Electricity and Magnetism 2 and Statistical Thermodynamics (MP232)
Solution Assignment 4

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Ex. 4.1: The ideal gas law

In an ideal gas, pressure p, volume V and temperature T in Kelvin satisfy the *Ideal Gas Law.* We give this law below in three different forms:

$$pV = Nk_BT \quad (1)$$
$$pV = nRT \quad (2)$$
$$pV = \frac{m}{M_{mol}}RT \quad (3)$$

In the first line, N is the number of particles that make up the quantity of gas and $k_B \approx 1.38 \times 10^{-23}$ is Boltzmann's constant.
In the second line, n is the number of mol of gas and $R \approx 8.31\, J/(Kmol)$ is the gas constant.
In the third line, m is the mass of the quantity of gas and M_{mol} is the mass of one mol of gas.
The number of particles in one mol of gas is Avogadro's number $N_A \approx 6.0221 \times 10^{23}$.
For dry air, we have, $M_{mol} \approx 29\, g/mol$.

a. Check that the three forms of the ideal gas law given above are all equivalent to each other.

   We have $n = \frac{N}{N_A}$ and, as can be checked from the numerical values given, $R = N_Ak_B$, so $nRT = \frac{N}{N_A}(N_Ak_B)T = Nk_BT$ and the first and second form of the ideal gas law are equivalent. Also, the number of mol n is equal to the mass of the gas divided by the mass per mol of gas, $n = \frac{m}{M_{mol}}$, so the last form is also equivalent.

b. If we keep the temperature and the amount of gas constant, what happens to the volume if we increase the pressure by a factor α, that is $p \to \alpha p$? Why can we not expect this behavior to be true for arbitrarily large α in a real gas?

   The volume will decrease by a factor α. If $p \to \alpha p$ then since $V = \frac{nRT}{p}$, we have $V = \frac{nRT}{p} \to \frac{nRT}{\alpha p} = \frac{1}{\alpha}V$. We cannot expect the volume to decrease linearly with pressure for very high pressures and small volumes, because the particles of the gas will start interacting strongly under those circumstances. The gas may even liquify or solidiy and then the volume will change comparatively little with increasing pressure.

c. If we keep the temperature and the volume of gas constant, what happens to the pressure if we increase the amount of gas by a factor α, that is $m \to \alpha m$? Why can we not expect this behavior to be true for arbitrarily large α in a real gas?

   The pressure will increase by a factor α. If $m \to \alpha m$ then since $p = \frac{mRT}{M_{mol}V}$, the pressure will change to αp. Again for very high pressures and small volumes, the particles of the gas will interact strongly and then adding more gas at constant volume and temperature will increase the pressure much faster than it would according to the ideal gas law.

d. If we keep the volume and the amount of gas constant, what happens to the pressure if we increase the temperature from $100\,K$ to $200\,K$?

Since T (the absolute temperature, in Kelvin) doubles, so does p

e. If we keep the volume and the amount of gas constant, what happens to the pressure if we increase the temperature from $100°C$ to $200°C$?

The absolute temperature changes from $373K$ to $473K$, so the pressure increases by a factor $\frac{473}{373}$.

f. Derive a formula for the density ρ of the gas from the ideal gas law (the density is the mass per unit volume). Use this to calculate the density of dry air at a temperature of $20°C$ and at atmospheric pressure (approximately 100 kPa).

the density ρ is given by $\rho = \frac{m}{V} = \frac{pM_{mol}}{RT}$, using the third form of the ideal gas law above. For dry air, we have $M_{mol} \approx 29\,g = 0.029\,kg$. Atmospheric pressure is approximately $10^5\,Pa$. For the temperature we have $20°C \approx 293K$ and $R \approx 8.31\,J/K$. Filling this into the equation for ρ, we find that $\rho_{air} \approx 1.2\,kg/m^3$

Ex. 4.2: Maxwell-Boltzmann velocity distribution

For a gas of N particles moving in three dimensions, the Maxwell-Boltzmann velocity distribution function f is of the form $f(\mathbf{v}) = Ce^{-\frac{mv^2}{2kT}}$, where $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$ and C is a constant (independent of v)

a. Show that the constant C must be given by $C = N\sqrt{(\frac{m}{2\pi kT})^3}$.
Hint: use that $\int_{-\infty}^{\infty} e^{-ax^2}\,dx = \sqrt{\frac{\pi}{a}}$

