Week 6 – Computer simulations

The new frontier: Nanoscience

Study of structure and properties of materials at the nanometer scale

Experimental methods: x-ray diffraction, nuclear magnetic resonance,…

Molecular structure obtained is often frozen, static.

How can we study its properties and dynamic response?

By simulating the system on a computer!

Several dynamics methods

• Ab initio molecular dynamics (quantum mech.)
• Molecular dynamics / Monte Carlo (classical mech.)
• Brownian dynamics (stochastic mech.)
Molecular dynamics (MD)
MD is the most popular method for simulation studies of nano systems
It is based on Newton’s equation of motion
For n interacting particles, one needs to solve n coupled DE:

\[ m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i = \sum_{j \neq i}^{n} \mathbf{F}_{ij}, \quad i = 1, \ldots, n \]

Analytically this is an intractable problem for n>2
But we can solve it easily on a computer using numerical methods
Current computers can handle n=10^5 – 10^6 particles, which is large enough for description of most nano-systems
Integration time, however, is still a bottleneck (10^6 steps @ 1 fs = 1 ns)
Integration algorithms

Given the position and velocities of n particles at time t,
at \ t+\Delta t \ they \ become

\[
v_i(t + \Delta t) = v_i(t) + \frac{F_i(t)}{m_i} \Delta t
\]

\[
r_i(t + \Delta t) = r_i(t) + v_i(t) \Delta t + \frac{F_i(t)}{2m_i} \Delta t^2
\]

Verlet algorithm:

\[
r_i(t - \Delta t) = r_i(t) - v_i(t) \Delta t + \frac{F_i(t)}{2m_i} \Delta t^2
\]

Add the two eq's \ \ \ \ r_i(t + \Delta t) = 2r_i(t) - r_i(t - \Delta t) + \frac{F_i(t)}{m_i} \Delta t^2

Velocity at \ t: \ v_i(t) = \frac{1}{2\Delta t}[r_i(t + \Delta t) - r_i(t - \Delta t)]
Leap-frog algorithm:

\[
v_i(t + \Delta t / 2) = v_i(t - \Delta t / 2) + \frac{F_i(t)}{m_i} \Delta t
\]

\[
r_i(t + \Delta t) = r_i(t) + v_i(t + \Delta t / 2) \Delta t
\]

Equivalent to the Verlet algorithm

\[
r_i(t + \Delta t) = r_i(t) + v_i(t - \Delta t / 2) \Delta t + \frac{F_i(t)}{m_i} \Delta t^2
\]

\[
r_i(t) = r_i(t - \Delta t) + v_i(t - \Delta t / 2) \Delta t
\]

Subtracting the two equations yields the Verlet result.

Velocity at \( t \):

\[
v_i(t) = \frac{1}{2} [v_i(t + \Delta t / 2) + v_i(t - \Delta t / 2)]
\]
To iterate these equations, we need to specify

- Initial conditions
- Force fields (potential functions)

Interaction of two atoms involves

- Coulomb potential \((1/r)\)
- Induced polarization \((1/r^2)\)
- Dispersion (van der Waals) \((1/r^6)\)
- Short range repulsion (exponential)

The first two can be described using classical electromagnetism

Polarization

\[ p_i = \alpha E_i \]

(\text{many-body})

\[ E_{pol} = \frac{1}{4\pi\varepsilon_0} \frac{1}{r^3} [3(p \cdot \hat{r})\hat{r} - p] \]
The last two interactions are quantum mechanical in origin.

Dispersion is a dipole-dipole interaction that arises from quantum fluctuations.

Short range repulsion arises from Pauli exclusion principle applied to electron clouds of atoms.

