Lecture 9: Equipartition Theorem

Polyatomic Partition Functions, Equipartition Theorem

Polyatomic Ideal Gas

Polyatomic Ideal gases have all degrees of freedom:

$$q = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vibr}} \cdot q_{\text{elec}}$$
$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vibr}} + \varepsilon_{\text{elec}}$$

Translational and Electronic partition functions behave similarity to diatomics, but will have more complex rotational and vibrational q's compared to diatomics

$$q_{trans} = \left[\int_0^\infty \exp\left(-\beta \frac{h^2}{8ma^2} n^2\right) dn\right]^3$$

$$\langle \varepsilon_{trans} \rangle = \frac{3}{2\beta} = \frac{3}{2} k_B T \qquad \frac{1}{2} k_B T \text{ per DOF}$$

$$q_{elec} = \sum_{i,levels} g_i e^{-\beta \varepsilon_i}$$

Virtually no contribution to ε

Polyatomic Vibrational Partition Function

Diatomic Vibrational q_{vib}

$$q_{\text{vib}} = \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}}$$

$$\langle E_{\text{vib}} \rangle = Nk_B \left(\frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1} \right)$$

$$C_{V,\text{vib}} = R \left(\frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2}$$

Single vibrational mode

Polyatomic Vibrational q_{vib}

$$q_{\text{vib}} = \prod_{j=1}^{\alpha} \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}}$$

$$\langle E_{\text{vib}} \rangle = Nk_B \sum_{j=1}^{\alpha} \left(\frac{\Theta_{\text{vib},j}}{2} + \frac{\Theta_{\text{vib},j}}{e^{\Theta_{\text{vib},j}/T} - 1} \right)$$

$$C_{V,\text{vib}} = Nk_B \sum_{j=1}^{\alpha} \left(\frac{\Theta_{\text{vib},j}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{(1 - e^{-\Theta_{\text{vib},j}/T})^2}$$

α vibrational modes

Polyatomic Rotational Partition Function

Case	Partition function	Example
Spherical top $I_A = I_B = I_C$	$q_{\text{rot}} = \dfrac{\pi^{1/2}}{\sigma} \left(\dfrac{T}{\Theta_{\text{rot}}} \right)^{3/2}$	CH_4
Symmetric top $I_A = I_B \neq I_C$	$q_{\text{rot}} = \dfrac{\pi^{1/2}}{\sigma} \left(\dfrac{T}{\Theta_{\text{rot},A}} \right) \left(\dfrac{T}{\Theta_{\text{rot},C}} \right)^{1/2}$	NH_3
Asymmetric top $I_A \neq I_B \neq I_C$	$q_{\text{rot}} = \dfrac{\pi^{1/2}}{\sigma} \left(\dfrac{T^3}{\Theta_{\text{rot},A}\Theta_{\text{rot},B}\Theta_{\text{rot},C}} \right)^{1/2}$	CH_3COOH

Heat Capacity

$$\begin{aligned} q &= q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{elec}} \\ &= \underbrace{\left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V}_{q_{\text{trans}}} \underbrace{\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_{\text{rot},A}\Theta_{\text{rot},B}\Theta_{\text{rot},C}}\right)^{1/2}}_{q_{\text{rot}}} \underbrace{\prod_{j=1}^{\alpha} \frac{e^{-\Theta_{\text{vib},j}/2T}}{1-e^{-\Theta_{\text{vib},j}/T}}}_{q_{\text{vib}}} \underbrace{\sum_i g_i e^{-\beta\varepsilon_i}}_{q_{\text{elec}}} \end{aligned}$$

$$\langle E \rangle = \frac{\partial \ln q^N/N!}{\partial \beta}$$

$$C_V = \frac{\partial \langle E \rangle}{\partial T}$$

so much math...

Equipartition Theorem

Equipartition Theorem

At the high temperature (classical) limit, each quadratic degree of freedom contributes $\frac{1}{2}k_\mathrm{B}T$ per particle (or $\frac{1}{2}RT$ per mole) to the average internal energy, and $\frac{1}{2}R$ per mole (or $\frac{1}{2}k_\mathrm{B}$ per particle) to molar heat capacity at constant volume

$$\begin{aligned}
\text{Translational:}\quad & KE = \frac{1}{2}mv^2 & & \frac{1}{2}k_\mathrm{B}T \text{ or } \frac{1}{2}R \text{ per DOF}\\
\text{Rotational:}\quad & KE = \frac{1}{2}I\omega^2 & & \frac{1}{2}k_\mathrm{B}T \text{ or } \frac{1}{2}R \text{ per DOF}\\
\text{Vibrational:}\quad & KE = \frac{1}{2}mv^2 \quad PE = \frac{1}{2}kx^2 & & k_\mathrm{B}T \text{ or } R \text{ per DOF}
\end{aligned}$$

Equipartition Theorem

Number of Degrees of Freedom

Motion	**Linear**	**Non-Linear**	**Contribution per DOF**
Translational	3	3	$\frac{1}{2}k_BT$ or $\frac{1}{2}R$
Rotational	2	3	$\frac{1}{2}k_BT$ or $\frac{1}{2}R$
Vibrational	$3N-5$	$3N-6$	k_BT or R
Total DOF	$3N$	$3N$	—

N is number of atoms

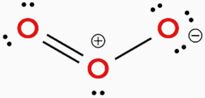
Linear molecules have a C_∞ rotation axis: can rotate any fraction of a full circle and the molecule will look the same

Example: Identifying Linear vs Non-linear

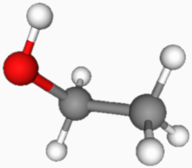
C_2H_2 (linear)

$\mathrm{H-C\equiv C-H}$

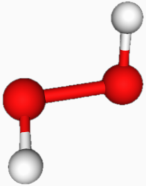
O_3 (non-linear)



C_2H_5OH (non-linear)



H_2O_2 (non-linear)



Example: Equipartition Theorem

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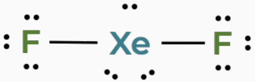

$$\begin{aligned}\overline{C_V} &= 3\cdot\frac{1}{2}R + 2\cdot\frac{1}{2}R + (3(3)-5)\cdot R \\ &= \frac{3}{2}R + R + 4R = \frac{13}{2}R\end{aligned}$$