Boltzmann factor

Everybody knows that air is rarer at higher place such as Mountain Everest. But, why? This is the question we will answer in this article.

See the figure. Inside air, we have designated an imaginary box, with area A and very small height Δh. Right below the box we have pressure P and right above the box we have pressure $P + \Delta P$. The difference is due to the weight of the air; PA must be bigger than $(P + \Delta P)A$ by the weight of the air inside the imaginary box for the force to be balanced. To obtain the weight of the air, let's recall Boyle-Charles law, which is slightly modified for our purpose here:

$$\frac{P}{kT} = \frac{N}{V} \tag{1}$$

This gives the number of molecules per unit volume. Then, as the volume in our case is $A\Delta h$, the number of molecules inside the box is given by following:

$$\frac{P}{kT} A\Delta h \tag{2}$$

Therefore, the weight is given by:

$$(\frac{P}{kT} A\Delta h)mg \tag{3}$$

Tying everything together, we have:

$$PA - (P + \Delta P)A = (\frac{P}{kT} A\Delta h)mg \tag{4}$$

$$\Delta P/P = -mg/kT\Delta h \tag{5}$$

Changing Δ to infinitesimal d, and integrating both-hand sides we have:

$$\ln P/P_0 = -mgh/kT \tag{6}$$

which implies:

$$P = P_0 \exp{(-mgh/kT)} \tag{7}$$

Now notice that (1) implies that the air density is proportional to the pressure. (In this article, we are assuming that the temperature is same.) Therefore, if we denote the air density by ρ we have:

$$\rho = \rho_0 \exp{(-mgh/kT)} \tag{8}$$

Now, we see that the higher the altitude the rarer the air. Notice that mgh is the potential energy. If we call this E, we can re-write the above equation as follows:

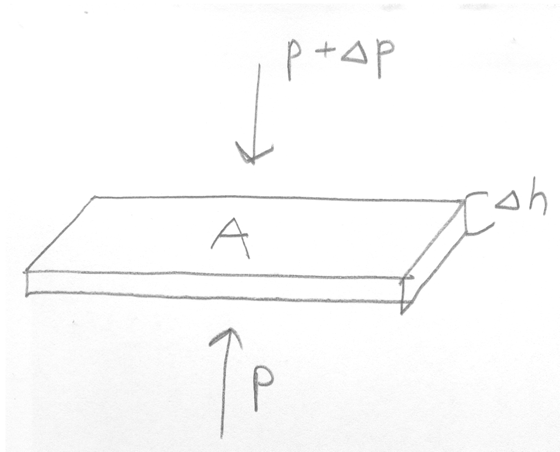

Figure 1: pressure balanced

$$\rho = \rho_0 \exp\left(-E/kT\right) \tag{9}$$

It clearly shows that air is rarer in higher altitude because of the high potential energy of the molecule. In all these derivations, we assumed that the temperature is constant for simplicity and clarity, but we could have obtained a more general formula, which is of no interest in this article. In any case, $\exp(-E/kT)$ is called "Boltzmann factor" and we will re-obtain this formula rigorously in our later article "Boltzmann factor" in the section "Statistical Mechanics."

Problem 1. A nitrogen molecule is heavier than an oxygen molecule. Given this, how does the ratio of nitrogen to oxygen change as you go high up in the sky? Does it increase or decrease?

Summary

- The higher altitude, the rarer the air, because of the higher potential energy of the air molecule. The Boltzmann factor $\exp(-E/kT)$ tells us that the higher the energy, the rarer the particles.