

Statistical and Low Temperature Physics (PHYS393)

## **2. Ideal Gas**

Kai Hock

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University of Liverpool

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## Density of States

## A particle in a 3-D box

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In an ideal gas, we assume that there is little interaction between atoms. We shall learn how to calculate the total energy and other properties, and apply this to electrons, phonons, photons, liquid helium, etc.

From the kinetic theory of gases, we know that the average energy of each atom in an ideal gas is

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T.$$

This means that the total energy is

$$U = \frac{3}{2}Nk_B T$$

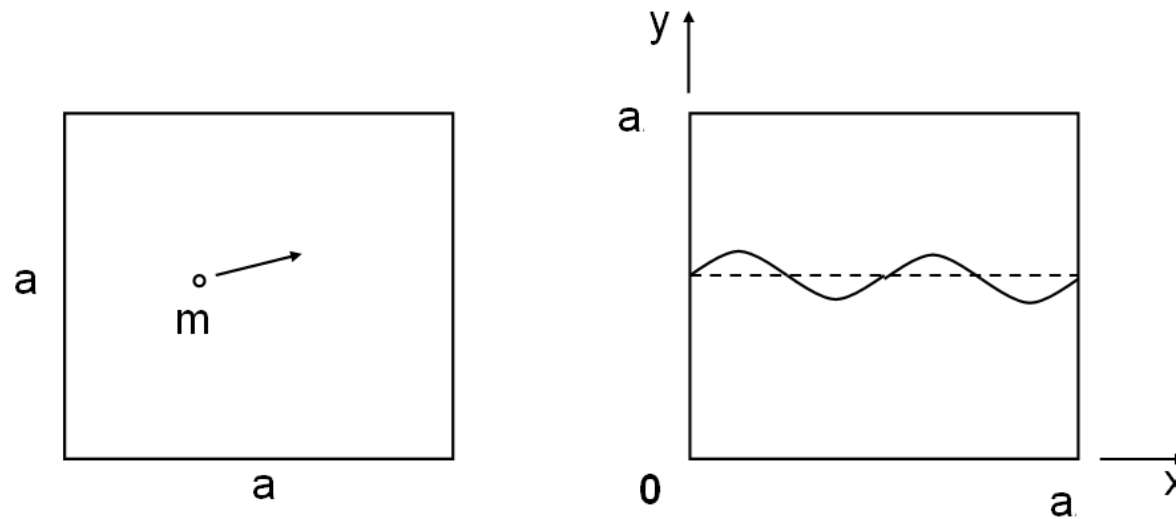
and the heat capacity is

$$C = \frac{dU}{dT} = \frac{3}{2}Nk_B.$$

## A particle in a 3-D box

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We first determine the energy states for a particle in a 3-D box.



We solve Schrödinger's equation for the particle:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V\psi = E\psi$$

where  $V$  is zero in the box, and infinite at the walls. So the wave function must have zero amplitude there.

## Energy states of the particle

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This is done in the standard way by trying the solution

$$\psi = \sin k_x x \sin k_y y \sin k_z z$$

where  $(k_x, k_y, k_z)$  are unknown constants. They can be determined from the boundary condition that the wave function must have zero amplitude at the wall.

In the  $x$  direction, suppose the walls are at  $x = 0$  and  $x = a$ . The condition can be written as:

$$\sin k_x a = 0.$$

This gives

$$k_x a = n_x \pi \quad \text{or} \quad k_x = \frac{n_x \pi}{a},$$

where  $n_x$  is a positive integer. This means that  $k_x$  is quantised. Similarly, for the  $y$  and the  $z$  directions, we find

$$k_y = \frac{n_y \pi}{a} \quad \text{and} \quad k_z = \frac{n_z \pi}{a}.$$

## Energy states of the particle

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We can then substitute the solution

$$\psi = \sin k_x x \sin k_y y \sin k_z z$$

into the Schrödinger's equation

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V\psi = E\psi$$

to find the energy. This gives

$$\frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = E.$$

It can also be written in the form

$$\frac{\hbar^2 k^2}{2m} = E$$

where

$$k^2 = k_x^2 + k_y^2 + k_z^2.$$

$k$  is called the wavevector.

