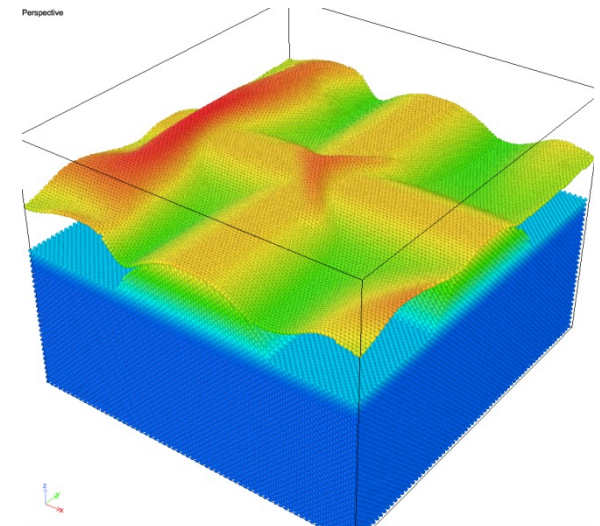# Molecular Dynamics (part 2)

Computational Material Science
Lecture 5

Last time

- Molecular dynamics simulations treat atoms as if they were Newtonian particles

- The goal of an MD simulation is to track the trajectory of all atoms while the system evolves in time. Atoms respond to external forces and to forces exchanged with other atoms.

- The equation of motion of all atoms is computed numerically using an integration scheme of the type of the Verlet algorithm.

Today

- Theoretical basis of molecular dynamics simulations

- Connection between macroscopic quantities and microscopic variables (statistical thermodynamics)

- Time averaging and ensemble averaging

Learning goals:

- Can distinguish and relate macroscopic and microscopic variables

- Capability of writing a molecular dynamics program.

The Hamiltonian

The Hamiltonian is a function of the total energy in a system.
If the system is Newtonian the potential energy only depends on the coordinates, and the kinetic energy only on the momenta. In this case the Hamiltonian takes the simple form:

$$\mathcal{H}(\mathbf{p}^N, \mathbf{r}^N) = K(\mathbf{p}^N) + U(\mathbf{r}^N)$$

In a Newtonian system the energy is conserved, which means that E is constant in time:

$$\frac{dE}{dt} = \frac{d\mathcal{H}}{dt} = 0$$

Demonstrate that for a one d.o.f. the energy is conserved

The Hamiltonian

The Hamiltonian is a function of the total energy in a system
If the system is Newtonian, the potential energy only depends on the coordinates, and the kinetic energy only on the momenta. In this case the Hamiltonian is very simple:

$$\mathcal{H}(\mathbf{p}^N, \mathbf{r}^N) = K(\mathbf{p}^N) + U(\mathbf{r}^N)$$

Conservation of energy: $\dfrac{dE}{dt} = \dfrac{d\mathcal{H}}{dt} = 0$ very important check in MD simulations!

Demonstrate that for a one d.o.f. the energy is conserved:

$$\mathcal{H} = \frac{1}{2}mv^2 + U(x)$$

$$\frac{d\mathcal{H}}{dt} = mv\frac{dv}{dt} + \frac{dU}{dt}$$

$$= mva + \frac{dU}{dx}\frac{dx}{dt} = mva - Fv$$

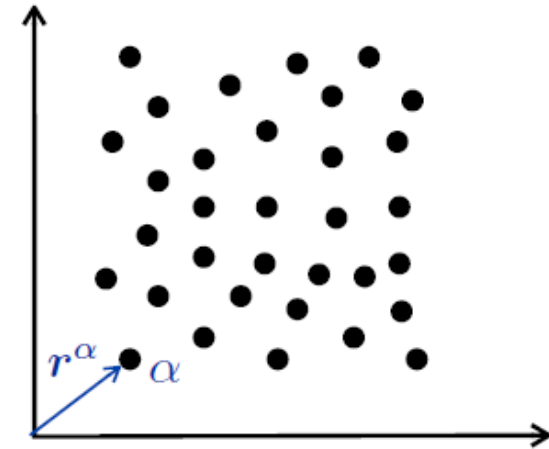$$= mva - mva = 0 \, ,$$

Hamilton's equations of motion

▶ The dynamical evolution of a system of N particles in a conservative force field is described by Hamilton's equations:

$$\dot{r}^\alpha = \frac{\partial \mathcal{H}}{\partial p^\alpha} \qquad \dot{p}^\alpha = -\frac{\partial \mathcal{H}}{\partial r^\alpha} \qquad \alpha = 1, \ldots, N$$

where

$$r^\alpha = \quad \text{position of particle } \alpha$$

$$p^\alpha = m^\alpha \dot{r}^\alpha = \quad \text{momentum of particle } \alpha$$

$$\mathcal{H} = \sum_\alpha \frac{p^\alpha \cdot p^\alpha}{2m^\alpha} + \widehat{\mathcal{V}}(r^1, \ldots, r^N) = \text{total energy (Hamiltonian)}$$

kinetic energy $\mathcal{T}$

potential energy

Phase space

▶ It is convenient to bundle the positions and momenta into two generalized vectors:

$$q = \{r_1^1,\ r_2^1,\ r_3^1,\ r_1^2,\ \ldots,\ r_3^N\} = \{q_1,\ldots,q_n\}, \qquad n = 3N$$

$$p = \{p_1^1,\ p_2^1,\ p_3^1,\ p_1^2,\ \ldots,\ p_3^N\} = \{p_1,\ldots,p_n\}$$

▶ The set of all possible values of (q, p) forms a 6N-dimensional space called phase space Γ.

