Derivation of Angle Force Field

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Angle Potential

$U(\theta) = K[1 - \cos(\theta - \theta_0)]$

where

$$\theta = \theta(\boldsymbol{r}_a, \boldsymbol{r}_b, \boldsymbol{r}_c) = \cos^{-1} \frac{\boldsymbol{r}_{ab} \cdot \boldsymbol{r}_{bc}}{r_{ab} r_{bc}}$$

$\boldsymbol{r}_{ab} = \boldsymbol{r}_a - \boldsymbol{r}_b, \ \ \boldsymbol{r}_{bc} = \boldsymbol{r}_b - \boldsymbol{r}_c$

Note that $\boldsymbol{r}_{ab} = \boldsymbol{r}_b - \boldsymbol{r}_a$ and $\boldsymbol{r}_{bc} = \boldsymbol{r}_c - \boldsymbol{r}_b$ are the conventional definition of the difference between vectors. Here, we adopt opposite sign definition as shown above. The differences in sign of $\boldsymbol{r}_{ab}$ and $\boldsymbol{r}_{bc}$ are cancelled out at the inner product $\boldsymbol{r}_{ab} \cdot \boldsymbol{r}_{bc}$. Therefore, we do not need to warry about the differences in sign of $\boldsymbol{r}_{ab}$ and $\boldsymbol{r}_{bc}$.

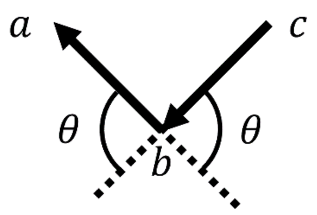

Figure 1. Schematic explanation of θ

Force field

$$\boldsymbol{F}(\boldsymbol{r}_a) = -\frac{dU}{d\boldsymbol{r}_a}, \qquad \boldsymbol{F}(\boldsymbol{r}_b) = -\frac{dU}{d\boldsymbol{r}_b}, \qquad \boldsymbol{F}(\boldsymbol{r}_c) = -\frac{dU}{d\boldsymbol{r}_c}$$

Derivation of $\boldsymbol{F}(\boldsymbol{r}_a)$

$$\boldsymbol{F}(\boldsymbol{r}_a) = -\frac{dU}{d\boldsymbol{r}_a} = -\frac{dU}{d\theta}\frac{d\theta}{d\boldsymbol{r}_a}$$

$$-\frac{dU}{d\theta} = -K\sin(\theta - \theta_0) = -K[\sin\theta\cos\theta_0 - \cos\theta\sin\theta_0]$$

$$\frac{d\theta}{d\boldsymbol{r}_a} = \frac{\partial \boldsymbol{r}_{ab}}{\partial \boldsymbol{r}_a}\frac{d\theta}{d\boldsymbol{r}_{ab}} = I\frac{d\theta}{d\chi}\frac{d\chi}{d\boldsymbol{r}_{ab}} = -\frac{1}{\sin\theta}\frac{d}{d\boldsymbol{r}_{ab}}\frac{\boldsymbol{r}_{ab} \cdot \boldsymbol{r}_{bc}}{r_{ab} r_{bc}}$$

$$\because \frac{\partial \boldsymbol{r}_{ab}}{\partial \boldsymbol{r}_a} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = I$$

$$\because \chi = \frac{\boldsymbol{r}_{ab} \cdot \boldsymbol{r}_{bc}}{r_{ab} r_{bc}} = \cos\theta$$

$$\because \frac{d\theta}{d\chi} = \frac{1}{d\chi/d\theta} = -\frac{1}{\sin\theta}$$

