Lecture Notes Thermal Physics

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1 Introduction: a short overview of important notions

The mole

A **mole** of a certain atom is equivalent to an **Avogadro number** N_a of atoms. Where $N_A = 6.022 \cdot 10^2 3$.

The ideal gas law

Suppose we have N particles in a gas, then we can relate the pressure, volume, temperature, and amount of particles as follows:

$$pV = Nk_BT \tag{1}$$

where k_B is Boltzmann's constant. In order to apply this formula one assumes that (i) there are no intermolecular forces and (ii) that the particles are point-like and have zero size.

Combinatorics

Suppose we have n atoms, and r of those atoms are for instance in an excited state. If we want to calculate the number of possible configurations Ω we apply the following formula,

$$\Omega = \frac{n!}{(n-r)!r!} \equiv {}^nC_r \tag{2}$$

Since factorials grow incredibly quick, we shall often use $\ln \Omega$ instead of Ω.

$$\ln \Omega = \ln(n!) - \ln([n-r]!) - \ln(r!) \tag{3}$$

We also have **Sterling's formula**:

$$\ln(n!) \approx n \ln n - n \tag{4}$$

2 Heat

Heat (Q, measured in Joules) is thermal energy in transit. Note that in contrast to for instance fuel in a car, one cannot say that something has a certain quantity of heat. One can only add heat to something, like adding fuel to a car.

2.1 Heat capacity

We can ask the question, how much heat needs to be supplied to an object tot raise its temperature by a small amount dT. The answer is $dQ = CdT$, such that we define the **heat capacity** C of an object using

$$C = \frac{dQ}{dT} \tag{5}$$

There is also c, the **specific heat capacity** in $\mathrm{J\,K^{-1}\,kg^{-1}}$. And the **molar heat capacity**, the heat capacity of one mole of a substance.

If we were to add heat to a system, we'd have to constrain, either the volume of the gas or the pressure of the gas to be fixed. We should therefore change the definition of heat capacity, we need new quantities: C_V, the heat capacity at constant volume, and C_p, the heat capacity at constant pressure.

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V \tag{6}$$

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p \tag{7}$$

In practice $C_p > C_V$, due to more heat being added whilst heating at constant pressure. While heating at constant volume will expend additional energy on doing work on the atmosphere as the gas expands.

3 Probability

3.1 Discrete probability distributions

Let x be a discrete random variable which takes values x_i with probability P_i. The sum of P_i's must always be $\sum P_i = 1$. And we define the **mean** of x to be

$$\langle x \rangle = \sum_i x_i P_i \tag{8}$$

and in general

$$\langle f(x) \rangle = \sum_i f(x_i) P_i \tag{9}$$

3.2 Continuous probability distributions

Let x be a continuous random variable which has a probability $P(x)\,dx$ of having a value between x and $x + dx$. We require that

$$\int P(x)\,dx = 1 \tag{10}$$

With the mean defined as

$$\langle x \rangle = \int x P(x)\,dx \tag{11}$$

and in general

$$\langle f(x) \rangle = \int f(x) P(x)\,dx \tag{12}$$

3.3 Linear transformation

If one want to relate say a random variable x to the random variable y by e.g. $y = ax + b$ then

$$\langle y \rangle = \langle ax + b \rangle = a \langle x \rangle + b \tag{13}$$

where a and b are just constants.

3.4 Variance

One measurement of spread in a distribution is the variance (the square root of it is the standard deviation), defined as

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 \tag{14}$$

3.5 Independent variables

If u and v are independent random variables the probability that they are in there respective range is given by

$$P_u(u)\,du\,P_v(v)\,dv \tag{15}$$

and by taking the double integral of that product we obtain

$$\langle uv \rangle = \langle u \rangle \langle v \rangle \tag{16}$$

3.6 Binomial distribution

It is a probability distribution based on **Bernoulli trials**, which are experiments with two outcomes, success and failure. Where the success happens with a probability p, and failure with probability $1-p$. The **binomial distribution** is the discrete probability distribution of getting k successes from n independent Bernoulli trials. It is defined as

$$P(n,k) = p^k(1-p)^{n-k}\left({}^nC_k\right) \quad \text{where} \quad {}^nC_k = \frac{n!}{(n-k)!k!} \tag{17}$$

and the mean of the distribution is $\langle k \rangle = np$ and the variance is $\sigma_k^2 = np(1-p)$.

