$$F = -kT \ln Q(V, T, N)$$

$$Q = \int \frac{[dp\, dq]}{C} e^{-\beta H}$$

$$\frac{[dp\, dq]}{C} \downarrow$$

for monoatomic mol (N molecules) $\qquad \dfrac{d^{3N}p\, d^{3N}q}{h^{3N} N!}$

diatomic mol (N molecules) $\qquad \dfrac{d^{6N}p\, d^{6N}q}{h^{6N} N!}$ ← integration over atoms

The same results hold for polyatomic molecules

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

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

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

$$E = \frac{\partial(\beta F)}{\partial \beta}$$

For the diatomic molecule $\beta F = N\left(\ln \rho + \ln \lambda_{eff}^3\right) - N$

$$= N\left(\ln \rho + 3\ln \lambda_1 + 3\ln \lambda_2 - \ln I\right) - N$$

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

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

$$E = 3NkT + \frac{N}{I} \int d^3y \, V e^{-\beta V} \quad \boxed{\text{average intramolecular energy}}$$

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

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

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

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

where we define

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

$$\left[\text{we interpret } e^{-\beta V} \text{ as a probability density}\right]$$

correctly: $\dfrac{e^{-\beta V(y)}}{\int d^3x \, e^{-\beta V(x)}}$ 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 $\Delta E \sim 0.2 - 0.3$ eV. The typical thermal energy is $kT = \frac{1}{40}$ 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)

distance
fixed

Then:
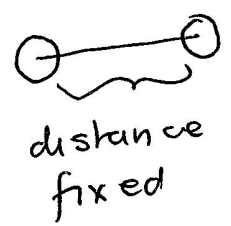
ⓐ 3 translation degrees of freedom of the MOLECULE

ⓑ 2 rotational degrees of freedom

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