Intra-molecular interactions

To this point, we have focused on inter-molecular interactions (i.e., between molecules).

What about forces within a molecule? (i.e., intra-molecular)

In some cases, these are not important.

e.g., - water at room temperature
- the vibrational frequencies of the O-H bonds and H-O-H angle are much higher than the intermolecular vibrational frequencies

In other cases, intramolecular interactions are critical

e.g., - butane C_4H_{10}
- there are two stable configurations of this molecule at room temperature

TRANS: 99% of molecules

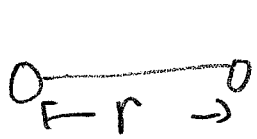
CIS: 1% of molecules

(H atoms not drawn)

- we need an intramolecular potential function that can differentiate between these two configurations
- consider: (a) bond length (2 atoms)
  (b) bond angles (3 atoms)
  (c) dihedral angles (4 atoms)

} all based on directly bonded atoms

(a) bond length (stretch)



$$u(r) = \frac{1}{2} k_s (r - r_0)^2$$

k_s: stretch; r_0: equilibrium value

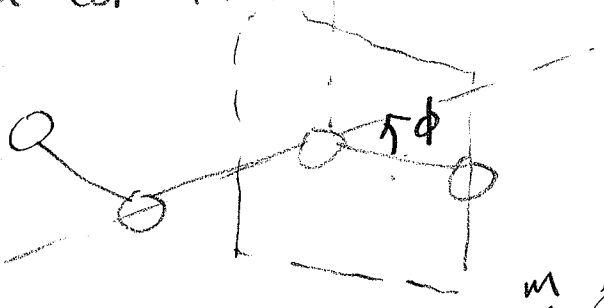
a simple harmonic potential

(b) bond angle (bend)

$$u(\theta) = \frac{1}{2} k_\theta (\theta - \theta_0)^2$$

k_θ: bend; θ_0: equilibrium value

(c) dihedral (or torsional) angle (four body term)



$$u(\phi) = \sum_{i=1}^{m} a_i \cos^i(\phi)$$

a_i: specific constants

Fa polynomial

For butane, m=4 will capture important physics

$$\rightarrow u(\phi) = a_1 \cos\phi + a_2 \cos^2\phi + a_3 \cos^3\phi + a_4 \cos^4\phi$$