4 Temperature and the Boltzmann factor

4.1 Thermal equilibrium

Suppose two bodies are in thermal contact with one another, heat will flow from the hotter to the colder body. At a certain moment no net flow of heat will happen, the energy and temperature will no longer change with time. This is called the **Thermal equilibrium**, the process of reaching it is called **thermalization**.

4.2 The zeroth law of thermodynamics

It says that two systems, each, separately in thermal equilibrium with a third, are in equilibrium with each other.

4.3 On thermometers

A working thermometer should have a heat capacity that is less than that of the measured object. Some common methods of measuring temperature include (i) the fact that liquids expand, (ii) that the resistance of certain materials depend on temperature, or (iii) letting liquid coexist with the vapour and measuring the pressure of the vapour.

4.4 Microstates and macrostates

Let's consider the example of a hundred coin flips. Here the **microstates** would be either heads or tails (note microstates are all equally likely). Macrostates would be the total outcome, so how many heads or tails (these are not equally likely).

4.5 The statistical definition of temperature

Let's imagine two systems in thermal contact, otherwise they are isolated. The total energy is $E = E_1 + E_2 = $ constant. The first system can be in any one of $\Omega_1(E_1)$ microstates and the second system can be in any one of $\Omega_2(E_2)$. The total system can then be in any of $\Omega_1(E_1)\Omega_2(E_2)$ microstates.

If we assume that the system is in thermal equilibrium, the energies E_1 and E_2 are fixed. To continue we'll try to maximize $\Omega_1(E_1)\Omega_2(E_2)$.

$$\frac{d}{dE_1}\left\{\Omega_1(E_1)\Omega_2(E_2)\right\} = \Omega_2(E_2)\frac{d\Omega_1(E_1)}{dE_1} + \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_2}\frac{dE_2}{dE_1} = 0 \quad (18)$$

Note that $dE_1 = -dE_2$ therefore $dE_1/dE_2 = -1$, since $E = E_1 + E_2$. We can use that to rewrite the previous expression to

$$\frac{1}{\Omega_1}\frac{d\Omega_1}{dE_1} = \frac{1}{\Omega_2}\frac{d\Omega_2}{dE_2} \quad \Rightarrow \quad \frac{d\ln\Omega_1}{dE_1} = \frac{d\ln\Omega_2}{dE_2} \quad (19)$$

Let $d\ln\Omega/dE$ be identified with a temperature T such that $T_1 = T_2$. We can then define temperature by

$$\frac{1}{k_BT} = \frac{d\ln\Omega}{dE} \quad \Rightarrow \quad \frac{1}{T} = \frac{dS}{dE} \quad (20)$$

Where S is called entropy. Often we will use

$$\beta \equiv \frac{1}{k_BT} \quad (21)$$

since it is a frequently used quantity.

4.6 Ensembles

Ensembles are idealizations consisting of a large number of virtual copies of a system, considered all at once, each which represent a possible state of the real system. The main ensembles are

1. Micro canonical ensemble: an ensemble of systems that each have the same fixed energy.

2. Canonical ensemble: an ensemble of systems, each that exchange its energy with a large reservoir of heat. This fixes the temperature.

3. Grand canonical ensemble: aside from the canonical ensemble also particles can be exchanged with the reservoir. This fixes the temperature and the chemical potential.

