Partition Function $Z = \sum_{i=1}^{\Omega} e^{-\frac{E_i}{k_B T}}$

Internal energy: $U = -\frac{\partial}{\partial \beta} \ln(Z)$

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$-\frac{\ln(Z)}{\beta} = F = A =$ Helmholtz Free Energy.

$F = -k_B T \ln(Z)$

$\Rightarrow Z = e^{-\beta F} = e^{-\frac{F}{k_B T}}$

Proof: $F = U - TS$ (Legendre Transformation)

$dF = -S\,dT - p\,dV + \mu\,dN$

$-S = \left(\frac{\partial F}{\partial T}\right)_{VN}$ $\quad \left(\frac{\partial F}{\partial V}\right)_{TN} = -p$ $\quad \left(\frac{\partial F}{\partial N}\right)_{TV} = \mu$

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$\left(\frac{\partial F}{\partial T}\right)_{VN} = -S = \frac{F-U}{T}$

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$F = A = \frac{-\ln(Z)}{\beta} = -k_B T \ln(Z)$

$\left(\frac{\partial A}{\partial T}\right)_{VN} = -k_B \ln(Z) - k_B T \frac{\partial}{\partial T} \ln(Z)$

$$\left(\frac{\partial A}{\partial T}\right)_{VN} = -k_B \ln(Z) - k_B T \left(\frac{\partial \beta}{\partial T}\right) \frac{\partial}{\partial \beta} \ln(Z)$$

$$\frac{\partial \beta}{\partial T} = \frac{\partial}{\partial T}\left(\frac{1}{k_B T}\right) = \frac{-1}{k_B T^2}$$

$$= -k_B \ln(Z) + \frac{k_B}{T} \frac{\partial}{\partial \beta} \ln(Z)$$

$$= \frac{A}{T} - \frac{U}{T} = \frac{A-U}{T}$$

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Maxwell-Boltzmann — distribution of speeds of molecules in an ideal gas at temp. $T$.

equipartition theorem: $\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} k_B T$

$v_x^2 + v_y^2 + v_z^2$

$$v_{rms} = \sqrt{\frac{3 k_B T}{m}}$$

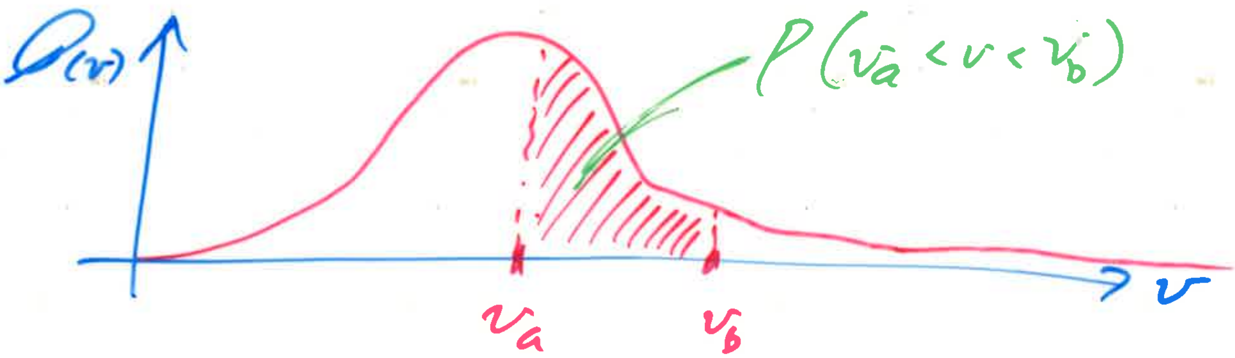
root mean square

not all molecules are traveling at $v_{rms}$

We seek a probability density function

$\frac{dP}{dv} = \rho(v)$ whose integral gives the probability of finding a value between $v_a$ and $v_b$.

$$P(v_a \le v \le v_b) = \int_{v_a}^{v_b} \rho(v)\, dv$$




e.g. The probability of finding a molecule moving with speed $v_c = 13.8721900\ldots$ m/s $= 0$

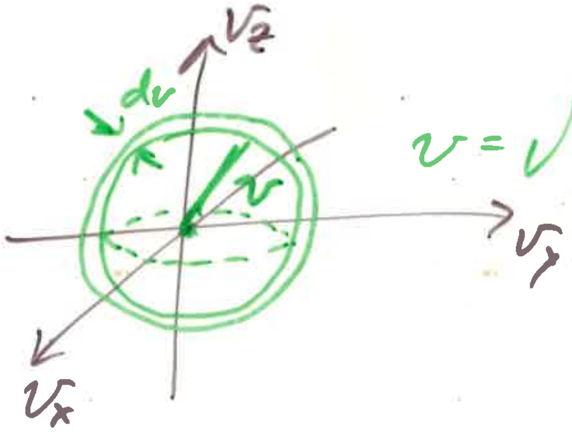
$$P(v = v_c) = \int_{v_c}^{v_c} \rho(v)\, dv = \emptyset$$

$P$ is dimensionless

$\rho(v)$ has dimension $\frac{T}{L}$, MKS unit $\frac{s}{m}$

$$\wp(v)\,dv = (\text{Normalization})\begin{pmatrix}\text{Probability of molecule}\\ \text{having velocity } \vec{v}\end{pmatrix}\begin{pmatrix}\text{number of vectors}\\ \vec{v} \text{ corresponding}\\ \text{to speed } v\\ \text{in 3 dimensions}\end{pmatrix} dv$$

$$= N \cdot e^{\frac{-\frac{1}{2}mv^2}{k_B T}}\, 4\pi v^2\, dv \qquad v^2 = \vec{v}\cdot\vec{v}$$




$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$

Get $N$ from unitarity

$$P(0 \le v < \infty) = 1 = \int_{v=0}^{\infty} \wp(v)\,dv$$

$$1 = \int_{v=0}^{\infty} N \exp\left[\frac{-\frac{1}{2}mv^2}{k_B T}\right] 4\pi v^2\, dv$$

$$\Longrightarrow N = \left(\frac{m}{2\pi k_B T}\right)^{3/2}$$

$$\mathcal{P}(v)\,dv = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left[\frac{-\frac{1}{2}mv^2}{k_B T}\right] 4\pi v^2\,dv$$


low $v$, $\frac{1}{2}mv^2 \ll k_B T$

high $v$ $\frac{1}{2}mv^2 \gg k_B T$

To find $v_{max}$: $\frac{d\mathcal{P}(v)}{dv} \overset{!}{=} 0 \Rightarrow v_{max} = \sqrt{\frac{2k_BT}{m}}$

most likely speed most likely velocity vector is zero $= \vec{v}$.

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Average speed: $\bar{v} = \int_{v=0}^{\infty} v\,\mathcal{P}(v)\,dv = \sqrt{\frac{8}{\pi}\frac{k_BT}{m}}$

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rms speed $v_{rms} = \sqrt{\int_{v=0}^{\infty} v^2\,\mathcal{P}(v)\,dv} = \sqrt{\frac{3k_BT}{m}}$