The quantity $f(\mathbf{v})dv_xdv_ydv_z$ is the number of particles with velocities in a very small box in velocity space, of volume $dv_xdv_ydv_z$, which contains the point $\mathbf{v}$. The total number of particles N should equal the sum of this quantity over all such boxes. In other words, N equals the integral of f over all of velocity space,

$$N = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(\mathbf{v})dv_xdv_ydv_z.$$

Now, using the property that $e^{a+b} = e^ae^b$ and the fact that $v^2 = v_x^2 + v_y^2 + v_z^2$ we can write $f(\mathbf{v}) = Ce^{-\frac{mv^2}{2kT}} = Ce^{-\frac{mv_x^2}{2kT}}e^{-\frac{mv_y^2}{2kT}}e^{-\frac{mv_z^2}{2kT}}$. Substituting this in the integral above, we see that we may pull the factors which depend only on v_x and v_y out of the integral over v_z and the factor which depends only on v_x out of the integral over v_y. This gives

$$N = C\int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2kT}}\,dv_x \int_{-\infty}^{\infty} e^{-\frac{mv_y^2}{2kT}}\,dv_y \int_{-\infty}^{\infty} e^{-\frac{mv_z^2}{2kT}}\,dv_z.$$

With a bit of thought, we realize that this triple integral is just the product of the three single integrals (as the notation already suggests) and also that each of the three single integrals will yield the same answer, so in fact, we have

$$N = C\left(\int_{-\infty}^{\infty} e^{-(\frac{m}{2kT})x^2}dx\right)^3 = C\left(\sqrt{\frac{2\pi kT}{m}}\right)^3$$

where we used the standard integral given in the hint, with $a = \frac{m}{2kT}$. This finally gives $C = N\sqrt{(\frac{m}{2\pi kT})^3}$ as claimed.

b. What is the most likely value of the velocity $\mathbf{v}$?

The most likely value is the velocity $\mathbf{v}$ for which there are the most particles with velocities in a small box of volume $\mathbf{dv}$ around $\mathbf{v}$. In other words, it is the velocity for which $f(\mathbf{v})$ is maximal. We have $f(\mathbf{v}) = Ce^{-\frac{mv^2}{2kT}}$ and we see that the exponent in the exponential is always negative, unless $v^2 = 0$. Since $e^x < 1$ for $x < 0$ and $e^0 = 1$, it follows that the maximal value of f occurs when $v^2 = 0$. Since $v^2 = v_x^2 + v_y^2 + v_z^2$, we see that $v^2 = 0$ implies that $\mathbf{v} = \mathbf{0}$. In other words, the most likely velocity is $\mathbf{0}$.

c. What is the most likely value of the speed v?
Hint: there are many different velocities corresponding to the same speed. The most likely speed is the speed v for which there are the most particles with speeds between v and $v + dv$, for fixed, infinitesimally small dv.

The most likely value of the speed $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$ is the value such that there are the most particles with speeds between v and $v + dv$. Therefore, let us calculate the number of particles with speeds between v and $v + dv$. We can write this number as $g(v)\,dv$, where $g(v)$ is a new distribution function, for speed instead of velocity. All particles with speeds between v and $v + dv$ have velocity vectors that lie between the sphere of radius v and the sphere of radius $v+dv$ in velocity space. To calculate the total number of particles with velocities in any region in velocity space, we simply integrate $f(\mathbf{v})$ over that region. In this case it is not so easy to calculate the integral of $f(\mathbf{v})$ in the region between two spheres exactly, but because dv is very small, we see that $f(v)$ is nearly constant over the integration region, so we can approximate the integral as just the product of $f(\mathbf{v})$ and the volume of the region between the spheres. This volume can be calculated exactly as the difference between the volumes of balls of radii v and $v + dv$, but it is also not too difficult to see that, for very small dv, it is just $4\pi v^2\,dv$, the product of the area $4\pi v^2$ of the spere of radius v and the thickness dv of the region between the speres. So we find that

$$g(v)\,dv = 4\pi v^2 f(v)\,dv$$

or

$$g(v) = 4\pi C v^2 e^{-\frac{mv^2}{2kT}}$$

The most likely speed is the speed for which $g(v)$ is maximal. To find out where g is maximal, we differentiate g with respect to v and set the result equal to zero. This gives

$$0 = \partial_v g = 4\pi C\left(2v - \frac{2mv^3}{2kT}\right)e^{-\frac{mv^2}{2kT}}.$$

