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 $\lambda_{\text{DB}} = \sqrt{h^2/2mk_BT}$, we may write

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

- The number of states are occupied/have energy within k_BT 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., $L \approx 1\,\text{m}$) 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, $\mathrm{e}^{-\lambda_{\text{DB}}^2 n_x^2/4L_x^2} \approx 1/\mathrm{e}$.
  - It follows that in a $1\,\text{m}^3$ 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

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

where the middle term approximates the number of states so that

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

- 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: $\frac{3}{2}k_B$.
  - H_2O: $\frac{3}{2}k_B + 3 \cdot k_B + 3 \cdot \frac{1}{2}k_B = 6k_B$.
  - O_2: $\frac{3}{2} + 1 \cdot k_B + 2 \cdot \frac{1}{2}k_B = \frac{7}{2}k_B$.
  - CO_2: $\frac{3}{2}k_B + 4 \cdot k_B + 2 \cdot \frac{1}{2}k_B = \frac{13}{2}k_B$.
  - $CHCl_3$: $\frac{3}{2}k_B + 9 \cdot k_B + 3 \cdot \frac{1}{2}k_B = 12k_B$.
- 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
$$q_{\text{elec}} = g_1 \mathrm{e}^{-(-D_e/k_BT)} + g_2 \mathrm{e}^{-E_2/k_BT}$$
  - If $\mathrm{d}T \ll (E_2 + D_e)$, then $q_{\text{elec}} = g_1 \mathrm{e}^{D_e/k_BT}$.
- 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

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

- The **rotational temperature** leads to

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

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

- **Rotational temperature**: The following quantity. *Denoted by* $\mathbf{\Theta_{rot}}$. *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

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

  - Thus,

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

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

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

2.3 Chapter 18: Partition Functions and Ideal Gases

From McQuarrie and Simon (1997).

1/23:

- 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

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

  - 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.,

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

1/24:

- Deriving the electronic molecular partition function of an atom in a monatomic ideal gas.
  - We express the partition function here in terms of levels, i.e., by

$$q_{\text{elec}}=\sum_i g_{ei}\mathrm{e}^{-\beta\varepsilon_{ei}}$$

    where g_{ei} is the degeneracy and ε_{ei} is the energy of the i^{th} electronic level.
  - Taking $\varepsilon_{e1}=0$ to be the zero of energy yields

$$q_{\text{elec}}=g_{e1}+g_{e2}\mathrm{e}^{-\beta\varepsilon_{e2}}+\cdots$$

    - Note that since ε's are usually on the order of tens of thousands of wavenumbers, $\mathrm{e}^{-\beta\varepsilon_{e2}}$ is around 10^{-5} for most atoms at ordinary temperatures, so only the first term in the summation is significantly different from zero.
    - For some gases such as halogens, other terms may be important, but even there the sum converges very rapidly.

- Using spectroscopic data, we can show that the fraction of atoms of most gases in the first excited state is very small.
  - For example, the fraction of helium atoms at 300 K in the first excited state is 10^{-334}.
  - For fluorine, however, the fraction is on the order of 10^{-2}, which is significant. In this case, we need to approximate q_{elec} with more than one or two terms.

- McQuarrie and Simon (1997) recalculates the average energy, heat capacity, and pressure of a monatomic ideal gas using the above results.
- Diatomics.
  - The translational partition function is

$$q_{\text{trans}}(V,T) = \left[\frac{2\pi(m_1+m_2)k_BT}{h^2}\right]^{3/2} V$$

  - We take the zero of rotational energy to be the $J=0$ state.
  - We take the zero of vibrational energy to be the bottom of the internuclear potential well of the lowest electronic state (so that the energy of the ground vibrational state is $h\nu/2$).
  - We take the zero of electronic energy to be the energy of the separated atoms at rest in their ground electronic state (so that the energy of the ground electronic state is $-D_e$[1]).

