The energy of the gas

- The energy of the gas U is the sum of the kinetic and potential energies

$$U = U(T, V; N)$$

- As before we will regard N as being fixed, And the dependence on volume simply reflects the change in density. Specifically the energy per volume takes the form:

$$\frac{U}{V} = e_v(T, n) \qquad e_v = \text{some function of temperature + density.}$$

energy per volume.

- If I double the system size, double the number of particles, at fixed temperature, the density remains the same and, energy per volume is the same. At small density, we expand in density

$$\frac{U}{V} = n\, e_0(T) + n^2 e_1(T) + n^3 e_2(T) + \ldots$$

- So the low density (ideal gas) expansion takes the form with $n = N/V$
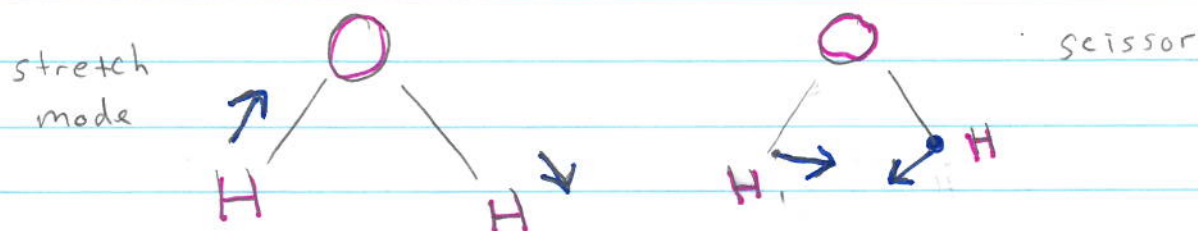
$$U(T,V) = N\left(e_0(T) + \frac{N}{V} e_1(T) + \ldots\ldots\right)$$

- First lets take first term. This is an ideal gas

$$U(T,V) = N e_0(t)$$

Ideal gas only

For a mono-atomic gas, $U = N \frac{3}{2} k_B T$; For a diatomic gas $U = N \frac{5}{2} k_B T$, specifying $f_0(T)$.

- What about more complicated gasses, such as H_2O?

stretch mode

scissor

It can rotate, the H's can vibrate. All of that complexity is incorporated in $e_0(T)$. The molecules are indepent of each other, but the system still needs to decide how to partition energy into the modes of the molecule.

- We note that for an ideal gas:

$$\frac{\partial U(T,V)}{\partial V} = 0$$

← the molecules are so far apart they don't talk to each other

And

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = N e_0'(T)$$

Ideal gas only

We will want to figure out how to calculate

$e_0(T)$, which is directly related to measured $C_p + C_v$

- For non ideal gasses: non-ideal gas

$$\boxed{\frac{\partial U}{\partial V} \neq 0}$$ and this reflects the potential energy between the molecules.

$$\frac{\partial U}{\partial V} \approx -\left(\frac{N}{V}\right)^2 e_1(T) \implies$$ for dilute gasses. This term clearly involves pairs of particles and scales as the (density)^2, reflecting the interactions

we won't calculate $f_1(T)$ in this course.

- Finally note that the curve $\dfrac{C_p^{1mol}}{R}$ is directly related to $e_0(T)$. For one mole

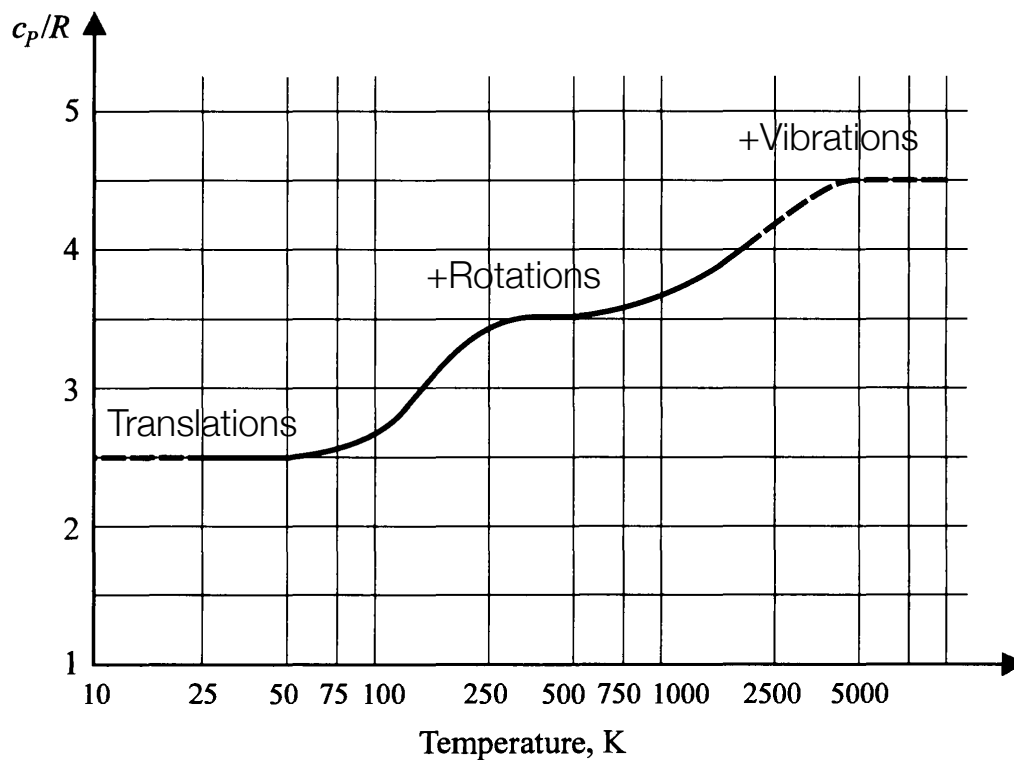$$C_V^{1mol} = N_A k_B \left(\frac{1}{k_B} \frac{de_0}{dT}\right) = R \left[\frac{1}{k_B} \frac{de_0}{dT}\right]$$

$$C_p^{1mol} = C_V^{1mol} + R = R \left[\frac{1}{k_B} \frac{de_0}{dT} + 1\right]$$
this what is plotted on C_p/R graph.

So we see that measurements about specific heats are directly telling us about U (or $e_0(T)$). (Reconsider what C_p for Hydrogen is telling you looking at the slide)

Specific Heat of H_2

c_P/R vs Temperature, K

Labels on curve: Translations, +Rotations, +Vibrations

The specific heats reflect the internal energy of the system

$$U = Ne_0(T)$$

We have for one mole ($R = N_A k$):

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = R\left(\frac{1}{k_B}\frac{de_0}{dT}\right)$$

and

$$C_p = C_V + R$$