

Week 2

Partition Functions and Ideal Gases

2.1 System Partition Functions

1/19:

- Decomposing the partition function of a molecule into the product of separate sums as partitioned by degrees of freedom (e.g., translation, rotation, vibration, and electronic).
- The partition functions of **independent**, distinguishable/indistinguishable molecules.
 - We should not double count the same states.
 - The $N!$ in $Q = q^N/N!$ is not important when calculating energy (because of the properties of the \ln function), but it is very important when calculating quantities such as entropy.
- **Independent** (particles): A set of particles that do not interact with one another.
- Discusses bosons and fermions.
 - We can have a two fermions in the state $|1, 1\rangle$ because it is a symmetric state.
- Recall the Fermi level, the boundary between the filled and unfilled electronic states in a solid.
 - If T is small, this level is a hard boundary.
 - If T is large, electrons can easily be excited and the Fermi level is a soft boundary.
- Does the 3D particle in a box derivation for the translation molecular partition function.
 - Note that since the de Broglie wavelength $\lambda_{\text{DB}} = \sqrt{h^2/2mk_B T}$, we may write

$$q_x = \sum_{n_x} e^{-h^2/8mk_B T L_x^2} = \sum_{n_x} e^{-\lambda_{\text{DB}}^2 n_x^2 / 4L_x^2}$$

- The number of states are occupied/have energy within $k_B T$ of the ground state.
 - $-\lambda_{\text{DB}}^2 n_x^2 / 4L_x^2$ is on the order of 1, implying that n_x is on the order of $2L/\lambda_{\text{DB}}$.
 - It follows if L is on a macroscopic scale (e.g., $L \approx 1$ m) and λ_{DB} is on a sub-angstrom scale that n_x is on the order of 10^{10} . When n_x is at such a scale, $e^{-\lambda_{\text{DB}}^2 n_x^2 / 4L_x^2} \approx 1/e$.
 - It follows that in a 1 m^3 box, we will have about 10^{30} states, so we really are in a regime where the number of states is larger than the number of molecules.
- More precisely, we want

$$N \ll n_x n_y n_z = \left(\frac{8mk_B T}{h^2} \right)^{3/2} L_x L_y L_z$$

where the middle term approximates the number of states so that

$$\frac{N}{V} \ll \left(\frac{8mk_B T}{h^2} \right)^{3/2}$$

- Approximating the translational energy with an integral.
 - Concludes with the translational partition function.
 - Since we can approach this problem from a classical perspective (as we did last Friday) or quantum mechanically (as we did today) to achieve the same result, this system again demonstrates the relation between quantum and classical mechanics.

2.2 Molecular Partition Functions

- 1/21: • We approximate the total molecular energy as

$$q = q_{\text{elec}} q_{\text{trans}} q_{\text{vib}} q_{\text{rot}}$$

- The heat capacity in the very high temperature limit where translations, rotations, and vibrations are classical.
 - Translational: $\frac{3}{2}k_B$.
 - Vibrational: Each degree of freedom ($3N - 5$ for a linear molecule and $3N - 6$ for a nonlinear molecule) contributes k_B .
 - Rotational: Each degree of freedom (2 for a linear molecule and 3 for a nonlinear molecule) contributes $\frac{1}{2}k_B$.
- We can use the above to calculate the heat capacity of various molecules at very high temperatures (note, however, that at such temperatures, molecules would likely dissociate; we're simply theoretically considering the classical limit here).
 - Ne: $\frac{3}{2}k_B$.
 - H₂O: $\frac{3}{2}k_B + 3 \cdot k_B + 3 \cdot \frac{1}{2}k_B = 6k_B$.
 - O₂: $\frac{3}{2} + 1 \cdot k_B + 2 \cdot \frac{1}{2}k_B = \frac{7}{2}k_B$.
 - CO₂: $\frac{3}{2}k_B + 4 \cdot k_B + 2 \cdot \frac{1}{2}k_B = \frac{13}{2}k_B$.
 - CHCl₃: $\frac{3}{2}k_B + 9 \cdot k_B + 3 \cdot \frac{1}{2}k_B = 12k_B$.
- Electronic partition function.
 - Consider the bottom D_e of the potential well of a diatomic.
 - D_0 is the ionization energy from the bottom state ($D_e \neq D_0$, but relations can be obtained via spectroscopy).
 - It follows that

$$q_{\text{elec}} = g_1 e^{-(D_e/k_B T)} + g_2 e^{-E_2/k_B T}$$
 - If $dT \ll (E_2 + D_e)$, then $q_{\text{elec}} = g_1 e^{D_e/k_B T}$.
- Vibrational partition function.
 - As before with the law of Dulong and Petit.
 - It's a special point where $T = h\nu/k_B$.
- Rotational partition function.
 - Almost always classical.
 - The rotational energy of a polyatomic molecule will almost always be $\frac{3}{2}k_B$.
 - Let's look at a heteronuclear diatomic, such as CO. Derives

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) e^{-\hbar^2 J(J+1)/2Ik_B T}$$

- The **rotational temperature** leads to

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) e^{\Theta_{\text{rot}}/T} = \frac{T}{\Theta_{\text{rot}}}$$

- Thus, at the temperature at which we exist, rotation is equivalent classically to quantum mechanically.

