History

- History of MD goes back $\sim$ 50 years when Alder & Wainwright formulated the method[10] [11]

- So, MD is a method developed for numerically solving a many-body problem.

- Numerical methods are needed since the $N > 3$ problem is not solvable analytically.

- Initial system of interest for MD was "a small number of elastic spheres" which represented molecules. Hence the name.

- First interaction models were simple square potentials describing hard spheres rather than atoms or molecules ("billiard ball physics").

- Nowadays MD is typically used for variety of systems from metals to large biomolecules in solution.

Important steps

- Metropolis MC 1953.

- Alder and Wainwright 1956: MD of hard spheres

- Rahman 1964: MD of liquid argon (Lennard-Jones)

- Rahman and Stillinger 1971: MD of liquid water

- McCammon et al. 1977: The first protein simulations

- Car and Parrinello 1985: ab initio MD

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[10] [J. Chem. Phys. 31, 459 (1959)]
[11] [J. Chem. Phys. 33, 1439 (1960)]

2 Phases of a MD simulation

The general phases of an MD simulation are

- Deciding the model

  - Intermolecular interactions
  - Intramolecular interaction

- Setting up the system

  - Geometry
  - Velocities
  - Simulation cell

- Equilibration = running MD to obtain equilibrium

  - May involve many stages, (like start with minimization)
  - Ends to a normally running MD
  - Ends with converged thermodynamical and structural parameters

- Production run

  - Continuing MD without any changes
  - Sampling and storing information

- Analysis

We will now have a look at the **equations of motion** from the point of view of classical analytical mechanics and our idea of dynamics performed with them. Then we will discuss **setting up, initializing and equilibrating** the system. In future we will then get stuck in numerical **integration of the equations of motion, evaluation of forces, and treating pressure and temperature**. After having understood how these all aspects constitute to the MD run for equilibrium system, we will discuss **fluctuations and error estimation for statistical observables** and discuss **energy minimalization** of structures. After understanding these basic concepts we will move a more detailed discussion about models for different systems.

3 Equations of Motion

For a system on N classical particles (here nuclei), there are

- $3N$ degrees of freedom in the position of the particles, marked $\mathbf{q}$ and

- $3N$ degrees of freedom in the velocities of the particles, marked $\dot{\mathbf{q}}$.

- In classical analytic mechanics these are treated independently

- Let us mark all these $6N$ degrees of freedom as $\mathbf{\Gamma}$, a point in *phase space*, that defines the state of our system.

- Here we assume that knowing $\mathbf{\Gamma}$, everything about the system is known (for any quantity $A = A(\mathbf{\Gamma})$).

- We define an *ensemble* as a collection of points $\mathbf{\Gamma}$, weighted with a probability density $\rho(\mathbf{\Gamma})$.

  - Depending on the macroscopic parameters, we have ρ_{NPT}, ρ_{NVT}, and in general ρ_{ens}

  - In the first lecture we already rushed in calculating ensemble average $\langle A \rangle$ as a time-average $\overline{A}$.

  - In general, ensemble averages are obtained

  $$\langle A \rangle_{ens} = \int A(\mathbf{\Gamma}) \rho_{ens}(\mathbf{\Gamma}) \mathrm{d}\mathbf{\Gamma}$$

  which relates ρ to thermodynamic potentials and partition functions.

- Some commonly used statistical ensembles

  - constant-NVE (microcanonical)

  - constant-NVT (canonical)

  - constant-NPT (isothermal-isobaric)

  - constant-μVT (grand canonical)

  Later on this course, we will discuss simulating different ensembles. At least the three first ones (NVE, NVT, and NPT) will be covered.

As time goes by, the system evolves. Especially, system originally at phase space point $\mathbf{\Gamma}$ moves to some other point $\mathbf{\Gamma}'$.

- More generally, function $\rho_{ens}(\mathbf{\Gamma})$ will evolve in time.

- However, systems are not destroyed or created (a good approximation) during the evolution (Liouville's theorem)

$$\frac{\mathrm{d}\rho_{ens}}{\mathrm{d}t}\bigg|_{\mathbf{\Gamma},t} = 0$$

- In addition, for an ensemble in equilibrium, characterized by $\rho_{ens}(\mathbf{\Gamma})$ all time dependence disappear,

$$\frac{\partial}{\partial t}\rho_{ens}(\mathbf{\Gamma}, t) = 0$$

and the time-evolution is very special, namely the propability stays constant

$$\rho_{ens}(\mathbf{\Gamma}, t) = \rho_{ens}(\mathbf{\Gamma}, 0).$$

- For every system moving from $\mathbf{\Gamma}$, there is a system entering $\mathbf{\Gamma}$ (otherwise the probality $\rho_{ens}(\mathbf{\Gamma}, t)$ would change with time). This creates a trajectory of states that may have several distinct loops, or that may be a long single loop in the whole accessible phase space. (More mathematical details in Tuckerman p. 66)

