


Lecture VII: Potential Energy Surfaces

Recap: Statistical Mechanics and Sampling

- **Statistical Mechanics:** The partition function, $Z = \sum_i e^{-\beta E_i}$, provides access to all thermodynamic properties.
- **Monte Carlo (MC):** The natural ensemble for MC is the canonical ensemble (NVT). It uses random sampling according to the Boltzmann distribution.
- **Molecular Dynamics (MD):** The natural ensemble for MD is the microcanonical ensemble (NVE). It generates a phase space trajectory by numerically solving Newton's equations of motion.

The different thermodynamic ensembles can be simulated using MD and MC as follows:

Ensemble	Description	MC Method	MD Method
NVE	Microcanonical	Difficult	Natural Ensemble
NVT	Canonical	Natural Ensemble	Requires a Thermostat
NPT	Isothermal-Isobaric	Possible	Requires a Thermostat & Barostat

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Note that in practice, temperature (T) and pressure (P) are not strictly constant in NVT and NPT simulations but fluctuate around an average value. These fluctuations are dependent on the size of the system.

Potential Energy Surfaces (PES)

To calculate the total energy, $E = K + V$, which is needed for any simulation, we must specify the potential energy, V . There are two general strategies for defining this potential.

1. **"Ab Initio" Methods:** Solve the electronic Schrödinger equation for the system at each configuration. This is computationally very expensive.
2. **Force Fields:** Use a pre-defined analytical function to describe the interatomic potential. This is much more efficient.

Force Fields

Force fields use analytical functions to describe the potential energy of interacting atoms or molecules.

Pair Potentials

These describe the interaction between pairs of particles.

- **Lennard-Jones (LJ) Potential:** A common model for van der Waals interactions.

$$V^{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

- **Buckingham Potential:** Another model for non-bonded interactions.

$$V^B(r) = be^{-ar} - \frac{c}{r^6} - \frac{d}{r^8}$$

- **Morse Potential:** Often used to model the interaction in a diatomic molecule.

$$V^M = D_e \left(1 - e^{-a(r-r_e)} \right)^2$$

- **Harmonic Oscillator Potential:** A simple model for covalent bonds, treating them as springs.

$$V^{HO} = \frac{1}{2}Kx^2$$

Determining Force Field Parameters

The parameters for these potential functions (e.g., ϵ , σ , K) can be determined in two main ways:

1. **Empirical Adjustment:** Parameters are adjusted until simulation results match experimental data (e.g., density, virial coefficients).
2. **Electronic Structure Fitting:** Parameters are fitted to reproduce the potential energy surface calculated from high-level "ab initio" methods.

Many-Body Effects and Molecular Mechanics (MM)

Simple pair potentials are often insufficient, especially for dense systems or complex molecules. The total potential energy can be expressed as a many-body expansion:

$$V(r_1, \dots, r_N) = \sum_i V_1(r_i) + \sum_{i < j} V_2(r_i, r_j) + \sum_{i < j < k} V_3(r_i, r_j, r_k) + \dots$$

Here, V_1 represents external fields, V_2 are pair potentials, V_3 are three-body terms, and so on.

For large molecules, **Molecular Mechanics (MM)** or **Valence Force Fields** are used. These models assume a fixed chemical bonding topology (e.g., an sp^3 carbon atom remains sp^3 throughout the simulation).

An example is the **CHARMM** force field, which has the following general form:

$$V = \sum_{\text{bonds}} V_{\text{bond}} + \sum_{\text{angles}} V_{\text{angle}} + \sum_{\text{dihedrals}} V_{\text{dihedral}} + \sum_{\text{non-bonded}} V_{\text{vdW}} + V_{\text{Coulomb}}$$

- **Bonds:** $\frac{1}{2}k_b(b - b_0)^2$
- **Angles:** $\frac{1}{2}k_\theta(\theta - \theta_0)^2$
- **Dihedrals:** $k_\phi(1 + \cos(n\phi - \delta))$
- **van der Waals (vdW):** Lennard-Jones potential
- **Coulomb:** $\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$

Other common force fields include **AMBER**, **OPLS**, and **GROMOS**.

Simplifications and Modern Approaches

To improve computational efficiency, several simplifications can be made:

- **Freezing Bonds:** Treating bond lengths as rigid reduces the degrees of freedom and allows for a larger simulation time step.
- **United Atoms:** Representing small groups of atoms (like a CH₂ group) as a single interaction site.
- **Coarse-Graining:** Representing very large groups or entire molecules as single particles.

Modern approaches to developing potentials include using highly flexible mathematical functions or machine learning models trained on "ab initio" data.

Boundary Conditions

To simulate a bulk system (like a liquid) without having most particles on a surface, **Periodic Boundary Conditions (PBC)** are used. The simulation box is replicated infinitely in all directions, so a particle that exits one side of the box immediately re-enters from the opposite side.

Handling Interactions in PBC

This infinite replication creates a problem: each particle would interact with an infinite number of other particles.

- **Short-Range Potentials:** For potentials that decay quickly (like Lennard-Jones), a **cutoff radius** (R_{cut}) is used. A particle only interacts with other particles within this radius. To be physically valid, the cutoff must be less than half the length of the simulation box ($R_{cut} < L/2$). This is known as the **minimum image convention**.
- **Long-Range Potentials:** For potentials that decay slowly (like Coulomb interactions), a simple cutoff is inaccurate. Methods like **Ewald summation** are used. This technique splits the calculation into two parts: a short-range part calculated directly in real space and a long-range part calculated in reciprocal space (k-space).