- **Rotational temperature:** The following quantity. Denoted by Θ_{rot} . Given by

$$\Theta_{\text{rot}} = \hbar^2 / 2Ik_B$$

- PGS will not specify whether we need a quantum vs. classical model.

- Homonuclear diatomic (e.g., H_2).

- The vibrational differences in energy become visible with spectroscopy.

- $q_{\text{rot}} = T/2\Theta_{\text{rot}}$.

- Partition functions:

- If the molecule is linear, it's of the form T/Θ_{rot} .

- If the molecule is nonlinear, it's of the form $T/2\Theta_{\text{rot}}$.

- Spherical top (e.g., CH_4):

$$\frac{\sqrt{\pi}}{\sigma} \left(\frac{T}{\Theta_{\text{rot}}} \right)^{3/2}$$

- Symmetric top (e.g., NH_3):

$$\frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_{\text{rot},a}^2 \Theta_{\text{rot},b}}}$$

- a and b are the two different symmetry axes.

- Asymmetric top (e.g., H_2O):

$$\frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_{\text{rot},a} \Theta_{\text{rot},b} \Theta_{\text{rot},c}}}$$

- Application to total energy and heat capacity of a molecule.

- We have that

$$q = \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \cdot V \cdot \sqrt{\frac{T^2}{\sigma \Theta_{\text{rot},a} \Theta_{\text{rot},b} \Theta_{\text{rot},c}}} \cdot \sum_1^{3N-6} \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}} \cdot g_1 e^{D_e/k_B T}$$

- Thus,

$$\langle E \rangle = k_B T^2 \frac{\partial \ln q}{\partial T} = k_B T^2 \frac{\partial}{\partial T} \left(\frac{3}{2} \ln T + \text{constant} + \frac{3}{2} \ln T + \text{vibration} - D_e \right)$$

- The energy of the vibration is $E = k_B \Theta_{\text{vib}} / (e^{\Theta_{\text{vib}}/k_B T} - 1) + k_B \Theta_{\text{vib}}/2$. It follows that

$$C = \frac{\partial E}{\partial T} = k_B \frac{\Theta_{\text{vib}}^2}{T^2} \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})}$$

2.3 Chapter 18: Partition Functions and Ideal Gases

From McQuarrie and Simon (1997).

- Herein, we will calculate the partition functions and heat capacities of ideal gases.
 - We heavily rely on the expression of the partition function for a system of independent, indistinguishable particles, which ideal gases are likely to satisfy because of their low density.
- Deriving the translational molecular partition function of an atom in a monatomic ideal gas.
 - As mentioned in Chapter 17, if we let the container be cubic, then

$$\varepsilon(n_x, n_y, n_z) = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$$

- It follows that

$$\begin{aligned} q_{\text{trans}} &= \sum_{n_x, n_y, n_z=1}^{\infty} e^{-\beta \varepsilon(n_x, n_y, n_z)} \\ &= \sum_{n_x=1}^{\infty} \exp\left(-\frac{\beta h^2 n_x^2}{8ma^2}\right) \sum_{n_y=1}^{\infty} \exp\left(-\frac{\beta h^2 n_y^2}{8ma^2}\right) \sum_{n_z=1}^{\infty} \exp\left(-\frac{\beta h^2 n_z^2}{8ma^2}\right) \\ &= \left[\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right) \right]^3 \end{aligned}$$

- The above sum cannot be evaluated in closed form. However, since later terms in the summation get very small, it is an excellent approximation to replace the summation with an integral, i.e.,

$$\begin{aligned} q_{\text{trans}} &= \left(\int_0^{\infty} e^{-\beta h^2 n^2 / 8ma^2} dn \right)^3 \\ &= \left(\sqrt{\frac{\pi}{4\beta h^2 / 8ma^2}} \right)^3 \\ &= \left(\sqrt{\frac{2\pi m}{\beta h^2}} \right)^3 a^3 \\ &= \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V \end{aligned}$$