▶ The dynamical evolution of a system is described by a trajectory $(q(t), p(t))$ through phase space.

p

$(q(t), p(t))$

q

6N-dimensional phase space Γ
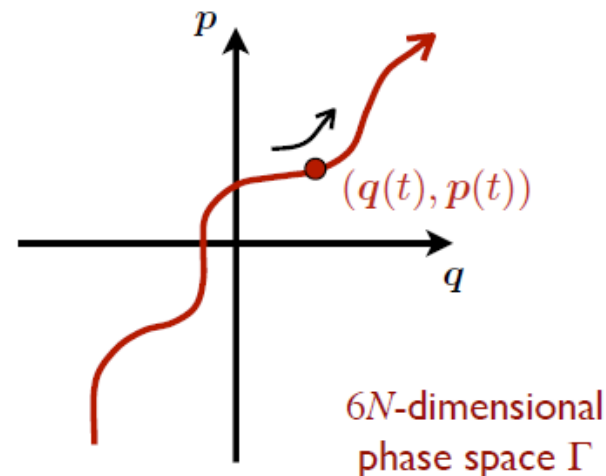
Properties of trajectories of Hamiltonian systems

▶ The trajectory through phase space of a Hamiltonian system has some important properties:

1. The solution $(q(t), p(t))$ to Hamilton's equations is unique.

   Implication: Only a single trajectory passes through each point in phase space and therefore trajectories cannot intersect.

2. The Hamiltonian $\mathcal{H}$ is constant along a trajectory.

   Implication: The total energy of a Hamiltonian system is conserved.

   Proof: The time rate of change of a time-independent Hamiltonian is

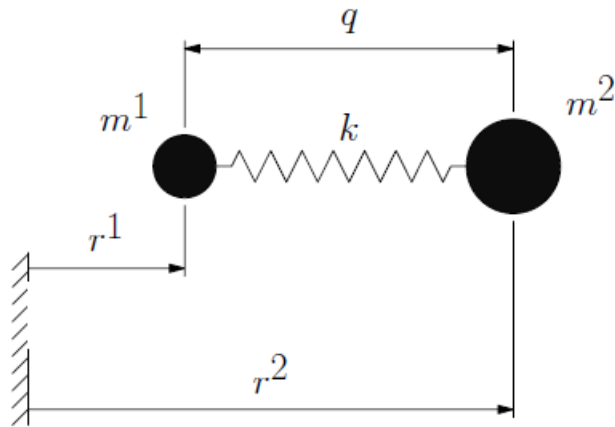 $$\frac{d\mathcal{H}}{dt} = \sum_{i=1}^{n}\left[\frac{\partial\mathcal{H}}{\partial q_i}\dot{q}_i + \frac{\partial\mathcal{H}}{\partial p_i}\dot{p}_i\right] = \sum_{i=1}^{n}\left[-\dot{p}_i\dot{q}_i + \dot{q}_i\dot{p}_i\right] = 0 \qquad \Rightarrow \qquad \mathcal{H} = \text{constant.}$$

3. Poincaré recurrence theorem: Given sufficient time, a Hamiltonian system with a bounded phase space will return to a state arbitrarily close to its initial state.

   Implication: Interesting philosophical questions regarding reversibility. However, for macroscopic systems, a "sufficient time" exceeds the age of the universe.
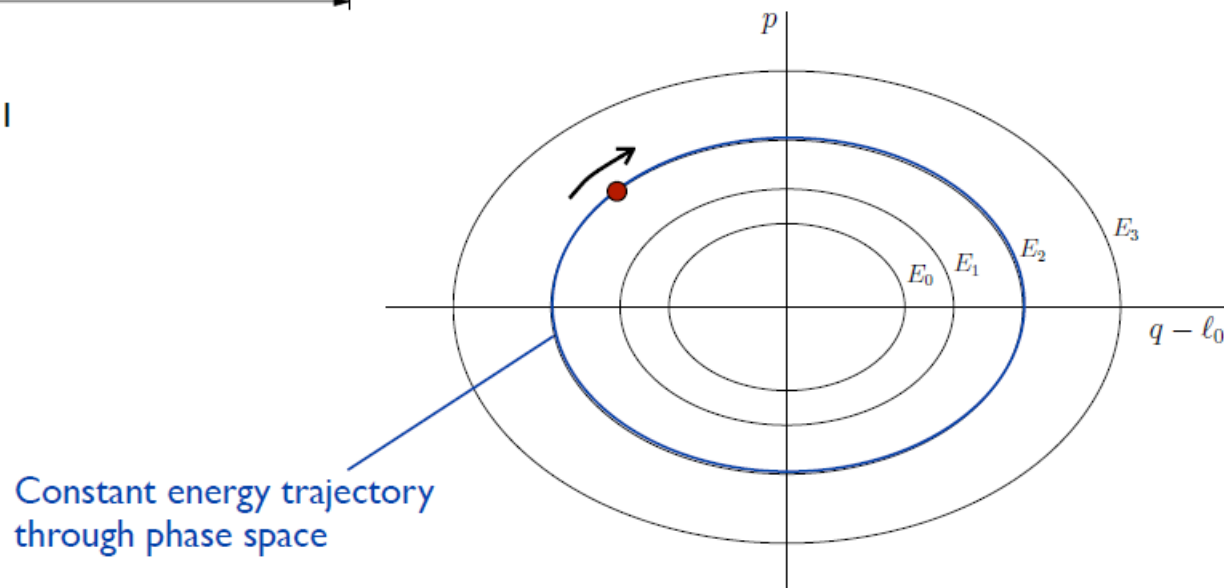
Example: the harmonic oscillator

▶ The only case that can be visualized is a 1D system like a harmonic oscillator

MM Fig. 7.1

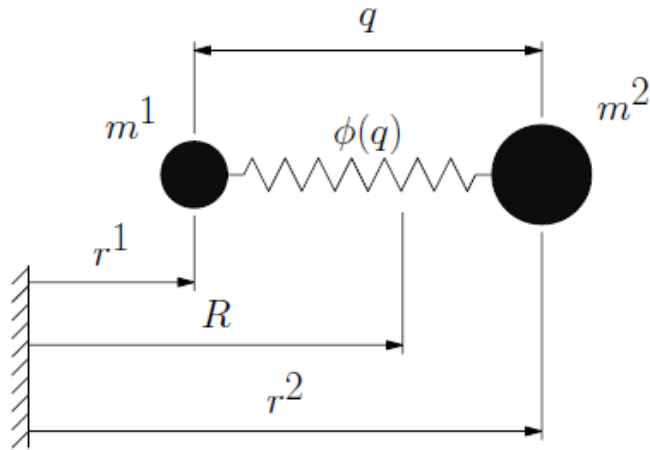$$\mathcal{H} = \frac{p^2}{2\mu} + \frac{1}{2}k(q - \ell_0)^2$$

$$q = r^2 - r^1 \qquad \mu = \frac{m^1 m^2}{m^1 + m^2} \qquad \text{reduced mass}$$