- Trajectories in phase space for equilibrium ensemble can be separated loops. Moreover, there can be bottlenecks between different regimes. See shaded areas. (source: Allen & Tildesley).
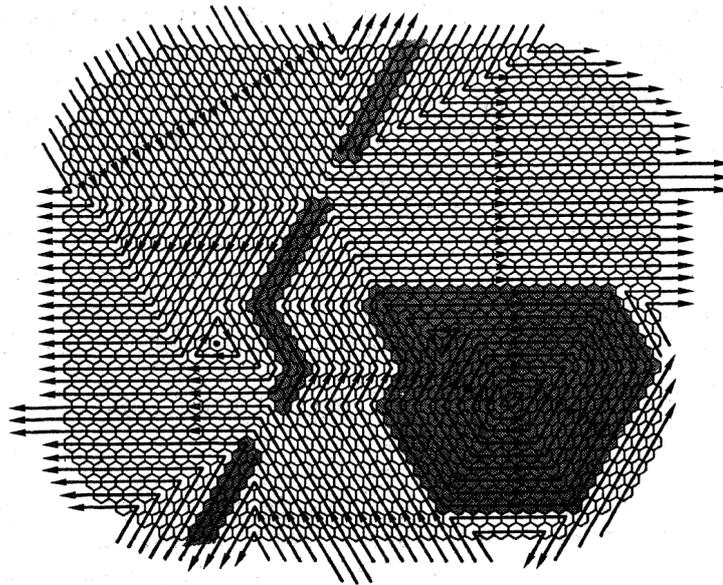
- In MD, we hope to hop on this loop and explore the phase space we can access. For NVE this is straightforward and simulation contains a physical interpretation.

- For other equilibrium ensembles the methodology is allowed involve a random element **or even be without a physical meaning** as long as

  - ρ_{ens} does not change in time
  - As simulation proceeds, any reasonable guess ρ should evolve to stationary solution
  - We should be able to argue that ergodicity holds – even though proving it is impossible

- With the conditions above, our method generates in the long run a trajectory sampling the ensemble with the desired ρ_{ens}

- Moreover for any $A = A(\mathbf{\Gamma})$,

$$\frac{1}{N} \sum_{\tau=1}^{N} A(\mathbf{\Gamma}(\tau)) \to \overline{A} = \langle A \rangle_{ens} = A_{obs},$$

$$N \to \infty$$

  where τ identifies the number of a particular time step in the simulation.

Note that people often talk about "Newtonian equations of motion" when discussing MD. This is to be understood as "classical equations of motion", i.e., non-relativistic, non-QM, motion. Obviously, it doesn't matter in which formalism the equations are given. Let us now turn to the equations of motion.

3.1 Lagrangian formalism of EoMs

- Let's start with the generalized way of representing the motion of particles, i.e., *Lagrangian equation of motion*

$$\frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial \mathcal{L}}{\partial \dot{q}_k} - \frac{\partial \mathcal{L}}{\partial q_k} = 0 \tag{3.1}$$

  where the Lagrangian function $\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}})$ is defined in terms of kinetic and potential energies

$$\mathcal{L} \equiv \mathcal{K} - \mathcal{U} \tag{3.2}$$

  and is a function of the *generalized coordinates* q_k and their time derivatives $\dot{q}_k$

- If, on the other hand, we consider a system of atoms in *Cartesian coordinates* $\mathbf{r}_i$ and define the kinetic energy – as usual – as

$$\mathcal{K} \equiv \sum_{i,\alpha} \frac{p_{i,\alpha}^2}{2m_i} \tag{3.3}$$

  where $p_i = m_i \mathrm{d}r_i / \mathrm{d}t$, i runs over the particles and α over the coordinates (x, y, z) and m_i denotes the mass of a particle i, then the equation of motion becomes

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i \tag{3.4}$$

where the force on atom i is (since $\nabla_{\mathbf{r}_i}\mathcal{K} = 0$)

$$\mathbf{f}_i = \nabla_{\mathbf{r}_i}\mathcal{L} = -\nabla_{\mathbf{r}_i}\mathcal{U} \tag{3.5}$$

The Lagrangian formalism results in $3N$ second-order differential equations, that can be solved numerical integration from a given starting point. This is an initial value problem.

3.2   Hamiltonian formalism EoMs

- Generalized momentum is defined as

$$p_k = \frac{\partial\mathcal{L}}{\partial\dot{q}_k} \tag{3.6}$$

  after which the Hamiltonian can be defined

$$\mathcal{H}(\mathbf{p},\mathbf{q}) = \sum_k \dot{q}_k p_k - \mathcal{L}(\mathbf{q},\dot{\mathbf{q}}) \tag{3.7}$$

- Taking total differential of the Lagrangian, inserting some manipulation and obtain the *Hamiltonian equations of motion*

$$\begin{aligned}
\dot{q}_k &= \frac{\partial\mathcal{H}}{\partial p_k} \\
\dot{p}_k &= -\frac{\partial\mathcal{H}}{\partial q_k}
\end{aligned} \tag{3.8}$$

- The Hamiltonian can be viewed as

$$\mathcal{H}(\mathbf{p},\mathbf{q}) \equiv \mathcal{K}(\mathbf{p}) + \mathcal{U}(\mathbf{q}) \tag{3.9}$$

  where $\mathcal{U}$ is assumed to be independent of velocities and time, $\mathcal{U} = \mathcal{U}(\mathbf{r})$. This coincides with our previous identification of the nuclear Schrödinger equation after the Born-Oppenheimer approximation.

