

Modern trends in Computational Materials Discovery

17 - 21 November 2022
Isfahan University of Technology, Isfahan, Iran

Molecular dynamics simulation as a tool for determining
physical properties of thermodynamic systems

Mehdi Neek-Amal, Shahid Rajaee University, Tehran
Friday, Nov. 18, 2022, ISFAHAN

Contents

Basics of Molecular Dynamics Simulations

Observables (what we can expect from MD)

MD as a minimization method

MD prediction for 2D-ice structure vs ab-initio result

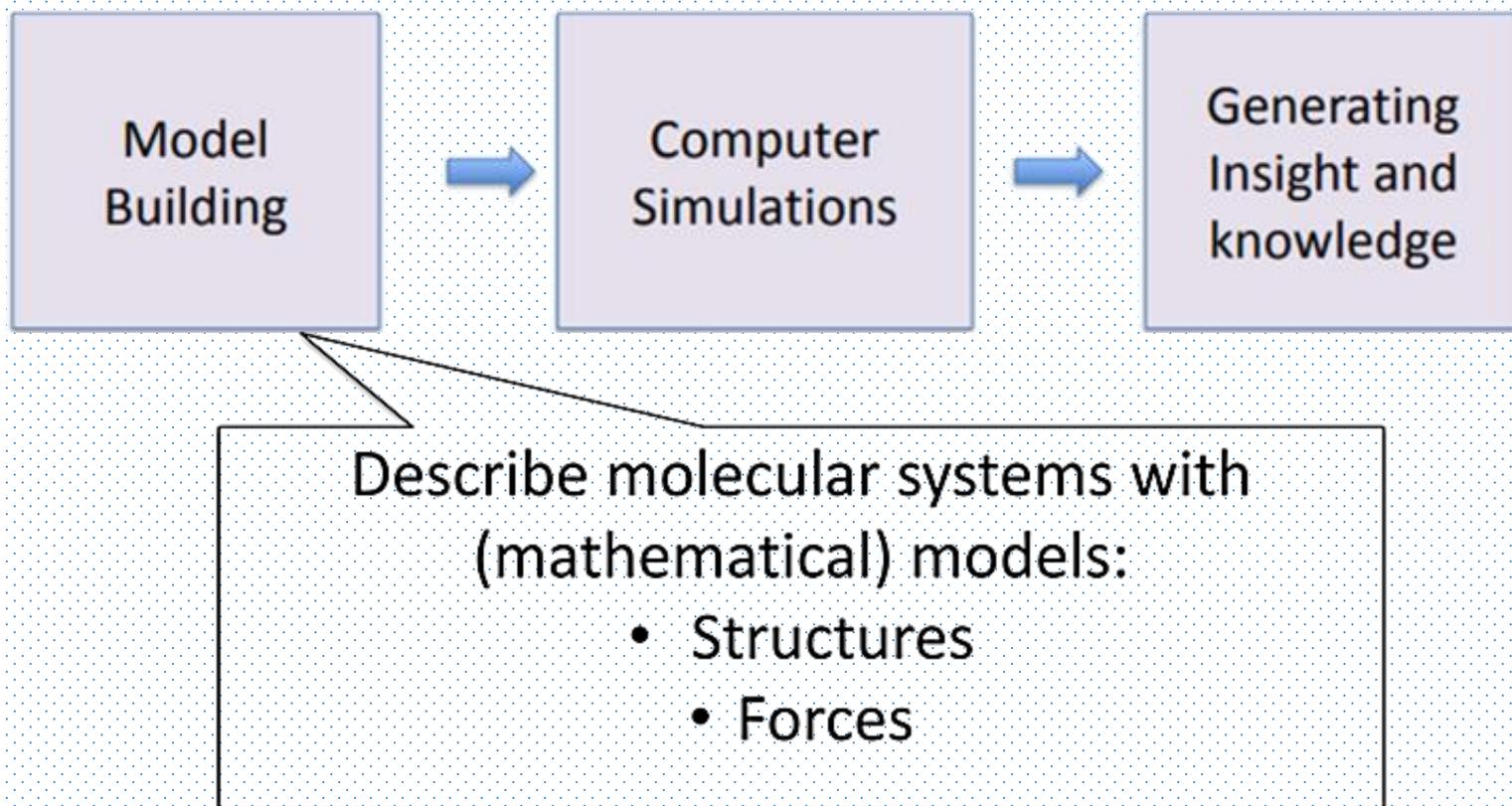
1-Basics of Molecular Dynamics Simulations

What is molecular modeling and simulation?

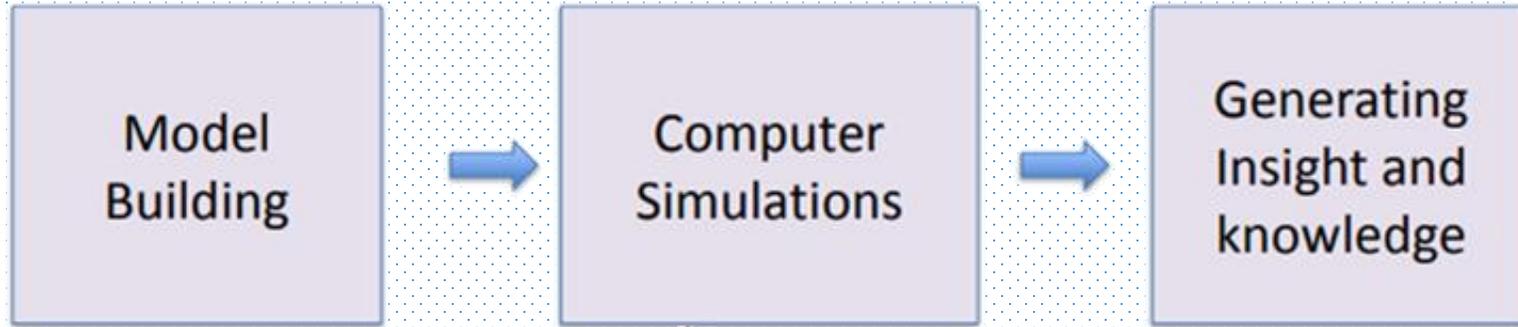
- Theoretical methods that allow describing of macroscopic observations with the use of microscopic description of matter.