$$\frac{d}{d\boldsymbol{r}_{ab}} \frac{\boldsymbol{r}_{ab} \cdot \boldsymbol{r}_{bc}}{r_{ab} r_{bc}} = \frac{d}{d\boldsymbol{r}_{ab}} \left(\frac{\boldsymbol{r}_{ab}}{r_{ab}}\right) \cdot \frac{\boldsymbol{r}_{bc}}{r_{bc}} = \left(I \frac{1}{r_{ab}} - \frac{\boldsymbol{r}_{ab} \boldsymbol{r}_{ab}}{r_{ab}^3}\right) \cdot \frac{\boldsymbol{r}_{bc}}{r_{bc}}$$

$$\because \frac{d}{d\boldsymbol{r}} \frac{\boldsymbol{r}}{r} = \frac{\boldsymbol{\partial r}}{\boldsymbol{\partial r}} \frac{1}{r} + \boldsymbol{r} \frac{d}{d\boldsymbol{r}} \frac{1}{r} = I \frac{1}{r} - \frac{\boldsymbol{r}\boldsymbol{r}}{r^3}$$

$$\frac{d\theta}{d\boldsymbol{r}_a} = -\frac{1}{\sin\theta} \left(\frac{\boldsymbol{r}_{bc}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{ab}}{r_{ab}^2} \cos\theta\right)$$

$$\therefore \boldsymbol{F}(\boldsymbol{r}_a) = -\frac{dU}{d\boldsymbol{r}_a} = +K[\cos\theta_0 - \cot\theta \sin\theta_0] \left(\frac{\boldsymbol{r}_{bc}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{ab}}{r_{ab}^2} \cos\theta\right)$$

Derivation of $\boldsymbol{F}(\boldsymbol{r_b})$

$$\boldsymbol{F}(\boldsymbol{r}_b) = -\frac{dU}{d\boldsymbol{r}_b} = -\frac{dU}{d\theta} \frac{d\theta}{d\boldsymbol{r}_b}$$

$$\begin{aligned}
\frac{d\theta}{d\boldsymbol{r}_b} &= \frac{\boldsymbol{\partial r}_{ab}}{\boldsymbol{\partial r}_b} \frac{d\theta}{d\boldsymbol{r}_{ab}} + \frac{\boldsymbol{\partial r}_{bc}}{\boldsymbol{\partial r}_b} \frac{d\theta}{d\boldsymbol{r}_{bc}} \\
&= -I \frac{d\theta}{d\boldsymbol{r}_{ab}} + I \frac{d\theta}{d\boldsymbol{r}_{bc}} \\
&= -\frac{d\theta}{d\chi} \frac{d\chi}{d\boldsymbol{r}_{ab}} + \frac{d\theta}{d\chi} \frac{d\chi}{d\boldsymbol{r}_{bc}} \\
&= +\frac{1}{\sin\theta} \frac{d}{d\boldsymbol{r}_{ab}} \frac{\boldsymbol{r}_{ab} \cdot \boldsymbol{r}_{bc}}{r_{ab} r_{bc}} - \frac{1}{\sin\theta} \frac{d}{d\boldsymbol{r}_{bc}} \frac{\boldsymbol{r}_{ab} \cdot \boldsymbol{r}_{bc}}{r_{ab} r_{bc}} \\
&= \frac{1}{\sin\theta} \left(\frac{\boldsymbol{r}_{bc}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{ab}}{r_{ab}^2} \cos\theta\right) - \frac{1}{\sin\theta} \left(\frac{\boldsymbol{r}_{ab}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{bc}}{r_{bc}^2} \cos\theta\right)
\end{aligned}$$

$$\begin{aligned}
\therefore \boldsymbol{F}(\boldsymbol{r}_b) &= -\frac{dU}{d\boldsymbol{r}_b} \\
&= -K[\cos\theta_0 - \cot\theta \sin\theta_0] \left(\frac{\boldsymbol{r}_{bc}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{ab}}{r_{ab}^2} \cos\theta\right) \\
&\quad +K[\cos\theta_0 - \cot\theta \sin\theta_0] \left(\frac{\boldsymbol{r}_{ab}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{bc}}{r_{bc}^2} \cos\theta\right) \\
&= -\boldsymbol{F}(\boldsymbol{r}_a) - \boldsymbol{F}(\boldsymbol{r}_c)
\end{aligned}$$