- For Cartesian coordinates (x, y, z), Hamilton's equations become

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} \tag{3.10}$$

$$\dot{\mathbf{p}}_i = -\nabla_{\mathbf{r}_i}\mathcal{U} = \mathbf{f}_i \tag{3.11}$$

The Hamiltonian formalsim results in $6N$ differential equations of first order and an initial value problem (Naturally, the Lagrangian equations above can be formulted using $6N$ first-order equations.) For following the trajectories of the particles in time, we need to either solve $3N$ **second-order differential equations** or equivalent set of $6N$ **first-order differential equations**.

- The equation of motion presented here reproduce the microcanonical ensemble (NVE)

- This is close to a real system because it's the solution for the N-body problem, and corresponds to the real atomic motion of an isolated system in fixed volume.

3.3   Integrating EoMs

Integrating equations of motion means dividing time to points t_i, separated by steps of Δt, and obtaining the next t_{i+1} one from the previous one t_i. As the equation contains inherently the physical information, our simulation is expected to be approximative solution to the problem.

The procedure is the following

(1) Set up the system

- for each step $t_i \rightarrow t_{i+1}$

(2) Evaluate forces

(3) Get new positions (integration)

(4) Calculate physical quantities and save desired information

(5) Decide whether to go to (2) or to stop.

The reason for considering $\mathcal{L}$ and $\mathcal{H}$ is, that to obtain other ensembles we will modify these functions and obtain new equations of motion to be integrated.

3.4 Potential energy

- As the first approximation, we assume the potential energy of the system to be a sum over particle-particle interactions as follows:

$$\mathcal{U}(\mathbf{r}) = \sum_i U_1(\mathbf{r}_i) + \sum_{i,j} U_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i,j,k} U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots \qquad (3.12)$$

- The first term corresponds to an external potential.

- Second one includes two-particle interactions, and third one corresponds to three-particle interactions.

- Typically, interactions between more particles than three are neglected, or included in an approximative way.

- How U_1, U_2, U_3 are defined will be discussed during later lectures.

- Note that the original QM Hamiltonian (1.4) has only 1-body and 2-body terms

$$H = \sum_I \frac{\hat{P}_I^2}{2M_I} + \frac{1}{4\pi\epsilon} \sum_{I<J} \frac{e^2 Z_I Z_J}{r_{IJ}} - \frac{1}{4\pi\epsilon} \sum_{i,I} \frac{e^2 Z_I}{r_{iI}} + \sum_i \frac{\hat{p}_i^2}{2m_e} + \frac{1}{4\pi\epsilon} \sum_{i<j} \frac{e^2}{r_{ij}}$$

- However in division of $\mathcal{U}(\mathbf{r})$ the 3-body and higher terms emerge from neglecting electrons in the equations of motion.

- It would be nice if terms higher than 2-body ones could be considered zero.

- Effective pair potential answers this call.

3.5 Conservation laws

- For a MD simulation to work, it has to preserve properties of a real system. In nature, symmetry is the general cause for conservation laws.

- Regarding equations of motion, there are some things to pay attention to:

  – If a generalized momentum p_k is conserved, the $\mathcal{L}$ and $\mathcal{H}$ must be
    independent on the corresponding generalized coordinate q_k (i.e.,
    $\dot{p}_k = -\partial\mathcal{H}/\partial q_k = 0$).

  – Hence, for any set of particles, it is possible to choose six gene-
    ralized coordinates corresponding to translations of the centre of
    mass, and rotations about it, for the system as whole (the rest
    $3N - 6$ coordinates involve the motion of the particles relative to
    each other).

  – In Cartesian coordinates with origin at the center of mass of the
    system these correspond to the total linear momentum $\mathbf{P}$ and total
   angular momentum $\mathbf{L}$.

  – These are defined as:

$$\mathbf{P} = \sum_i \mathbf{p}_i$$
$$\mathbf{L} = \sum_i \mathbf{r}_i \times \mathbf{p}_i = \sum_i \mathbf{r}_i \times m_i\dot{\mathbf{r}}_i \tag{3.13}$$

  – For a completely isolated system:

    * **P and L are conserved**
    * **Hamiltonian $\mathcal{H}$ is independent on time**, i.e., $\mathrm{d}\mathcal{H}/\mathrm{d}t = 0$
      (total energy is constant).
    * Further, **the equations of motion are reversible in time**.
      I.e., by changing the signs of all momenta, particles would
      retrace their trajectories.

  – For a periodic boundary conditions $\mathbf{L}$ is not conserved.

During the course, we will face ensembles other than constant-NVE (shortly
NVE) describing an isolated system. **A successfull atomistic simulation
reproduces all relevant conservation laws!**

3.6   Implementation and application

The MD algorithm can be summarized as a flowchart.
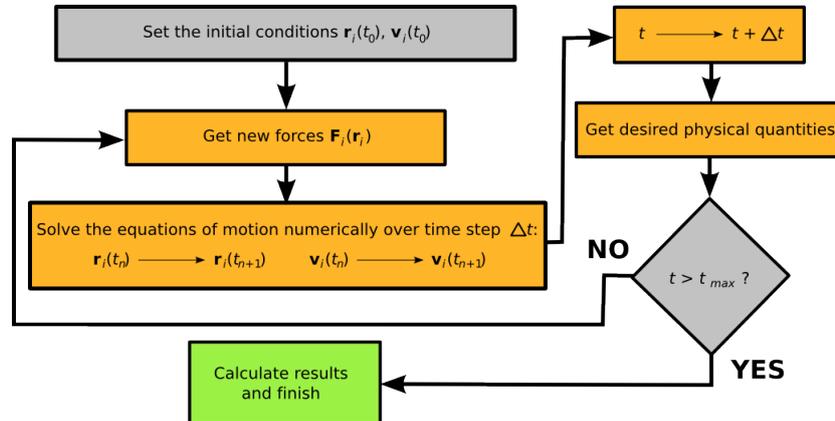
4   Setting up the simulation System

