Lecture 21
CH-4114
Molecular Simulation

"Everything that living things do can be understood in terms of the jigglings and wigglings of atoms."

- Richard P. Feynman

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Pressure Calculation, Coupling and Concept of Barostat:

The NPT Ensemble and Volume Fluctuation

- **NPT Ensemble (Isothermal-Isobaric):** This ensemble maintains a constant number of particles (N), constant pressure (P), and constant temperature (T). To keep the pressure constant, the **volume (V) of the simulation box is allowed to fluctuate.**

- **Isothermal Compressibility (β_T):** The extent to which the volume fluctuates is an inherent property of the system, mathematically defined by the isothermal compressibility:

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

Weak Coupling to a Pressure Bath

The core idea of the Berendsen method is to **"weakly couple"** the system's pressure, P, to an external reference pressure, P_0. This coupling is designed to make the pressure relax exponentially towards the target pressure.

- **Relaxation Term:** The text uses the equation:

$$\frac{dP}{dt} \propto \frac{P_0 - P}{\tau_P}$$

This means the rate of change of pressure ($\frac{dP}{dt}$) is proportional to the difference between the target pressure (P_0) and the current pressure (P), scaled by a **pressure relaxation time constant (τ_P)**. The term τ_P dictates how quickly the system pressure reacts to the bath.

Berendsen Pressure Coupling

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The Target: Exponential Pressure Relaxation

The Berendsen method postulates that the system's instantaneous pressure (P) should relax toward the target pressure (P_0) exponentially with a time constant τ_P:

$$\left.\frac{dP}{dt}\right|_{\text{bath}} = \frac{P_0 - P}{\tau_P} \quad (1)$$

Recall how this is analogous to Berendsen Temperature Coupling

$$\frac{dT}{dt} = \frac{1}{\tau_T}(T_0 - T)$$

Solve for T(t)

This differential equation has an exponential relaxation solution:

$$T(t) = T_0 + [T(0) - T_0]e^{-t/\tau_T}$$

So the system temperature relaxes exponentially toward the bath temperature T_0.

Velocity rescaling form (used in MD)

Since $E_k \propto v^2 \propto T$, controlling T means **rescaling velocities** at each time step:

Let λ be the scaling factor for velocities at time t:

$$\mathbf{v}'_i = \lambda \mathbf{v}_i$$

Then $T' = \lambda^2 T$.

Berendsen Pressure Coupling

The Mechanism: Coordinate and Volume Scaling

In Molecular Dynamics (MD), the pressure is changed by continuously scaling the simulation box volume (V).

The Berendsen barostat applies an extra velocity term to the equation of motion for each coordinate $\mathbf{x}$ (where $\mathbf{x}$ is x, y, z for a given particle), proportional to a scaling factor α:

$$\dot{\mathbf{x}} = \mathbf{v} + \alpha \mathbf{x} \quad (2)$$

The rate of change of a linear dimension (e.g., box length L) is $\dot{L} = \alpha L$.

For a 3D isotropic system, the rate of change of the **volume** ($V = L^3$) is:

$$\frac{dV}{dt} = \frac{d(L^3)}{dt} = 3L^2 \frac{dL}{dt} = 3L^2(\alpha L) = 3\alpha L^3$$

$$\frac{dV}{dt} = 3\alpha V \quad (3)$$

3. The Constraint: Isothermal Compressibility

Thermodynamically, the change in volume is related to the change in pressure via the **isothermal compressibility (β_T)**:

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Rearranging this to relate the time derivatives $\frac{dP}{dt}$ and $\frac{dV}{dt}$:

$$\frac{dV}{dt} = -\beta_T V \frac{dP}{dt} \quad (4)$$

(*Note: This relationship assumes the system is close to equilibrium, which is the underlying approximation of the Berendsen method*).

Combining the Terms (Derivation of α)

Now, we equate the two expressions for the rate of change of pressure ($\frac{dP}{dt}$):

- Substitute the coupling requirement (1) for $\frac{dP}{dt}$ into the thermodynamic relation (4):

$$\frac{dV}{dt} = -\beta_T V \left(\frac{P_0 - P}{\tau_P} \right)$$

$$\frac{dV}{dt} = \frac{\beta_T V}{\tau_P}(P - P_0) \quad (5)$$

- Finally, equate the volume change derived from the scaling (3) with the combined expression (5):

$$3\alpha V = \frac{\beta_T V}{\tau_P}(P - P_0)$$

- Solving for α by dividing both sides by $3V$:

$$\alpha = \frac{\beta_T}{3\tau_P}(P - P_0)$$

Key Insight

$$\alpha = \frac{\beta_T}{3\tau_P}(\mathbf{P} - \mathbf{P_0})$$

➤ This factor α (alpha) is a simple scalar that dictates the velocity by which all coordinates and box vectors are scaled at each time step to drive the pressure toward the target value P_0.

