

Derivation of Angle Force Field

2022/12/19 Takahiro Murashima

murasima@cmpt.phys.tohoku.ac.jp

Angle Potential

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

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

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

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

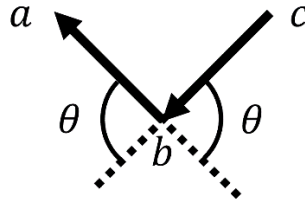


Figure 1. Schematic explanation of θ

Force field

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

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

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

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

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

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

$$\therefore \chi = \frac{\mathbf{r}_{ab} \cdot \mathbf{r}_{bc}}{r_{ab} r_{bc}} = \cos \theta$$

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

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

$$\therefore \frac{d}{d\mathbf{r}} \frac{\mathbf{r}}{r} = \frac{\partial \mathbf{r}}{\partial \mathbf{r}} \frac{1}{r} + \mathbf{r} \frac{d}{d\mathbf{r}} \frac{1}{r} = I \frac{1}{r} - \frac{\mathbf{r} \mathbf{r}}{r^3}$$

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

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

Derivation of $\mathbf{F}(\mathbf{r}_b)$

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

$$\frac{d\theta}{d\mathbf{r}_b} = \frac{\partial \mathbf{r}_{ab}}{\partial \mathbf{r}_b} \frac{d\theta}{d\mathbf{r}_{ab}} + \frac{\partial \mathbf{r}_{bc}}{\partial \mathbf{r}_b} \frac{d\theta}{d\mathbf{r}_{bc}} = -I \frac{d\theta}{d\mathbf{r}_{ab}} + I \frac{d\theta}{d\mathbf{r}_{bc}} = -\frac{d\theta}{d\chi} \frac{d\chi}{d\mathbf{r}_{ab}} + \frac{d\theta}{d\chi} \frac{d\chi}{d\mathbf{r}_{bc}}$$

$$= +\frac{1}{\sin \theta} \frac{d}{d\mathbf{r}_{ab}} \frac{\mathbf{r}_{ab} \cdot \mathbf{r}_{bc}}{r_{ab} r_{bc}} - \frac{1}{\sin \theta} \frac{d}{d\mathbf{r}_{bc}} \frac{\mathbf{r}_{ab} \cdot \mathbf{r}_{bc}}{r_{ab} r_{bc}}$$

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

$$\therefore \mathbf{F}(\mathbf{r}_b) = -\frac{dU}{d\mathbf{r}_b}$$

$$= -K[\cos \theta_0 - \cot \theta \sin \theta_0] \left(\frac{\mathbf{r}_{bc}}{r_{ab} r_{bc}} - \frac{\mathbf{r}_{ab}}{r_{ab}^2} \cos \theta \right)$$

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

Derivation of $\mathbf{F}(\mathbf{r}_c)$

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

Summary

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

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

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