As our simulation will probe the phase space $\{\mathbf{\Gamma}\}$ (hopefully in ergodic fashion), we need a point $\mathbf{\Gamma}(0) = (\mathbf{r}(0), \mathbf{p}(0))$ to start from. We need

- Obtain a structure (a "configuration") $\mathbf{r}(0)$

- Define a cell where the dynamics takes place

- Initialize momenta $\mathbf{p}(0)$

before we can start evaluating forces for the first time and integrating the equations of motion.

4.1   Starting structure

Selecting the starting structure (initial configuration) can be essential in terms of success of the MD simulation. Therefore choosing initial configuration $\mathbf{r}(0)$ for the system should be performed with care.

- The initial structure should be close to the structure to be simulated

  - Short distance in phase space, and shorter and feasible equilibration run

  - Face-centered cubic structure for fcc crystal

- The initial structure should be "realistic"

  – No atomic overlapping causing pathologically high energies
  – "Hot spot"/ "Bad contact"
  – Energy minimization can help

For selection of a starting structure all available knowledge used be used.

- X-ray diffraction structure can be helpful. Common sense too.

- If no knowledge, fcc lattice can be chosen

  – Avoid bad contacts
  – Density close to experimental
  – Molecular orientation random
  – Rod-shaped molecules parallel

- For molecules in solvent, in addition fulfill

  – Molecular structure from other sources (exp. QM-calc. etc.)
  – Solvent molecules from pure-solvent-MD. Remove solvent molecules overlapping with the solute.

Initial structure should fit in (and possibly fill) the chosen simulation cell volume.

4.2   Simulation cell

Now we have set a configuration where to start. 1/3 of setting the system is now done. Next, consider the cell and boundary conditions.

4.2.1   Relative coordinates

Let's consider an orthogonal simulation cell as a simple example. Actually, some codes do not go beyond this (only orthogonal cells implemented).

- Now, we have a box of size $L_x \times L_y \times L_z$ [Å^3] with lattice vectors:

$$\mathbf{e}_x = \hat{\mathbf{x}}, \qquad \mathbf{e}_y = \hat{\mathbf{y}} \qquad \text{and} \qquad \mathbf{e}_z = \hat{\mathbf{z}}. \qquad (4.1)$$

- Next, we define the positions for the atoms inside the cell:

$$\mathbf{r}_i = \sum_\alpha x_{i,\alpha} L_\alpha \mathbf{e}_\alpha \tag{4.2}$$

  where $x_{i,\alpha} \in [0,1]$ are relative coordinates for atom i (and α runs over Cartesian coordinates x,y,z).

This trick allows us scaling the box size if needed. That would be done simply changing the box lengths L_x, L_y, L_z,. As relative coordinates $x_{i,\alpha} \in [0,1]$, this would squeeze the system uniformly.

4.2.2 Periodic boundary conditions (pbc)

- For a N-atomic system with pair potentials, one in principle needs to care about N^2 interactions for each time step Δt.

  - The number of terms in $\sum_{i=1}^{N} \sum_{j=i+1}^{N} U_2(\mathbf{r}_i, \mathbf{r}_j)$ is approximately $\frac{N^2}{2}$

- Obviously, this would become a problem for large N (like $N > 10^6$).

  - 1 liter of water in a cube has 3.3×10^{25} molecules
  - 2×10^{19} are within 10 molecular radii from wall
  - 1 out of 1.5 million senses walls
  - For a box of 1000 molecules not a single one fulfills this $=>$ bulk properties are not obtained
  - Simulation of droplets is feasible though

- Simulations of molecules on vacuum is not correct. From solutions of small molecules to large proteins, interaction with sufficiently many solvent molecules is needed for the solute to be in proper regime of phase space.

- Fortunately, most atomic interactions diminish quickly with increasing inter-atomic distance ($r \to \infty$).

- Because $\mathcal{U}(r) \xrightarrow[r\to\infty]{} 0$, we can limit the interactions to a sphere close to each particle. This transforms the scalability from quadratic N^2 to linear N.

- For example,

  - metals are closely-packed, but atoms at $r > 5$ Å are typically well-enough screened $\rightarrow \sim 80N$ *interactions*

  - for water we need a couple of solvation shells $=> 100N$ interactions.

- worst case appears for ionic bonding; Coulomb's law behaves as $\mathcal{U} \propto r^{-1}$
  $\rightarrow$ *cutting the interactions is impossible.* (There is still a solution...)

Obviously, it is impossible to model most of the real system sizes. Hence, we need to carefully consider how our **simulation model** can be made to represent a larger system.

- For example, if we are interested in bulk properties, we can introduce periodic boundary conditions to estimate the behaviour of an **infinite** system.

