Temperature and Pressure Controls

Ensembles

1. \((E, V, N)\) microcanonical (constant energy)
2. \((T, V, N)\) canonical, constant volume
3. \((T, P, N)\) constant pressure
4. \((T, V, \mu)\) grand canonical

• #2, 3 or 4 are often better for macroscopic properties
• Today we will learn how we can do #2 and #3 with MD.
Constant Temperature MD

- Problem in MD is to control the temperature.

- How to start the system?
  Sample the velocities from a Maxwellian (Gaussian) distribution.
  (we will learn how to do this next time)

\[
P(v) \, dv = C \exp\left(-\frac{mv^2}{k_B T}\right) \, dv
\]

- If we start from a perfect lattice as the system becomes disordered, it will suck up the kinetic energy and cool down.
- Vice versa for starting from a gas.

- QUENCH method.
- Andersen Thermostat
- Nose-Hoover Thermostat
Quench method (Berendsen)

- Run for a while, compute kinetic energy, then rescale the momentum to correct temperature $T$, repeat as needed.

\[ k_B T_I = \frac{1}{3N - 3} \sum_i m_i v_i^2 \]

\[ v_i^{\text{new}} = v_i^{\text{old}} \sqrt{\frac{T}{T_I}} \]

• Control is at best $O(1/N)$, not real-time dynamics.
Brownian dynamics/Andersen thermostat

• *Put a system in contact with a heat bath*
• Leads to discontinuous velocities.
• Not necessarily a bad thing, but requires some physical insight into how the bath interacts with the system.
  – For example, this is appropriate for a large molecule (protein or colloid) in contact with a solvent.
  – Other heat baths in nature are given by phonons, photons,...
• We will discuss Brownian dynamics later in the course.
• Andersen thermostat:
  – With some probability, resample velocities from a Maxwell dist. (see FS 6.1.1)
Nose-Hoover thermostat (FS 6.1.2)

- MD in canonical distribution (T,V,N)
- Introduce a *friction* force $\zeta(t)$

\[
\frac{dp}{dt} = F(q,t) - \zeta(t)p(t)
\]

Dynamics of friction coefficient to get canonical ensemble.

\[
Q \frac{d\zeta}{dt} = \sum_i \frac{1}{2} m_i v_i^2 - \frac{3N}{2} k_B T
\]

Feedback makes K.E. = 3/2 kT

\[
\frac{d\zeta}{dt} = 0 \quad \text{Dynamics at steady-state}
\]

$Q$ = fictitious “heat bath mass”. Large $Q$ is weak coupling.


**Nose-Hoover thermodynamics**

- Energy of physical system fluctuates. However energy of system plus heat bath is conserved.

\[ H' = H + \frac{Q}{2} \zeta^2 + 3Nk_B T \ln(s) \quad \text{where} \quad \frac{d \ln s}{dt} = \zeta \]

- Derive equation of motion from this Hamiltonian. (see text)

\[
\frac{dr}{dt} = \frac{p}{m} \quad \frac{dp}{dt} = F - \zeta p \quad \frac{d\zeta}{dt} = \frac{1}{Q} \left( \sum_i \frac{p_i^2}{m_i} - 3Nk_BT \right)
\]

- Hopefully system is ergodic.

Then stationary state is canonical distribution

\[ \exp \left\{ -\beta \left( V + \frac{1}{2m} p^2 + \frac{Q}{2} \zeta^2 \right) \right\} \]
Effect of thermostat

System T fluctuates but how quickly?

Q=1
Q=100

DIMENSION 3
TYPE argon 256 48.
POTENTIAL argon argon 1 1.1 1.2 2.5
DENSITY 1.05
TEMPERATURE 1.15
TABLE_LENGTH 100000
LATTICE 4 4 4 4
SEED 10
WRITE_SCALARS 25
NOSE 100.
RUN MD 2200 .05

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Thermostats are needed in non-equilibrium situations where there might be a flux of energy in/out of the system.