4.7 The canonical ensemble

To examine the canonical ensemble we shall imagine a reservoir with energy $E - \epsilon$, where ϵ is the energy of the system and E the total energy. (We shall assume that for each allowed energy there is one microstate.) The probability $P(\epsilon)$ that the system has energy ϵ is proportional to $\Omega(E - \epsilon)$ times the number microstates, which is one.

$$P(\epsilon) \propto \Omega(E - \epsilon) = \Omega(E)e^{-\epsilon/k_B T} \tag{22}$$

$$P(\epsilon) \propto e^{-\epsilon/k_B T} \tag{23}$$

Which is called the **Boltzmann distribution** and $e^{-\epsilon/k_B T}$ is called the **Boltzmann factor**. If a system is in contact with a reservoir and has a microstate r, with energy E_r, then

$$P(\text{microstate } r) = \frac{e^{E_r/k_B T}}{\sum_i e^{E_i/k_B T}} = \frac{e^{E_r/k_B T}}{Z} \tag{24}$$

where Z is called the **partition function**.

5 The Maxwell-Boltzmann distribution

5.1 Multilevel systems and the Boltzmann distribution

Suppose you have a system with multiple energy levels, then the higher the state the smaller the occupancy and the higher the temperature, the more probable it is that higher states are occupied. This statement is summarized by

$$\frac{N_i}{N_j} = e^{-\frac{E_i - E_j}{k_B T}} \tag{25}$$

5.2 The velocity distribution

The velocity distribution is defined as the fraction of molecules with velocities between $\boldsymbol{v}$ and $\boldsymbol{v} + d\boldsymbol{v}$. Assuming we are only looking in one direction, say x, then the velocity distribution is given as

$$g(v_x) \propto e^{-mv_x^2/2k_B T} \quad \Rightarrow \quad g(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mv_x^2/2k_B T} \tag{26}$$

The rightmost expression is found by normalization. For this distribution we have that

$$\langle v_x \rangle = 0 \tag{27}$$

$$\langle |v_x| \rangle = \sqrt{\frac{2k_B T}{\pi m}} \tag{28}$$

$$\langle v_x^2 \rangle = \frac{k_B T}{m} \tag{29}$$

$$\tag{30}$$

Now to generalize, and go back to the original statement, between $\boldsymbol{v}$ and $\boldsymbol{v}+d\boldsymbol{v}$

$$g(v_x)\,dv_x\,g(v_y)\,dv_y\,g(v_z)\,dv_z \propto e^{-mv^2/2k_BT}\,dv_x\,dv_y\,dv_z \qquad (31)$$

5.3   The speed distribution

Now we are looking at the molecules between v and $v + dv$. Which in velocity space is a spherical shell of radius v, with thickness dv. The volume of that part of the shell is given as $4\pi v^2\,dv$. Such that the speed distribution is given as

$$f(v)\,dv \propto v^2\,dv\,e^{-mv^2/2k_BT} \qquad (32)$$

Note that the 4π is absorbed into the proportionality. Now to normalize it, integrate from 0 to ∞ (since $v > 0$):

$$\int_0^\infty f(v)\,dv = 1 \quad\Rightarrow\quad f(v)\,dv = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2}v^2\,e^{-mv^2/2k_BT}\,dv \qquad (33)$$

This expression is called the Maxwell-Boltzmann distribution. For which

$$\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}} \qquad (34)$$

$$\langle v^2\rangle = \frac{3k_BT}{m} \qquad (35)$$

$$v_{rms} = \sqrt{\langle v^2\rangle} \propto m^{-1/2} \qquad (36)$$

From this we can derive an expression for the mean kinetic energy of a gas molecule:

$$\langle T\rangle = \frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_BT \qquad (37)$$

We can also derive the value of v such that $f(v)$ is at a maximum, this is simply

$$\frac{df}{dv} = 0 \quad\Rightarrow\quad v_{max} = \sqrt{\frac{2k_BT}{m}} \qquad (38)$$

Such that $v_{max} < \langle v\rangle < v_{rms}$.