- This approach involves "copying" the simulation cell to each of the periodic directions (1–3) so that our initial system "sees" another system, exactly like itself, in each direction around it.
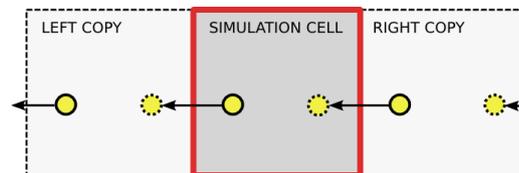
- If an atom moves out, if comes back in from the other side.

- In the pbc model we need to consider the main box only

  - Coordinates of atoms in other boxes obtained owing to implied periodicity
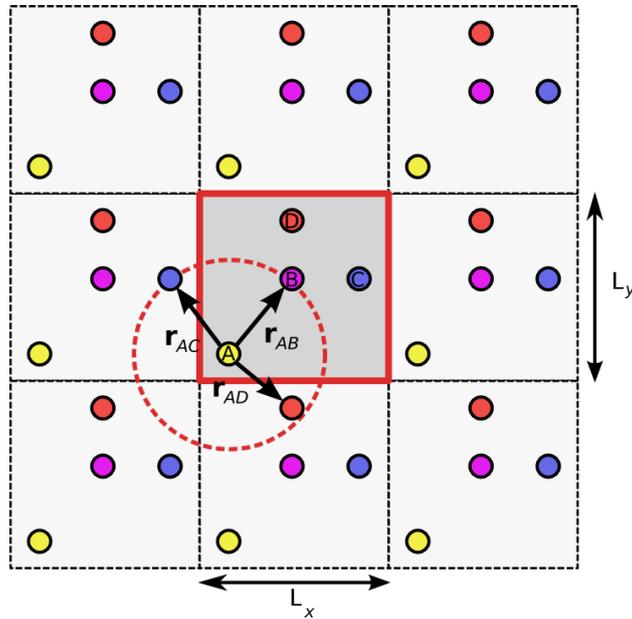
- Note that the nearest neighbors of atom A, except for B, are now in the neighbouring "virtual" cells instead of the original cell.

- Obviously, this has to be taken into account when evaluating the potential $\mathcal{U}(r)$.

4.2.3 Minimum image convention for cubic pbc

- Orthorhombic box in 3D has 26 neighbouring boxes. Rectangular box in 2D has 8 neighboring boxes.

- The closest image of a certain molecule is not necessary in the box

- However, the closest image (and that only) should be used for force evaluation

    – For cubic box, a good rule of thumb is not to do anything above distances of $L/2$ if no special reasons exists.

    – For orthorhombic box, $\min(L_x, L_y, L_z)/2$ is the corresponding choice.

- Using cubic or orthorhombic boxes is a good idea in most cases

    – Savings in number of atoms can be counteracted by laborous geometry handling. For further processing this is easier too.

- For a cubic box geometry (lenght L), and two given two coordinates $\mathbf{r}_i$ and $\mathbf{r}_j$, the minimum image vector $\mathbf{r}_{ij}^{(MI)}$ can be calculated by first calculating the separation vector $\mathbf{r}_{ij}$

$$
\begin{aligned}
x_{ij} &= x_i - x_j & (4.3) \\
y_{ij} &= y_i - y_j & (4.4) \\
z_{ij} &= z_i - z_i & (4.5)
\end{aligned}
$$

- and then $\mathbf{r}_{ij}^{(MI)}$

$$
\begin{aligned}
x_{ij}^{(MI)} &= x_{ij} - L * \texttt{round}(x_{ij}/L) & (4.6) \\
y_{ij}^{(MI)} &= y_{ij} - L * \texttt{round}(y_{ij}/L) & (4.7) \\
z_{ij}^{(MI)} &= z_{ij} - L * \texttt{round}(z_{ij}/L), & (4.8)
\end{aligned}
$$

where function $\texttt{round}()$ is standard rounding operator to the closest integer. The above equations are quaranteed to give the closest image in 3D cubic system, no matter how far the two points are. The Euclidian norm is (of course you know it!!!)
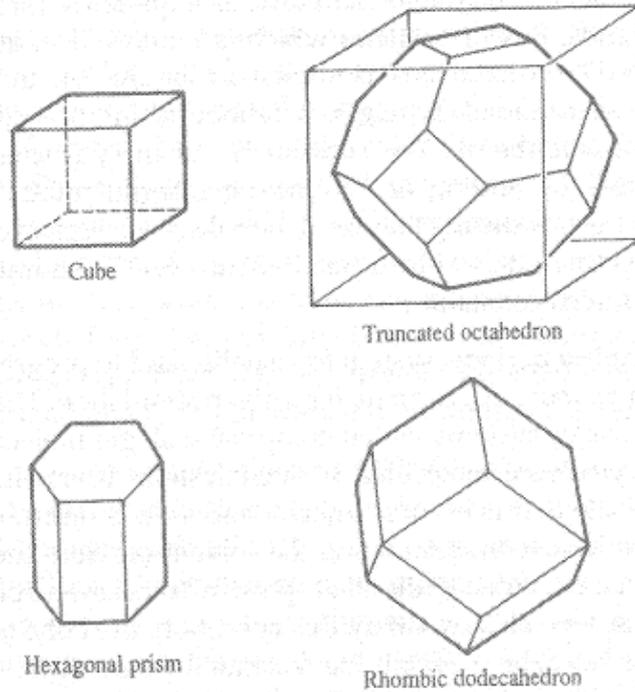
$$
r_{ij}^{(MI)} = \left| \mathbf{r}_{ij}^{(MI)} \right| = \sqrt{(x_{ij}^{(MI)})^2 + (y_{ij}^{(MI)})^2 + (z_{ij}^{(MI)})^2} \qquad (4.9)
$$

- Things can be this elegant in cubic cell whereas they can be much more labourous in a more complicated unit cell.