## Density of states.

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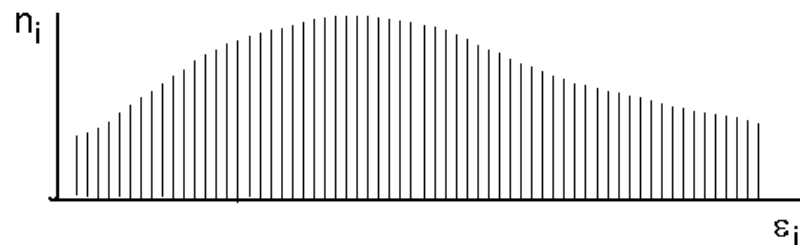
To find the total energy of  $N$  particles, we need to add up all their energies:

$$U = \sum n_i \varepsilon_i.$$

where  $\varepsilon_i$  is the energy of level  $i$  and  $n_i$  is the number of particles at that level.

At room temperature, many of these levels could be occupied. This is because for an ideal gas, spacing between energy levels is much smaller than the average energy of a particle.

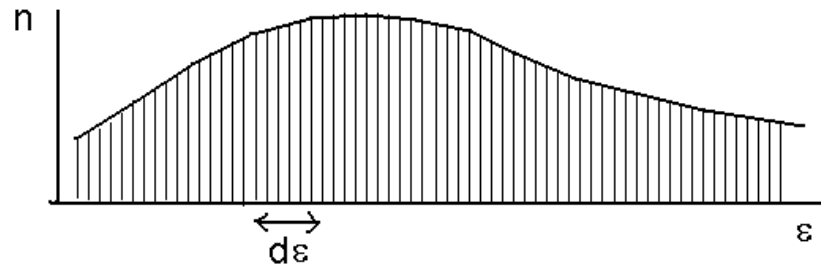
As a result, a plot of  $n_i$  against  $\varepsilon_i$  may look like this.



## Density of states.

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This suggests that we may approximate the graph to a curve, and the sum to an integral.



Within a small interval  $d\varepsilon$ , the energy  $\varepsilon$  is nearly constant. If we know the number of particles in this interval, we can multiply by  $\varepsilon$  to find the total.

Because of the quantisation condition, there can only be a certain number of states in  $d\varepsilon$ . For each state, there is a certain probability that it would be occupied. Lets start by find the number of states.



## Counting states

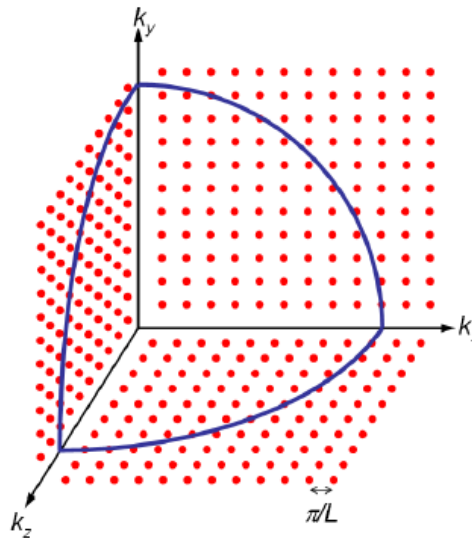
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The wavevectors

$$k_x = \frac{n_x \pi}{a}$$

are quantised at uniform intervals in all three directions.

we can imagine a  $k$  space in which the the  $x$  coordinate is  $k_x$ , and so on. If we use a point to represent each state, we would get a lattice like this.



## Counting states

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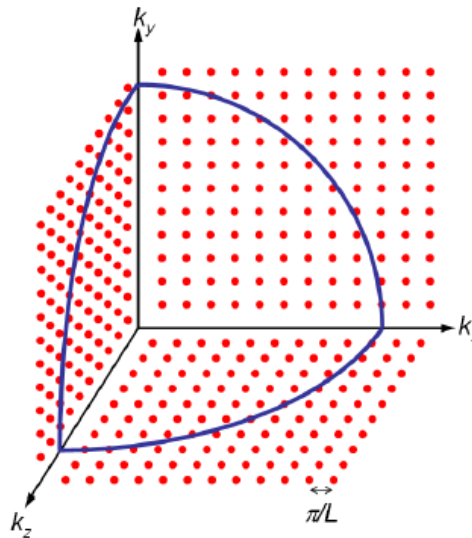
First, we find the number of all states below energy  $\varepsilon$ . This energy is related to the wavevector  $k$  by