➤ Interpretation of the Terms:$(P - P_0)$: The sign of α(alpha) depends on the pressure difference. If $P > P_0$, α is positive, leading to an expansion ($\dot{x} > 0$), which reduces the pressure.

➤ τ_p: The coupling time constant. A smaller τ_p results in a larger α, meaning stronger, faster coupling.

➤ β_T: The isothermal compressibility. A system that is highly compressible (large β_T) requires a larger α for a given pressure change.

Computing Pressure: The Virial Theorem

The final expression for pressure in an MD simulation that relates macroscopic pressure (P) to microscopic properties (particle positions $\mathbf{r}$ and forces $\mathbf{F}$) is:

$$P = \frac{NkT}{V} + \frac{1}{3V} \sum_{i<j} \langle \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \rangle$$

Origin: Statistical Mechanics/Mayer's Cluster Expansion

This formula effectively breaks the pressure into two intuitive components:

1. The Ideal Gas Component ($\mathbf{P}_{\text{Ideal}}$)

This component accounts for the kinetic energy of the particles, representing the pressure that would exist even if the particles had no interactions (an ideal gas).

- **Starting Point:** The ideal gas law is $PV = NkT$.

2. The Interaction Component ($\mathbf{P}_{\text{Interaction}}$)

This component accounts for the effects of inter-particle forces ($\mathbf{F}_{ij}$) on the system pressure. This is where the **Virial Theorem** comes in.

- **The Virial ($\mathbf{W}$):** In classical mechanics, the Virial is defined as the sum of the product of coordinates and forces. The Virial Theorem connects the system's kinetic energy ($\sum \frac{1}{2} m_i \mathbf{v}_i^2 = \frac{3}{2} NkT$) to the system's Virial W:

$$\sum_i \langle \mathbf{r}_i \cdot \mathbf{F}_i \rangle = -3PV$$

This is the core result that links microscopic forces to macroscopic pressure, P.

- **Breaking Down the Force ($\mathbf{F_i}$):** The total force $\mathbf{F}_i$ on any particle i has two origins:

  1. **External Force ($\mathbf{F}_i^{\text{ext}}$):** The force exerted by the walls of the container, which is directly related to the system pressure P.

  2. **Internal Force ($\mathbf{F}_i^{\text{int}}$):** The forces exerted on particle i by all other particles j (i.e., $\mathbf{F}_i^{\text{int}} = \sum_{j \neq i} \mathbf{F}_{ij}$).

Virial Contribution to Pressure in Molecular Dynamics or Monte Carlo Simulations Using Truncated Lennard-Jones (LJ) potentials.

- In simulations, we can't sum over all infinite pairs of particles — so we **truncate** the potential at a cutoff r_c.
  However, there are still weak attractive interactions beyond r_c that **contribute to energy and pressure**.
- In our early classes we have shown energy correction.
- To estimate and fix pressure now, we compute their **mean-field (analytical)** contribution assuming that Beyond r_c , the radial distribution function $g(r) \approx 1$) i.e., particles are uniformly distributed).
- This approximation gives rise to "tail corrections" for **energy** and **pressure**.

Virial Expression for Pressure:

In statistical mechanics, the pressure P of a system can be related to the virial as:

$$P = \rho k_B T + \frac{1}{3V} \left\langle \sum_{i<j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \right\rangle$$

When using a **Lennard-Jones potential:**

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

And the corresponding force $F(r) = -\frac{dU}{dr}$, the virial integral for $r > r_c$ can be evaluated analytically under the assumption of a **uniform particle distribution** beyond r_c.

Plug into the Pressure Tail Integral

$$P_{\text{tail}} = -\frac{2\pi}{3}\rho^2 \int_{r_c}^{\infty} r^3 \frac{dU(r)}{dr} dr$$

Substitute and simplify:

$$P_{\text{tail}} = \frac{8\pi\epsilon}{3}\rho^2 \int_{r_c}^{\infty} \left[12\frac{\sigma^{12}}{r^{10}} - 6\frac{\sigma^6}{r^4} \right] dr$$

Integrate term by term:

$$\int_{r_c}^{\infty} r^{-10} dr = \frac{1}{9r_c^9}, \qquad \int_{r_c}^{\infty} r^{-4} dr = \frac{1}{3r_c^3}$$

$$P_{\text{tail}} = \frac{8\pi\epsilon}{3}\rho^2 \left[12\frac{\sigma^{12}}{9r_c^9} - 6\frac{\sigma^6}{3r_c^3} \right]$$

