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 , μ) 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)

$$P(v) = Ce^{-\frac{mv^2}{k_B T}} dv$$

  - 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.

$$k_B T_I = \frac{\sum_i m_i v_i^2}{3N-3} \qquad v_i^{new} = \sqrt{\frac{T}{T_I}} v_i^{old}$$

Instantaneous T_I

- Control is at best O(1/N), not real-time dynamics.

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DIMENSION 3
TYPE argon 256 48.
POTENTIAL argon argon 1 1. 1. 2.5
DENSITY 1.05
TEMPERATURE 1.15
TABLE_LENGTH 10000
LATTICE 4 4 4 4
SEED 10
WRITE_SCALARS 25
WRITE_COORD 25
QUENCH 100
RUN MD 400 .05
QUENCH 0
RUN MD 1800 .05
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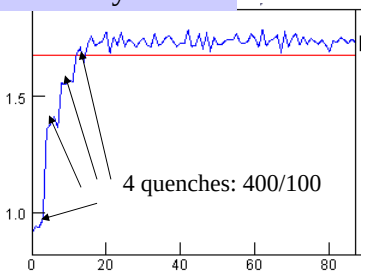


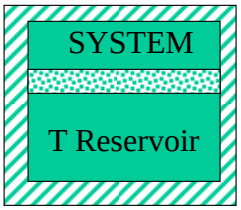
Brownian dynamics/Andersen thermostat

- *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 **ζ(t)**

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



Dynamics of friction coefficient to get canonical ensemble.

$$Q\frac{d\zeta}{dt} = \sum \frac{1}{2} m_i v_i^2 - \frac{3N}{2} k_B T$$

Feedback makes K.E.=3/2 kT

$$\frac{d\zeta}{dt} = 0$$ 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*.

$$H' = H + \frac{Q}{2}\zeta^2 + gk_B T \ln(s) \quad and \quad \frac{d\ln(s)}{dt} = \zeta$$

- Derive equation of motion from this Hamiltonian.
  - dr/dt=p, dp/dt= F - p_ζ /Q, dζ/dt=p_ζ/Q etc. (see text)
- Hopefully system is *ergodic*.

Then stationary state is canonical distribution

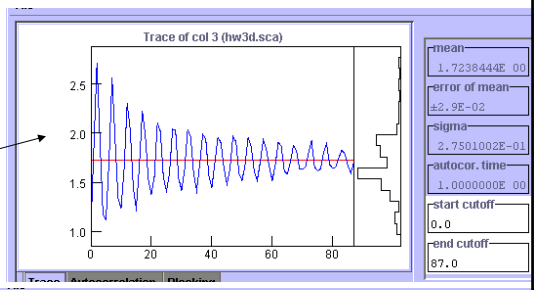
$$\exp[-\beta(V + \frac{1}{2m}p^2 + \frac{Q}{2}\zeta^2)]$$

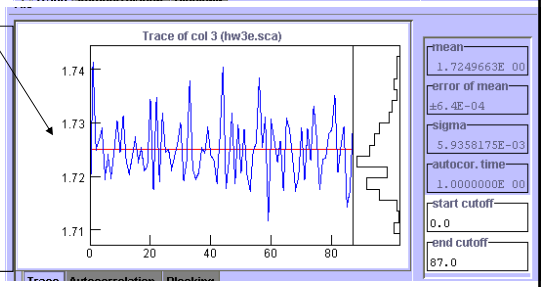
Effect of thermostat

System T fluctuates but how quickly?