$$\varepsilon = \frac{\hbar^2 k^2}{2m}.$$

$k$  is in turn related to the components by

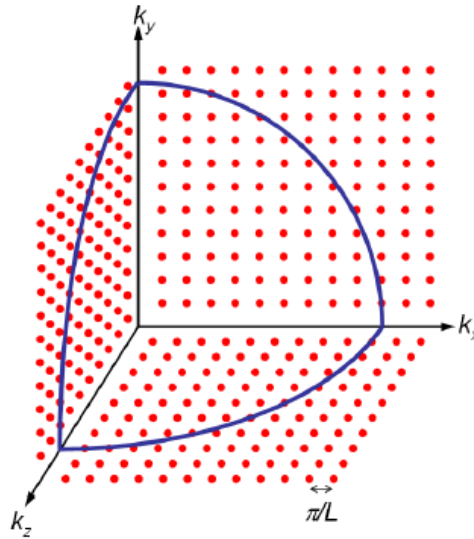
$$k^2 = k_x^2 + k_y^2 + k_z^2.$$

This describes a sphere in  $k$  space.



# DOS

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Because  $k_x$ ,  $k_y$  and  $k_z$  are all positive, only the points within 1/8 of the sphere of radius  $k$ , where  $k$  is the wavevector for  $\varepsilon$ .

Since the spacing between points is  $\pi/a$ , the volume associated with each point is  $(\pi/a)^3$ . Therefore, the total number of states is one eighth of the sphere volume divided by  $(\pi/a)^3$ :

$$G(k) = \frac{1}{8} \times \frac{4}{3}\pi k^3 \div \left(\frac{\pi}{a}\right)^3.$$

We find that the total number of states below  $k$  is

$$G(k) = \frac{Vk^3}{6\pi^2},$$

where  $V$  is the volume  $a^3$  of the box.

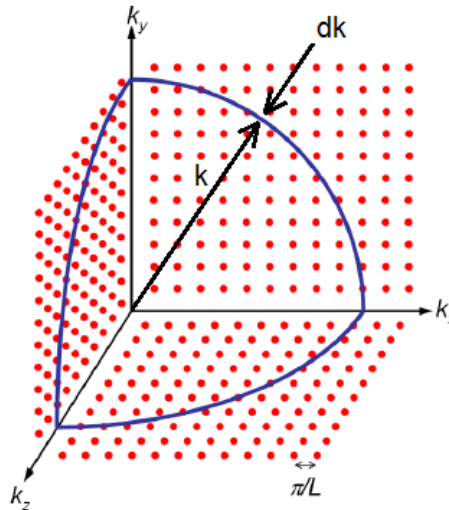
Suppose  $k$  is increased by  $dk$ . Then the number of states increases by  $dG$ . So the density of states is

$$g(k) = \frac{dG(k)}{dk} = \frac{Vk^2}{2\pi^2}.$$

# DOS

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We have derived  $g(k)$  by first deriving  $G(k)$ . We can also derive  $g(k)$  directly.



Consider a spherical shell in  $k$  space with a thickness  $dk$ . The states in the shell lie between wavevectors  $k$  and  $k + dk$ .

Each state is associated with volume  $(\pi/a)^3$ . So the number of states in the shell is volume of the shell divided by  $(\pi/a)^3$ .

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Volume of the spherical shell is  $4\pi k^2 dk$ . We only take 1/8 of this because only positive components of  $k_x, k_y, k_z$  are needed.

$$\text{number of states in } dk = \frac{1}{8} \times 4\pi k^2 dk \div \left(\frac{\pi}{a}\right)^3$$

$$g(k) = \frac{\text{number of states in } dk}{dk}$$

$$g(k) = \frac{1}{8} \times 4\pi k^2 \div \left(\frac{\pi}{a}\right)^3$$

$$g(k) = \frac{V k^2}{2\pi^2}.$$

where volume  $V = a^3$ .

We have earlier defined the DOS in terms of energy,  $\varepsilon$ .

To convert the variable from  $k$  to  $\varepsilon$ , we must use the method for probability density function:

$$g_{\varepsilon}(\varepsilon)d\varepsilon = g_k(k)dk.$$

The subscripts are added here to emphasise that  $g(\varepsilon)$  and  $g(k)$  are different functions.