Tail Correction to Pressure (WLRC):

$$P_{\text{tail}} = \frac{16}{9}\pi\rho^2\sigma^3\epsilon\left(2\left(\frac{\sigma}{r_c}\right)^9 - 3\left(\frac{\sigma}{r_c}\right)^3\right)$$

This corresponds to the formula:

$$\text{WLRC} = \frac{16}{9}\pi\rho N\sigma^3\left(2\left(\frac{\sigma}{r_c}\right)^9 - 3\left(\frac{\sigma}{r_c}\right)^3\right)$$

Where:

- $\rho = N/V$ is the number density
- σ: LJ parameter
- r_c: cutoff radius
- $\left(\frac{\sigma}{r_c}\right)^3 = SR3$, and $\left(\frac{\sigma}{r_c}\right)^9 = SR9$ **Code Implementation**
- ϵ is absorbed in unit conversion or set to 1 (reduced units)

This is derived by integrating the virial component of the force over the spherical shell beyond r_c assuming a constant density (mean-field approximation).

Dimensions and Units 1. Magnitudes

- Important extensive quantities small in magnitude
  - when expressed in macroscopic units
- Small numbers are inconvenient
- Two ways to magnify them
  - work with atomic-scale units
    - ps, amu, nm or Å
  - make dimensionless with characteristic values
    - model values of size, energy, mass

Symbol	Definition	Value
1. Constants		
k	Boltzmann's constant	1.3806×10^{-23} J/(molec·K)
N_0	Avagadro's number	6.022×10^{23}
2. Simulation Variables		
N	Number of molecules	$\sim 10^3$
V	Simulation cell volume	$\sim 10^{-24}$ m^3
m	Molecular mass	$\sim 10^{-25}$ kg/molec
ρ	Number density	$\sim 10^{27}$ molec/m^3
E	Energy (total)	$\sim 10^{-20}$ J/molec
t	time	$\sim 10^{-12}$ s
3. Model Variables		
σ	Size variable	$\sim 5 \times 10^{-10}$ m
ϵ	Energy variable	$\sim 10^{-21}$ J/molec
r_b	Bond distance	$\sim 10^{-10}$ m
k_v	Vibrational spring constant	$\sim 10^3$ J/m^2

Dimensions and Units 2. Scaling

- In simulations it is often convenient to express quantities such as temperature, density, pressure and the like in reduced units. This means that we choose a convenient unit of energy, length and mass and then express all the other quantities in terms of these basic units. A natural choice of our basic units is the following
  - size σ
  - energy ε
  - mass m

In terms of these basic units, all other units follow

Symbol	Meaning	Definition
r^*	dimensionless distance	r/σ
E^*	dimensionless energy	E/ϵ
T^*	dimensionless temperature	kT/ϵ
U^*	dimensionless internal energy	U/ϵ
t^*	dimensionless time	$t/[\sigma(m/\epsilon)^{0.5}]$
v^*	dimensionless velocity	$v/(\epsilon/m)^{0.5}$
F^*	dimensionless force	$F\sigma/\epsilon$
p^*	dimensionless pressure	$P\sigma^3/\epsilon$
D^*	dimensionless self diffusion coefficient	$D/[\sigma(\epsilon/m)^{0.5}]$

Why reduced Units?

- Many combinations of ρ, T, ε and σ all correspond to the same state in reduced units. This is the law of corresponding states: the same simulation can of a LJ model can be used to study the Argon at 60 K and density 840 kg/m3 and Xe at 112 K and a density at 1617 kg/m3. In reduced unit both simulations corresponds to the state point $\rho = 0.5$ and $T = 0.5$. Scaling by model parameters

- In reduced units almost all quantities of interest are of order 1 (say between 10-3 and 103). Hence if we suddenly find very large (or very small) number in our simulations, suspect some error somewhere.

- Simulation results obtained in reduced units can be translated back into real units.

See the following table

Conversion of reduced Units to real Units for LJ argon system: $\varepsilon/k_B = 119.8$ K, $\sigma = 3.405 \times 10^{-10}$ m, m = 0.03994 kg/mol

Quantity	Reduced Units	Real Units
Temperature	$T^* = 1$	$T = \varepsilon/k_B = 119.8$ K
Density	$\rho^* = 1$	$\rho = 1680$ kg/m³
Time	$\delta t^* = 0.005$	$\delta t = 1.09 \times 10^{-14}$ s
Pressure	$P^* = 1$	$P = 41.9$ MPa

Thank you for joining CH4114!

May you look back on this class and recognize the **valuable transformation** that took place here.

---- Susmita Roy