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Lect 2. Boltzmann and Maxwell distributions

1. Boltzmann distribution — gas in a gravity field

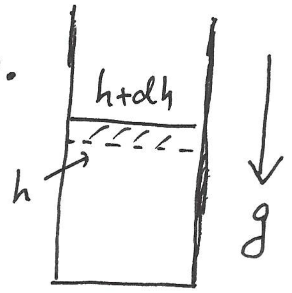
2. From Boltzmann $\longrightarrow$ Maxwell distribution

3. Gaussian integral

4. Probability distribution function

§ Boltzman distribution

- Consider a gas in the gravity field at thermal equilibrium. The temperature is the same, but the density may not be uniform. The pressure difference between the height h and $h+dh$, is due to the gravity of gas molecule within the thickness of dh.



$$p(h) - p(h+dh) = mng\,dh = -\frac{dP}{dh}\,dh$$

$$P(h) = n(h)\,k_B T \Rightarrow \frac{dP}{dh} = \frac{dn}{dh}\,k_B T \Rightarrow \frac{dn}{dh} = -\frac{1}{k_B T}\,mng$$

$$\frac{1}{n}\frac{dn}{dh} = -\frac{mg}{k_B T} \Rightarrow \frac{d\ln n}{dh} = -\frac{mg}{k_B T}$$

$$n = n_0\, e^{-\frac{mgh}{k_B T}}$$

Here, "mgh" can be viewed as the gavity potential energy, which can be generalized to other potential, say, electric potential energy, etc.

Then a characteristic height $h_0 = \frac{k_B T}{mg}$ can be defined.

$$\boxed{h_0 = \frac{k_B T}{mc^2} \cdot c^2/g}$$

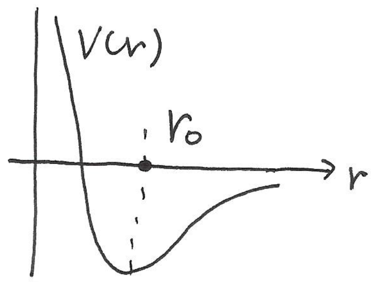
$T = 300K$

$m: O_2 \approx 32\,\text{GeV} \approx 3\times10^{10}\,\text{eV} \sim 3\times10^{14}\,\text{K}$

$$\Rightarrow h_0 \approx \frac{3\times10^2}{3\times10^{14}} \times 10^{16} \qquad c^2/g \approx \frac{9\times10^{16}}{10} \sim 10^{16}\,\text{m}$$

$\approx 10^4\,\text{m}$. $\Rightarrow$ O_2 density reduces to $1/e \approx 37\%$ at 10km height!

• intermolecular interaction



In gases, the interactions among gas molecules can often be neglected, but in liquids they cannot be neglected. The interactions are typically pair-wised,

Then the probability for find a configuration with the intermolecule distance r_{ij},

$$P(\{r_{ij}\}) \propto e^{-\sum_{i,j} V(r_{ij})/k_B T}.$$

If $k_B T \leq |V(r_0)|$, the relative probability to find a molecules at small distances around r_0 will be large. The system could be in a liquid state. On the other hand, if $k_B T \geq |V(r_0)|$, the molucles will tend to go at large distance, since there are more volume.

and $\int d^3\vec{r}_1 \ldots d^3\vec{r}_N$ (the integral measures are large at r_{ij} is large).

Say, for 2 molecules $\int d^3\vec{r}_1 \int d^3\vec{r}_2 = \int d^3\vec{R} \int d^3\vec{r}$, and $\int d^3\vec{r} = \int r^2 dr \int d\Omega$.

Hence, as varying temperture, the interaction $\sum_{i<j} V(r_{ij})$ could have different effect. At high temperatures, the inter-molecular distance in large, the system is a gas. While as temperature goes down, interactions will reorganize them to favor $V(r_{ij})$ reaching minima. The system would go to liquid, and even solid. This is a complicated problem

— "many body problem" or "a condensed matter physics".

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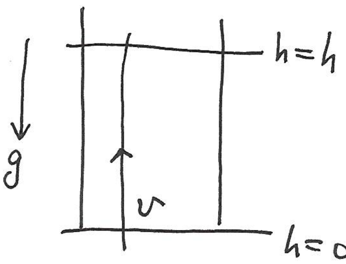
§ Maxwell distribution

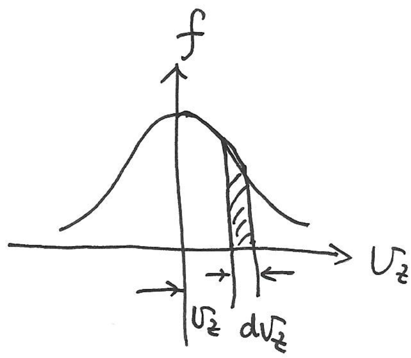
We have derived Maxwell's distribution in HW. Now let us examine it from a different viewpoint. Consider a gas in the gravity field.

- Define $\ell(h, v_z)$ is the number of molecules per unit time per unit volume passing the horizontal plane at the height of h with the vertical velocity larger than v_z.



