ENERGY AND SPECIFIC HEAT (CANONICAL ENSEMBLE)

\[ F = -kT \ln Q_N(V, T, N) \]

\[ Q = \int \frac{[dpdq]}{C} e^{-\beta H} \]

for monoatomic mol (N molecules)

\[ \int \frac{d^3N \, dp \, dq}{\hbar^3 N \, N!} \]

for diatomic mol (N molecules)

\[ \int \frac{d^6N \, dp \, dq}{\hbar^5 N \, N!} \]

The same results hold for polyatomic molecules

\[ \frac{\partial (\beta F)}{\partial \beta} = -\frac{\partial}{\partial \beta} \left[ -\ln Q(V, T, N) \right] \]

\[ = \frac{1}{Q} \int \frac{[dpdq]}{C} H \, e^{-\beta H} = \langle H \rangle \]

For any type of system, we can always compute the energy using

\[ E = \frac{\partial (\beta F)}{\partial \beta} \]

For the diatomic molecule, \( \beta F = N(\mu + 3 \lambda_{eff}) - N \)

\[ = N(\mu + 3 \lambda_1 + 3 \lambda_2 - \mu I) - N \]

\[ E = N \left( 3 \frac{1}{\lambda_1} \frac{\partial \lambda_1}{\partial \beta} + 3 \frac{1}{\lambda_2} \frac{\partial \lambda_2}{\partial \beta} - \frac{1}{I} \frac{\partial I}{\partial \beta} \right) \]

\[ = N \left( \frac{3}{2} kT + \frac{3}{2} kT + \frac{1}{I} \int d^3y \, V \, e^{-\beta V} \right) \]
\[ E = 3NkT + \frac{N}{I} \int d^3y \, V e^{-\beta V} \]

consistent with equipartition: the molecule has 6 degrees of freedom (three translational degrees of freedom for each atom)

\[ C_V = \frac{1}{N} \frac{\partial E}{\partial T} = 3k - \frac{1}{kT^2} \left( \frac{1}{\int d^3y e^{-\beta V}} \right) \int d^3y V e^{-\beta V} \int d^3y e^{-\beta V} \]

\[ \frac{\partial}{\partial \beta} \left( \frac{\int d^3y V e^{-\beta V}}{\int d^3y e^{-\beta V}} \right) = - \frac{\int d^3y V^2 e^{-\beta V}}{\int d^3y e^{-\beta V}} + \left( \frac{\int d^3y V e^{-\beta V}}{\int d^3y e^{-\beta V}} \right)^2 \]

\[ = - \left( \langle V^2 \rangle - \langle V \rangle^2 \right) = - \langle (V - \langle V \rangle)^2 \rangle \]

where we define

\[ \langle A \rangle = \frac{\int d^3y \, A(x) e^{-\beta V}}{\int d^3y e^{-\beta V}} \]

[we interpret \( e^{-\beta V} \) as a probability density.]

\[ \text{correctly:} \frac{e^{-\beta V(y)}}{\int d^3x e^{-\beta V(x)}} \text{ is a prob. dens.} \]

It follows

\[ C_V = 3k + \frac{k}{(kT)^2} \langle (V - \langle V \rangle)^2 \rangle \]

The last term is positive and therefore

\[ C_V \geq 3k \]
This result is in contrast with experiments.
For $O_2, N_2$ at room temperature $C_v = \frac{5}{2} k$.

**THE PROBLEM IS IN OUR CLASSICAL APPROXIMATION.**
We are assuming that we can model the molecule as a purely classical system. This is always correct if $T$ is large enough.

However, at room temperature the vibrational part of the molecule is **not** classical.

In $O_2$ and $N_2$ the spacing of the vibrational level is $\Delta E \approx 0.2 - 0.3$ eV. The typical thermal energy is $kT = \frac{T}{40}$ eV.

Thus, we are very far from the classical limit that requires $\Delta E \ll kT$.

At room temperature all molecules are in the vibrational ground state and the bond length is essentially fixed.

At this values of $T$, a good model is a sort of barbell (the one used in gyms for the weights)

Then:

(a) 3 translation degrees of freedom of the **molecule**

(b) 2 rotational degrees of freedom

$\Rightarrow C_v = \frac{5}{2} k$ because of equipartition theorem