Elements of Molecular simulations

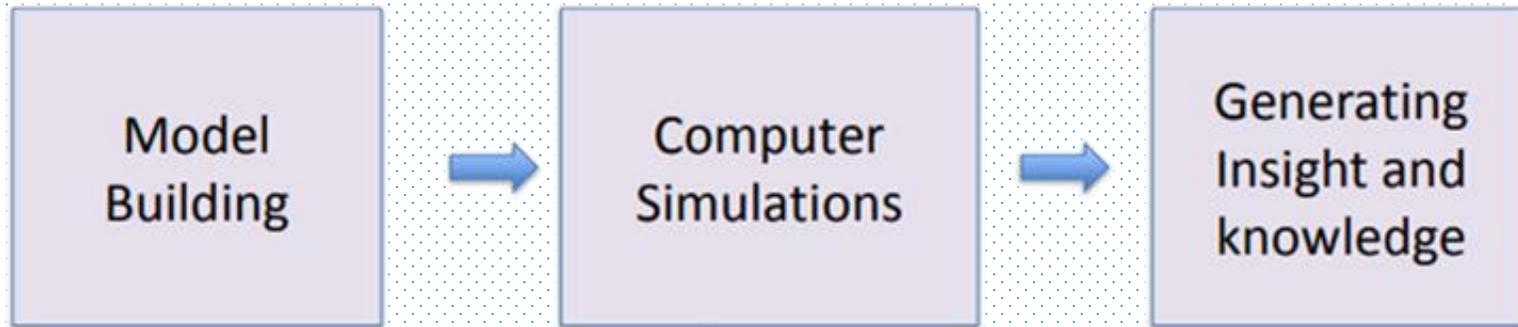


Elements of Molecular simulations



Explore all possible conformations of molecules and fluctuations with **numerical simulation algorithms (SAMPLING)**

Elements of Molecular simulations



Analyze and interpret data
Difficulty: complex information [from a vast number of conformations (10^{23})] / properties that could be comprehended and tested

Statistical Mechanics

Why Not Quantum Mechanics?

- Modeling the motion of a complex molecule by solving the wave functions of the various subatomic particles would be accurate...

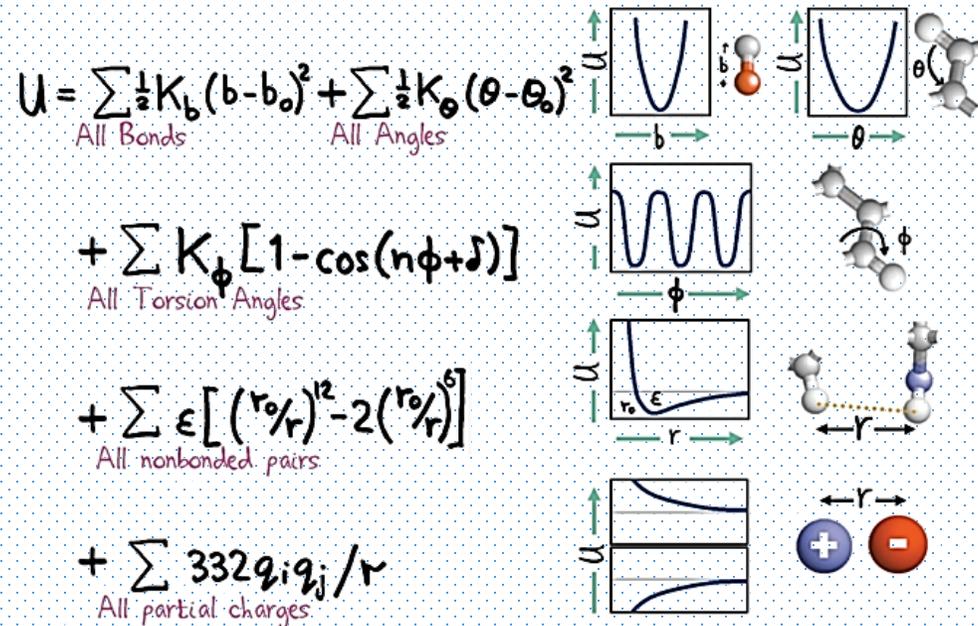
$$\frac{-\hbar^2}{2m} \nabla^2 \Psi + U(x, y, z) \Psi(x, y, z) = E \Psi(x, y, z)$$

- But it would also be **very** hard to program and take more computing power than anyone has!

The good news is

“the development of multiscale models
for complex chemical systems”

wins noble prize



The Nobel Prize in Chemistry 2013



© Nobel Media AB. Photo: A. Mahmoud
Martin Karplus
Prize share: 1/3



© Nobel Media AB. Photo: A. Mahmoud
Michael Levitt
Prize share: 1/3



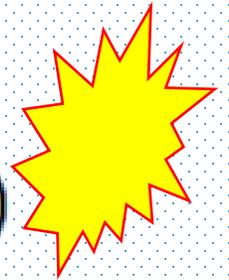
© Nobel Media AB. Photo: A. Mahmoud
Arieh Warshel
Prize share: 1/3

The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel "for the development of multiscale models for complex chemical systems"

Computational chemistry and computational physics don't always get the respect they deserve! This is not one of those times, as the [Royal Swedish Academy of Sciences](#) has awarded the 2013 Nobel Prize in Chemistry to three theoretical chemists

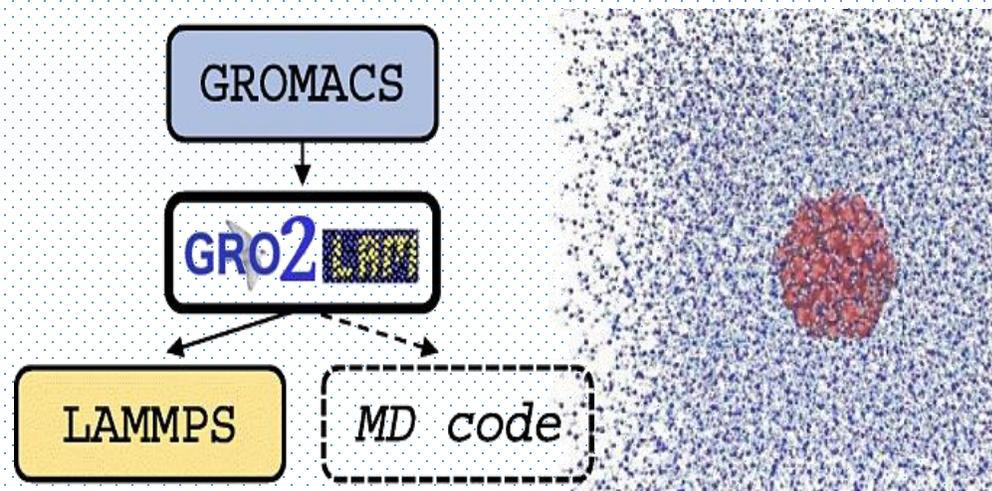
What is Classical Molecular Dynamics?

- ▶ Simulation of explicit particles (atoms, ions, ...)
- ▶ Particles interact via relatively simple analytical potential functions
- ▶ Newton's equations of motion are integrated for all particles simultaneously
- ▶ 100-1,000,000's of particles depending on model
- ▶ Time 10 ps to 1 μ s depending on model (typically ns)



Why Classical Molecular Dynamics?

- ▶ Not too expensive
- ▶ There are many user-friendly codes that can be linked to each other



- ▶ MD can be used to pre-optimize structures for ab-initio simulation (multi-scale idea)

Phase Space and Time Averages

- ▶ A system containing N atoms has $6N$ values defining the state of the system ($3N$ coordinates (\mathbf{r}), $3N$ momenta (\mathbf{p}))
- ▶ Each combination of coordinates and momenta define a point in the $6N$ -dimensional *phase space*: Γ_N
- ▶ Consider a property that can be described as a function of the coordinates and momenta, $A(\Gamma)$, (for instance the total energy or the (instantaneous) pressure)
- ▶ The average value of the property can then be written as:

$$A_{\text{obs}} = \langle A \rangle_{\text{time}} = \langle A(\Gamma(t)) \rangle_{\text{time}} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A(\Gamma(t)) dt$$

- ▶ The *ergodic hypothesis*: "The long time average is equal to the ensemble average in the limit of an infinite number of members in the ensemble"

Molecular Dynamics

- ▶ A MD simulation generates a sequence of points in phase space connected in time
- ▶ The result is a *trajectory* of all particles in the system as a function of time
- ▶ Time averages and other properties can be calculated from this trajectory
- ▶ Motion of the system through phase space is governed by Hamiltonian equations of motion :

$$\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i} = \mathbf{f}_i$$

- ▶ The Hamiltonian :

$$H(\mathbf{r}, \mathbf{p}) = K(\mathbf{p}) + V(\mathbf{r})$$

$$K(\mathbf{p}) = \sum_i^N \frac{\mathbf{p}_i^2}{2m_i}$$

- ▶ V is a potential energy function

- ▶ Newtons equations of motion :

$$\dot{x} = \frac{\partial H}{\partial p_x} = \frac{p_x}{m} = v_x$$

$$\dot{p}_x = -\frac{\partial H}{\partial x} = -\frac{\partial V(x)}{\partial x} = F = ma_x$$

Force Calculation

The force on an atom is determined by

$$\mathbf{F}_i = -\nabla U(\mathbf{r}) = -\sum_{j \neq i}^N \frac{\partial u(r_{ij})}{\partial r_{ij}} \hat{\mathbf{r}}_{ij}$$

$U(\mathbf{r})$: potential function

N : number of atoms in the system

\mathbf{r}_{ij} : vector distance between atoms i and j

Using Classical Potential

Born-Oppenheimer Approximation

- ▶ Electrons move much faster than the nuclei
- ▶ QM: Solve Schrodinger equation for static nuclei
- ▶ MD: Nuclei experience electrons as an average field

■ Consider electron motion for fixed nuclei ($\frac{m_e}{M} \rightarrow 0$)

$$\Psi(\mathbf{R}_i, \mathbf{r}_\alpha) = \Phi(\mathbf{R}_i) \varphi(\mathbf{r}_\alpha, \mathbf{R}_i)$$

■ Assume total wavefunction as

$\Phi(\mathbf{R}_i)$: Nuclei wavefunction

$\varphi(\mathbf{r}_\alpha, \mathbf{R}_i)$: Electron wavefunction
parametrically depending on \mathbf{R}_i

■ The equation of motion for nuclei is given by

$$H_N = \sum_i \frac{P_i^2}{2M_i} + U(\mathbf{R}_i) \quad (\text{approximated to classical motion})$$

MD Potentials

Classical Potential

- ▶ The potential energy can be divided into interactions between pairs, triplets, ... of particles :

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

U_1 : Single particle potential

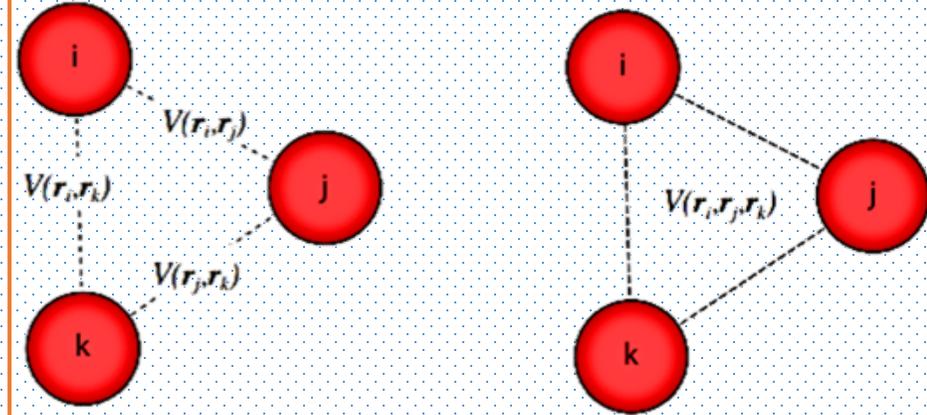
Ex) external electric field, zero if no external force

U_2 : Pair potential only depending on

$$\mathbf{F}_{ij} = -\nabla_{\mathbf{r}_i} U(r_{ij})$$

U_3 : Three-body potential with an angular dependence

$$\mathbf{F}_i = -\nabla_i \left[\sum_j (V_{ij} + V_{ji}) + \sum_j \sum_k V_{jki} \right]$$



MD Potential parametrizations

Empirical Potential

functional form for the potential
fitting the parameters to experimental data
Ex) Lennard-Jones, Morse, Born-Mayer

Semi-empirical Potential

calculate the electronic wavefunction
for fixed atomic positions from QM
Ex) EAM, Glue Model, Tersoff

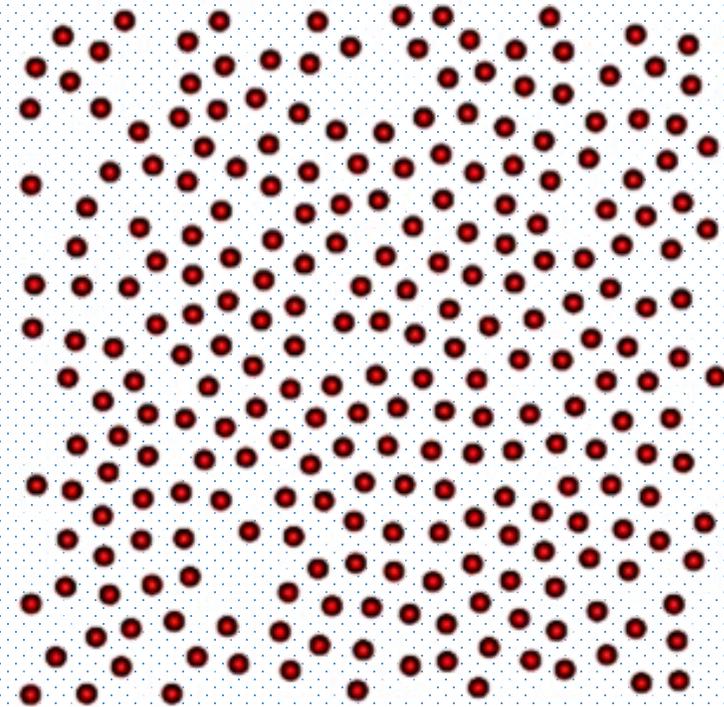
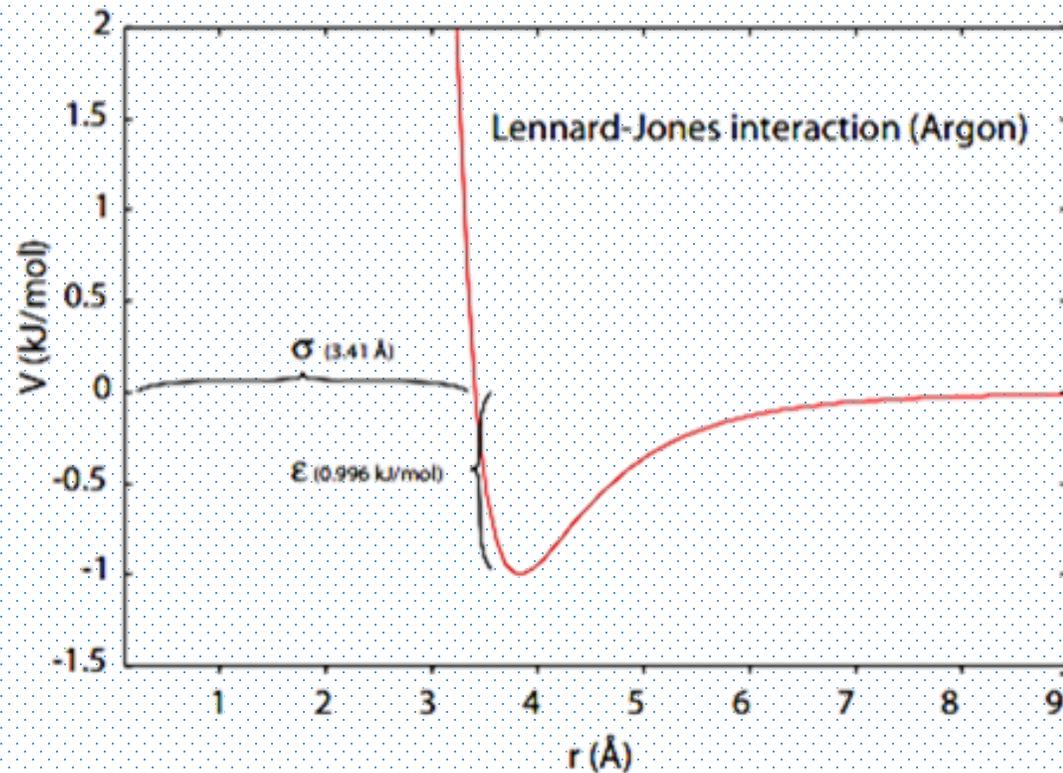
Ab-initio MD

direct QM calculation of electronic structure
Ex) Car-Parrinello using plane-wave pseudopotential

The Lennard-Jones Potential

$$V_{ij}(r_{ij}) = 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right)$$

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$$



Two dimensional simulation of argon

Tersoff Potential

- cluster-functional potential
- environment dependence without absolute minimum at the tetrahedral angle
- The more neighbors, the weaker bondings

$$U = U_{repulsive}(r_{ij}) + b_{ijk} U_{attractive}(r_{ij})$$

b_{ijk} : environment-dependent parameter weakening the pair interaction when the coordination number increases. It is a function that in **Tersoff-type potentials depends inversely on the number of bonds to the atom**, the bond angles between sets of three atoms, and optionally on the relative bond lengths.

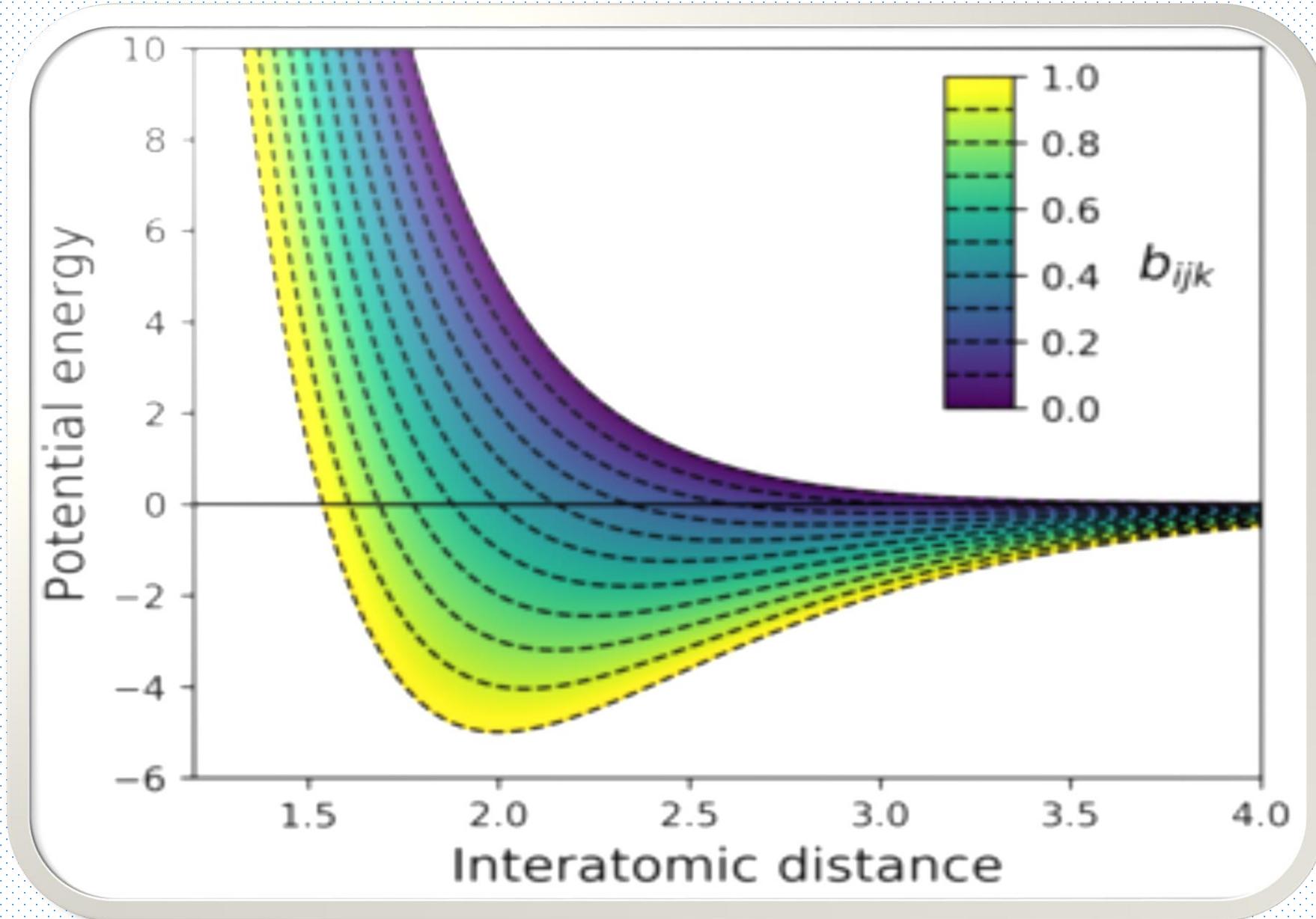
Tersoff Potential

$$U_{ij} = f_C(r_{ij})[a_{ij}f_R(r_{ij}) + b_{ij}f_A(r_{ij})]$$

where

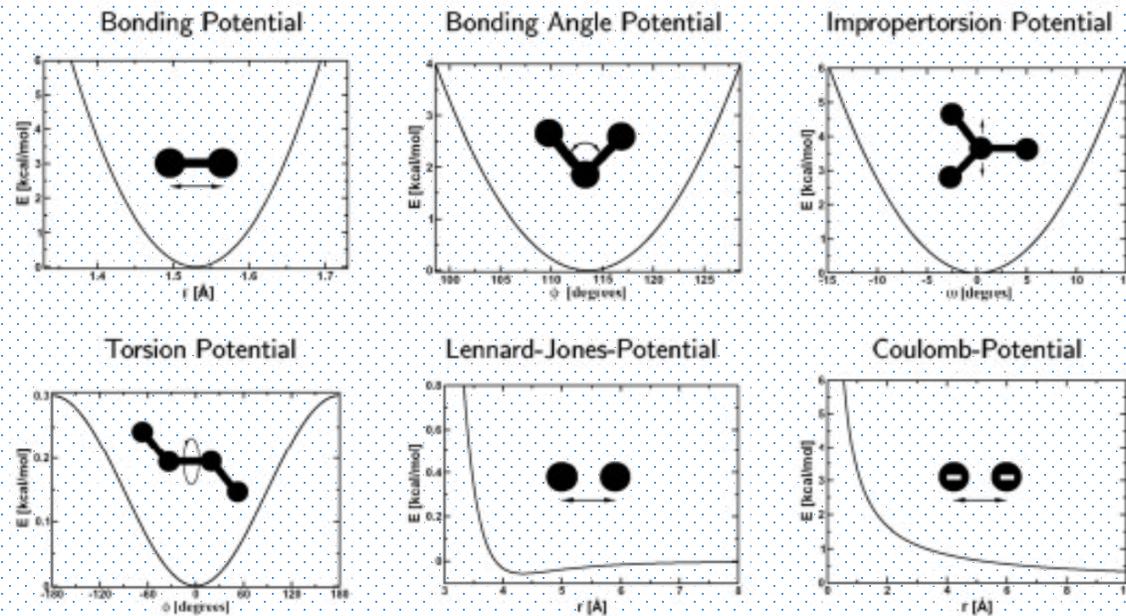
repulsive part $f_R(r) = Ae^{-\lambda_1 r}$ attractive part $f_A(r) = -Be^{-\lambda_2 r}$

potential cutoff function $f_C(r) = \begin{cases} 1, & r \leq R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi}{2} \frac{(r - R)}{D}\right), & R - D < r < R + D \\ 0, & r \geq R + D \end{cases}$



Potential energy per bond, illustrating of how the value of the bond order in a Tersoff-type potential shifts the potential energy minimum.

A standard FF:



$$E = \sum_b k_b (r - r_b)^2 + \sum_\theta k_\theta (\theta - \theta_0)^2 + \sum_\omega k_\omega (\omega - \omega_0)^2$$
$$+ \sum_\phi k_\phi (1 - \cos(n\phi - \delta)) + \sum_{i < j} 4 \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] + \sum_{i < j} \frac{q_i q_j}{r}$$

But the best force field does not exist!

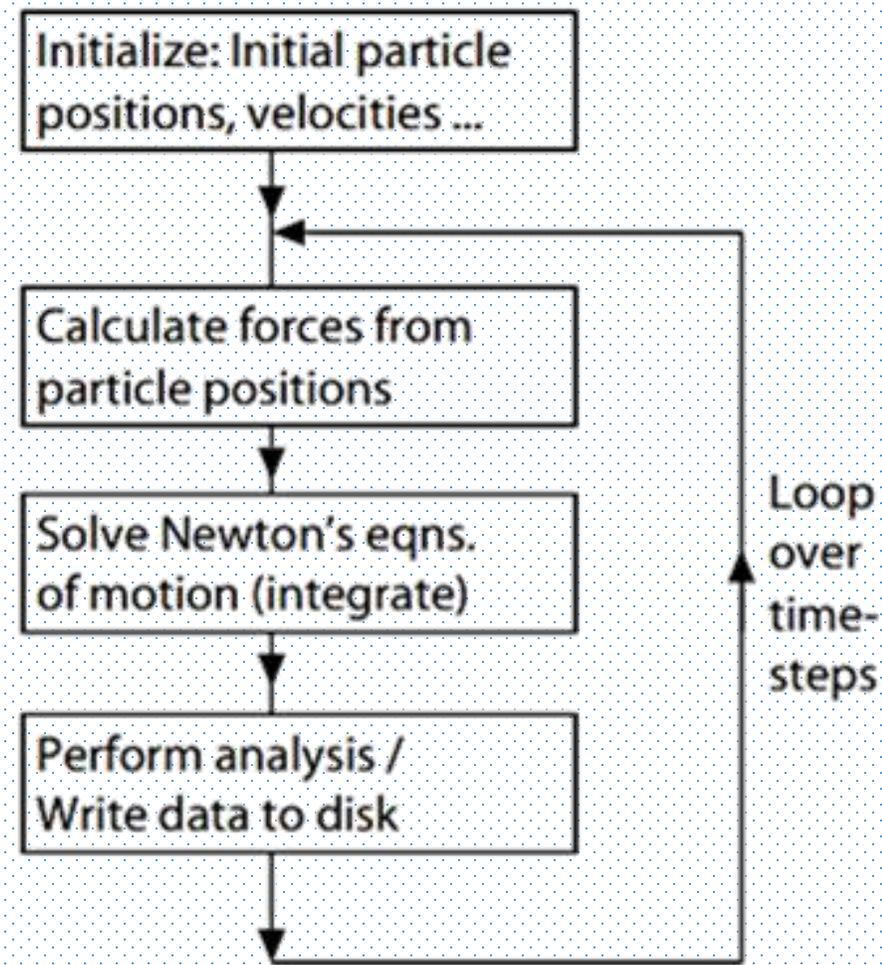
The choice will depend on the type of molecular system and the type of properties we are interested in!

The Initial Configuration

- ▶ For a solid it may be possible to start from the experimentally determined structure
- ▶ For a liquid it is also common to start from a “solid” lattice, and letting the structure melt
- ▶ For a liquid it is also possible to start from a “random” placement of molecules (this may be tricky)
- ▶ If previous simulation data is available, one might modify a configuration to suit the new simulation, for instance by replacing one or a few particles
- ▶ Macromolecule in liquid: Use experimental coordinates of macromolecule from solid phase structure determination, surround it by liquid

Steps in Performing an MD Simulation

- ▶ Selection of interaction model
- ▶ Selection of boundary conditions
- ▶ Selection of initial conditions (positions, velocities ...)
- ▶ Selection of ensemble (NVE, NVT, NPT ...)
- ▶ Selection of target temperature, density/pressure ...
- ▶ Selection of integrator, thermostat, barostat ...
- ▶ Perform simulation until equilibration is reached (property dependent)
- ▶ Perform production simulation to collect thermodynamic averages, positions, velocities
- ▶ Analyze the results via post-processing



The Initial Velocities

- ▶ The velocities of the particles is related to the kinetic energy :

$$K = \sum_i^N \frac{m_i v_i^2}{2}$$

- ▶ The kinetic energy is related to the temperature :

$$2 \langle K \rangle = g k_B T = 3 N k_B T$$

- ▶ Assign velocities according to a Boltzmann distribution :

$$P(v_i) = \left(\frac{m_i}{2\pi k_B T} \right)^{1/2} e^{-\frac{m_i v_i^2}{k_B T}}$$

- ▶ Alternatively assign particle velocities from a uniform distribution. They will obtain a Boltzmann distribution after a short time.

Temperature Control

Velocity Scaling

- Scale velocities to the target T
- Efficient, but limited by energy transfer
- Larger system takes longer to equilibrate

Nose-Hoover thermostat

- Fictitious degree of freedom is added
- Produces canonical ensemble (NVT)
- Unwanted kinetic effects from T oscillation

- It is often necessary to adjust the initial velocities so the total linear momentum of the system is zero :

$$\mathbf{p} = \sum_i^N \mathbf{p}_i = \sum_i^N m_i \mathbf{v}_i = \mathbf{0}$$

- This momentum corresponds to translation of the *whole system*
- Having $\mathbf{p} \neq \mathbf{0}$ in simulations of “liquid” water, has been referred to as a “flying ice cube”
- Newton’s equations of motion will preserve the *linear momentum* resulting in a NVE \mathbf{P} ensemble, resulting in a system with three fewer degrees of freedom
- For a system with periodic boundary conditions, the *angular momentum* will not be conserved

Integrating the Equations of Motion

- ▶ Motion of all particles is coupled (many-body problem), This is impossible to solve analytically ...
- ▶ Solve using finite differences
- ▶ Positions, velocities ... approximated as a Taylor series:

$$r(t + \Delta t) = r(t) + \Delta t v(t) + \frac{1}{2} \Delta t^2 a(t) + \frac{1}{6} \Delta t^3 b(t) + \frac{1}{24} \Delta t^4 c(t) + \dots$$

$$v(t + \Delta t) = v(t) + \Delta t a(t) + \frac{1}{2} \Delta t^2 b(t) + \frac{1}{6} \Delta t^3 c(t) + \dots$$

$$a(t + \Delta t) = a(t) + \Delta t b(t) + \frac{1}{2} \Delta t^2 c(t) + \dots$$

$$b(t + \Delta t) = b(t) + \Delta t c(t) + \dots$$

Integration Method

- Finite difference method
- Numerical approximation of the integral over time

Verlet Method

- Better long-term energy conservation
- Not for forces depending on the velocities

Predictor-Corrector

- Long-term energy drift (error is linear in time)
- Good local energy conservation (minimal fluctuation)

Velocity Verlet Method

- From the initial $\mathbf{r}_i(t)$, $\mathbf{v}_i(t)$

$$\mathbf{a}(\mathbf{r}) = \frac{1}{m} \mathbf{F}(\mathbf{r}(t))$$

- Obtain the positions and velocities at $t + \Delta t$

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2} \mathbf{a}(\mathbf{r})\Delta t^2$$

$$\mathbf{a}(t + \Delta t) = \frac{1}{m} \mathbf{a}(\mathbf{r}(t + \Delta t))$$

$$\mathbf{v}(t + \Delta t/2) = \mathbf{v}(t)\Delta t + \frac{1}{2} \mathbf{a}(\mathbf{r})\Delta t$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t + \Delta t/2) + \frac{1}{2} \mathbf{a}(t + \Delta t)\Delta t$$

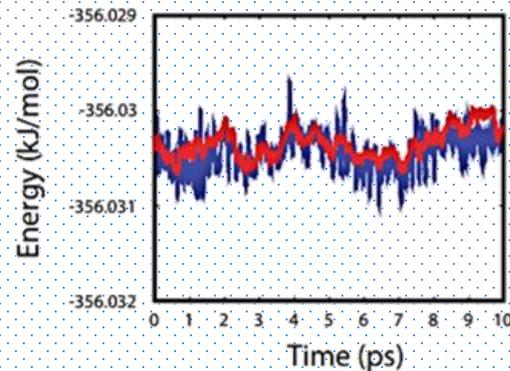
MD Time Step

► Choosing the Timestep

- A balance is needed in choosing the timestep. A too short timestep lead to a very expensive solution of the equations of motion, and leads to a limited coverage of phase space. A much too small timestep might lead to round-off errors.
- Too large of a timestep leads to instabilities

