Statistical and Low Temperature Physics (PHYS393)

1. Basic Statistical Mechanics

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Learning Aims: You will learn to

Explain the meaning of probability. Calculate probabilities for simple examples.

Explain how number of particles at each energy level depends on probability.

Use Boltzmann distribution to calculate number of particles at each energy level.

Use Boltzmann distribution to calculate total energy.

Probability and Statistics

Suppose there are 10 balls in bag: 3 red, 7 blue. If I pick a ball at random, would it be red or blue?

We don't know. But we know that if I pick a ball 10 times (replacing it each time), then 3 out of 10 times it would be red. 7 out of 10 times it would be blue.

Roughly.

This idea is quantified by the definition of probability:

$$\text{probability of an event} = \frac{\text{number of possible outcomes for that event}}{\text{total number of possible outcomes}}.$$

So

$$\text{probability of red ball} = \frac{3}{10},$$

$$\text{probability of blue ball} = \frac{7}{10}.$$

If I pick and replace the ball 100 times, I would get red balls approximately

$$\frac{3}{10} \times 100 = 30$$

times. Approximately, but most likely a bit more or a bit less.

So if I say 3/10 of the times I get red, then there is some error in this statement.

In reality, I might get 29 red balls, or 33 red balls, or some other random numbers of red balls. But chances are, it would not be too far from 30. It can be proven that if you repeat the experiment many times, the average of all the numbers of red balls that you picked each time would approach 30.

We call 3/10 the expected value of the proportion of red balls. In some sense, it is an average.

It is often convenient just to think of 3/10 as the proportion of red balls we would get, as along as we remember that it is an average, and the actual number could be different. Since the actual proportion takes a range of random values, we can think in terms of the standard deviation σ.

σ is a kind of average of the difference between a random variable and its expected value (or mean). We may think of it as a measure of the error of an observed quantity.

It has been shown in statistics that σ gets smaller as the number N of of times I pick and replace the ball gets larger. In fact, the error in the proportion goes as $1/\sqrt{N}$.

If I pick and replace the ball 100 times, and I say that 3/10 of the times I get red, then my error is about $1/\sqrt{100}$ which is 10%.

But if I pick and replace the ball 10^{24} times, and I say that 3/10 of the times I get red, then the error is only $1/\sqrt{10^{24}}$. This is so small that I can neglect the error and treat 3/10 as an accurate answer.

Why would I even think about picking a ball 10^{24} times from a bag?

Because 10^{24} is close to the Avogadro constant 6.022×10^{23}, the typical number of atoms in any object that we would pick up - a cup of tea, an apple, or a piece of cake.

There is a connection between the number of times I pick a ball from a bag, and the number of atoms in an object.

We know from quantum mechanics that the atoms and electrons have energies at discrete levels. If we can somehow know the probability of the particles at each level, then we can calculate the expected value of the total energy of the particles. Because the number of atoms is so large, the percentage error would be negligible.

Once we know the total energy of the particles in a body, many thermodynamic properties can be calculated.

Basic Statistical Mechanics

Suppose that a solid body contains 10 atoms, and each atom has 2 energy levels: the lower level ε_1 and higher level ε_2. At a certain temperature, an atom can either be at ε_1 or ε_2.

The atoms interact with each other through electromagnetic fields. Each atom can gain or lose some energy to another atom, and change from one level to the other.

At a particular point in time, each atom is at a particular energy level ε_1 or ε_2. So the 10 atoms have a particular arrangement in energy levels. This arrangement is called a **microstate**.

At another point in time, the energy of each atom could have changed. The 10 atoms would have a different arrangement in energy levels. This is possible as long total energy is conserved. This new arrangement would be a different microstate.

Which of these microstates is more likely? We will never really know. However, physicists made a very good guess: They assumed that all the microstates are equally likely.

By making this assumption, they calculated the thermodynamic properties of many things. The answers agreed well with experiments, so physicists are now convinced that this assumption is correct. They even promoted it to a principle:

> “The principle of a priori probability.”

We want to know the number of atoms at each energy level (ε_1, ε_2). Once we know this, we can calculate the total energy of the body, and other thermodynamic properties.

Suppose that the numbers are (n_1, n_2). This set of numbers of atoms at different levels is called a **macrostate**.

Each macrostate can correspond to different microstates. For example, if the macrostate is (7, 3), it means that 7 atoms are at ε_1 and 3 atoms are at ε_2. However, the 3 atoms at ε_2 can be any of the 10 atoms.

For each macrostate, there are different arrangements, or microstates. We can find the number of different microstates using the mathematics of combinations and permutations.

Since we assume that each microstate is equally likely, we can then find the probability of each macrostate:

$$\text{probability of } (n_1, n_2) = \frac{\text{number of possible microstates for } (n_1, n_2)}{\text{total number of possible microstates}}$$

We want to find the macrostate (n_1, n_2) with the highest probability. When the number of atoms is very large (e.g. 10^{24}), this macrostate is given by this formula:

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

where i = 1, 2.

This is called the Boltzmann distribution.

$$n_i = A\,\mathsf{exp}(-\varepsilon_i/k_B T)$$

This distribution is obtained using these assumptions:

1. Each microstate is equally likely.
2. The number of particles (atoms) is very large.
3. The total energy or temperature is constant.
4. The number of particles (atoms) is fixed.
5. The positions of the atoms are fixed (distinguishable - so we can tell one from another).

The mathematics used to derive this formula is called Lagrange's multipliers. Details available in previous years' lecture notes.

The examples so far are about atoms with two energy levels.

$$n_i = A\,\mathrm{exp}(-\varepsilon_i/k_B T).$$

The Boltzmann distribution also applies to particles with any number of energy levels, so that i = 1, 2, 3, ...

We are mainly interested in the total number of particles and the total energy. These are related to the number n_i of particles at each energy level.

The total number is the sum of particles at all levels:

$$N = n_1 + n_2 + n_3 + ... = \sum_i n_i.$$

For the total energy, there are n_1 atoms at level ε_1, so the energy at level 1 is $n_1\varepsilon_1$. Likewise for level 2, and so on.

The total energy is the sum of energies at all levels:

$$U = n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + ... = \sum_i n_i\varepsilon_i.$$

Note that the number n_i given by Boltzmann distribution

$$n_i = A\,\text{exp}(-\varepsilon_i/k_BT).$$

is an expected value, just like the expected number of red balls when you pick 10 balls from a bag with red and blue balls.

This means that at different points in time, n_i could change. This means there is some error in the above formula. However, we know that the percentage error goes as $1/\sqrt{N}$, where N here is the total number of particles.

Since N is about 10^{24} for typical objects, the percentage error is extremely small, and we usually neglect this.

The Boltzmann distribution is true for a number of systems, such as:

- atoms in a solid, and
- particles in an ideal gas.

If is not true for some systems, e.g.:

- electrons in metals, and
- atoms at extremely low temperatures.

In the last two cases, the distributions are different. We shall learn more about these distributions later on.

Worked Examples

Example 1

There is one mole of atoms at a temperature of 1 K. Each atom has energy levels -10^{-23} J and 10^{-23} J. Find the number of atoms at each level.

Solution

The formula is Boltzmann distribution

$$n_i = A\,\mathrm{exp}(-\varepsilon_i/k_B T).$$

Given
$\varepsilon_1 = -10^{-23}$ J, $\varepsilon_2 = 10^{-23}$ J, and T = 1 K.

We also know that $n_1 + n_2 = N_A$ (Avogadro constant).

We need to find the numbers n_1 and n_2. But what is A?

Lets write out all equations:

$$n_1 + n_2 = N_A$$

$$n_1 = A\,\mathrm{exp}(-\varepsilon_1/k_B T)$$

$$n_2 = A\,\mathrm{exp}(-\varepsilon_2/k_B T)$$

There are three unknowns: n_1, n_2 and A. Divide the last two equations:

$$\frac{n_1}{n_2} = \mathrm{exp}((\varepsilon_2 - \varepsilon_1)/k_B T).$$

Let this above fraction be r. So the total is N_A is divided into the ratio $r : 1$. Therefore

$$n_1 = \frac{r}{r+1} \times N_A = 4.876 \times 10^{23}$$

$$n_2 = \frac{1}{r+1} \times N_A = 1.145 \times 10^{23}$$

Example 2

Following from the previous example, find the total energy of the atoms.

Solution

There are n_1 atoms with energy ε_1, so the energy of these atoms is $n_1\varepsilon_1$

There are n_2 atoms with energy ε_2. so the energy of these atoms is $n_2\varepsilon_2$.

Therefore the total energy is

$$U = n_1\varepsilon_1 + n_2\varepsilon_2.$$

Using the values from the previous example, we get

$$U = (4.876 \times 10^{23})(-10^{-23}) + (1.145 \times 10^{23})(10^{-23}) = 6.021J.$$

Example 3

Following from the previous example, find the probability that an atom is at level 1, and the probability that it is at level 2.

Solution

The total number of atoms is N_A.

There are n_1 atoms at level 1 and n_2 atoms at level 2.

An atom can change level with time. So any one time, probability that it is at level 1 is

$$\frac{\text{number of possible atoms at level 1}}{\text{total number of atoms}} = \frac{n_1}{N_A} = \frac{4.876 \times 10^{23}}{6.022 \times 10^{23}}$$

Probability that it is at level 2 is

$$\frac{\text{number of possible atoms at level 2}}{\text{total number of atoms}} = \frac{n_2}{N_A} = \frac{1.145 \times 10^{23}}{6.022 \times 10^{23}}$$

Example 4

There are a number of atoms at a temperature of 1 K. Each atom has energy levels -10^{-23} J and 10^{-23} J. Find the probability that an atom is at each level.

Solution

This time, we are not given the total number of particles. We still have the Boltzmann distribution:

$$n_1 = A\,\mathrm{exp}(-\varepsilon_1/k_B T)$$

$$n_2 = A\,\mathrm{exp}(-\varepsilon_2/k_B T)$$

but we cannot find A if we don't know the the total number of particles.

But we know that the probability that an atom is at level 1 is

$$\frac{\text{number of possible atoms at level 1}}{\text{total number of atoms}} = \frac{n_1}{n_1 + n_2}$$

If we substitute the Boltzmann distribution, A cancels out!

$$\frac{n_1}{n_1 + n_2} = \frac{\cancel{A}\,\mathrm{exp}(-\varepsilon_1/k_B T)}{\cancel{A}\,\mathrm{exp}(-\varepsilon_1/k_B T) + \cancel{A}\,\mathrm{exp}(-\varepsilon_2/k_B T)}$$

We do know the energy levels and temperature, so we can now calculate this. In the same way, the probability that an atom is at level 2 is

$$\frac{n_2}{n_1 + n_2} = \frac{\cancel{A}\,\mathrm{exp}(-\varepsilon_2/k_B T)}{\cancel{A}\,\mathrm{exp}(-\varepsilon_1/k_B T) + \cancel{A}\,\mathrm{exp}(-\varepsilon_2/k_B T)}$$

The answers are 4.876/6.022 and 1.145/6.022 respectively.