4.2.4   Options for simulation boxes

There are 5 choices for boxes to be used

- Cubic (and orthogonal, orthorhombic)

- Truncated octahedron

- Hexagonal prism

- Rhombic dodecahedron

- "Elongated"dodecahedron

Source: R. Leech, Molecular modeling, principles and applications

Although the cubic and its orthogonal variants are easy to use, for certain cases it is advantageous to use other ones. Generally this occurs when number of solvent molecules needs to be minimized.

- Truncated octahedron and Rhombic dodecahedron closer to spherical

    - No wasting effort on molecules in corners of the cube

    - Spherical molecules, proteins

    - Truncated octahedron easier to code

- Hexagonal prism good for DNA

Minimum image vectors and other formulations can be found in literature (Leech or Allen & Tildesley)

4.2.5   Other boundary conditions

- **Open boundaries.** In this case, if a particle reaches a boundary, it will be lost.

  – Obviously, this only works for a system where the particles themselves are more or less stationary.

  – Clearly, one would get problems modeling, e.g., a fluid with open boundaries.

- **Partially Open Boundaries** Some directions open, some not.

  – For surfaces, one can use pbc for directions parallel to surface and open boundaries for the direction normal to the surface.

  – A way to go round is to set large lenght in z-direction (perpendicular to surface) and use 3D pbc.

- **Vacuum**

  – Sometimes the system has to be put in vacuum

  – Typical example is an enzyme with little water

- **Fixed Boundaries**

  – Fixed boundaries, i.e., prevent the particle motion at or close to a boundary.

  – Unphysical, to be avoided at all cost.

Periodic boundary conditions and cutting interactions have advantages. For large enough systems, we truly obtain linear scaling, which is

- rare yet desirable for microscopic simulation

- owing to neglecting electrons. This allows us going to scales where interactions can be cut.

In addition the use of pbc allows simulation of bulk with a "small"number of molecules.

4.2.6   Size effects

The size of the used simulation box might introduce artifacts.

- Phenomena that have fluctuation wavelength $\lambda > L$ can not be described

- Phonons (sound waves)

- Strained systems

- Phase transitions

- Large temperature gradients

- If the box is not big enough, there may be non-physical interactions over the cell boundaries – even if the interaction is shorter ranged.

- The solution is to study system of numerous sizes.

    - The cell size should not affect real results.

- In the best case, results allow for a prediction for an infinite system.

4.3   Initializing atom velocities

The last step in setting up the simulation system is to generate velocities for the atoms.

- MD simulations are typically carried above 0K.

- Need to know how to initiate with a certain temperature of the system. (Especially NVE simulations.)

- The best guess is the Maxwell-Boltzmann distribution (exact for noninteracting gases)

$$\rho(v_{i,\alpha}) = \sqrt{\frac{m_i}{2\pi k_{\mathrm B}T}} \exp\left(-\frac{1}{2}\frac{m_i v_{i,\alpha}^2}{k_{\mathrm B}T}\right) \tag{4.10}$$

which is simply the Gaussian function (or **normal distribution**)

$$\psi(x)_{\mu,\sigma} = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-(x-\mu)/2\sigma^2\right] \tag{4.11}$$

with $\mu = 0$, $x = v_{i,\alpha}$ and $\sigma = \sqrt{k_{\mathrm B}T/m_i}$.

- A gaussian random number x generated with zero mean $\mu = 0$ and unit variance $\sigma = 1$ can be transformed to a random number x' of another normal distribution with μ' and uσ' by transformation

$$x' = \mu' + \sigma' x \tag{4.12}$$

meaning that given zero-mean, unit-variance numbers, we can obtain a starting velocity distribution by scaling with $\sigma' = \sqrt{\frac{k_{\mathrm B}T}{m_i}}$ (Note that $\mu'=0$)

- In practice, we assign each velocity component of each particle separately:

$$v_{i,\alpha} = \sqrt{\frac{k_{\mathrm B}T}{m_i}} u_{\mathrm G} \tag{4.13}$$

where indepent gaussian ($\mu = 0, \sigma = 1$) random numbers $u_{\mathrm G}$ are obtained from gaussian (pseudo) random number generator.

- For example given two uniformly distributed random numbers ξ_1 and ξ_2 between 0 and 1, numbers
  $x_1 = \sqrt{-2\ln\xi_1}\cos(2\pi\xi_2)$ and $x_2 = \sqrt{-2\ln\xi_1}\sin(\pi\xi_2)$
  are gaussian random numbers with $\mu = 0$ and $\sigma = 1$.

- More about generating random numbers on Monte Carlo course, or in book "Numerical Recipes" available freely in the web.

- **It is not a good idea to trust a random random-number generator=).**

- Check that the (pseudo) random number generator you are using, was developed for scientific use and explicitly stated to be OK for your purpose.

