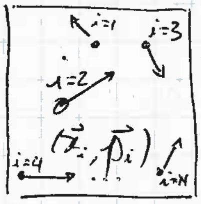
3-4. 理想気体

2012-05-18

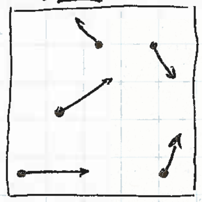
$$\mathcal{H} = \frac{1}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2}$$

(体積 V の容器の中)

名前を付けた配位は $N!$ 通り出てくる。



$i=1,\dots,N$



同種粒子は区別しない

$$Z = \sum_{\boxed{\text{ALL STATES}}} e^{-\beta\mathcal{H}} = C\frac{1}{N!}\int_V d\vec{x}_i \int d\vec{p}_i\, e^{-\beta\mathcal{H}}$$

$$= C\left[\int_V dx_i\,dy_i\,dz_i \int dp_i^x\,dp_i^y\,dp_i^z\right] e^{-\beta\frac{1}{2m}\left(p_1^{x\,2}+\cdots+p_N^{z\,2}\right)}$$

$$= CV^N\left[\int_{-\infty}^{\infty} dp_i^x\, e^{-\beta\frac{1}{2m}(p_i^x)^2}\right]^{3N} = CV^N\left(\sqrt{2\pi m k_B T}\right)^{3N}$$

$$= CV^N(2\pi m k_B T)^{3N/2} = C\frac{V^N}{N!}(2\pi m k_B T)^{\frac{3N}{2}} \approx C\frac{V^N}{N^N e^{-N}}(2\pi m k_B T)^{\frac{3N}{2}} \quad \cdots (*)$$

$$F = -k_B T \ln Z = -k_B T\left\{\ln C + N\ln V + \frac{3N}{2}\ln(2\pi m k_B T)\right\}$$

$$\frac{\partial F}{\partial V} = -P = -k_B T N\frac{1}{V} \implies PV = Nk_BT$$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = -\frac{3N}{2}\frac{\partial}{\partial\beta}\ln\frac{1}{\beta} = \frac{3N}{2}\frac{1}{\beta} = \frac{3N}{2}k_BT$$

気体定数 $R = N_A k_B \longrightarrow \langle E\rangle = \frac{3}{2}\underset{\text{モル数}}{n}RT$

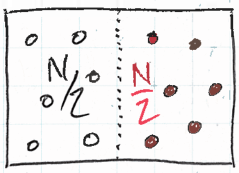
$$S = \frac{\langle E\rangle - F}{T} = \frac{3}{2}Nk_B + k_B\left\{\ln C + \underline{N\ln V} + \frac{3N}{2}\ln(2\pi m k_B T)\right\}$$

密度: $\rho = \frac{N}{V}$ を一定にして N を変化: $k_B N\ln\rho \sim \underset{?}{\underline{N\ln N}}$

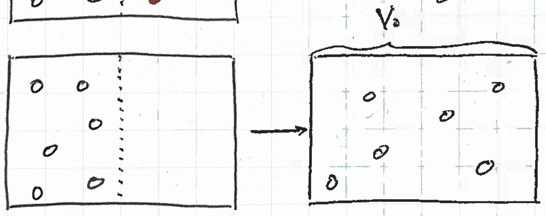
$$(*) \implies Z = C\left(\frac{V}{N}\right)^N (2\pi m k_B T)^{\frac{3}{2}N} e^N \implies F = -k_BT\left\{\ln C + N\ln\left(\frac{V}{N}\right) + \frac{3}{2}N\ln(2\pi m k_B T) + N\right\}$$

ギブスのパラドックス

$\boxed{PV=Nk_BT}$



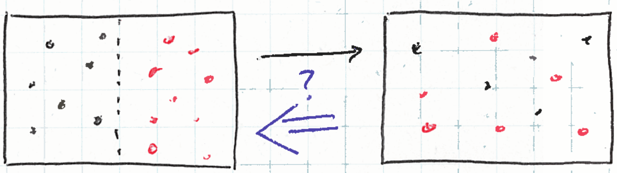
$$\Delta S=\int_{\frac{V_0}{2}}^{V_0}\left(\frac{\partial S}{\partial V}\right)dV=\int_{\frac{V_0}{2}}^{V_0}\left(\frac{\partial P}{\partial T}\right)dV \overset{\downarrow}{=} \int_{\frac{V_0}{2}}^{V_0}\frac{Nk_B}{2V}\,dV$$



$$=\frac{N}{2}k_B\ln V\Big|_{\frac{V_0}{2}}^{V_0}=\frac{N}{2}k_B\ln 2$$

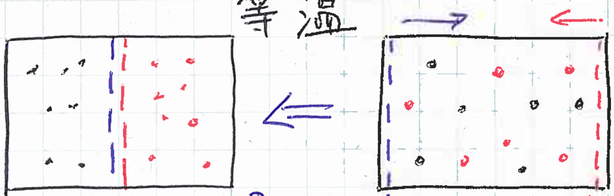
$$\Delta S=Nk_B\ln 2$$

自由膨張



$\Delta S=Nk_B\ln 2$ …混合のエントロピー

等温



黒だけ通す A　　B 赤だけ通す

分離に必要な仕事

Aのする仕事：$\displaystyle\int_{V}^{\frac{V}{2}}P\,dV=\int_{V}^{\frac{V}{2}}\frac{N}{2}\frac{k_BT}{V}dV=\frac{N}{2}k_BT\ln 2$