## Changing variables

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Rearranging,

$$g_{\varepsilon}(\varepsilon) = g_k(k) \frac{dk}{d\varepsilon}.$$

We can now substitute the relation

$$\varepsilon = \frac{\hbar^2 k^2}{2m}$$

to find  $g_{\varepsilon}(\varepsilon)$ . The answer is

$$g(\varepsilon) = \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2}$$

where we have dropped the subscript again, as is the normal practice. For comparison:

$$g(k) = \frac{V k^2}{2\pi^2}.$$

If you substitute  $\varepsilon$  for  $k$  in  $g(k)$ , you DO NOT get  $g(\varepsilon)$ .  $g(k)$  and  $g(\varepsilon)$  are DIFFERENT functions!



## Changing variables

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It is also useful to have the formula for total number states

$$G(k) = \frac{1}{8} \times \frac{4}{3} \pi k^3 \div \left(\frac{\pi}{a}\right)^3.$$

in terms of energy.

Since no  $\varepsilon$  or  $k$  intervals are involved, we can simply substitute

$$\varepsilon = \frac{\hbar^2 k^2}{2m}.$$

The answer is

$$G(\varepsilon) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}.$$

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## Most Likely Macrostate

## Ideal gas energy states

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We first show that it is very unlikely for two atoms to occupy the same energy state.

At a temperature  $T$ , we know from simple kinetic theory of ideal gas that the average energy of a gas atom is about  $3k_B T/2$ .

First, we need to know how many energy states there are below this energy at room temperature. We can use the formula we have derived:

$$G(\varepsilon) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}$$

by setting  $\varepsilon = 3k_B T/2$ .

## Ideal gas energy states

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$$G(3k_B T/2) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}$$

Putting in the numbers for one mole of ideal gas at room temperature, we find that the number of states below  $3k_B T/2$  is about  $10^{30}$ .

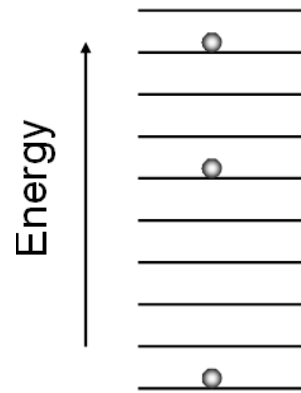
1 mole of gas contains about  $10^{24}$  atoms.

This means we have about  $10^{30} \div 10^{24} = 10^6$  states per atom.

## Ideal gas energy states

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This means we have about 1 million energy states for every atom.



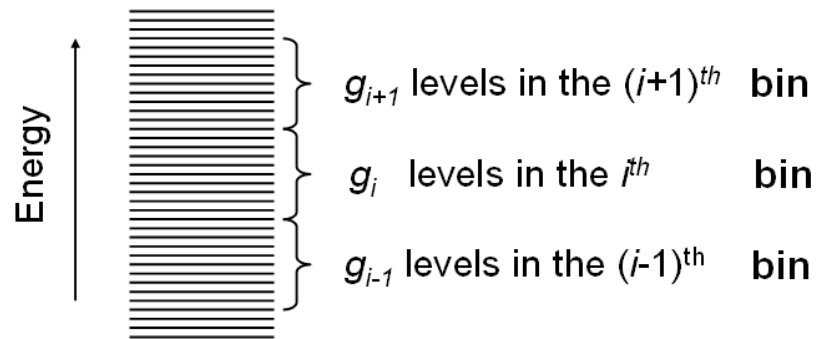
So it is extremely unlikely that two atoms would ever occupy the same energy state.

We are now going to derive the energy distribution of these atoms.

## Grouping energy levels into bundles

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We shall borrow the idea from histograms - divide the energy levels into bins, or bundles.



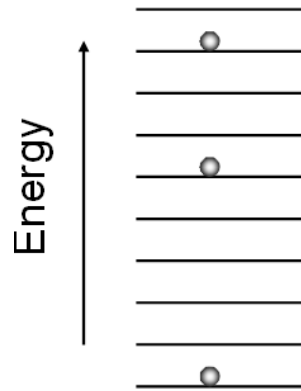
Suppose each bundle covers an energy interval  $d\varepsilon$ .

We want to find out how many ways we can arrange a number of atoms in a particular bundle.

