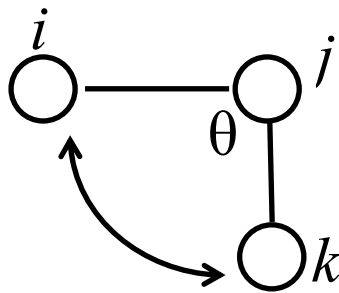


Forces, triangles and angles, vectors till you bleed

Andrew Torda, April 2009



The problem ..

The energy is $U_{angle}(\vec{r}_i, \vec{r}_j, \vec{r}_k) = \frac{k}{2} (\cos \theta_{ijk} - \cos \theta_0)^2$

And the derivative is

$$\vec{F}_{angle_i} = \frac{-\partial U_{angle}(\vec{r}_i)}{\partial \vec{r}_i}$$

Ending up as

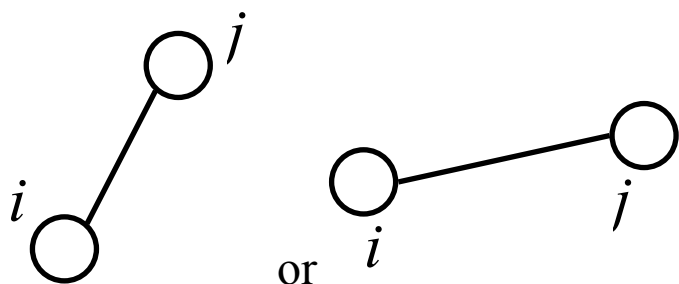
$$= -k (\cos \theta_{ijk} - \cos \theta_0) \left(\frac{\vec{r}_{kj}}{r_{kj}} - \frac{\vec{r}_{ij}}{r_{ij}} \cos \theta_{ijk} \right) \frac{1}{r_{ij}}$$

How do we get this ?

- Remember quotient rule
- Expand the $\cos \theta$ term
- Get derivative of top and bottom

First, some fundamentals we will need later.

- $\frac{\partial r_{ij}}{\partial \vec{r}_i}$ how does the distance between two atoms change as one atom



moves ? Will depend on the vector \vec{r}_{ij} so

$$\frac{\partial r_{ij}}{\partial \vec{r}_i} = \frac{\vec{r}_{ij}}{r_{ij}} \quad (1)$$

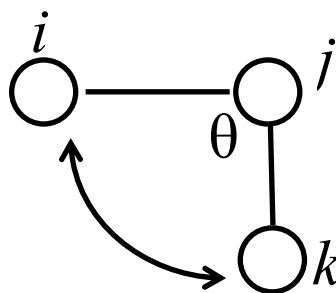
See the formal explanation on page 5.

- remember $\vec{r}_{ij} - \vec{r}_{ik} = \vec{r}_{kj}$ (2)

think of the triangle.

- the "quotient rule" $\frac{d}{dx} \frac{u}{v} = \frac{1}{v} \frac{du}{dx} - \frac{u}{v^2} \frac{dv}{dx}$ (3)

- Difficult term $\frac{\partial \cos \theta}{\partial \vec{r}_i}$ (note subscript - we are working with particle i).



- cosine rule, $\cos \theta = \frac{r_{ij}^2 + r_{kj}^2 - r_{ik}^2}{2r_{ij}r_{kj}}$

$$\text{set } u = r_{ij}^2 + r_{kj}^2 - r_{ik}^2$$

$$\begin{aligned} \text{Then } \frac{\partial u}{\partial \vec{r}_i} &= 2\vec{r}_{ij} - 2\vec{r}_{ik} && \text{from (2)} \\ &= 2\vec{r}_{kj} \end{aligned}$$

$$\text{Set } v = 2r_{ij}r_{kj}$$

$$\text{And } \frac{\partial v}{\partial \vec{r}_i} = \frac{2r_{kj}\vec{r}_{ij}}{r_{ij}} \quad \text{using chain rule and (1)}$$

$$\frac{\partial \cos \theta}{\partial \vec{r}_i} = \frac{1}{v} \frac{du}{dx} - \frac{u}{v} \frac{1}{v} \frac{\partial v}{\partial x} \quad \text{from quotient rule (3).}$$

$$\begin{aligned} \frac{\partial \cos \theta}{\partial \vec{r}_i} &= \frac{1}{2r_{ij}r_{kj}} 2\vec{r}_{kj} - \cos \theta \frac{1}{2r_{ij}r_{kj}} \frac{2r_{kj}\vec{r}_{ij}}{r_{ij}} \\ &= \frac{1}{r_{ij}} \frac{\vec{r}_{kj}}{r_{kj}} - \frac{1}{r_{ij}} \frac{\vec{r}_{ij}}{r_{ij}} \cos \theta \\ &= \left(\frac{\vec{r}_{kj}}{r_{kj}} - \frac{\vec{r}_{ij}}{r_{ij}} \cos \theta \right) \frac{1}{r_{ij}} \end{aligned}$$

