $v_{\text{mp}} < \bar{v} < v_{\text{rms}}$.

Consequences of Maxwell-Boltzmann Distribution

- The average kinetic energy of the molecules is

$$\bar{K} = \frac{\bar{p}^2}{2m} = \frac{3}{2}kT,$$

which is also the result we get from the theorem of equipartition of energy.

- For a classical molecule in equilibrium at temperature T , each independent mode of motion has an average energy of $(1/2)kT$. Here the three translational degrees of freedom give rise to a total energy $(3/2)kT$.
- We can calculate the standard deviation in the spread of momenta of the Maxwell-Boltzmann distribution as

$$\sigma_p = \sqrt{\overline{p^2} - \bar{p}^2} = \sqrt{3 - \frac{8}{\pi}} \sqrt{mkT}.$$

Conditions for which Maxwell-Boltzmann Distribution holds

- We have made an important assumption in deriving the Maxwell-Boltzmann distribution. We assumed that the particles (or the molecules) are **distinguishable**. That is, we have the ability to tell apart one molecule from another.
- But all the molecules are **identical**. So how can we tell them apart?
- Suppose the distance between the molecules is reasonably large (much larger than the quantum mechanical uncertainty in the position of the molecules).
- Then we can, in principle, label the molecule at x_1 to be 1, molecule at x_2 to be 2 and so on at $t = 0$. Then we assume that as the molecules 1, 2 etc move about, we can keep track of them.
- Impossible to do it practically for an Avagadro number of molecules but, **in principle**, it is possible.
- So the condition for the validity of Maxwell-Boltzmann distribution is

$$\Delta x \ll d$$

Conditions for which Maxwell-Boltzmann Distribution holds

- To estimate Δx , we calculate Δp_x .

$$\Delta p_x = \sqrt{\bar{p}_x^2 - \bar{p}_x^2}.$$

- For gas molecules, motion in any of the three directions is equivalent hence $\bar{p}_x^2 = \bar{p}_y^2 = \bar{p}_z^2$. Since $\bar{p}^2 = \bar{p}_x^2 + \bar{p}_y^2 + \bar{p}_z^2$, we get $\bar{p}_x^2 = \bar{p}^2/3$.
- In a large box of molecules, there are as many molecules moving in the positive x-direction as in the negative x-direction. Therefore the average value of p_x is zero. Similarly $\bar{p}_y = 0 = \bar{p}_z$.
- Note that the average value of the momentum vector $\vec{p} = 0$ but the average value of the magnitude of the momentum $\bar{p} \neq 0$ as we calculated before.
- We get $\Delta p_x = \sqrt{mkT}$, hence

$$\Delta x \sim \frac{\hbar}{\Delta p_x} = \frac{\hbar}{\sqrt{mkT}}.$$

Conditions for which Maxwell-Boltzmann Distribution holds

- The average volume occupied by a molecule is V/N and hence the average distance between two molecules is $(V/N)^{1/3}$.
- The condition for the validity of Maxwell-Boltzmann distribution becomes

$$\frac{\hbar}{\sqrt{mkT}} \ll \left(\frac{V}{N}\right)^{1/3} \quad \text{or} \quad \left(\frac{N}{V}\right) \frac{\hbar^3}{(mkT)^{3/2}} \ll 1. \quad (1)$$

- Maxwell-Boltzmann distribution holds for
 - 1 low particle density
 - 2 high temperature
 - 3 high particle mass
- If the above inequality does not hold, the assumption of distinguishability does not hold and we can not use Maxwell-Boltzmann distribution.