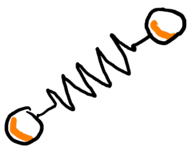
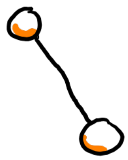
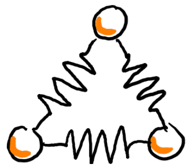
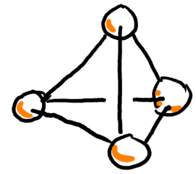
If the microscopic world was classical, predict $U_{\text{classical}}(T)$ for the following "toy molecules" in the gas phase.

(a)  (b)  (c)  (d) 

- Each ball is a point mass m with no moment of inertia.
- The zig-zag lines are springs which are freely jointed at the balls.
- Vibrational motion of the springs is very small ($\ll$ the length of the spring).
- The springs can extend and compress, but cannot twist or flex.
- The straight lines are rigid rods.

Solution

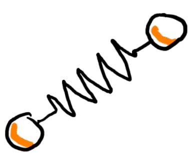


Figure 1: $f = 7$

Molecule (a) There are a couple of ways to count the degrees of freedom of this molecule. Firstly, we can use the velocities of the two atoms separately:

$$E = \underbrace{\frac{1}{2}mv_{1x}^2 + \frac{1}{2}mv_{1y}^2 + \frac{1}{2}mv_{1z}^2}_{\text{Translational K.E. of atom 1}} + \underbrace{\frac{1}{2}mv_{2x}^2 + \frac{1}{2}mv_{2y}^2 + \frac{1}{2}mv_{2z}^2}_{\text{Translational K.E. of atom 2}} + \underbrace{\frac{1}{2}k(\ell - \ell_0)^2}_{\text{P.E. of spring}} \tag{1}$$

which gives seven degrees of freedom.

The other way to do this would use center of mass velocity and angular momentum:

$$E = \underbrace{\frac{1}{2}(2m)v_x^2 + \frac{1}{2}(2m)v_y^2 + \frac{1}{2}(2m)v_z^2}_{\text{Translational K.E. of entire molecule}} + \underbrace{\frac{1}{2}\frac{L_x^2}{I_x} + \frac{1}{2}\frac{L_y^2}{I_y}}_{\text{Rotational K.E.}} + \underbrace{\frac{1}{2}m\left(\frac{1}{2}\frac{d\ell}{dt}\right)^2 + \frac{1}{2}k(\ell - \ell_0)^2}_{\text{K.E. + P.E. of spring}} \tag{2}$$

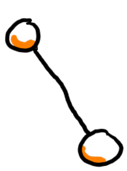


Figure 2: $f = 5$

Molecule (b) Here we really need to use center-of-mass velocity and angular momentum:

$$E = \frac{1}{2}(2m)v_x^2 + \frac{1}{2}(2m)v_y^2 + \frac{1}{2}(2m)v_z^2 + \frac{1}{2}\frac{L_x^2}{I_x} + \frac{1}{2}\frac{L_y^2}{I_y} \tag{3}$$

The tricky thing here is that we only have two degrees of rotational freedom because there is no opportunity to rotate around its axis.

Molecule (c) Here we really need to use center-of-mass velocity and angular momentum:

$$\begin{aligned}E &= \frac{1}{2}mv_{1x}^2 + \frac{1}{2}mv_{1y}^2 + \frac{1}{2}mv_{1z}^2 \\ &+ \frac{1}{2}mv_{2x}^2 + \frac{1}{2}mv_{2y}^2 + \frac{1}{2}mv_{2z}^2 \\ &+ \frac{1}{2}mv_{3x}^2 + \frac{1}{2}mv_{3y}^2 + \frac{1}{2}mv_{3z}^2 \\ &+ \frac{1}{2}k(\ell_1 - \ell_0)^2 + \frac{1}{2}k(\ell_2 - \ell_0)^2 + \frac{1}{2}k(\ell_3 - \ell_0)^2 \end{aligned} \tag{4}$$

We have three springs and three kinetic energy terms per atom, giving 12 degrees of freedom.

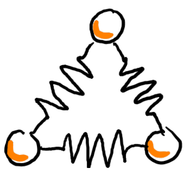


Figure 3: $f = 12$

Molecule (d) Here we really need to use center-of-mass velocity and angular momentum:

$$E = \frac{1}{2}(2m)v_x^2 + \frac{1}{2}(2m)v_y^2 + \frac{1}{2}(2m)v_z^2 + \frac{1}{2}\frac{L_x^2}{I_x} + \frac{1}{2}\frac{L_y^2}{I_y} + \frac{1}{2}\frac{L_z^2}{I_z} \tag{5}$$

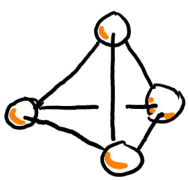


Figure 4: $f = 6$

You might expect this molecule with four atoms to be way more complicated than the two atom rigid molecule, but it's not!