Constant energy trajectory through phase space
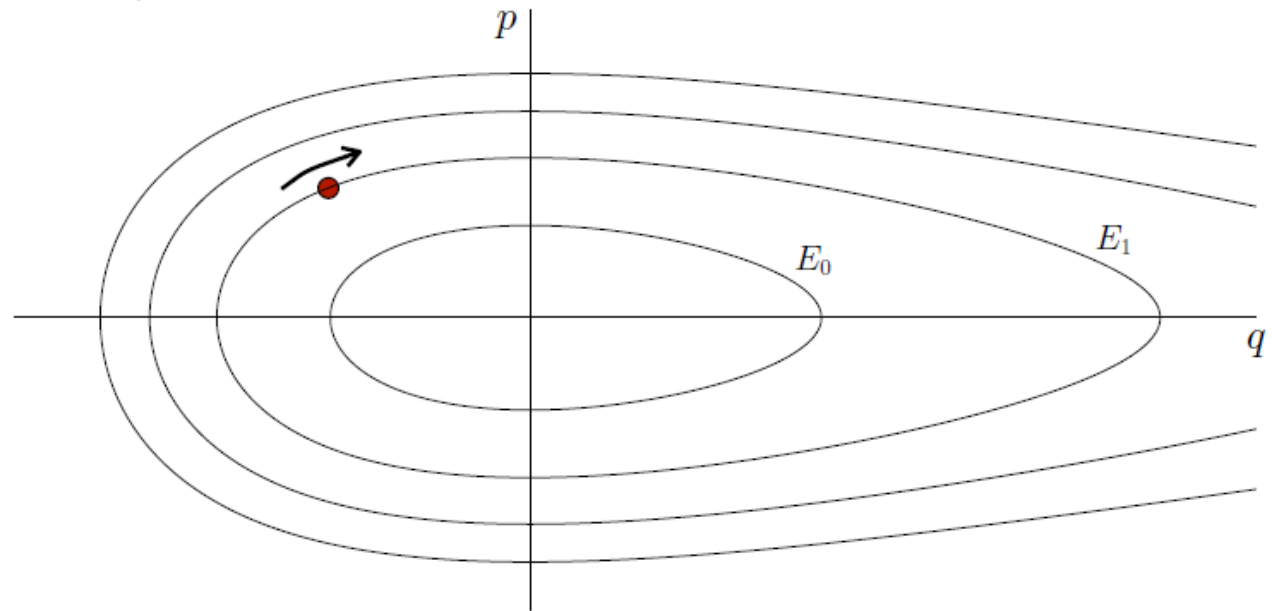
Example: Lennard-Jones oscillator

▶ Lennard-Jones oscillator is qualitatively the same, but with asymmetric trajectories.

$$\mathcal{H} = \frac{p^2}{2\mu} + \phi(q)$$

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

MM Fig. 7.1

Examining the reliability of a simulation

A key question in an MD simulation is whether the algorithm used to integrate the equation of motion is of sufficient accuracy.

If the trajectories of a few atoms have errors it is generally no problem as long as the average quantities in the system are correct.
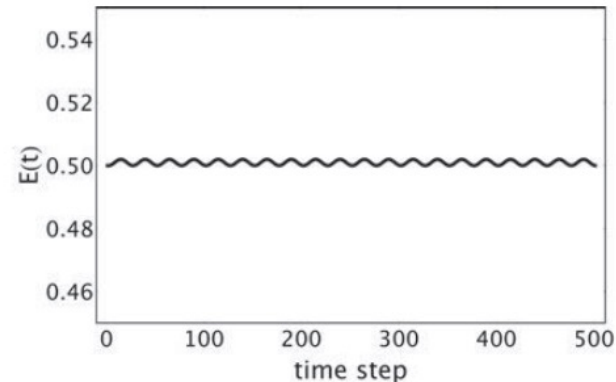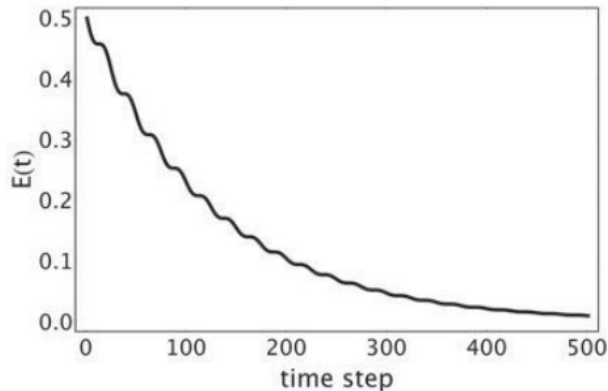

Which simulation is wrong here? What could be wrong?

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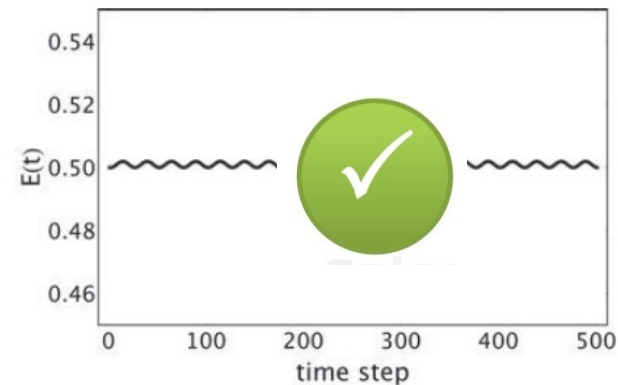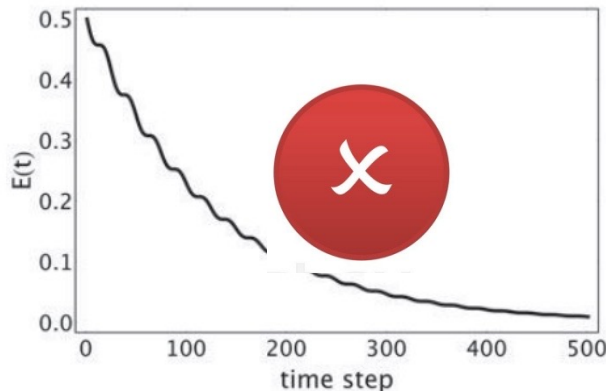

Which simulation is wrong here? What could be wrong?