## Energy levels as partitions

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Consider the  $i^{\text{th}}$  bundle. There are  $g_i$  energy states and  $n_i$  atoms.



Recall that it is extremely unlikely for two atoms to be in the same state.

Think of each state as a partition. The partition and the atom are like two different objects. We need to find the number of ways to arrange  $n_i$  atoms and  $g_i$  partitions in a row.

## Number of arrangements

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There are  $n_i$  atoms and  $g_i$  partitions.

We can use the combination formula  ${}^n C_r = \frac{n!}{r!(n-r)!}$ .

This gives, for one bundle,  $\frac{(n_i+g_i)!}{n_i!g_i!}$  ways.

To find the total number of arrangements for all bundles, we must multiply together the answer for every bundle:

$$\Omega = \prod_i \frac{(n_i + g_i)!}{n_i!g_i!} \quad (1)$$

Since the number of energy states in each bundle is much larger than the number of atoms,  $g_i \gg n_i$ , we can simplify this.



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Expand

$$\Omega = \prod_i \frac{(g_i + n_i) \dots (g_i + 1)(g_i) \dots (1)}{n_i! g_i!} = \prod_i \frac{(g_i + n_i) \dots (g_i + 1)}{n_i!}$$

Since  $g_i \gg n_i$ ,  $(g_i + n_i) \approx g_i$  and  $(g_i + 1) \approx g_i$ . Therefore

$$\Omega = \prod_i \frac{g_i^{n_i}}{n_i!}$$

This gives the number of microstates in the macrostate  $n_i$ .

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$$\Omega = \prod_i \frac{g_i^{n_i}}{n_i!}$$

If a macrostate is specified by  $(n_1, n_2, n_3, \dots)$ , or  $n_i$  in short, then the above expression gives the number of microstates in the macrostate.

We are interested in the most likely distribution of  $(n_1, n_2, n_3, \dots)$ , or the most probable macrostate.

We can once again apply the Lagrange multiplier to find this.

## Most probable macrostate for the ideal gas

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We apply the Lagrange multiplier method as follows:

1. Instead of  $\Omega$ , maximise  $\ln \Omega$ .
2. Apply Stirling's approximation:

$$\ln \Omega = \sum_i [n_i \ln g_i - n_i \ln n_i + n_i] = \sum_i n_i \ln(g_i/n_i) + N$$

3. The number of particles is fixed:

$$N = \sum_i n_i$$

4. The total energy is fixed:

$$U = \sum_i n_i \varepsilon_i.$$

5. Define the Lagrange function as  $\ln \Omega + \lambda_1 N + \lambda_2 U$ .
6. To find the maximum, differentiate with respect to  $n_i$ :

$$\ln g_i - \ln n_i + \lambda_1 + \lambda_2 \varepsilon_i = 0$$

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## Most probable macrostate for the ideal gas

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We have found

$$\ln g_i - \ln n_i + \lambda_1 + \lambda_2 \varepsilon_i = 0$$

Rearranging, we get

$$n_i = A g_i \exp(\lambda_2 \varepsilon_i),$$

where

$$A = \exp(\lambda_1).$$

In the same way as before, by using our knowledge of entropy, we can show that

$$\lambda_2 = -\frac{1}{k_B T}.$$

This gives the Boltzmann distribution again:

$$n_i = A g_i \exp(-\varepsilon_i / k_B T),$$

## Approximate to continuous energy

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We are mainly interested in the energy range of the order of  $k_B T$  (which means up to a few times of that). Most of the atoms would fall in this range.

We have seen previously that there is a very large number of energy states in this range.

Since the energy levels are so closely spaced, we can approximate them to continuous energy.

We have previously obtained the density of states, which is the number of states per unit energy,  $g(\varepsilon)$ .

Consider the  $i^{\text{th}}$  bundle. Assume that this occupies an energy interval of  $d\varepsilon$ .

The number of energy states is then given by  $g_i = g(\varepsilon)d\varepsilon$ .

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## Approximate to continuous energy

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In a similar way, we can define a number density  $n(\varepsilon)$  as the number of particles per unit energy.