Usually they are combined using a 12-6 Lennard-Jones (LJ) potential

\[
U_{LJ} = 4\varepsilon \left[ \left( \sigma/r \right)^{12} - \left( \sigma/r \right)^{6} \right]
\]

Here \(\varepsilon\) corresponds to the depth of the potential at the minimum, \(2^{1/6}\sigma\)

Combination rules for different atoms:

\[
\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad \sigma_{ij} = \sqrt{\sigma_i \sigma_j}
\]
12-6 Lennard-Jones potential

$\varepsilon = \frac{1}{4}, \quad \sigma = 3$
In molecules, atoms are bonded together with covalent bonds. If the bonds are very strong, the molecule can be treated as rigid e.g. water; to account for the dipole moment, partial charges are assigned to the H and O atoms.

For softer and flexible bonds, a harmonic approximation is invoked

\[
U_{\text{bond}} = \frac{1}{2} k_r (r_{ij} - r_0)^2
\]

\[
U_{\text{bend}} = \frac{1}{2} k_\theta (\theta_{ijk} - \theta_0)^2
\]

\[
U_{\text{tors}} = k_\phi \cos(n\phi - \phi_0)
\]

This is a good approximation for most covalent bonds in polymers and biomolecules (proteins, lipids, etc.)
Monte Carlo (MC)

Metropolis algorithm:

Given \( n \) particles interacting with a potential energy \( U \)

Probability: \( P \propto e^{-U/kT} \)

- Assume some initial configuration with energy \( U_0 \)
- Move the particles by small increments to new positions with energy \( U_1 \)
- If \( U_1 < U_0 \), accept the new configuration
- If \( U_1 > U_0 \), select a random number \( r \) between 0 and 1, and accept the new configuration if

\[
\exp[-(U_1 - U_0)/kT] > r
\]
Brownian dynamics (BD)

In order to deal with the time bottle-neck in MD, one has to simplify the simulation system (coarse graining). This is achieved by describing parts of the system as continuum with dielectric constants.

Examples:

• transport of ions in electrolyte solutions (water $\rightarrow$ continuum)

• protein folding (water $\rightarrow$ continuum)

• function of transmembrane proteins (lipid $\rightarrow$ continuum)

To include the effect of the atoms in the continuum, modify the Newton’s eq. of motion by adding frictional and random forces:

Langevin equation

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i - \gamma_i m_i \mathbf{v}_i + \mathbf{R}_i$$
Frictional forces:

Friction dissipates the kinetic energy of a particle, slowing it down.

Consider the simplest case of a free particle in a viscous medium

\[ m \frac{d^2 \mathbf{r}}{dt^2} = -m \gamma \mathbf{v} \quad \rightarrow \quad \frac{dv}{dt} = -\gamma v \]

Solution with the initial values of \( \mathbf{v}(0) = v_0, \quad \mathbf{r}(0) = 0 \)

\[ \mathbf{v}(t) = v_0 e^{-\gamma t} \]

\[ \mathbf{r}(t) = \frac{v_0}{\gamma} \left( 1 - e^{-\gamma t} \right) \]

In liquids frictional forces are quite large, e.g. in water \( 1/\gamma \approx 20 \) fs

From \[ \frac{1}{2} m v^2 = \frac{3}{2} kT \quad \rightarrow \quad v \approx 500 \text{ m/s} \quad \text{and} \quad \frac{v}{\gamma} \approx 0.1 \AA \]
Random forces:

Frictional forces would dissipate the kinetic energy of a particle rapidly.

To maintain the average energy of the particle at 1.5 kT, we need to kick it with a random force at regular intervals.

This mimics the collision of the particle with the surrounding particles, which are taken as continuum and hence not explicitly represented.

Properties of random forces:

1. Must have zero mean (white) \( \langle R_i \rangle = 0, \quad i = x, y, z \)

2. Uncorrelated with prior velocities \( \langle v_i(0)R_j(t) \rangle = 0 \)

3. Uncorrelated with prior forces \( \langle R_i(0)R_j(t) \rangle = 2m\gamma kT \delta(t)\delta_{ij} \) (Markovian assumption)
Fluctuation-dissipation theorem:

Because the frictional and random forces have the same origin, they are related

\[ m\gamma = \frac{1}{2kT} \int_{-\infty}^{\infty} \langle R(0)R(t) \rangle \, dt \]