An excessively large time step (first thing to check), a poor integration scheme for the equations, an error in the programme.

Time step

Although constant on average, the energy fluctuates over time around its average at equilibrium.
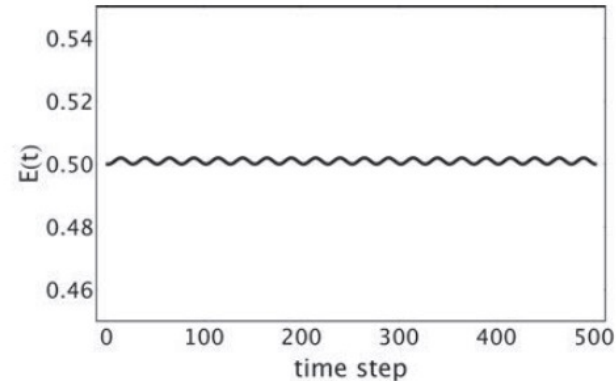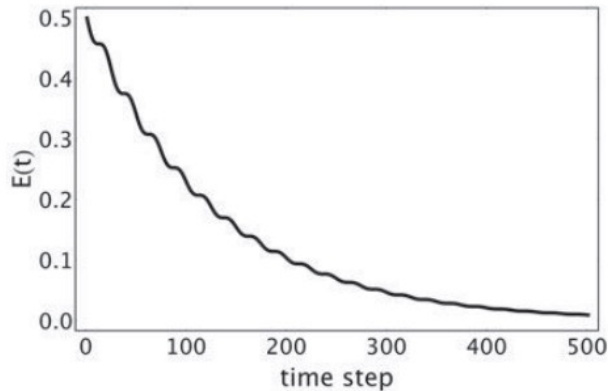
$$(\max E - \min E)/\langle E \rangle \sim 10^{-4}$$

δt: $10^{-15} - 10^{-14}$ seconds ⮕ MD simulations should be used for short time events

Schematics of an MD code

- Atomistic model; requires atomistic microstructure and atomic position at beginning
- Step through time by integration scheme
- Repeated force calculation of atomic forces
- Explicit notion of chemical bonds – captured in interatomic potential
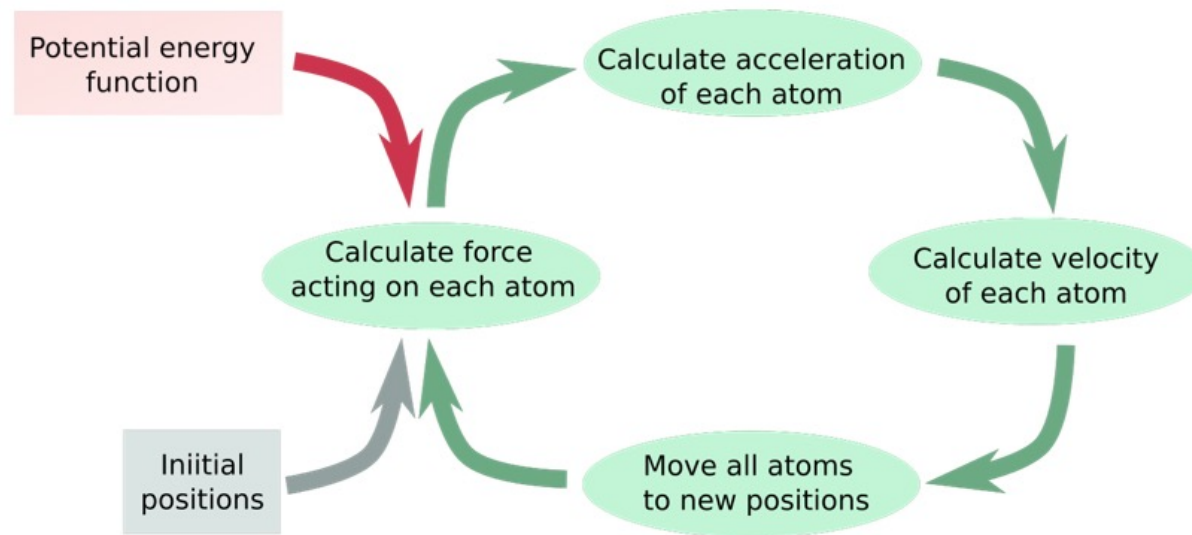
Flow diagram of MD simulation

Initial conditions for an MD simulation

Problem definition:
1) Material
2) Potential
3) Number of atoms, volume, and shape of the unit cells
4) Specify boundary conditions
5) If somewhere periodic ensure commensurability
6) Make sure the number of atoms is sufficiently large to be representative of the system studied
7) Check on symmetries
8) Make a smart choice of the initial positions
9) …and of initial velocities (e.g. the Maxwell-Boltzmann distribution)

Steps in an MD simulation

Warning: wait until equilibrium is reached before taking any averages!

