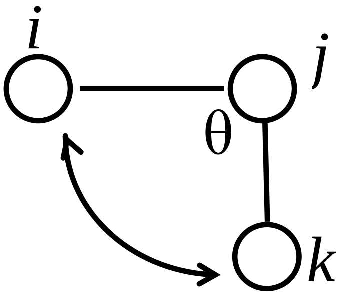
Forces, triangles and angles, vectors till you bleed

Andrew Torda, April 2010



<u>The problem</u> ..

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

And the derivative is

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

Ending up as

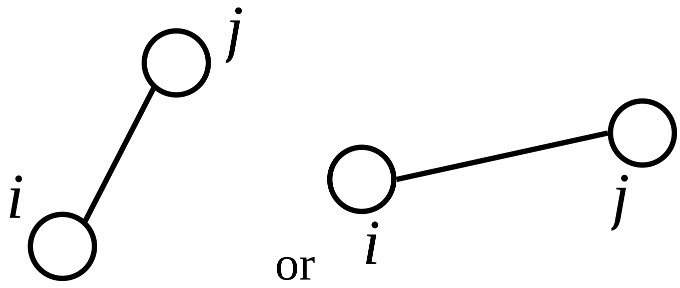
$$= -k\left(\cos\theta_{ijk} - \cos\theta_0\right)\left(\frac{\vec{r}_{kj}}{r_{kj}} - \frac{\vec{r}_{ij}}{r_{ij}}\cos\theta_{ijk}\right)\frac{1}{r_{ij}}$$

How do we get this ?

- Remember quotient rule
- Expand the cos θ 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

$$\frac{\partial r_{ij}}{\partial \vec{r}_i} = \frac{\vec{r}_{ij}}{r_{ij}} \tag{1}$$

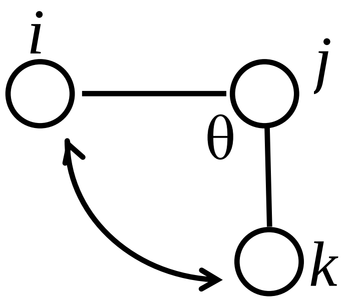
See the formal explanation on page 5.

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

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

Then $\dfrac{\partial u}{\partial \vec{r}_i} = 2\vec{r}_{ij} - 2\vec{r}_{ik}$ from (2)

$= 2\vec{r}_{kj}$

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

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

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

$$\frac{\partial \cos\theta}{\partial \vec{r}_i} = \frac{1}{2r_{ij}r_{kj}} 2\vec{r}_{kj} - \cos\theta \frac{1}{2r_{ij}r_{kj}} \frac{2r_{kj}\vec{r}_{ij}}{r_{ij}}$$

$$= \frac{1}{r_{ij}} \frac{\vec{r}_{kj}}{r_{kj}} - \frac{1}{r_{ij}} \frac{\vec{r}_{ij}}{r_{ij}} \cos\theta$$

$$= \left(\frac{\vec{r}_{kj}}{r_{kj}} - \frac{\vec{r}_{ij}}{r_{ij}} \cos\theta \right) \frac{1}{r_{ij}}$$

Final form

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

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

$$= k\left(\cos\theta_{ijk} - \cos\theta_0\right)\frac{\partial \cos\theta}{\partial \vec{r}_i}$$

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

<u>Are we finished ?</u>

- $\vec{F}_i \neq -\vec{F}_j$
- 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

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

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

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

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

so, one component of the vector, $\dfrac{dr_{ij}}{dx_i}$ 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

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

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