Derivation of $\boldsymbol{F}(\boldsymbol{r_c})$

$$\boldsymbol{F}(\boldsymbol{r}_c) = -\frac{dU}{d\boldsymbol{r}_c} = -\frac{dU}{d\theta} \frac{d\theta}{d\boldsymbol{r}_c} = -\frac{dU}{d\theta} \frac{\boldsymbol{\partial r}_{bc}}{\boldsymbol{\partial r}_c} \frac{d\theta}{d\boldsymbol{r}_{bc}} = -K[\cos\theta_0 - \cot\theta \sin\theta_0] \left(\frac{\boldsymbol{r}_{ab}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{bc}}{r_{bc}^2} \cos\theta\right)$$

Summary

$$U(\theta) = K[1 - \cos(\theta - \theta_0)], \;\; \theta = \theta(\boldsymbol{r}_a, \boldsymbol{r}_b, \boldsymbol{r}_c) = \cos^{-1}\frac{\boldsymbol{r}_{ab} \cdot \boldsymbol{r}_{bc}}{r_{ab} r_{bc}}$$

$$\begin{aligned}
\boldsymbol{F}(\boldsymbol{r}_a) &= +K[\cos\theta_0 - \cot\theta \sin\theta_0] \left(\frac{\boldsymbol{r}_{bc}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{ab}}{r_{ab}^2}\cos\theta\right) \\
\boldsymbol{F}(\boldsymbol{r}_b) &= -K[\cos\theta_0 - \cot\theta \sin\theta_0] \left(\frac{\boldsymbol{r}_{bc}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{ab}}{r_{ab}^2}\cos\theta\right) \\
&\quad\; +K[\cos\theta_0 - \cot\theta \sin\theta_0] \left(\frac{\boldsymbol{r}_{ab}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{bc}}{r_{bc}^2}\cos\theta\right) \\
&= -\boldsymbol{F}(\boldsymbol{r}_a) - \boldsymbol{F}(\boldsymbol{r}_c) \\
\boldsymbol{F}(\boldsymbol{r}_c) &= \; -K[\cos\theta_0 - \cot\theta \sin\theta_0] \left(\frac{\boldsymbol{r}_{ab}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{bc}}{r_{bc}^2}\cos\theta\right)
\end{aligned}$$

For a general angle potential $U(\theta)$ with $\theta = \cos^{-1}\frac{\boldsymbol{r}_{ab} \cdot \boldsymbol{r}_{bc}}{r_{ab} r_{bc}}$, the following representations can be useful:

$$\begin{aligned}
\boldsymbol{F}(\boldsymbol{r}_a) &= \frac{dU}{d\theta}\frac{1}{\sin\theta}\left(\frac{\boldsymbol{r}_{bc}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{ab}}{r_{ab}^2}\cos\theta\right) \\
\boldsymbol{F}(\boldsymbol{r}_b) &= -\frac{dU}{d\theta}\frac{1}{\sin\theta}\left(\frac{\boldsymbol{r}_{bc}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{ab}}{r_{ab}^2}\cos\theta\right) \\
&\quad\; +\frac{dU}{d\theta}\frac{1}{\sin\theta}\left(\frac{\boldsymbol{r}_{ab}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{bc}}{r_{bc}^2}\cos\theta\right) \\
&= -\boldsymbol{F}(\boldsymbol{r}_a) - \boldsymbol{F}(\boldsymbol{r}_c) \\
\boldsymbol{F}(\boldsymbol{r}_c) &= \; -\frac{dU}{d\theta}\frac{1}{\sin\theta}\left(\frac{\boldsymbol{r}_{ab}}{r_{ab} r_{bc}} - \frac{\boldsymbol{r}_{bc}}{r_{bc}^2}\cos\theta\right)
\end{aligned}$$