So the number of atoms in the bundle would be

$$n_i = n(\varepsilon)d\varepsilon.$$

Therefore, the distribution that we have obtained,

$$n_i = Ag_i \exp(-\beta\varepsilon_i),$$

can be rewritten as

$$n(\varepsilon)d\varepsilon = Ag(\varepsilon) \exp(-\varepsilon_i/k_B T)d\varepsilon$$

## Approximate to continuous energy

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Substituting the formula for  $g(\varepsilon)$ , we get

$$n(\varepsilon) = A \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2} \exp(-\varepsilon/k_B T)$$

Note that the total number of atoms is then given by integrating over all energy:

$$N = \int_0^{\infty} n(\varepsilon) d\varepsilon$$

This relation is known as the normalisation condition.

## Maxwell-Boltzmann distribution

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The unknown constant  $A$  can be determined by integrating the normalisation condition (with the help of the table of integrals):

$$A = \frac{N}{V} \left( \frac{h^2}{2\pi m k_B T} \right)^{3/2}$$

This gives

$$n(\epsilon) = \frac{2\pi N}{(\pi k_B T)^{3/2}} (\epsilon)^{1/2} \exp(-\epsilon_i/k_B T)$$

The energy is just the kinetic energy,  $\epsilon = mv^2/2$ . So

$$n(v) = N \left( \frac{2}{\pi} \right)^{1/2} \left( \frac{m}{k_B T} \right)^{3/2} \exp(-mv^2/2k_B T) v^2$$

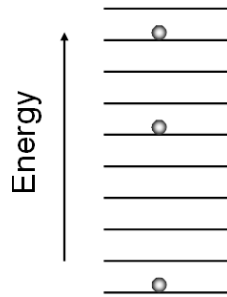
This is the Maxwell-Boltzmann distribution of speeds.



## When would it break down?

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We have assumed that: "It is extremely unlikely that two atoms would ever occupy the same energy state."



Recall that we have arrived at this by looking at the number of states below the mean energy  $3k_B T/2$ , when  $T$  is at room temperature.

If  $T$  is very small, there may be far fewer states below the mean energy. Then it would be very likely for two atoms to occupy the same state, and the Maxwell-Boltzmann distribution would not be valid.

Instead, quantum statistics - such as Fermi-Dirac or Bose-Einstein - have to be used. We shall learn about these later.

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**Boltzmann constant**

## Boltzmann constant

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We can now return to the earlier lectures on derivation of the Boltzmann distribution

$$n_i = A \exp(-\varepsilon_i/k_B T)$$

and tie up a loose end.

We can now find the total energy in an ideal gas. Replace the sum

$$U = \sum n_i \varepsilon_i$$

by the integral

$$U = \int_0^\infty n(\varepsilon) \varepsilon d\varepsilon.$$

Substitute the formula for number density:

$$U = \int_0^\infty \frac{2\pi N}{(\pi k_B T)^{3/2}} (\varepsilon)^{1/2} \exp(-\varepsilon/k_B T) \varepsilon d\varepsilon.$$

## Boltzmann constant

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Integrating this gives the formula for the total energy that we know from kinetic theory of gases:

$$U = \frac{3}{2}Nk_B T$$

This is evidence that the Boltzmann distribution for the ideal gas is correct.

Differentiating with respect to  $T$  gives the heat capacity:

$$C = \frac{3}{2}Nk_B.$$

The measured value is:

$$C = \frac{3}{2}nR.$$

$R$  is the gas constant and has the value of  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .

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Recall that  $k_B$  is related to one of the Lagrange multipliers. We can find it by comparing the measured  $C$  above, with the formula derived using the Boltzmann distribution.

Comparing

$$C = \frac{3}{2}Nk_B$$

and

$$C = \frac{3}{2}nR,$$

we find

$$Nk_B = nR.$$

Since the number of moles  $n$  is related to the number of particles  $N$  by

$$n = \frac{N}{N_A},$$

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we have

$$Nk_B = \frac{N}{N_A}R$$

and finally, we obtain the value for  $k_B$ :

$$k_B = \frac{R}{N_A},$$

which is indeed the Boltzmann constant as we have assumed.