Since the exponential is never zero, we find that $v - \frac{mv^3}{2kT} = 0$ and so $v = 0$ or $v^2 = \frac{2kT}{m}$ which would imply $v = \sqrt{\frac{2kT}{m}}$. It is now not so difficult to see (for example by making a sketch of $g(v)$) that the maximum of $g(v)$ is actually at the nonzero value, $v_{ml} = \sqrt{\frac{2kT}{m}}$. In fact, at $v = 0$, we have $g(v) = 0$. The reason the most likely speed is not at zero, like the most likely velocity, is because, even though any particular velocity with speed v_{ml} is less likely to occur than a velocity near $\mathbf{v} = \mathbf{0}$, there are many more velocities corresponding to nonzero speeds than there are corresponding to speeds near zero.

d. What is the most likely value of the kinetic energy $\frac{1}{2}mv^2$ of a single particle? Does it correspond to the kinetic energy of a particle at the most likely speed?

The kinetic energy of a particle is $E = \frac{1}{2}mv^2$. The most likely kinetic energy is the energy E such that there are the largest number of particles with energies between E and $E+dE$. We can write this number as $h(E)\,dE$, where $h(E)$ is another new distribution function, for energy instead of speed or velocity. Particles with energies between E and $E+dE$ have speeds between $\sqrt{2E/m}$ and $\sqrt{2(E+dE)/m}$, since $E = \frac{1}{2}mv^2$ implies $v = \sqrt{2E/m}$. Since dE is very small, we can replace the square root by its first order Taylor expansion, which gives

$$\sqrt{2(E+dE)/m} = \sqrt{2E/m}\sqrt{1+\frac{dE}{E}} \approx \sqrt{2E/m}\left(1+\frac{dE}{2E}\right) = \sqrt{2E/m} + \frac{dE}{\sqrt{2mE}}$$

We must calculate the number of particles with speeds between $v(E) = \sqrt{2E/m}$ and $v(E+dE) = \sqrt{2E/m} + \frac{dE}{\sqrt{2mE}} = v(E) + \frac{dE}{mv(E)}$. We can do this as in the previous part, by integrating f over the region in velocity space between spheres of radii $v(E)$ and $v(E+dE)$. The distance between these spheres now depends on v, it is $\frac{dE}{mv(E)}$. For small dE, we see that the number of particles we are looking for is given by $h(E)dE = g(v(E))\frac{dE}{mv(E)}$, so $h(E) = \frac{g(v(E))}{mv(E)} = \frac{g(v(E))}{\sqrt{2mE}}$. Here $g(v)$ is the distribution function for speeds introduced in the previous part and substituting $g(v) = 4\pi C v^2 e^{-\frac{mv^2}{2kT}} = \frac{8\pi C}{m} E e^{-\frac{E}{kT}}$, we find that

$$h(E) = 4\sqrt{2}\frac{\pi C}{m\sqrt{m}}\sqrt{E}e^{-\frac{E}{kT}}$$

To find the most likely energy, we find the maximum of $h(E)$. At the maximum, we have

$$0 = \partial_E h = \frac{4\sqrt{2}\pi C}{m\sqrt{m}}\left(\frac{1}{2\sqrt{E}} - \frac{\sqrt{E}}{kT}\right)e^{-\frac{E}{kT}}.$$

This happens only when $E = \frac{kT}{2}$ and so the most likely energy is $E_{ml} = \frac{kT}{2}$. The corresponding velocity is $\sqrt{\frac{2E_{ml}}{m}} = \sqrt{\frac{kT}{m}}$. This is smaller than the most likely velocity $v_{ml} = \sqrt{\frac{2kT}{m}}$. The difference is caused by the fact, for given dE and dv, the volume available in velocity space for particles with energies between E and $E+dE$ grows more slowly with E than the velocity space volume for particles with speeds between v and $v+dv$ grows with v.
A faster but perhaps less insightful way to do the same thing is this. We have

$$g(v)\,dv = g(\sqrt{2E/m})\frac{dv}{dE}\,dE = g(\sqrt{2E/m})\frac{d\sqrt{2E/m}}{dE}\,dE = \frac{g(\sqrt{2E/m})}{\sqrt{2mE}}dE$$

This gives the same function $h(E)$ as before and the rest of the calculation is then unchanged .