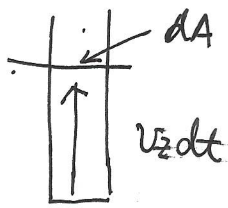
- Define the distribution function $f(v_z)$, satisfying $\boxed{\int_{-\infty}^{+\infty} dv_z\, f(v_z) = 1}$,

  $f(v_z)\,dv_z$: the probability for a molecule's v_z lying from v_z to $v_z + dv_z$



$$d(\#\text{ of molecules}) = dA\, dt\, v_z\, n(h)\, f(v_z) dv_z$$

$$\boxed{\ell(h, v_z) = n(h) \int_{v_z}^{+\infty} dv_z \quad v_z\, f(v_z)}$$



Hence,

$$\boxed{\frac{\ell(h,\, v_z = 0)}{\ell(h=0,\, v_z = 0)} = \frac{n(h)}{n(h=0)}}$$

where $n(h)$ is the molecule density at the height h.

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At $h=0$, if the molecule's velocity $v_z > u = \sqrt{2gh}$, then it can pass the height h with non-zero vertical velocity >0. Then

$$l(0,u) = l(h,0) \quad \text{with } \frac{1}{2}mu^2 = mgh \text{ and } u>0.$$

$$\Rightarrow \frac{l(0,u)}{l(0,0)} = \frac{l(h,0)}{l(0,0)} = \frac{n(h)}{n(0)} = e^{-mgh/k_BT} = e^{-\frac{1}{2}mu^2/k_BT}$$

$$\Rightarrow \text{define } F(u) = \int_u^{+\infty} dv_z\, v_z f(v_z) = C\, e^{-\frac{1}{2}mu^2/k_BT},$$

with $C = F(u=0)$ is a constant.

$$\text{Then } \frac{dF(u)}{du} = -u f(u) = -muC\, e^{-\frac{1}{2}mu^2/k_BT}$$

$$\Rightarrow f(u) \propto e^{-\frac{1}{2}mu^2/k_BT}.$$

$$\text{or } f(v_z) = \frac{e^{-\frac{\beta}{2}mv_z^2}}{\int_{-\infty}^{+\infty} dv_z\, e^{-\frac{\beta}{2}mv_z^2}} \quad \text{with } \beta = \frac{1}{k_BT}.$$

* Knowledge of Gaussian integral

$$a = \int_{-\infty}^{+\infty} dx\, e^{-x^2} \Rightarrow a^2 = \int_{-\infty}^{+\infty} dx\, dy\, e^{-(x^2+y^2)} = \int_0^{+\infty} r\,dr\,d\theta\, e^{-r^2}$$

$$= \frac{1}{2}\int_0^{+\infty} dy\, e^{-y} \cdot 2\pi = \pi$$

$$\Rightarrow \int_{-\infty}^{+\infty} dx\, e^{-x^2} = \sqrt{\pi}$$

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$$\int_{-\infty}^{+\infty} dx\, e^{-ax^2} = \int_{-\infty}^{+\infty} \frac{dy}{\sqrt{a}}\, e^{-y^2} = \sqrt{\frac{\pi}{a}} \Rightarrow \int_{-\infty}^{+\infty} dv_z\, e^{-\frac{\beta m}{2} v_z^2} = \sqrt{\frac{2\pi}{m\beta}}$$

$y = \sqrt{a}\, x$

define $f(a) = \int_{-\infty}^{+\infty} dx\, e^{-ax^2} \Rightarrow \frac{df(a)}{da} = -\int_{-\infty}^{+\infty} dx\, x^2 e^{-ax^2} = -\frac{1}{2}\frac{\sqrt{\pi}}{a^{3/2}}$

$$\Rightarrow \boxed{\int_{-\infty}^{+\infty} dx\, x^2 e^{-ax^2} = \frac{\pi^{1/2}}{2a^{3/2}}}$$

* **Maxwell distribution summary**

$$f(v_z) = \left(\frac{2\pi}{m\beta}\right)^{-1/2} e^{-\frac{\beta}{2} m v_z^2}$$

$$\Rightarrow f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{\beta}{2} m (v_x^2 + v_y^2 + v_z^2)}.$$

$$\boxed{\int dv_x = \int \frac{dp_x}{m}.}$$

or we switch to momentum p_x, p_y, p_z

$$\boxed{f(p_x, p_y, p_z) = \left(\frac{1}{2\pi m k_B T}\right)^{3/2} e^{-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)}}$$

$$\int_{-\infty}^{+\infty} dp_x\, dp_y\, dp_z\, f(p_x, p_y, p_z) = 1$$

$\vec{p} = (p_x, p_y, p_z)$

$f(p_x, p_y, p_z)\, dp_x\, dp_y\, dp_z$

probability lying in this volume element in momentum space

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x Distribution of speed u

$$\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int dv_x dv_y dv_z \; e^{-\frac{m}{2k_BT}(v_x^2+v_y^2+v_z^2)^2} = 1$$

$$\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_0^{+\infty} v^2 dv \int d\Omega \; e^{-\frac{m}{2k_BT}v^2} = \int_0^{+\infty} dv \; e^{-\frac{mv^2}{2k_BT}} \cdot v^2 \cdot (4\pi)\left(\frac{m}{2\pi k_BT}\right)^{3/2} = 1$$

$$\Rightarrow \boxed{f(v) = v^2 e^{-\frac{mv^2}{2k_BT}} \cdot \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_BT}\right)^{3/2}}$$