1) Initialize positions and momenta
2) Calculate the initial K, U, and forces on each atom Fi
3) For n_equil time steps:
   - Solve for $\{\mathbf{r}_i(t+\delta t)\}$ and for $\{\mathbf{p}_i(t+\delta t)\}$
   - Calculate K, U, E, f_i
   - Check for drift of values
   - When equilibrated, restart
4) For n time steps:
   - Solve for $\{\mathbf{r}_i(t+\delta t)\}$ and for $\{\mathbf{p}_i(t+\delta t)\}$
   - Calculate K, U, E, f_i and other quantities of interest
   - Accumulate values of K, U, etc. for averaging
5) Analyse data: averages, correlations…

Simulation

Let's take Lennard-Jones

$$\phi(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

$$\phi^*(r_{ij}^*) = 4\left[\left(\frac{1}{r_{ij}^*}\right)^{12} - \left(\frac{1}{r_{ij}^*}\right)^{6}\right]$$

$$\mathbf{f}_{ij}^*(r_{ij}^*) = -\frac{24}{r_{ij}^2}\left[2\left(\frac{1}{r_{ij}^*}\right)^{12} - \left(\frac{1}{r_{ij}^*}\right)^{6}\right]\mathbf{r}_{ij}^*$$

Value	In reduced units
Potential energy	$U^* = U/\epsilon$
Temperature	$T^* = k_B T/\epsilon$
Density	$\rho^* = \rho\sigma^3$
Pressure	$P^* = P\sigma^3/\epsilon$
Time	$t^* = t/t_o$, where $t_o = \sigma\sqrt{m/\epsilon}$

$$k_B = 8.617 * 10^{-5} \; eV/K$$

Phase space and trajectories

The time dependent properties of a system made of N atoms are fully defined by the 6N mechanical degrees of freedom of the system (microstate):

$$(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N) \qquad\qquad (\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, \ldots, \mathbf{p}_N)$$

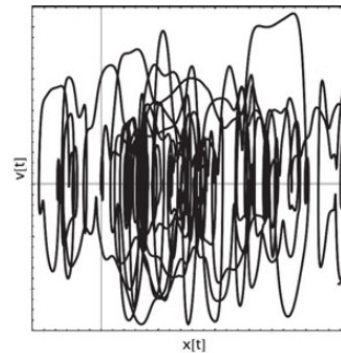These are 6N coordinates in phase space. The locus of the points in phase space is called trajectory.
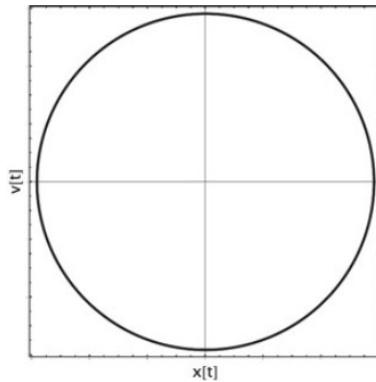
Phase space and trajectories

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$$(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N) \qquad\qquad (\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, \ldots, \mathbf{p}_N)$$

These are 6N coordinates in phase space. The locus of the points in phase space is called trajectory.

Harmonic oscillator

One coordinate of one atom in an MD simulation over a fraction of femtosecond (collisions+long range effects)

How do we make sense out of all the information we will produce through the MD simulation, i.e. the trajectories of all those atoms?

Connection to thermodynamics

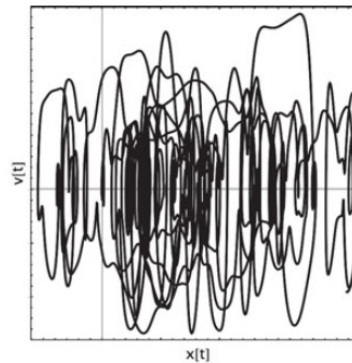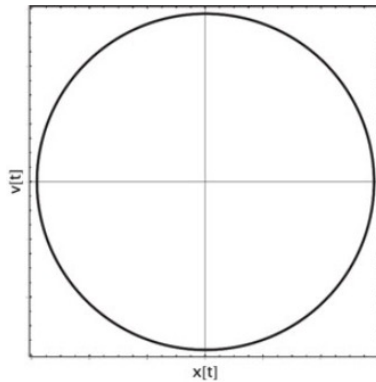Although in MD we can keep track of the motion of N atoms, knowledge of their individual trajectories does not give us much information on the properties of the full crystal unless we rely on statistics. Here statistical thermodynamics comes out VERY handy.

Basic thermodynamics quantities:

N = number of particles	$E = U + K$ = internal energy
V = volume	S = entropy
P = pressure	$H = E + PV$ = enthalpy
T = temperature	$A = E - TS$ = Helmholtz free energy
μ = chemical potential	$G = E - TS + PV$ = Gibbs free energy

E, H, A are extensive quantities, T, P, μ intensive.
Statistical mechanics relates macroscopic properties of a system with microscopic variables through averaging. It links the degrees of freedom of atoms in a system to the thermodynamic quantities that describe it (pressure, volume…)
Statistical thermodynamics describes the behavior of systems in equilibrium

Statistical mechanics

Macrostate: the thermodynamic state of a system. It depends on the constraints acting on it: (N, V, T) or (N, P, T)

Microstate: instantaneous value of internal variables (at time t the positions and momenta of the N atoms). Microstates change with time as the system evolves

▸ We are interested in predicting a macroscopic observable $\mathcal{A}$ from an associated phase function $A(\boldsymbol{q}, \boldsymbol{p})$.

We postulate:

$$\mathcal{A} = \bar{A} = \lim_{t \to \infty} \frac{1}{t} \int_0^t A(\boldsymbol{q}(\tau), \boldsymbol{p}(\tau)) \, d\tau$$

Examples of phase functions:

Physical Significance	$\mathcal{A}$	$A(q,p)$
Temperature	$k_{\mathrm{B}}T$	$(2/3N) \sum_\alpha \|p^\alpha\|^2 / 2m^\alpha = 2\mathcal{T}/3N$
Pressure	p	$(1/3V) \sum_\alpha [\|p^\alpha\|^2 / m^\alpha - q^\alpha \cdot \nabla_{q^\alpha} \mathcal{V}(q)]$

Ensemble average

To connect microstates with macrostates the most intuitive idea is to take time averages:

$$E_{obs} = \langle E \rangle = \frac{1}{t_o} \int_0^{t_o} E(t')dt' \qquad E(t) = K(\mathbf{p}^N(t)) + U(\mathbf{r}^N(t))$$

One can also keep track of the number of times a system goes back to a given configuration

$$\langle E \rangle = \frac{1}{N_{config}} \sum_{\alpha=1}^{N_{config}} n_\alpha E_\alpha = \sum_{\alpha=1}^{N_{config}} \rho_\alpha E_\alpha \qquad \sum_{\alpha=1}^{N_{config}} \rho_\alpha = 1$$

number of time a system was in a given configuration

probability density

The probability density will depend on the constraint imposed on the system.