Final form

$$U_{angle}(\vec{r}_i, \vec{r}_j, \vec{r}_k) = \frac{k}{2} (\cos \theta_{ijk} - \cos \theta_0)^2$$

$$\begin{aligned}\vec{F}_{angle_i} &= \frac{-\partial U_{angle}(\vec{r}_i)}{\partial \vec{r}_i} \\ &= k (\cos \theta_{ijk} - \cos \theta_0) \frac{\partial \cos \theta}{\partial \vec{r}_i} \\ &= -k (\cos \theta_{ijk} - \cos \theta_0) \left(\frac{\vec{r}_{kj}}{r_{kj}} - \frac{\vec{r}_{ij}}{r_{ij}} \cos \theta_{ijk} \right) \frac{1}{r_{ij}}\end{aligned}$$

Are we finished ?

- $\vec{F}_i \neq -\vec{F}_j$
- similar maths for either \vec{F}_j or \vec{F}_k
- we do not have to do all three $\vec{F}_j + \vec{F}_i + \vec{F}_k = 0$

What happens if this is not true ?

Variations

Vectors vs scalars - do we always need vectors ?

If we want forces - yes. Do we always need forces ? No.

Example - For two atoms with a Lennard-Jones interaction

- what is the distance of lowest energy ?
- how close can they approach if the energy has some numbers (kT) ?

What changes ?

- Vectors - work with $\frac{\partial U}{\partial \vec{r}_i}$
- Scalar properties - work with something like $\frac{dU}{dr_{ij}}$
- Can it become more complicated ? not here

Partial derivative of a scalar with respect to a vector

How to remember how this works.

$$\frac{\partial r_{ij}}{\partial \vec{r}_i} = \frac{\vec{r}_{ij}}{r_{ij}}$$

if we write \vec{r}_i explicitly as the vector $\begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix}$. The top of the formula is a

scalar distance between i and j which can be expanded as

$$r_{ij} = \left((x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 \right)^{1/2}.$$

To write this out in great detail, you could say,

$$\frac{\partial r_{ij}}{\partial \vec{r}_i} = \frac{\vec{r}_{ij}}{r_{ij}}$$

$$\frac{\partial r_{ij}}{\partial \vec{r}_i} = \begin{bmatrix} \frac{dr_{ij}}{dx_i} \\ \frac{dr_{ij}}{dy_i} \\ \frac{dr_{ij}}{dz_i} \end{bmatrix} \quad (4)$$

so, one component of the vector, $\frac{dr_{ij}}{dx_i}$ you would say

$$\begin{aligned} \frac{dr_{ij}}{dx_i} &= \frac{d\left(\left(x_i - x_j\right)^2 + \left(y_i - y_j\right)^2 + \left(z_i - z_j\right)^2\right)^{1/2}}{dx_i} \\ &= \frac{1}{2} \left(\left(x_i - x_j\right)^2 + \left(y_i - y_j\right)^2 + \left(z_i - z_j\right)^2\right)^{-1/2} 2\left(x_i - x_j\right) \\ &= \frac{\left(x_i - x_j\right)}{r_{ij}} \end{aligned}$$

If we were do the same for the y component, you would get

$$\frac{dr_{ij}}{dy_i} = \frac{\left(y_i - y_j\right)}{r_{ij}} \text{ and the same for the } z \text{ component. Putting this into (4), we}$$

$$\text{have } \frac{\partial r_{ij}}{\partial \vec{r}_i} = \begin{bmatrix} \frac{dr_{ij}}{dx_i} \\ \frac{dr_{ij}}{dy_i} \\ \frac{dr_{ij}}{dz_i} \end{bmatrix} = \begin{bmatrix} \frac{\left(x_i - x_j\right)}{r_{ij}} \\ \frac{\left(y_i - y_j\right)}{r_{ij}} \\ \frac{\left(z_i - z_j\right)}{r_{ij}} \end{bmatrix} = \frac{\vec{r}_{ij}}{r_{ij}}$$