Chapter 3.8: Quantized rotation

0.) Kinetic degrees of freedom

$$Z_1 = \frac{V}{\lambda_T^3} \qquad \lambda_T = \sqrt{\frac{2\pi}{m k_B T}}$$

Possible internal degrees of freedom of gases

1.) Rotations

classically $\varepsilon_{rot} = \frac{\vec{L}^2}{2I}$ $\vec{L}$ = angular momentum

2.) Vibrations

classically $\varepsilon_{vib} = \frac{\Delta p^2}{2m} + \frac{1}{2} m \omega^2 \Delta x^2$

3.) Spin $\hat{\vec{S}}$ $\rightarrow$ magnetic moment $\vec{\mu} = g \mu_B \vec{S}$ $\rightarrow$ later

$$H_B = -\vec{\mu} \cdot \vec{B} \qquad H_{int} = J \vec{S}_A \cdot \vec{S}_B$$

4) Electronic excitation

very high energy $\rightarrow$ ignored for gases

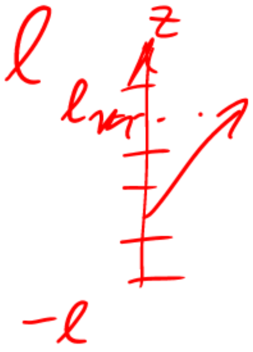
Quantum description of angular momentum

total angular momentum $\hat{L}^2 = \hbar^2 \ell(\ell+1)$

$\ell = 0, 1, 2, 3, \ldots$

$$\varepsilon_\ell = \frac{\hat{L}^2}{2I} \quad \to \quad \frac{\hbar^2 \ell(\ell+1)}{2I}$$

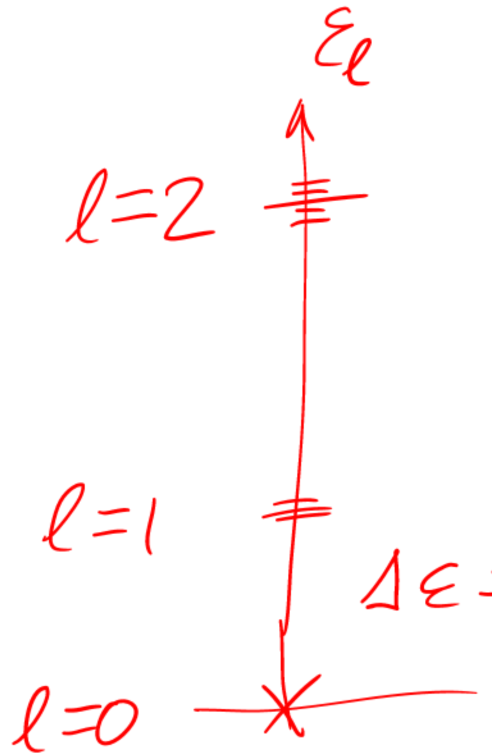
direction $-\ell \le m \le \ell$



$2\ell+1$ "directional" states (degenerate)

$$Z_{rot} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} e^{-\beta \varepsilon_\ell}$$

$$= \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\ell(\ell+1)\frac{\Theta_{rot}}{T}}$$



$\Delta\varepsilon = 2k_B\Theta_{rot}$

rotational temperature scale

$$\Theta_{rot} = \frac{\hbar^2}{2Ik_B}$$

if $T \gg \Theta_{rot}$ $\to$ integral

if $T \ll \Theta_{rot}$ $\to$ sum

Sum cannot be expressed exactly as simple functions

Maclaurin Series

$$Z_{rot} = \sum_{\ell=0}^{\infty} f(\ell) \simeq \int_0^{\infty} d\ell\, f(\ell) + \frac{f(0)}{2} - \frac{f'(0)}{12} + \frac{1}{720} f'''(0) + \ldots$$

$$f(\ell) = (2\ell+1)\, e^{-\ell(\ell+1)\Theta_{rot}/T}$$

$$f(0) = 1;\quad f'(0) = 2 - \frac{\Theta_{rot}}{T};\quad f'' \ldots$$

$$x = \ell(\ell+1)$$

$$dx = (2\ell+1)\, d\ell$$

$$\int_0^{\infty} d\ell\, f(\ell) = \int_0^{\infty} dx\, e^{-x\frac{\Theta_{rot}}{T}} = \frac{T}{\Theta_{rot}}$$

expansion requires higher orders

$$\ln(1+\varepsilon) \simeq \varepsilon - \frac{\varepsilon^2}{2} + \ldots$$

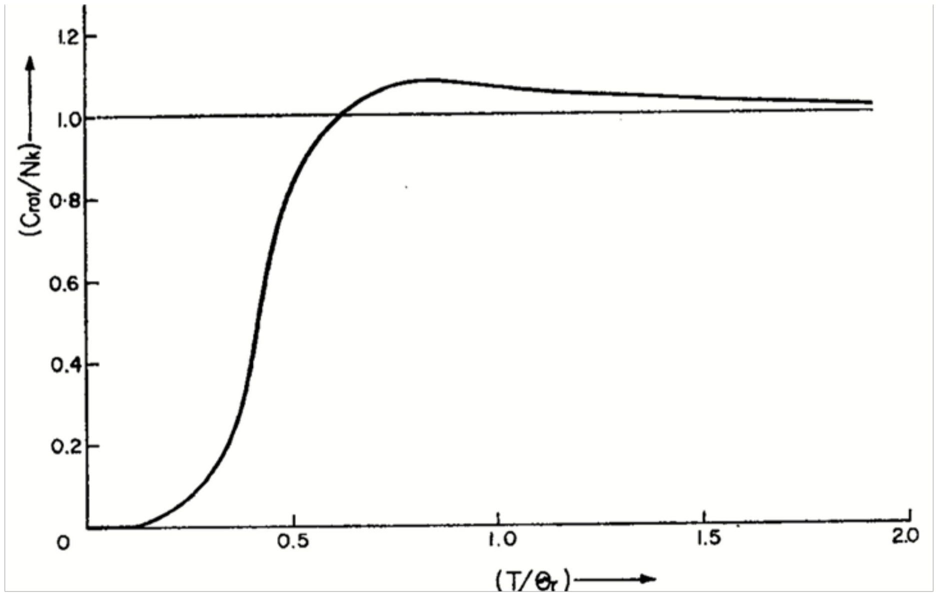
$$\ln Z_{rot} \simeq \ln\left(\frac{T}{\Theta_{rot}}\right) + \frac{\Theta_{rot}}{3T} + \frac{1}{90}\left(\frac{\Theta_{rot}}{T}\right)^2 + \ldots$$

$$E_{rot} = -\frac{\partial \ln Z_{rot}}{\partial \beta} = k_B T - \frac{k_B \Theta_{rot}}{3} - \frac{1}{45}\frac{k_B \Theta_{rot}^2}{T} + \ldots$$

$$C_V = \frac{\partial E}{\partial T} = k_B + \frac{k_B}{45}\left(\frac{\Theta_{rot}}{T}\right)^2$$

Low temperature expansion:

$$Z_{rot} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} e^{-\beta \varepsilon_\ell}$$



Molecules of identical atoms