Q=1

Q=100



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DENSITY 1.05
TEMPERATURE 1.15
TABLE_LENGTH 10000
LATTICE 4 4 4 4
SEED 10
WRITE_SCALARS 25
NOSE 100.
RUN MD 2200 .05
```


- *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

1. *S. Nose, J. Chem. Phys. 81, 511 (1984); Mol. Phys. 52, 255 (1984).*
2. *W. Hoover, Phys. Rev. A31, 1695 (1985).*

Comparison of Thermostats

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

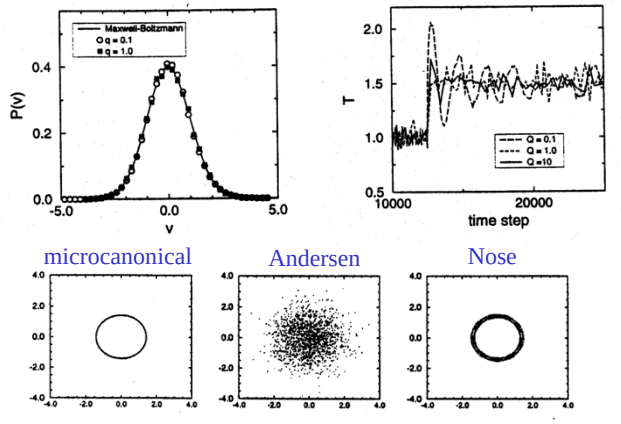
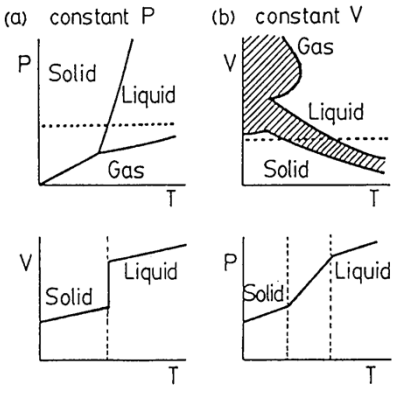


Figure 6.7: Trajectories of the harmonic oscillator: (from left to right) in the microcanonical ensemble, using the Andersen method, and using the Nosé-Hoover method. The y axis is the velocity and x axis is the position.

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.

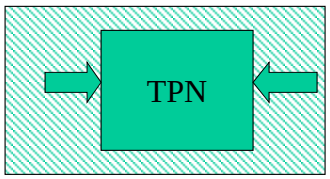


Constant Pressure (FS 6.2)

- 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.*

$$P = \frac{1}{3\Omega}\left[2K - \sum_{i<j} r_{ij}\frac{d\phi}{dr}\right]$$



• *Unit cell shape can also change.*

– System can switch between crystal structures.

– Method is very useful is 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.

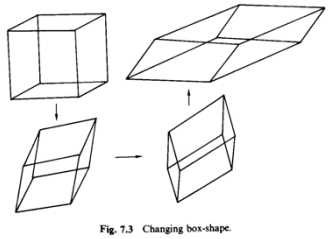


Fig. 7.3 Changing box-shape.

To implement, consider

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

$$\vec{r} = \overline{\overline{L}}\vec{s} \qquad \vec{s} = \left[\overline{\overline{L}}\right]^{-1}\vec{r}$$

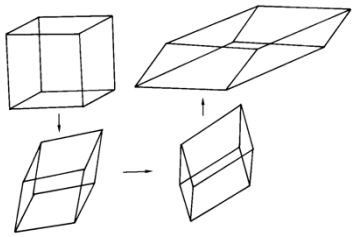


Fig. 7.3 Changing box-shape.

- 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

ω is the response (or mass) of the surrounding medium.

• Usual **F = ma** but also *force from boundaries*

$$\frac{d\vec{p}_i}{dt} = \vec{F}_i - \left(\overline{\overline{L}}^{T}\right)^{-1} \frac{d\overline{\overline{L}}}{dt}\vec{p}_i$$

• Feedback keeps box size in equilibrium

$$\omega \frac{d^2\overline{\overline{L}}}{dt^2} = (\overline{\overline{\pi}} - P\overline{\overline{I}})\Omega\left(\overline{\overline{L}}^{T}\right)^{-1}$$

• Stress tensor, π

$$\overline{\overline{\pi}} = \frac{1}{\Omega}\sum[\vec{r}_i\vec{F}_i + m_i\vec{v}_i\vec{v}_i]$$

• The new distribution is

$$\exp\left[-\beta(H + P\Omega + \omega\overline{\overline{L}}\overline{\overline{L}}^{T}\right]$$

Parrinello-Rahman simulation

• **500 KCl ions at 300K**

• First P = 0

• Then P = 44 kB

• System spontaneously changes from ***rocksalt*** to ***CsCl*** structure

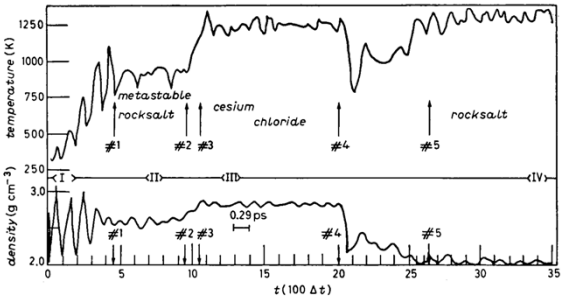


Fig. 2. – Time history of a compression and decompression molecular-dynamics run on KCl. Points plotted are 25 Δt apart, hence the nonsmooth appearance. In regions I to IV the pair correlations were monitored; these have not been shown in this lecture. Significance of the numbered vertical arrows is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

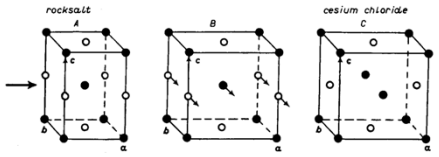


Fig. 3. – Detail of rocksalt to cesium chloride change found to occur in the MD calculation. Thick arrow in A indicates a dilatation resulting in B. Fine arrows in B indicate displacements of particles with a common c direction co-ordinate, resulting in the final structure C. A is rocksalt, C is cesium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

Features of Constant Pressure/Variable Structure Simulations

- 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

1. *H. C. Andersen, J. Chem. Phys. 72, 2384 (1980).*
2. *M. Parrinello and A. Rahman, J. Appl. Phys. 52, 7158 (1981).*
3. *R. Martonak* Eur. Phys. J. B **79, 241–252 (2011)**

- Homework 3 due Friday, Feb 22