From Atoms to Materials: Predictive Theory and Simulations

Week 4: Connecting Atomic Processes to the Macroscopic World
Lecture 4.5: Isothermal & Isobaric MD Simulations

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MD at constant temperature

Canonical (NVT) ensemble averages

What do we expect from an NVT MD simulation?

• Average kinetic energy should correspond to desired temperature

\[ \langle k \rangle_m = \frac{3}{2} N_{\text{eff}} kT \]

• Dynamics of system to be consistent with the canonical distribution

\[ P_m(\{\mathbf{r}_i\}; \{\mathbf{p}_i\}) = \frac{1}{Z} \cdot \exp \left(-\beta H(\{\mathbf{r}_i\}; \{\mathbf{p}_i\})\right) \]
Isothermal MD: Andersen approach

Coupling of system with heat bath:
Stochastic collisions between randomly selected particles with the bath that result in a new velocity consistent with the desired temperature

1. Integrate equations of motion for time $\Delta t$

2. Number of atoms that underwent collisions during $\Delta t$ is: $\nu \Delta t$ – select them randomly

3. Assign new velocities to selected atoms from a Maxwell-Boltzmann distribution at temperature $T$

**PROS:**
Leads to canonical distribution

**CONS:**
Collisions affect atomic dynamics (e.g. diffusion coefficient)

Isothermal MD: Berendsen approach

Can we modify the equations of motion to obtain desired temperature?

**Berendsen thermostat**

- Direct feedback to control temperature
- \( \gamma \) is a heat flow variable (can be negative or positive)
- \( \gamma \) defined in terms of instantaneous temperature \( (T) \) and thermostat temperature \( (T_0) \)
- MD temperature converges to desired thermostat temperature

\[
\dot{R}_i = \frac{P_i}{m_i}
\]

\[
\dot{P}_i = F_i - \gamma \cdot P_i
\]

\[
\gamma(t) = \frac{T(t) - T_0}{T(t)}
\]

**PROS:**

- Thermalizes system to desired temperature efficiently

**CONS:**

- Does not lead to the canonical distribution

Isothermal MD: Nosé-Hoover approach

Berendsen thermostat

\[ \dot{R}_i(t) = \frac{\dot{P}_i(t)}{M_i} \]
\[ \dot{P}_i(t) = F_i(t) - \gamma(t)P_i(t) \]
\[ \gamma(t) = \nu \frac{T(t) - T_0}{T(t)} \]

• Heat flow variable has its own equation of motion: integral feedback
• Enables kinetic energy fluctuations

PROS:
• Leads to canonical distribution
• Time reversible

CONS:
• Approach to equilibrium: can lead to oscillations
• Persistent, non-canonical oscillations can occur if care is not taken

Molecular dynamics in various ensembles

Thermostats:
- Andersen: stochastic, based on collisions
- Berendsen: direct feedback to control kinetic energy
- Nose-Hoover: extended Lagrangian, integral feedback

Barostats:
- Hoover, Rahman and Parrinello
- Cell volume (liquids) or cell parameters (in solids) are allowed to fluctuate to equilibrate the system to an external stress state
Further reading

• Andersen, J. Chem. Phys. 72, 2384 (1980)


• Parrinello and Rahman, J. Appl. Phys. 52, 7182 (1981)


• Melchionna, Cicotti and Holian, Mol Phys. 78, 533 (1993)
