

7. Classical Force Fields

Observables in classical statistical mechanics

- ▶ for a system with constant number of particles N , volume V , and temperature T , the Boltzmann distribution on the positions of the particles is

$$p(\mathbf{r}_1, \mathbf{r}_2, \dots) = \frac{\exp(-\beta U(\mathbf{r}_1, \mathbf{r}_2, \dots))}{Q_{\text{pos}}},$$

where $Q_{\text{pos}} = \int \exp(-\beta U(\mathbf{r}_1, \mathbf{r}_2, \dots)) d\mathbf{r}_1 d\mathbf{r}_2 \dots$

- ▶ the average value of an observable A is

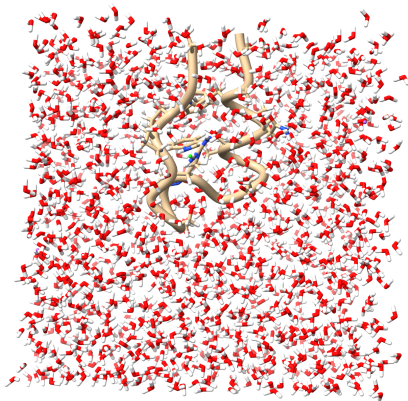
$$\langle A \rangle = \frac{\int \exp(-\beta U(\mathbf{r}_1, \mathbf{r}_2, \dots)) A(\mathbf{r}_1, \mathbf{r}_2, \dots) d\mathbf{r}_1 d\mathbf{r}_2 \dots}{\int \exp(-\beta U(\mathbf{r}_1, \mathbf{r}_2, \dots)) d\mathbf{r}_1 d\mathbf{r}_2 \dots}$$

- ▶ need to specify the potential energy function $U(\mathbf{r}_1, \mathbf{r}_2, \dots)$ for the system

Classical force fields

- ▶ in classical molecular simulations, the potential energy function $U(\mathbf{r}_1, \mathbf{r}_2, \dots)$ is often approximated using empirical potentials
- ▶ such empirical potentials are called classical force fields
- ▶ approximate the true potential energy of a system for which the exact calculation requires quantum mechanics
- ▶ are much faster to evaluate than quantum mechanical methods
- ▶ are often parameterized to reproduce quantum mechanical calculations or experimental data

Potential energy terms in classical force fields



$$\begin{aligned}
 U = & \sum_{\text{All Bonds}} \frac{1}{2} K_b (b - b_0)^2 + \sum_{\text{All Angles}} \frac{1}{2} K_\theta (\theta - \theta_0)^2 \\
 & + \sum_{\text{All Torsion Angles}} K_\phi [1 - \cos(n\phi + \delta)] \\
 & + \sum_{\text{All nonbonded pairs}} \epsilon \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right] \\
 & + \sum_{\text{All partial charges}} \frac{332 q_i q_j}{r}
 \end{aligned}$$

Figure: A small protein in a water box

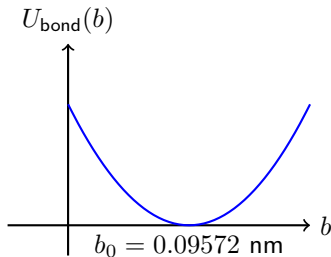
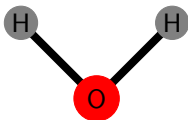
Bonds in classical force fields

- ▶ harmonic bond stretching

$$U_{\text{bond}(b)} = \frac{1}{2}k_b(b - b_0)^2$$

- ▶ example: O-H bond in water

$$b_0 = 0.09572 \text{ nm}, \quad k_b = 376560 \text{ kJ mol}^{-1} \text{ nm}^{-2}$$



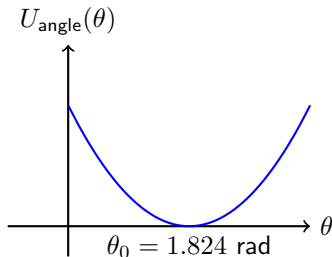
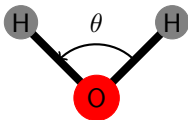
Angles in classical force fields

- ▶ harmonic angle bending

$$U_{\text{angle}(\theta)} = \frac{1}{2}k_{\theta}(\theta - \theta_0)^2$$

- ▶ example: H-O-H angle in water

$$\theta_0 = 1.824 \text{ rad}, \quad k_{\theta} = 460.24 \text{ kJ mol}^{-1} \text{ rad}^{-2}$$



Torsions in classical force fields

- ▶ periodic torsion potential

$$U_{\text{torsion}}(\phi) = k_{\phi}[1 + \cos(n\phi - \delta)],$$

where ϕ is the torsion angle, n is the periodicity, and δ is the phase shift

- ▶ example: O=C-NH₁-H

$$U_{\text{torsion}}(\phi) = 10.46[1 + \cos(2\phi - 180^{\circ})] \text{ kJ mol}^{-1}$$