赤粒子の圧力 $P=\frac{N/2}{V}k_BT$

Bのする仕事：　………　$\frac{N}{2}k_BT\ln 2$

$$\Longrightarrow \Delta W=Nk_BT\ln 2=T\Delta S$$

3-5. Maxwell-Boltzmann 分布

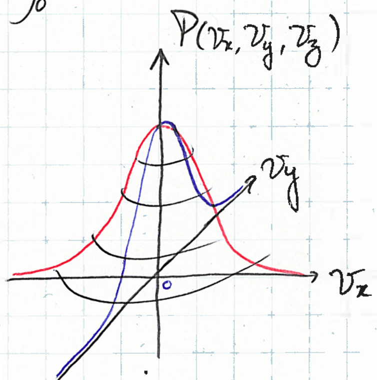
$$P(v_x, v_y, v_z)\,dv_x dv_y dv_z \propto e^{-\frac{m}{2k_BT}(v_x^2+v_y^2+v_z^2)}$$

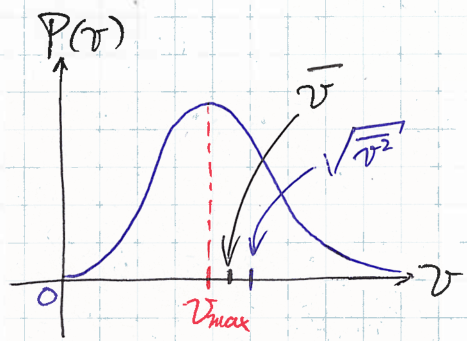
$$= \left(\sqrt{\frac{m}{2k_BT\pi}}\right)^3 e^{-\frac{m}{2k_BT}(v_x^2+v_y^2+v_z^2)} dv_x dv_y dv_z$$

$$P(v)\,dv = 4\pi v^2 \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{m}{2k_BT}v^2} dv$$

v: 速さ $=\sqrt{v_x^2+v_y^2+v_z^2}$; $dv_x dv_y dv_z = v\sin\theta\, d\phi\, v\, d\theta\, dv$

$$\int_0^{\pi} d\theta \int_0^{2\pi} d\phi\; v^2 \sin\theta\, dv = 4\pi v^2 dv$$





$$\bar{v} = \int_0^\infty v P(v)\, dv = \int_0^\infty 4\pi v^3 \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{m}{2k_BT}v^2} dv$$

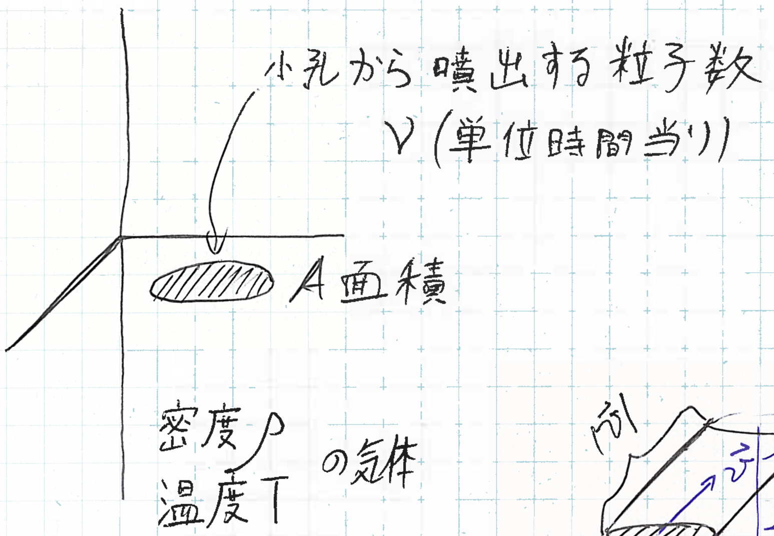
$$= \sqrt{\frac{8k_BT}{m\pi}}$$

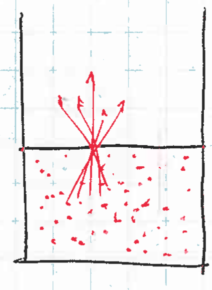
$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \;;\; \int_{-\infty}^{\infty} x e^{-ax^2} dx = \cdots \;;\; \begin{cases} \int_{-\infty}^{\infty} x^{2n+1} e^{-ax^2} dx = \cdots \\ \int_{-\infty}^{\infty} x^{2n} e^{-ax^2} dx = \cdots \end{cases}$$

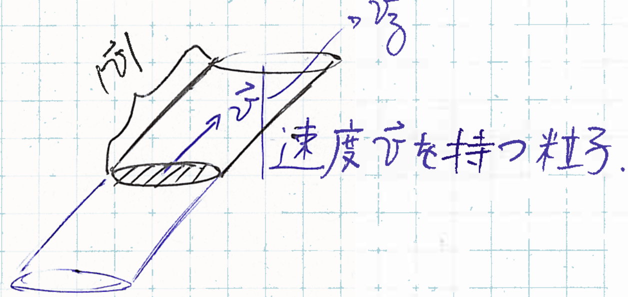
$$\overline{v^2} = \int_0^\infty v^2 P(v)\, dv = \frac{3k_BT}{m}$$

$$\frac{\partial P(v)}{\partial v} = 0 \Rightarrow v_{max} = \sqrt{\frac{2k_BT}{m}}$$

KNUDSEN の実験







$$\nu = \rho A \int_0^\infty dv_z \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \; v_z \, e^{-\frac{m}{2k_BT}(v_x^2+v_y^2+v_z^2)}$$

$$= \rho A \sqrt{\frac{k_B T}{2\pi m}} \propto \sqrt{T}$$

$$\uparrow$$

$$(PV = Nk_BT)\ \rho = \frac{N}{V}$$