In liquids the decay time is very short, hence one can approximate the correlation function with a delta function

\[ \langle R(0)R(t) \rangle = 2m\gamma kT\delta(t) \]
Random forces have a Gaussian probability distribution

\[ w(R_i) = \frac{1}{\sqrt{2\pi \langle R_i^2 \rangle}} \exp\left(-\frac{R_i^2}{2\langle R_i^2 \rangle}\right) \]

\[ \langle R_i^2 \rangle = \frac{2m\gamma kT}{\Delta t} \]

This follows from the fact that the velocities have a Gaussian distribution

\[ g(v_i) = N \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mv_i^2}{2kT}\right) \]

In order to preserve this distribution, the random forces must be distributed likewise.
A simple example: force-free particle

Since \( \mathbf{F} = 0 \), \( \langle x \rangle = \langle y \rangle = \langle z \rangle = 0 \)

But because \( \mathbf{R} \neq 0 \), \( \langle x^2 \rangle \neq 0 \), \( \langle y^2 \rangle \neq 0 \), \( \langle z^2 \rangle \neq 0 \)

\[
\ddot{x} = -\nu \dot{x} + \frac{R_x}{m} \quad \rightarrow \quad x \ddot{x} = -\nu x \dot{x} + \frac{R_x}{m} x
\]

\[
\frac{d}{dt}(x \dot{x}) - \dot{x}^2 = -\nu x \dot{x} + \frac{R_x}{m} x
\]

Ensemble average

\[
\frac{d}{dt} \langle x \dot{x} \rangle - \frac{kT}{m} = -\nu \langle x \dot{x} \rangle + \frac{1}{m} \langle R_x \rangle \langle x \rangle \rightarrow 0
\]

Integrate

\[
\langle x \dot{x} \rangle = \frac{kT}{m \gamma} \left( 1 - e^{-\nu t} \right)
\]
Using \( \frac{d}{dt} \langle x^2 \rangle = 2 \langle x \dot{x} \rangle \) in the previous result gives

\[
\frac{d}{dt} \langle x^2 \rangle = \frac{2kT}{m\gamma} \left( 1 - e^{-\gamma t} \right)
\]

\[
\langle x^2 \rangle = \frac{2kT}{m\gamma} \left[ t - \frac{1}{\gamma} \left( 1 - e^{-\gamma t} \right) \right]
\]

Consider the limits

1) Ballistic limit : \( t \ll \frac{1}{\gamma} \) \( \rightarrow \) \( \langle x^2 \rangle = \frac{kT}{m} t^2 \)

2) Diffusion limit : \( t \gg \frac{1}{\gamma} \) \( \rightarrow \) \( \langle x^2 \rangle = \frac{2kT}{m\gamma} t \)

Fick’s law for self - diffusion : \( \langle x^2 \rangle = 2Dt \) \( \rightarrow \) \( D = \frac{kT}{m\gamma} \) Einstein relation
Integration algorithms

More complicated because one has to integrate over the random force.

The simplest is a leap-frog algorithm

\[
\dot{v}_i = -\gamma v_i + \frac{1}{m} (F_i + R_i), \quad i = x, y, z
\]

\[
v_i(t + \Delta t / 2) = v_i(t - \Delta t / 2) e^{-\gamma \Delta t} + \frac{F_i(t) + R_i(t)}{m} \Delta t
\]

\[
x_i(t + \Delta t) = x_i(t) + v_i(t + \Delta t / 2) \Delta t
\]

This algorithm is alright for short time steps, i.e. a few fs.

For longer time steps, one needs to use a more accurate integration algorithm.
Statistical analysis of trajectory data

A typical simulation consists of two stages:

1. Equilibration
2. Production run

The trajectory data generated during the production run is used in statistical analysis of the system:

- Thermodynamic average and standard deviation (fluctuations)
- Pair distribution functions (structural information)
- Time correlation functions (dynamical information)

Ergodic theorem: ensemble average = time average