It is time-reversible, deterministic and goes to the canonical distribution but:

How natural is the thermostat?
- Interactions are non-local. They propagate instantaneously
- Interaction with a single heat-bath variable-dynamics can be strange. Be careful to adjust the “mass”

REFERENCES FS 6.1.2
Comparison of Thermostats

Nose-Hoover (deterministic) vs. Andersen (stochastic)

Figure 6.7: Trajectories of the harmonic oscillator: (from left to right) in the microcanonical ensemble, using the Andersen method, and using the Nosé-Hoover method. The y axis is the velocity and x axis is the position.

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Constant pressure or constant volume

- At constant pressure phase transitions are sharp.

- At constant volume, a two phase region (shaded region) is seen.

- In a finite cell, one will have droplets/crystallites form, but surface tension will make a barrier to the formation of them.

- An additional problem is the shape of simulation cell, that will favor certain crystal structures.
To generalize MD, follow similar procedure as for thermostats for constant P. Size of the box is coupled to internal pressure.

Volume is coupled to Virial Pressure.

\[ P = \frac{1}{3\Omega} \sum_i \left( \frac{p_i^2}{m_i} + r_i \cdot F_i \right) \]

Unit cell shape can also change.
- System can switch between crystal structures.
- Method is very useful in studying the transitions between crystal structures.
- Dynamics is unrealistic: Just because a system can fluctuate from one structure to another does not mean that the probability will be high.

Fig. 7.3 Changing box-shape.
To implement, consider

- **Internal coordinates**: $0 < s < 1$
- **Physical coordinates**: $r$

\[ \vec{r} = L \vec{s} \quad \vec{s} = L^{-1} \vec{r} \]

- $L$ is a 3 x 3 time-dependent symmetric matrix.
- Symmetric to eliminate rotation of cell.
- **Do periodic boundary conditions with $s$.** (simple)
- **Calculate energy and forces with $r$.**
Equations of motion

$\omega$ is the response (or mass) of the surrounding medium.

- Usual $F = ma$ but also force from boundaries

- Feedback keeps box size in equilibrium

- Stress tensor, $\sigma$

- The new distribution is

$$\frac{d\vec{p}}{dt} = \vec{F} - \mathcal{L}^{-T} \frac{d\vec{L}}{dt} \vec{p}$$

$$\omega \frac{d^2 \vec{L}}{dt^2} = (\sigma - \mathcal{P} \mathcal{L}^{-T}) \Omega \mathcal{L}^{-T}$$

$$\sigma = \frac{1}{\Omega} \sum_i \left[ \vec{r}_i \vec{F}_i + m_i \vec{v}_i \vec{v}_i \right]$$

$$\exp\left\{-\beta \left( H + P \Omega + \omega \mathcal{L} \mathcal{L}^T \right)\right\}$$
• 500 KCl ions at 300K
• First P = 0
• Then P = 44 kB
• System spontaneously changes from rocksalt to CsCl structure

Fig. 2. – Time history of a compression and decompression molecular-dynamics run on KCl. Points plotted are 25 Δt apart, hence the nonsmooth appearance. In regions I to IV the pair correlations were monitored; these have not been shown in this lecture. Significance of the numbered vertical arrows is discussed in the text.

Fig. 3. – Detail of rocksalt to cesium chloride change found to occur in the MD calculation. Thick arrow in A indicates a dilatation resulting in B. Fine arrows in B indicate displacements of particles with a common c direction co-ordinate, resulting in the final structure C. A is rocksalt, C is cesium chloride (see text).
Can “automatically” find new crystal structures

Nice feature is that the boundaries are flexible

But one is not guaranteed to get out of local minimum

One can get the wrong answer. Careful free energy calculations are needed to establish stable structure.

All such methods have non-physical dynamics since they do not respect locality of interactions but non-physical effects are small: $O(1/N)$.

REFERENCES