Instead of following the same system for a very long time, we create a large number (ensemble) of identical systems and let them evolve independently. Although identical, systems will be in different states.

The idea of Gibbs was to substitute averages in time with averages over configurations, i.e. averages over the number of states that the system will be in.

Ensemble average

For continuum systems the sum becomes an integral. So to be proper:

▶ Define as an ensemble, the set of all microstates (q, p) that are consistent with the applied macroscopic constraints (e.g. N, V, E, T).

▶ Define a phase average as

$$\langle A; f \rangle \equiv \int_{q_1} \cdots \int_{q_n} \int_{p_1} \cdots \int_{p_n} A(q, p) f(q, p) \, dq_1 \cdots dq_n dp_1 \cdots dp_n$$

$$= \int_{\Gamma} A(q, p) f(q, p) \, dq dp$$

where $f(q, p) \, dq dp =$ probability of finding the system in region
$$([q, q + dq], [p, p + dp])$$

└─→ distribution function, which satisfies: $\int_{\Gamma} f(q, p) \, dq dp = 1$

Ergodicity

▶ A basic assumption at the heart of statistical mechanics:

Ergodic hypothesis: phase averages = infinite time averages

$$\langle A \rangle = \bar{A} = \lim_{t \to \infty} \frac{1}{t} \int_0^t A(\boldsymbol{q}(\tau), \boldsymbol{p}(\tau)) \, d\tau$$
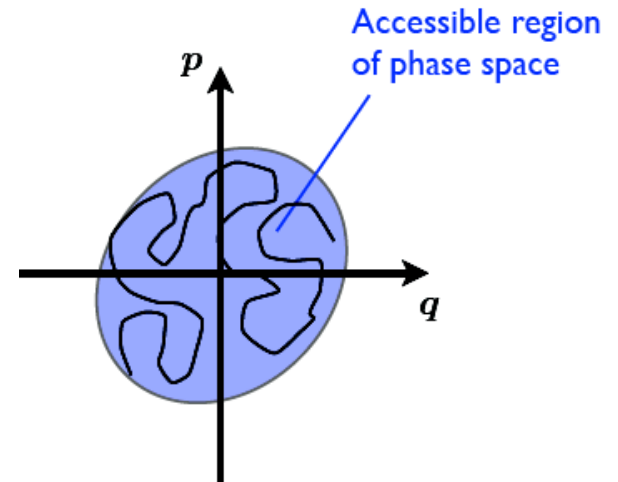
- This hypothesis was initially motivated by the assumption that Hamiltonian systems are ergodic, i.e. that given sufficient time a system will visit all points in phase space consistent with the imposed macroscopic constraints.

  This was proven to be impossible independently by Rosenthal and Plancherel in 1913.

- Current understanding is based on the law of large numbers and the theory of the thermodynamic limit.

  As the number of degrees of freedom increases the distribution function collapses to a delta function. Thus, the phase function being averaged is very close to the observable. This is in fact the essence of equilibrium.

Accessible region of phase space

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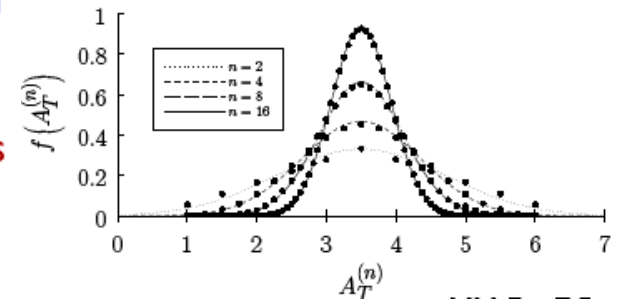
Weighting functions

Consider the probability ρ_α of being in a certain state. We cannot tell which factors influence the probability, how this probability depends for instance on thermodynamic variables.

Let's assume that we can introduce a weighting function w_α, which will tell us how thermodynamics influences the probability, and we assume the probability to be proportional to the weighting function

$$\rho_\alpha = \frac{w_\alpha}{\sum_\alpha w_\alpha} = \frac{1}{Q} w_\alpha \qquad \text{partition function:} \quad Q = \sum_\alpha w_\alpha$$

Given that:
$$\langle E \rangle = \frac{1}{N_{config}} \sum_{\alpha=1}^{N_{config}} n_\alpha E_\alpha = \sum_{\alpha=1}^{N_{config}} \rho_\alpha E_\alpha$$

The average of a quantity is then given by: $\langle B \rangle = \frac{1}{Q} \sum_\alpha w_\alpha B_\alpha$

Each ensemble is characterized by a given set of constraints and by different weighting functions and partition function.

Canonical ensemble
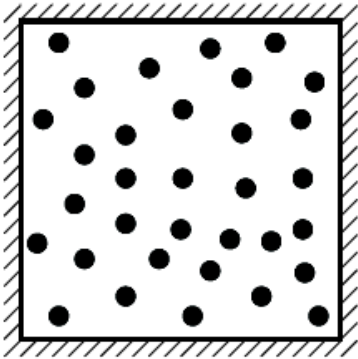
The canonical ensemble is a collection of systems with constant number of particles, volume, and temperature (NVT)

$$w_\alpha = e^{-E_\alpha / k_B T}$$

$$\boxed{Q_{NVT} = \sum_\alpha e^{-E_\alpha / k_B T}}$$

We can evaluate the relative probability of two states (configurations):

$$\frac{\rho_{\alpha*}}{\rho_\alpha} = \frac{e^{-\beta E_{\alpha*}}}{Q} \frac{Q}{e^{-\beta E_\alpha}} = e^{-\beta(E_{\alpha*} - E_\alpha)}$$

$$\langle E \rangle = \frac{1}{Q_{NVT}} \sum_\alpha e^{-E_\alpha / k_B T} E_\alpha$$

$$Q_{NVT} = \frac{1}{N! h^{3N}} \iint e^{-\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)/k_B T} d\mathbf{r}^N d\mathbf{p}^N$$

