Interatomic Potentials

We'll consider a potential of the OPLS-AA (Optimized Potential for Liquid Simulations, All Atom) model form:

$$E_{\text{bond}} = \sum_{\text{bonds}} K_r(r - r_{\text{eq}})^2$$

$$E_{\text{angle}} = \sum_{\text{angles}} K_\theta(\theta - \theta_{\text{eq}})^2$$

$$E(\phi) = \sum_{n=1}^{3} \frac{V_n}{2}\left(1 + \cos(n\phi + f_n)\right)$$

$$E_{ab} = \sum_{i}^{\text{on } a}\sum_{j}^{\text{on } b}\left[\frac{q_i q_j e^2}{r_{ij}} + 4\epsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right)\right]$$

These are the bond-stretching, bond-bending, torsion, and non-bonding terms. This is from OPLS-AA paper.

We want to write out expressions for the energies and forces in terms of atomic positions $\{\mathbf{r}_i\}$. The force on atom i is

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} E_{\text{total}}$$

Bond-stretching

The distance between two atoms, $\mathbf{r}_1$ and $\mathbf{r}_2$ is

$$r = |\mathbf{r}_1 - \mathbf{r}_2| = r_{12}$$

Both the bond-stretching and non-bonded terms are only functions of distance, so we'll consider a contribution to the energy of the form $v(r)$. The force is, by chain rule,

$$\mathbf{F}_{\text{i}} = -\nabla_{\mathbf{r}_i} v(r) = -\left.\frac{dv}{dr}\right|_{r=|\mathbf{r}_1-\mathbf{r}_2|} \nabla_{\mathbf{r}_i}|\mathbf{r}_1 - \mathbf{r}_2|$$

The derivative dv/dr is straightforward. For the second term,

$$\nabla_{\mathbf{r}_1} = \frac{\mathbf{r}_2 - \mathbf{r}_1}{|\mathbf{r}_2 - \mathbf{r}_1|} = \frac{\mathbf{r}_{21}}{r_{21}} = \hat{\mathbf{r}}_{21}$$

which is the normalized vector pointing from atom 1 to atom 2. By antisymmetry,

$$\nabla_{\mathbf{r}_2} = \frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{\mathbf{r}_{12}}{r_{12}} = \hat{\mathbf{r}}_{12}$$

which is the normalized vector pointing from atom 2 to atom 1.

Bond-bending

If we have three atoms with atom 2 at the "center" of a bond with atoms 1 and 3, with vectors $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{r}_{32} = \mathbf{r}_3 - \mathbf{r}_2$, then the angle θ_{123} is given by

$$\cos\theta_{123} = \frac{\mathbf{r}_{12} \cdot \mathbf{r}_{32}}{r_{12} r_{32}} = \hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{32}$$

To get the forces, we need to know $\nabla_{\mathbf{r}_i} \theta_{123}$ for each of the three atoms. A little bit of calculus is needed; first, let $x = \cos\theta$,

$$\frac{d}{dx} \arccos x = -\frac{1}{\sqrt{1-x^2}} = -\frac{1}{\sin\theta}$$

Then, we can take the derivative of $\cos\theta_{123}$ with respect to each atom position. First,

$$\begin{aligned}
\nabla_{\mathbf{r}_1} \theta_{123} &= \nabla_{\mathbf{r}_1} \arccos\left(\frac{\mathbf{r}_{12} \cdot \mathbf{r}_{32}}{r_{12} r_{32}}\right) = -\frac{1}{\sin\theta_{123}} \nabla_{\mathbf{r}_1} \left(\frac{\mathbf{r}_{12} \cdot \mathbf{r}_{32}}{r_{12} r_{32}}\right) \\
&= -\frac{1}{\sin\theta_{123}} \left\{ \frac{1}{r_{12}} \frac{\mathbf{r}_{32}}{r_{32}} - \frac{1}{r_{12}} \left(\frac{\mathbf{r}_{12} \cdot \mathbf{r}_{32}}{r_{12} r_{32}}\right) \frac{\mathbf{r}_{12}}{r_{12}} \right\} \\
&= -\frac{1}{r_{12} \sin\theta_{123}} \left(\hat{\mathbf{r}}_{32} - \cos\theta_{123} \hat{\mathbf{r}}_{12}\right)
\end{aligned}$$

Similarly,

$$\nabla_{\mathbf{r}_3} \theta_{123} = -\frac{1}{r_{32} \sin\theta_{123}} \left(\hat{\mathbf{r}}_{12} - \cos\theta_{123} \hat{\mathbf{r}}_{32}\right)$$

And finally,

$$\nabla_{\mathbf{r}_2} \theta_{123} = -\nabla_{\mathbf{r}_1} \theta_{123} - \nabla_{\mathbf{r}_3} \theta_{123}$$

Note the geometry here! The vector $(\hat{\mathbf{r}}_{32} - \cos\theta_{123} \hat{\mathbf{r}}_{12})$ is a vector that is perpendicular to the vector $\mathbf{r}_{12}$ in the plane of the atoms 1-2-3, and it's magnitude is $\sin\theta_{123}$. All that remains is to take the derivative of energy with respect to angle to apply the chain rule.

Torsion

The torsion angle requires a chain of four atoms 1-2-3-4 with their corresponding positions. The torsion angle ϕ is defined as the angle between the planes formed by atoms 1-2-3 and the atoms 2-3-4. Using our previous definitions of position vectors and relative vectors, the (unnormalized) normal vector of the 1-2-3 atom plane is

$$\mathbf{n}_{123} = \mathbf{r}_{12} \times \mathbf{r}_{32}$$

and for the 4-3-2 plane it is

$$\mathbf{n}_{432} = \mathbf{r}_{43} \times \mathbf{r}_{23}$$

Thus, the torsion angle ϕ is

$$\cos\phi = -\frac{\mathbf{n}_{123} \cdot \mathbf{n}_{432}}{|\mathbf{n}_{123}||\mathbf{n}_{432}|}$$

The derivatives are complicated; see Blondel and Karplus, *J. Comp. Chem.* **17**, 1132 (1996) for details; Eqn. 27, written in our notation, is:

$$\nabla_{\mathbf{r}_1}\phi = \frac{r_{23}}{n_{123}^2}\mathbf{n}_{123}$$

$$\nabla_{\mathbf{r}_4}\phi = \frac{r_{23}}{n_{432}^2}\mathbf{n}_{432}$$

$$\nabla_{\mathbf{r}_2}\phi = -\nabla_{\mathbf{r}_1}\phi + \frac{\mathbf{r}_{12}\cdot\mathbf{r}_{32}}{n_{123}^2 r_{23}}\mathbf{n}_{123} - \frac{\mathbf{r}_{43}\cdot\mathbf{r}_{23}}{n_{432}^2 r_{23}}\mathbf{n}_{432}$$

$$\nabla_{\mathbf{r}_3}\phi = -\nabla_{\mathbf{r}_4}\phi - \frac{\mathbf{r}_{12}\cdot\mathbf{r}_{32}}{n_{123}^2 r_{23}}\mathbf{n}_{123} + \frac{\mathbf{r}_{43}\cdot\mathbf{r}_{23}}{n_{432}^2 r_{23}}\mathbf{n}_{432}$$