We have discussed separation of variables into center-of-mass coordinates and relative coordinates. The same procedure applies to polyatomic ideal gases as to diatomic ideal gases. The translation partition function for polyatomic ideal gases has the same exact form as that for diatomic ideal gas or the monatomic ideal gas.

The rigid-rotator approximation can be applied as was the case for the diatomic ideal gas. For linear molecules there are two axes for rotation and two degrees of freedom associated with rotation. For non-linear molecules there are the axes and the moments of inertia. In a polyatomic molecule there is more than one vibrational mode. Thus, the number of degrees of freedom needs to be considered.

For a molecule with \( n \) atoms there will be \( 3n \) degrees of freedom. These can be attributed as follows:

<table>
<thead>
<tr>
<th>Type</th>
<th>Translation</th>
<th>Rotation</th>
<th>Vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>3</td>
<td>2</td>
<td>3n-5</td>
</tr>
<tr>
<td>Non-linear</td>
<td>3</td>
<td>3</td>
<td>3n-6</td>
</tr>
</tbody>
</table>

**Treatment of the vibrational potential**

We can expand the vibrational potential energy function for a polyatomic molecule in a Taylor's series as was done for the diatomic molecule. However, there will be \( 3n \) coordinates.

The harmonic approximation makes the assumption that terms higher than second order are zero. The first derivative term is zero at the minimum of the potential energy surface.

**Internal coordinates**

We have treated the motion of atomic masses thus far using Cartesian coordinates. It is convenient to transform from Cartesian coordinates to internal coordinates. Internal coordinates consist of bond stretching, valence angle bending, out-of-plane wagging and torsions. These have the following forms
The transformation from Cartesian to internal coordinates is convenient because we often find it easier to define the force constants for stretches and bends than to try and determine their value in Cartesian space.

The parameters in typical forcefields are also given in terms of the internal coordinates specified above. These comprise the intramolecular portion of the forcefield.
Normal Coordinates

In the normal coordinate system each vibrational frequency is associated with a collective motion of the atoms in the molecule. Each normal coordinate is orthogonal to all of the others. In a normal mode of vibration the atoms all move with the same frequency and phase, however, the amplitudes and directions of their motions differ. We can exemplify this with water. Since there are 3 atoms in water and it is a non-linear molecule, there are 3 vibrational degrees of freedom. These result in three normal modes of vibration shown below.

The potential energy contribution of the each of the internal coordinates to the normal mode can be computed. This is known as the potential energy distribution (PED). For example, for the symmetric stretch the PED of the mode is 50% O-H1 stretch and 50% O-H2 stretch. Within this approximation we can separate the hamiltonian into terms for each
vibrational normal mode.

The solutions are

The frequency \( n_j = \frac{\omega_j}{2p} \) where

The vibrational partition function for a polyatomic molecule becomes the product of partition functions for each vibrational normal mode.

We can define the vibrational temperature

The partition function can be expressed in terms of the vibrational temperature.

**Calculation of average quantities from the vibrational partition function**

The average energy can be calculated from

We insert the vibrational partition function to obtain
The vibrational entropy is

which after a little algebra becomes

The heat capacity can be calculated from

Recognizing that the average energy is the energy calculated above, \( E_{\text{vib}} \).

There is a great deal of utility for thermodynamic functions calculated from the vibrational normal modes of a molecule. The vibrational energy and entropy depend on the shape a multidimensional potential energy surface. If one performs a conformational search of macromolecule it is one obtains energies and structures but little direct information concerning the shape of the potential energy surface for each conformation. The vibrational entropy gives a means determining whether there are significant entropic differences in the structures and therefore whether certain conformations will be favored based on the entropy.

However, it is possible to take appropriate linear combinations of the coordinates so that the cross terms are eliminated and the classical Hamiltonian as well as the operator corresponding to it contains no cross terms and in terms of the new coordinates, the Hamiltonian can be written as,

\[
H = \sum_{i=1}^{f} \frac{h^2}{2 \mu_i} \frac{\partial}{\partial q_i^2} + \sum_{i=1}^{f} \frac{k_i}{2} q_i^2 \tag{3.81}
\]

Here, the degrees of freedom \( f \) is \( 3n - 5 \) for a linear molecule and \( 3n - 6 \) for a nonlinear molecule. Here, \( k_i \) is the force constant and \( \mu_i \) is the reduced mass for that particular vibrational mode which is referred to as a normal mode. The Equation \( \text{(3.81)} \) represents \( f \) linearly independent harmonic oscillators and the total energy for such a system is

\[
\epsilon_{\text{vib}} = \sum_{i=1}^{f} \left( v_i + \frac{1}{2} \right) h \nu_i
\]

The vibrational frequencies are given by

\[
\nu_i = \frac{1}{2 \pi} \sqrt{\frac{k_i}{\mu_i}}
\]

The vibrational partition function is given by the product of \( f \) vibrational functions for each frequency.
\[ q_{vib} = \prod_{i=1}^f \frac{e^{-\Theta_{vib,i}/2T}}{1-e^{-\Theta_{vib,i}/T}} \] \label{Qvib1}

with

\[ \Theta_{vib,i} = \frac{h\nu_i}{k_B} \]

As with the previous discussion regarding \textit{simple diatomics}, \(\Theta_{vib,i}\) is called the characteristic vibrational temperature. The molar energies and the heat capacities are given by

\[ \langle E_{vib} \rangle = Nk \sum_{i=1}^f \left[ \frac{\Theta_{vib,i}}{2} + \frac{\Theta_{vib,i} e^{-\Theta_{vib,i}/T}}{1-e^{-\Theta_{vib,i}/T}} \right] \]

and

\[ \bar{C}_V = Nk_B \sum_{i=1}^f \left( \frac{\Theta_{vib,i}}{T} \right)^2 \frac{e^{-\Theta_{vib,i}/T}}{(1-e^{-\Theta_{vib,i}/T})^2} \]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{water_vibrational_modes.png}
\caption{The three vibrational modes of water, the symmetric stretch (3656.7 cm\(^{-1}\), 5160 K), the asymmetric stretch (3755.8 cm\(^{-1}\), 5360 K) and the bending mode (1594.8 cm\(^{-1}\), 2290 K) are shown. The vibrational frequencies and the characteristic temperature for each mode are shown in parenthesis. Although not shown in the animation, the oxygen atom also moves with each of these normal modes.}
\end{figure}

Example \(\text{(NO}_2\text{)}\)

The three characteristic vibrational temperatures for \(\text{(NO}_2\text{)}\) are 1900 K, 1980 K and 2330 K. Calculate the vibrational partition function at 300 K.

\textbf{Solution}

The vibrational partition is (Equation \ref{Qvib1})

\[ q_{vib} = \prod_{i=1}^f \frac{e^{-\Theta_{vib,i}/2T}}{1-e^{-\Theta_{vib,i}/T}} \]

If we calculate \(q_{vib}\) by taking the zero point energies as the reference points with respect to which the other energies are measured

\[ q_{vib} = \prod_{i=1}^f \frac{1}{1-e^{-\Theta_{vib,i}/T}} = \left( \frac{1}{1-e^{-1900/300}} \right) \left( \frac{1}{1-e^{-1980/300}} \right) \left( \frac{1}{1-e^{-2330/300}} \right) \]
\[ = (1.0018) \times (1.0014) \times (1.0004) = 1.0035 \]

The implication is that very few vibrational states of \( \text{NO}_2 \) (other than the ground vibrational state) are accessible at 300 K. This is standard of the vibrations of most molecules.

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**Contributors**

- [http://www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf](http://www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf)