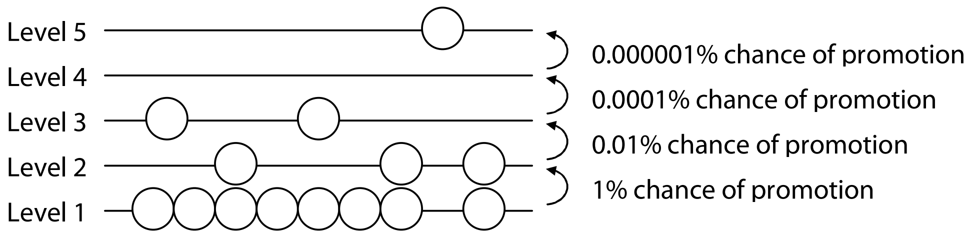
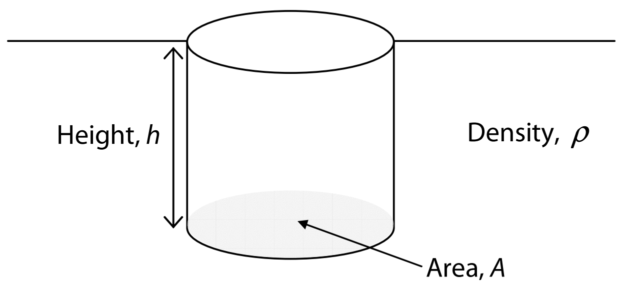
Maxwell-Boltzmann distribution



In the simple model already discussed for energy levels there are a given number of distinct levels, and the chance of promotion from one level to another can be modelled by a probability, say 1% with exponential decrease. Only a tiny proportion of molecules get enough energy to participate in processed involving overcoming an energy barrier.

The pressure due to a fluid



Consider a cylinder within a fluid. For equilibrium of area *A*, the weight of fluid above *A* must be equal to the pressure upward times area *A*. (*p* is the pressure exerted by the cylinder on the base, equal to height *h* times density ρ times gravity *g*.)

Weight of fluid above area A $\quad pA$

$$mg \quad pA$$

But $m \quad \rho Ah$

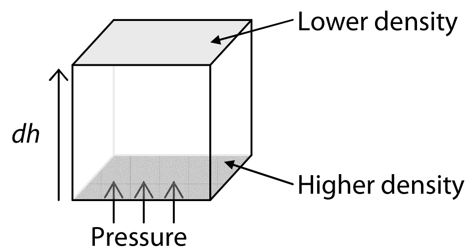
So $\rho Ahg \quad pA$

$$p \quad h\rho g$$

The behaviour of the atmosphere as an example of the Maxwell-Boltzmann distribution

A model for the distribution of molecules in an isothermal (constant temperature) atmosphere (i.e. molecules higher up require a greater GPE (gravitational potential energy) and so there are fewer of them).

Consider part of the atmosphere.



dh[*] is a small increase in the height of the atmosphere.

$$\text{Given } pV \quad NkT \qquad p \quad \tfrac{N}{V} kT$$
$$p \quad nkT$$

Where *n* here is not the number of moles but the number density, the number of moles per unit of volume.

$$dp \quad kT \; dn$$

dp is a small change in pressure and is *kT* times the small change in the number density.

As earlier $p \quad h\rho g$ so $dp \qquad \rho g \;\; dh$ as a small change in height upwards will result in a lower pressure (so there is a negative sign), but $\rho \quad nm$ (where *n* is the number density and *m* the mass of one molecule, so *nm* is the density, the mass per unit volume) so $dp \qquad nmg \;\; dh$.

$$\begin{matrix} dp \quad kT \;\; dn \\ dp \qquad nmg \;\; dh \end{matrix} \qquad kT \;\; dn \qquad nmg \;\; dh$$

Dealing with the expression $kT \;\; dn \qquad nmg \;\; dh$ can be done below (Mathematics module P3 – separable variables integration).

$$kT \;\; dn \qquad nmg \;\; dh$$
$${}^{n}_{n_0} \frac{1}{n} \; dn \qquad {}^{h}_{0} \frac{mg}{kT} \;\; dh$$
$$\ln n \, {}^{n}_{n_0} \qquad \frac{mgh}{kT} \, {}^{h}_{0}$$
$$\ln \frac{n}{n_0} \qquad \frac{mgh}{kT}$$
$$\frac{n}{n_0} \quad e^{\frac{mgh}{kT}}$$

Where n_0 is the concentration at the bottom (shown darker grey on initial diagram) and *n* the concentration at the top. *h* is the height at the top and 0 is the initial height (so *h* represents increase in height).

The ratio of the number of molecules at a higher level to those at a lower level depends on the ratio of *mgh*, the gravitational potential energy, to *kT*, the thermal energy.

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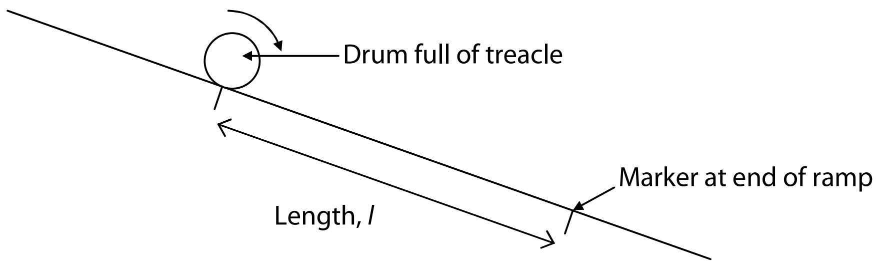
[*] *dh* can be thought of as a mathematical sophistication of the concept of h, a change in height. This is true for all other uses of the letter *d* in this document.

To turn this into a general statement (not just about the atmosphere and energy barriers of gravitational nature), replace *mgh* by *E*, energy. Therefore, for a population of two levels, separate by an energy gap *E*, $\frac{n}{n_0} \quad e^{\frac{E}{kT}}$.

Further examples



An energy barrier is created by the hexagonal shape of glucose molecules creating a barrier for neighbouring molecules to pass each other. Recording the time taken for the drum to roll down the ramp when full of treacle, then with maple syrup (at room temperature, 24°C) and then after being heated to 55°C we get the following results.

Temperature / °C	**Time / s**	
	Maple Syrup	**Treacle**
24	2.62	27.9
55	2.44	19.9

To calculate activation energy E *next lesson.*

These notes are from a lesson on 26/11/2004.