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## Worked Examples

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## Example 1

Show that the partition function of an ideal gas:

$$Z = \int_0^{\infty} \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2} \exp(-\varepsilon/k_B T) d\varepsilon$$

is given by:

$$Z = V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2}.$$

[You are given that

$$\int_{-\infty}^{\infty} x^{2n} e^{-a^2 x^2} dx = \frac{(2n)! \pi^{1/2}}{n! (2a)^{2n} a}$$

]



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First, move the constant factors outside the integral:

$$Z = \frac{4m\pi V}{h^3} (2m)^{1/2} \int_0^{\infty} \varepsilon^{1/2} \exp(-\varepsilon/k_B T) d\varepsilon$$

There is no power of 1/2 in the integration formula that is given. So we start with the substitution

$$\varepsilon = x^2$$

Then

$$\begin{aligned} Z &= \frac{4m\pi V}{h^3} (2m)^{1/2} \int_0^{\infty} x \exp(-x^2/k_B T) \cdot 2x dx \\ &= \frac{4m\pi V}{h^3} (2m)^{1/2} 2 \int_0^{\infty} x^2 \exp(-x^2/k_B T) dx \end{aligned}$$

Next, set  $n$  to 1 in the given formula:

$$\int_{-\infty}^{\infty} x^2 e^{-a^2 x^2} dx = \frac{2\pi^{1/2}}{(2a)^2 a}$$

The lower of limit of this integral is  $-\infty$ . To make this agree with the integral for the partition function  $Z$  ...

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We change the lower limit to 0 and halve the right hand side, and the formula becomes:

$$\int_0^{\infty} x^2 e^{-a^2 x^2} dx = \frac{\pi^{1/2}}{(2a)^2 a}$$

Now comparing with the partition function again:

$$Z = \frac{4m\pi V}{h^3} (2m)^{1/2} 2 \int_0^{\infty} x^2 \exp(-x^2/k_B T) dx$$

the integrals become the same if we set

$$a^2 = \frac{1}{k_B T}$$

Substituting this into the formula gives

$$\int_0^{\infty} x^2 e^{-x^2/k_B T} dx = \frac{\pi^{1/2}}{4} (k_B T)^{3/2}$$

Substituting this into partition function intergral, ...

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We get

$$Z = \frac{4m\pi V}{h^3} (2m)^{1/2} 2^{\frac{\pi^{1/2}}{4}} (k_B T)^{3/2}$$

Simplifying,

$$Z = V \left( \frac{2m\pi k_B T}{h^2} \right)^{3/2}$$

we get the formula for the partition function.

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## Example 2

What is the root-mean-square speed of a helium atom at room temperature?

[Given that the relative atomic mass of helium is 4.

Atomic mass unit  $u$  is  $1.6605 \times 10^{-27}$  kg.

Boltzmann's constant  $k_B$  is  $1.3807 \times 10^{-23}$  J K<sup>-1</sup>. ]

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First, we find the mean of  $v^2$ . This is can be obtained by

$$\bar{v^2} = \frac{1}{N} \int_0^\infty v^2 n(\varepsilon) d\varepsilon.$$

We have multiplied  $v^2$  by the number particles at each energy interval  $d\varepsilon$ , and divided by the total number  $N$ .

The energy of the atom in an ideal gas is just the kinetic energy,

$$\varepsilon = \frac{1}{2} m v^2.$$

If we rewrite the above integral for  $v^2$  in terms of the energy, we get

$$\bar{v^2} = \frac{2}{Nm} \int_0^\infty \varepsilon n(\varepsilon) d\varepsilon.$$

This integral is just the total energy  $U$ , i.e.

$$\bar{v^2} = \frac{2}{Nm} U.$$

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We have previously obtained the energy  $U$  from the partition function:

$$U = \frac{3}{2}Nk_B T.$$

So the mean square speed is

$$\bar{v}^2 = \frac{2}{Nm} \frac{3}{2}Nk_B T = \frac{3k_B T}{m}$$

The root-mean-square speed is then

$$\sqrt{\bar{v}^2} = \sqrt{\frac{3k_B T}{m}}.$$

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We can now calculate the root-mean-square speed. The mass of the helium atom is

$$4u = 4 \times 1.6605 \times 10^{-27} = 6.642 \times 10^{-27} \text{ kg.}$$

Taking the room temperature as 298 K, the answer is

$$\begin{aligned} \sqrt{v^2} &= \sqrt{\frac{3k_B T}{m}} \\ &= \sqrt{\frac{3 \times 1.3807 \times 10^{-23} \times 298}{6.642 \times 10^{-27}}} \\ &= 1363 \text{ m/s} \end{aligned}$$