Link to thermodynamics through the Helmholtz free energy: $A = -k_B T \ln Q_{NVT}$

If the potential energy depends only on position the two integrals over momenta and positions can be separated and multiplied with each other

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Canonical ensemble (NVT)

The integrals can be evaluated analytically

Only positions $\quad \langle U \rangle = \dfrac{1}{Z_{NVT}} \displaystyle\int e^{-U(\mathbf{r}^N)/k_B T} U(\mathbf{r}^N) d\mathbf{r}^N \qquad Z_{NVT} = \displaystyle\int e^{-U(\mathbf{r}^N)/k_B T} d\mathbf{r}^N$

Only momenta $\quad \langle K \rangle = \dfrac{\int \exp(-K(\mathbf{p}^N)/k_B T) K(\mathbf{p}^N) d\mathbf{p}^N}{\int \exp(-K(\mathbf{p}^N)/k_B T) d\mathbf{p}^N}$

$$\int_{-\infty}^{\infty} \exp(-ax^2) dx = \sqrt{\pi/a}.$$

Gaussian integral

Important result! Used in MD to calculate the temperature

$$\langle K \rangle = \frac{3}{2} N k_B T$$

Pressure

$$\mathcal{P} = \frac{N}{V} k_B T - \frac{1}{3V} \left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \nabla_i U \right\rangle$$

$$\mathcal{P} = \frac{N}{V} k_B T - \frac{1}{3V} \left\langle \sum_{i=1}^{N} \sum_{j>i}^{N} r_{ij} \frac{d\phi}{dr_{ij}} \right\rangle$$

Microcanonical ensemble

The microcanonical ensemble is a collection of systems with constant particles, volume, and energy (NVE), a standard choice in MD simulations.

$$w_{NVE} = \delta\left(\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) - E\right),$$

All states for which E is the prescribed value are equally probable, all other states forbidden

$$Q_{NVE} = \frac{1}{N!h^{3N}} \int \delta\left(\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) - E\right) d\mathbf{r}^N d\mathbf{p}^N$$

$$S = k_B \ln Q_{NVE}$$

connection with thermodynamics

What is constant and what fluctuates at equilibrium?

Microcanonical ensemble

The microcanonical ensemble is a collection of systems with constant particles, volume and energy (NVE). This is the ensemble of standard MD simulations

$$w_{NVE} = \delta\big(\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) - E\big) ,$$

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$$S = k_B \ln Q_{NVE}$$

connection with thermodynamics

What is constant and what fluctuates at equilibrium?

N,V, E constant, K, U, P, T fluctuate around an average value

Comparing canonical and microcanonical

$$\varepsilon_n = n\varepsilon_0$$

System defined by the instantaneous microstate {E1, E2, E3}
The total energy is $E = E1+E2+E3 = \varepsilon_0 (n1+n2+n3) = 9\varepsilon_0$

Suppose the instantaneous state is measured M times, then the probability of an atom to be in state n is ρ_n : the number of times the atom was in state n divided by M
The average energy for each atom is $\quad \rho_n \epsilon_n$
The average energy is $\quad \langle E \rangle = N \rho_n \epsilon_n$

For the microcanonical ensemble: E constant-> allowed states are {3,3,3}, {2,4,3}, etc. all with equal probability
Consistently with our idea of entropy the number of allowed states increases with E

For the canonical ensemble: all micro-states are possible but they have different probabilities. The probability of a microstate α is $\exp(-\beta E_\alpha)/Q$
The probable states are subset of all states.

$$Q = \sum_\alpha \exp(-\beta E_\alpha)$$

From statistical mechanics to MD

Important for MD simulations:
By keeping track of the velocities and positions of the atoms during the simulations for a certain time at equilibrium, we gain information on the macroscopic quantities of interest, as temperature and pressure.

$$\langle K \rangle = \frac{3}{2} N k_B T$$

$$\mathcal{P} = \frac{N}{V} k_B T - \frac{1}{3V} \left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \nabla_i U \right\rangle$$

$$\mathcal{P} = \frac{N}{V} k_B T - \frac{1}{3V} \left\langle \sum_{i=1}^{N} \sum_{j>i}^{N} r_{ij} \frac{d\phi}{dr_{ij}} \right\rangle$$

Take home messages

- Statistical mechanics provides us with a link between microscopic and macroscopic thermodynamics variables

- This allows us to calculate thermodynamic quantities in an MD simulation through averaging over time

- Averages should be taken after the simulation has equilibrated, i.e. when quantities fluctuate around a constant mean

Create your own MD code

1. Initialize positions (done!) and velocities (done)

2. Initialize energies (almost done) and forces (to be done today)

3. Apply the Verlet algorithm to find trajectories of atoms (next class)

4. Calculate forces and energies at new positions (next class)

Careful with reduced units

Ne $\varepsilon = 0.0031\ eV$ $\sigma = 2.74\ \overset{o}{A}$

Xe $\varepsilon = 0.02\ eV$ $\sigma = 3.98\ \overset{o}{A}$

Cu $\varepsilon = 0.415\ eV$ $\sigma = 2.277\ \overset{o}{A}$

$$T = T^{*}\varepsilon / k_B$$

$$k_B = 8.617 \cdot 10^{-5}\ eV/k$$

Value	In reduced units
Potential energy	$U^{*} = U/\epsilon$
Temperature	$T^{*} = k_B T/\epsilon$
Density	$\rho^{*} = \rho\sigma^3$
Pressure	$P^{*} = P\sigma^3/\epsilon$
Time	$t^{*} = t/t_o$, where $t_o = \sigma\sqrt{m/\epsilon}$