- Parallel MD runs for statistics require careful choice of random numbers.

  * The whole method assumes random selection of starting points $\mathbf{\Gamma}(0)$.

- For a single MD run that is not so critical. Even a uniform distribution would yield MB-distribution after a couple of hundred steps.

• To prevent the system from drifting during the simulation, the velocities are often adjusted to give zero total momentum after initializing the temperature. For the total momentum $\mathbf{P} = \sum_i m_i \mathbf{v_i}$
this is done by

$$\mathbf{v}_i^{(NPT\mathbf{P})} = \mathbf{v}_i - \mathbf{v}^{(av)} \qquad (4.14)$$

where

$$\mathbf{v}^{(av)} = \frac{\mathbf{P}}{\sum_i m_i}.$$

Now velocities $\mathbf{v}_i^{(NPT\mathbf{P})}$ give zero total momentum. This should be a conserved quantity in all cases. (As always i refers to individual atom ($\mathbf{v}_i$ has 3 dimensions))

5 Thermalization/equilibration

For the simulation system to reach equilibrium (to thermalize) from starting point $\mathbf{\Gamma}(0)$ just generated, the MD simulation needs to be run some time. During the equilibration run

- Particles interact and share energy

- Memory of the initial state is lost

- System moves to microstates corresponding to equilibrium ensemble.

Naturally, the time needed varies from system to system. Parameters to be monitored are

- Kinetic energy

- Potential energy

- Total energy

- Velocities

- Temperature

- Pressure

- Density

- and possibly some other system dependent quantities

After successful equilibration, the parameters

- should not exhibit any drifts.

- can have fluctiations

- should have the intended values as their average

The equilibrium temperature of the NVE system started with kinetic energy from (4.10) may differ from the initial value, depending on the initial configuration. Velocities thermalize very quickly, though, compared to spanning the position space.

5.1 Calculation of temperature

In a system of N particles, there are $(N_f = 3N - N_c)$ degrees of freedom.

- For a system in vacuum $N_c = 6$ corresponding conserved linear momentum and angular momentum

- For a system with pbc $N_c = 3$ corresponding conserved linear momentum

- Each one of the N_f terms of momentum in the Hamiltonian has equal average energy.

  - This is based on the **equipartition theorem** which states that the average kinetic energy per degree of freedom is $\left\langle \frac{1}{2} m_i v_{i,\alpha}^2 \right\rangle = \frac{1}{2} k_B T$

- Instantaneous temperature of the system can be direcly obtained from the kinetic energies of the particles:

$$T(t) \equiv \frac{1}{k_B N_f} \sum_{i,\alpha} m_i v_{i,\alpha}^2(t) \tag{5.1}$$

which can be used, among many other important things, to study thermalization of the simulation.

- An example of T fluctuation:
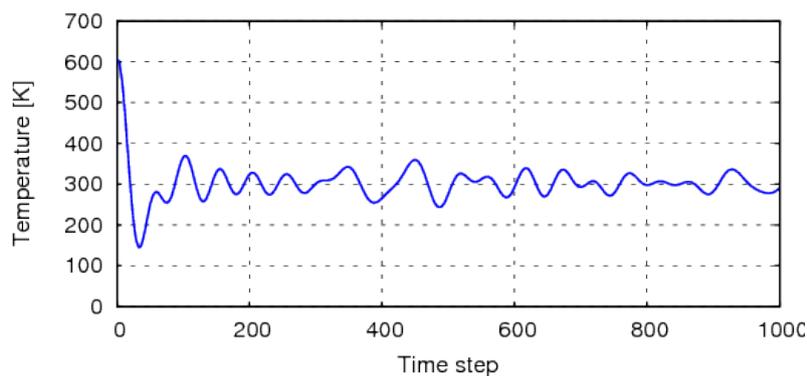
Clearly, the system is not thermalized in the beginning of the run.

5.2   Initial configuration and equilibrium

As we stated already, the initial phase space point $\mathbf{\Gamma}(0)$ should be chosen close to the equilibrium. This is easier said than done.

5.2.1   Systems in potential energy minima

In the beginning of the simulation, the system may be in a minimum energy geometry or close to it – or in a configuration of relatively high potential energy. These naturally affect the simulation.

- Let us consider a crystal lattice in minimum energy $\mathcal{U}(\mathbf{r}_0)$, obtained in configuration $\mathbf{r}_0$.

- In order to allow the atoms to move, they must leave their equilibrium positions $\mathbf{r}_0$.

