

Molecular Dynamics

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Molecular Dynamics

- Molecular dynamics involves following the microscopic behavior at the atomistic level, by making the Born-Oppenheimer approximation and solving $F = ma$ for all the nuclei present.
- One can calculate the forces using either empirical or quantum methods, but empirical methods are almost always used for reasons of computational efficiency.
- Empirical force fields are the subject of Molecular Mechanics



Molecular Dynamics

- Accounts for thermal motion of atoms and molecules.
- Direct output is position and velocity as a function of time. This is known as Phase Space.
- Provides information about possible conformations, thermodynamic properties, and dynamic behavior of molecules.



Equation of Motion

- Start with Newton's Law: $F = ma$
- Force is: $F_i = -\frac{\partial V}{\partial r_i}$
- Rewrite as: $a_i = \frac{F_i}{m_i}$
- Solve: $\frac{d^2 x_i}{dt^2} = \frac{F_i}{m}$



Force Calculations

Fundamental Assumptions

- Born-Oppenheimer (As always)
- Force constants and bond lengths largely the same from one molecule to the next. This is called transferability.
- The bonds and other interactions can be characterized algebraically.



Potential Energy

- Terms include:
 - Bonds
 - Angles
 - Dihedrals
 - Non-bonded

$$V = \sum_{\text{Bonds}} K_r (r - r_{eq})^2 + \sum_{\text{Angles}} K_\theta (\theta - \theta_{eq})^2 + \sum_{\text{Dihedrals}} V_n (1 + \cos(n\phi - \gamma)) \\ + \sum_{i=1}^{N-1} \sum_{j>i}^N \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} + \frac{q_i q_j}{r_{ij}} \right]$$



Developing a Force Field

- Like all curve fitting procedures, the proof is in the pudding.
- The results must match the reality that is desired.
- If Z is a least squared penalty function, then we seek to minimize Z subject to the weights we place on the various observables

$$Z = \left[\sum_i^{\text{Observables}} \sum_j^{\text{Occurrences}} \frac{(\text{calc}_{ij} - \text{expt}_{ij})^2}{w_i^2} \right]^{1/2}$$

(Fox and Kollman, *J. Phys. Chem. B* **1998**, *102*, 8070-8079)

Force Fields

- There are many published force fields.
- Each have been developed for a specific purpose.
- More common ones include the MM series, Amber, Charmm, and OPLS.