$Ne \nearrow$

$$T = \frac{0.8 \times 0.0031\ eV}{8.617 \times 10^{-5} eV/K} = 28.8\ K$$

$T^{*} = 0.8 \quad \xrightarrow{Xe}$

$$T = \frac{0.8 \times 0.02\ eV}{8.617 \times 10^{-5} eV/K} = 165.7\ K$$

$Cu \searrow$

$$T = \frac{0.8 \times 0.415\ eV}{8.617 \times 10^{-5} eV/K} = 3852\ K$$

InitMDLJ

```
function[n,sx,sy,sz,vx,vy,vz]= initLJMD(nc,tin)
%  created scaled coordinates in an fcc lattice
nc=5;
tin=0.6;
ncell=4; % number of atoms in a cell
x=[0 .5 0 .5];
y=[0 .5 .5 0];
z=[0 0 .5 .5];
i1=0;
n = ncell*nc^3;
sx=zeros(n,1);
sy=zeros(n,1);
sz=zeros(n,1);
vx=zeros(n,1);
vy=zeros(n,1);
vz=zeros(n,1);
for k=1:nc
    for l = 1:nc
        for m = 1:nc
            for i = 1:ncell
                i1=i1+1;
                sx(i1) = (x(i) + k-1)/nc;
                sy(i1) = (y(i) + l-1)/nc;
                sz(i1) = (z(i) + m-1)/nc;
            end
        end
    end
end
```

```matlab
%  pick velocities from Maxwell-Boltzmann distribution
%  for any temperature we want.
%  Then we will calculate the kinetic energy and thus
%  the temperature of these atoms and then we will
%  rescale the velocities to the correct temperature
k = 0;
px = 0;
py = 0;
pz = 0;
for i=1:n
    vx(i) = sqrt(-2*log(rand))*cos(2*pi*rand);
    vy(i) = sqrt(-2*log(rand))*cos(2*pi*rand);
    vz(i) = sqrt(-2*log(rand))*cos(2*pi*rand);
    px = px + vx(i);
    py = py + vy(i);
    pz = pz + vz(i);
end
histogram(vx);
hold;
% set net momentum to zero and calcuate K
px = px/n;
py = py/n;
pz = pz/n;
for i=1:n
    vx(i) = vx(i)-px;
    vy(i) = vy(i)-py;
    vz(i) = vz(i)-pz;
    k = k + vx(i)^2 + vy(i)^2 + vz(i)^2;
end
k = .5*k;
% kinetic energy of desired temperature (tin)
kin = 3*n*tin/2;
% rescale velocities
sc=sqrt(kin/k);
for i=1:n
    vx(i) = vx(i)*sc;
    vy(i) = vy(i)*sc;
    vz(i) = vz(i)*sc;
end
histogram(vx);
```

In class exercise 1

Calculate the energy (lattice sums) and the <u>forces on each atom</u>, for a periodic FCC crystal with interatomic interactions described by Lennard-Jones. Use the minimum image convention to compute the forces.

Reminder: Lennard-Jones potential and forces in reduced units

$$\phi^*(r_{ij}^*) = 4\left[\left(\frac{1}{r_{ij}^*}\right)^{12} - \left(\frac{1}{r_{ij}^*}\right)^{6}\right]$$

$$\mathbf{f}_{ij}^*(r_{ij}^*) = -\frac{24}{r_{ij}^2}\left[2\left(\frac{1}{r_{ij}^*}\right)^{12} - \left(\frac{1}{r_{ij}^*}\right)^{6}\right]\mathbf{r}_{ij}^*$$

In class exercise 1

Force acting on an atom at a given time for a Lennard-Jones potential in reduced units:

$$\vec{F}_i = \sum_{j \neq i} \vec{f}_{ij} = \sum_{j \neq i} \left(-\frac{1}{r_{ij}} \frac{d\varphi}{dr_i} \right) \vec{r}_{ij} = \sum_{j \neq i} \frac{24}{r_{ij}^2} \left(2 \left(\frac{1}{r_{ij}} \right)^{12} - \left(\frac{1}{r_{ij}} \right)^6 \right) \vec{r}_{ij}$$

$$P = \frac{N}{V} k_B T + \frac{1}{3V} \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{24}{r_{ij}^2} \left(2 \left(\frac{1}{r_{ij}} \right)^{12} - \left(\frac{1}{r_{ij}} \right)^6 \right) \right\rangle$$

```
%   we calculate force (fx,fy,fz), energy (u), and
%   part of the pressure (w)
%
function[u,w,fx,fy,fz]= fLJsum(a,n,rc,x,y,z)
%   set force components, potential energy, and pressure to 0
%   fx,fy,fz are each vectors, with an entry for every atom
```

```matlab
%  we calculate force (fx,fy,fz), energy (u), and
%      part of the pressure (w)
function[u,w,fx,fy,fz]= fLJsum(a,n,rc,x,y,z)
%  set force components, potential energy, and pressure to 0
fx=zeros(n,1);
fy=zeros(n,1);
fz=zeros(n,1);
u = 0;
w = 0;
for i = 1:n-1  % note limits
    ftx = 0;
    fty = 0;
    ftz = 0;
    for j=i+1:n  %  note limits
% mimimum image convention
        dx = x(j) - x(i);
        dy = y(j) - y(i);
        dz = z(j) - z(i);
        dx = dx - round(dx);
        dy = dy - round(dy);
        dz = dz - round(dz);
        dist = a*sqrt(dx^2 + dy^2 + dz^2);
        if dist <= rc
```

```matlab
            if dist <= rc
                dphi = (2/dist^(12)-1/dist^6);
                ffx = dphi*a*dx/dist^2;
                ffy = dphi*a*dy/dist^2;
                ffz = dphi*a*dz/dist^2;
                ftx = ftx + ffx;
                fty = fty + ffy;
                ftz = ftz + ffz;
                phi = (1/dist^(12)-1/dist^6);
                u = u +  phi;
                w = w + dphi;
%   add -f to sum of force on j
                fx(j) = fx(j) - ffx;
                fy(j) = fy(j) - ffy;
                fz(j) = fz(j) - ffz;
            end
        end
    %   sum up force on i (fi)
        fx(i) = fx(i) + ftx;
        fy(i) = fy(i) + fty;
        fz(i) = fz(i) + ftz;
end
%   need to multiply LJ by 4 and force and pressure by 24
%   also need to correct sign in f
u = 4*u;
w = 24*w;
for i=1:n
    fx(i) = -24*fx(i);
    fy(i) = -24*fy(i);
    fz(i) = -24*fz(i);
end
```