- This means that the energy of the system increases $\mathcal{U}(\mathbf{r}_0) \rightarrow \mathcal{U}(\mathbf{r}_1)$.
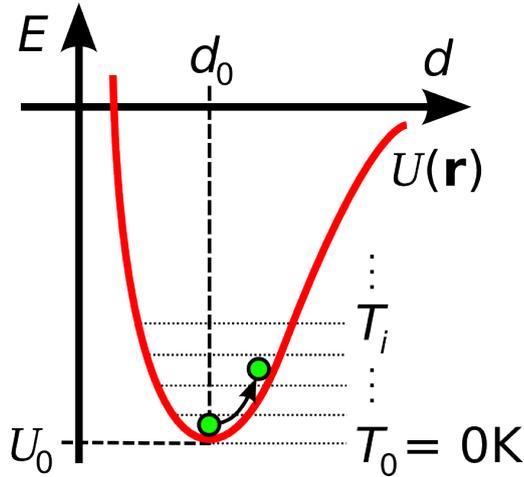
- As the system is not at $\mathbf{r}_0$ all the time and since $\mathcal{U}(\mathbf{r}_1) > \mathcal{U}(\mathbf{r}_0)$

$$\langle \mathcal{U} \rangle > \mathcal{U}(\mathbf{r}_0) \tag{5.2}$$

- If system is modeled as NVE ensemble, the total energy $\mathcal{H} = \mathcal{K} + \mathcal{U}$ is conserved and

$$E_{tot} = \langle \mathcal{H} \rangle = \langle \mathcal{K} \rangle + \langle \mathcal{U} \rangle = \mathcal{K}(\mathbf{p}_0) + \mathcal{U}(\mathbf{r}_0) \tag{5.3}$$

$$\langle \mathcal{K} \rangle = E_{tot} - \langle \mathcal{U} \rangle < E_{tot} - \mathcal{U}(\mathbf{r}_0) = \mathcal{K}(\mathbf{p}_0) \tag{5.4}$$

- The system transforms some of its initial kinetic energy to potential energy and temperature is lower than the initial temperature.

5.2.2 Harmonic approximation

Let us consider the previous case in more detail

- Around minimum, potential can be approximated harmonic with respect to each generalized coordinate

- Classical virial theorem states, that for any generalized coordinate q_k or momentum p_k

$$\langle p_k \partial \mathcal{H}/\partial p_k \rangle_{NVE} = k_{\mathrm{B}}T \qquad (5.5)$$
$$\langle q_k \partial \mathcal{H}/\partial q_k \rangle_{NVE} = k_{\mathrm{B}}T \qquad (5.6)$$

For proof, see Tuckerman p. 80

- Considering a system with Hamiltonian (and marking $i, \alpha =: k$)

$$\mathcal{H} = \sum_{i,\alpha} \frac{p_{i,\alpha}^2}{2m_i} + \sum_{i,\alpha} \frac{kq_{i,\alpha}^2}{2},$$

$$\langle p_k \partial \mathcal{H}/\partial p_k \rangle_{NVE} = \langle p_k p_k/m_i \rangle_{NVE} = 2\left\langle \frac{p_k^2}{2m_i} \right\rangle_{NVE} = k_{\mathrm{B}}T \qquad (5.7)$$

$$\langle q_k \partial \mathcal{H}/\partial q_k \rangle_{NVE} = \langle kq_k q_k \rangle_{NVE} = 2\left\langle \frac{kq_k^2}{2} \right\rangle_{NVE} = k_{\mathrm{B}}T \qquad (5.8)$$

- This means that to every $p_{i,\alpha}$ or $q_{i,\alpha}$ that has a quadratic term in Hamiltonian, has average energy of $\frac{1}{2}k_{\mathrm{B}}T$. Here $\mathcal{U}(\mathbf{r}_0) = 0$.

- For a simulation of a large system starting from minimum of a harmonic potential, $\langle \mathcal{K} \rangle \approx 3N/2k_{\mathrm{B}}T \approx \langle \mathcal{U} \rangle$ and

$$\langle \mathcal{K} \rangle = E_{tot} - \langle \mathcal{U} \rangle = \mathcal{K}(\mathbf{p}_0) - \langle \mathcal{U} \rangle \approx \mathcal{K}(\mathbf{p}_0) - \langle \mathcal{K} \rangle$$

$$\langle \mathcal{K} \rangle \approx \frac{1}{2}\mathcal{K}(\mathbf{p}_0)$$

- **When a simulation is started with a perfect crystal structure, the kinetic energy – and temperature – drop by a factor of two. The initialized temperature must be twice the desired one.**

5.2.3   Molecular liquids

For simulation of molecular liquid, the initial configuration may not be the potential energy minimum.

- For molecular liquids, the simplest way to thermalize is to run the simulation until drifts disappear.

- Achieving proper temperature in NVE is more tricky.

  - Trying different initial velocities
  - Scaling velocities during the run
  - Coupling to fictious degrees of freedom (a thermostat, lecture 5)

5.2.4   A word of warning

The treatment above has been completely classical. No quantization of molecular vibrations has been made and all nuclei are behaving according to the laws of classical mechanics.

- Whenever zero-point effects (lowest vibrational state, its energy, quantization of energy levels) are relevant, our model will fail.

5.3 Summary

- MD dates back to late 50's, when it was developed for simple molecular systems.

- The idea is to solve numerically the classical equations of motion for the given system ($3N$ differential equations of second order or $6N$ first-order ones).

- For each time step t_i, the new atomic coordinates are evaluated and the state of the system is calculated at $t_{i+1} = t_i + \Delta t$.

- For modeling a large system using only a small number of atoms, periodic boundaries are used (when possible).

- The velocities can be initialized according to Maxwell-Boltzmann distribution, but thermalization of the system is still needed.

- In MD, we are interested in the trajectory $\{\mathbf{\Gamma}(t)\}$, as t runs from t_0 to t_f and quantities we obtain onway.

- For sampling equilibrium ensembles, MD is first run from a initial configuration to equilibrium after which production run is performed for data collection.