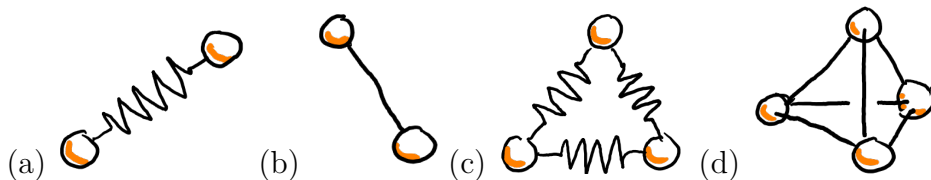
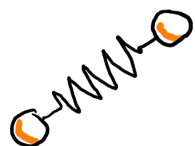


If the microscopic world was classical, predict  $U_{\text{classical}}(T)$  for the following “toy molecules” in the gas phase.



- 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



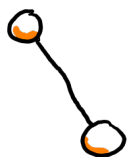
**Molecule (a)** There are a couple of ways to count the degrees of freedom of this molecule. Firstly, we can use the velocities of the two atoms separately:

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

Figure 1:  $f = 7$  which gives seven degrees of freedom.

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

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



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

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

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

Figure 2:  
 $f = 5$

**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.

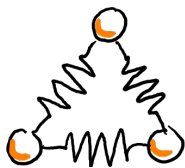
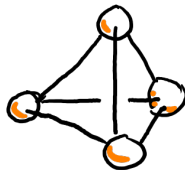


Figure 3:  $f = 12$

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



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

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

Figure 4:  $f = 6$