- **Vibrational temperature**: The following quantity. *Denoted by* $\mathbf{\Theta}_{\text{vib}}$. *Given by*

$$\Theta_{\text{vib}} = \frac{h\nu}{k_B}$$

- Deriving the vibrational molecular partition function of a molecule in a diatomic ideal gas.

$$\begin{aligned}
q_{\text{vib}}(T) &= \sum_{v=0}^{\infty} \mathrm{e}^{-\beta(v+1/2)h\nu}\\
&= \mathrm{e}^{-\beta h\nu/2}\sum_{v=0}^{\infty}\mathrm{e}^{-\beta h\nu v}\\
&= \mathrm{e}^{-\beta h\nu/2}\frac{1}{1-\mathrm{e}^{-\beta h\nu}}\\
&= \frac{\mathrm{e}^{-\beta h\nu/2}}{1-\mathrm{e}^{-\beta h\nu}}
\end{aligned}$$

- In terms of Θ_{vib},

$$\begin{aligned}
q_{\text{vib}}(T) &= \frac{\mathrm{e}^{-\Theta_{\text{vib}}/2T}}{1-\mathrm{e}^{-\Theta_{\text{vib}}/T}}\\
\langle E_{\text{vib}}\rangle &= Nk_B\left(\frac{\Theta_{\text{vib}}}{2}+\frac{\Theta_{\text{vib}}}{\mathrm{e}^{\Theta_{\text{vib}}/T}-1}\right)\\
\overline{C}_{\text{V,vib}} &= R\left(\frac{\Theta_{\text{vib}}}{T}\right)^2\frac{\mathrm{e}^{-\Theta_{\text{vib}}/T}}{(1-\mathrm{e}^{-\Theta_{\text{vib}}/T})^2}
\end{aligned}$$

- Note that the high temperature limit of $\overline{C}_{\text{V,vib}}$ is R, and $\overline{C}_{\text{V,vib}}$ attains $R/2$ at $T = 0.34\,\Theta_{\text{vib}}$.
- Calculating the fraction of molecules in the ground vibrational state reveals that generally, most molecules are in the ground vibrational state.

[1] See Figure 9.7 of Labalme (2021).

- Exceptions include Br_2, the smaller force constant and larger mass of which lead to a smaller value of Θ_{vib}.

- **Rotational temperature**: The following quantity. *Denoted by* $\mathbf{\Theta}_{\text{rot}}$. *Given by*

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

  - B is the rotational constant (see Chapter 5) in the above equation.

- Deriving the rotational molecular partition function of a molecule in a diatomic ideal gas.
  - We have

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

  - As with the translational partition function, for $\Theta_{\text{rot}} \ll T$ (which is true for normal temperatures), we may approximate the above sum via an integral. This approximation is known as the high-temperature limit, and under it,

$$\begin{aligned} q_{\text{rot}}(T) &= \int_0^{\infty}(2J+1)\mathrm{e}^{-\Theta_{\text{rot}}J(J+1)/T}\,\mathrm{d}J \\ &= \int_0^{\infty}\mathrm{e}^{-\Theta_{\text{rot}}x/T}\,\mathrm{d}x \\ &= \frac{T}{\Theta_{\text{rot}}} = \frac{8\pi^2 Ik_BT}{h^2} \end{aligned}$$

  - For low temperatures or molecules with large values of Θ_{rot} we evaluate some number of terms of the sum directly, but we will not consider these cases further.

- It follows from the above that

$$\langle E_{\text{rot}}\rangle = Nk_BT \qquad\qquad \overline{C}_{V,\text{rot}} = R$$

  - Each of the two rotational degrees of freedom of a diatomic contributes $R/2$ to $\overline{C}_{V,\text{rot}}$.

- Contrary to the other component parts of energy, higher energy rotational states are significantly occupied.

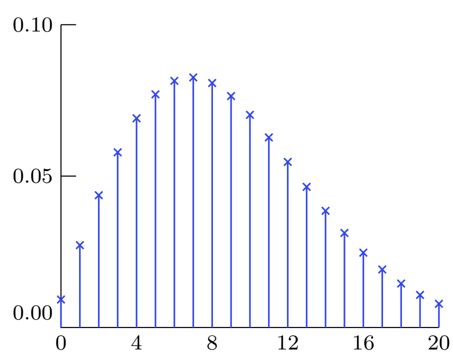

Figure 2.1: The fraction of molecules in the J^{th} rotational level for CO at 300 K.

  - We have that the fraction f_J of molecules in the J^{th} vibrational state is

$$f_J = \frac{(2J+1)\mathrm{e}^{-\Theta_{\text{rot}}J(J+1)/T}}{q_{\text{rot}}} = (2J+1)(\tfrac{\Theta_{\text{rot}}}{T})\mathrm{e}^{-\Theta_{\text{rot}}J(J+1)/T}$$

  - We can estimate the most probable value of J by solving $\partial f_J/\partial J = 0$, which gives $J = 7$ in agreement with Figure 2.1.