► Velocity Verlet Integrator

$\Delta t = 1$ fs (blue)



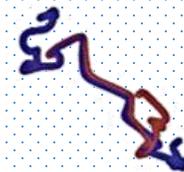
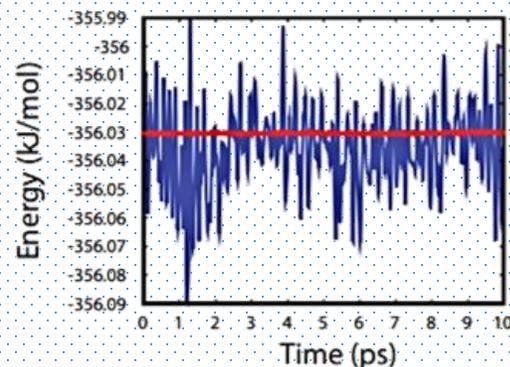
Too long Δt : energy is not conserved

$\Delta r / \Delta t \leq 1/20$ of the nearest atom distance

In practice $\Delta t \leq 4$ fs.

► Velocity Verlet Integrator

$\Delta t = 10$ fs (blue)



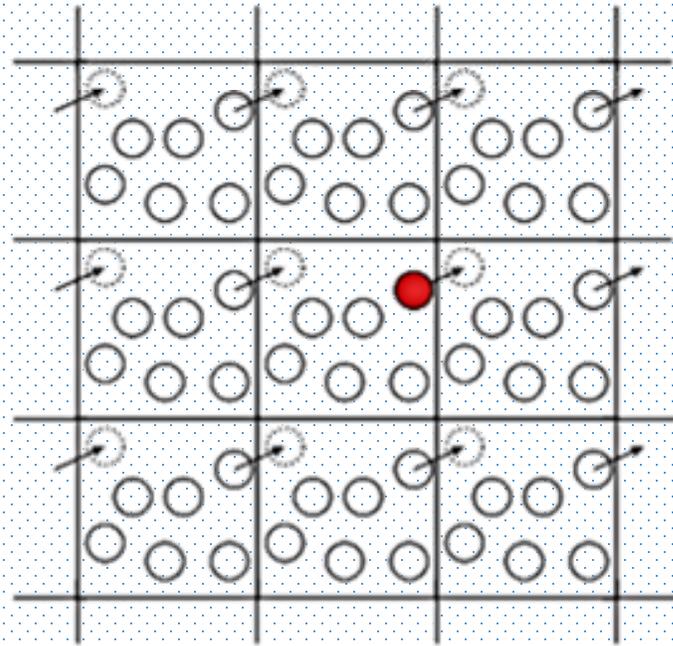
Total MD time is limited to < 100 ns

Statistical Mechanical Ensembles

- ▶ The “natural” ensemble for MD is the microcanonical ensemble: NVE (constant number of particles, constant volume, constant energy)
- ▶ Typical experiments: Constant pressure and/or temperature
- ▶ Canonical ensemble: NVT (constant number of particles, volume, temperature); Isobaric, isothermal (Gibbs): NPT (constant number of particles, pressure, temperature)
- ▶ Some ways to include such effects in MD
 - ▶ Stochastic events (change kinetic energy of single particle)
 - ▶ Periodic rescaling of velocities ($2K = gk_B T$)
 - ▶ Ad hoc partial rescaling of velocities (Berendsen’s thermal bath)
 - ▶ Extended system methods: Include extra variables in the equations of motion such as the volume of the system

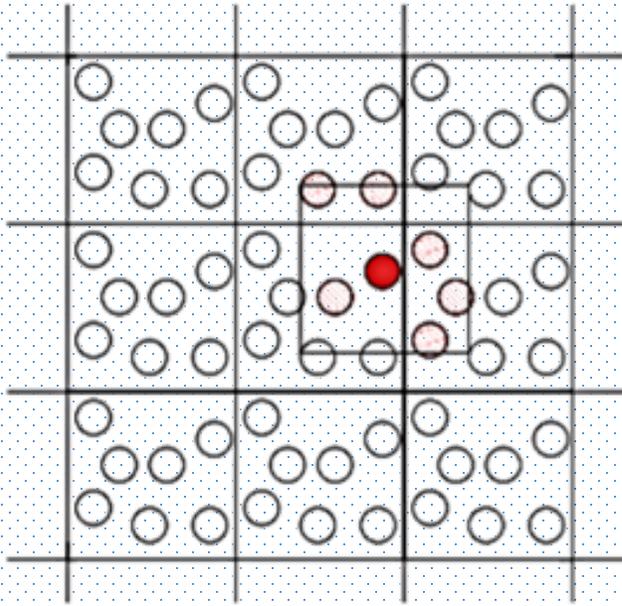
Periodic Boundary Conditions

- ▶ A “real” system might contain about $N_A = 6 \cdot 10^{23}$ molecules
- ▶ Simulation may contain about 100-1,000,000 molecules
- ▶ A small cube of 10x10x10 molecules has about half of the molecules on the surface
- ▶ Not appropriate to study “bulk” properties
- ▶ Periodic boundary conditions:
 - ▶ Small box replicated in all directions
 - ▶ A particle that leaves the box on one side is replaced by an image particle that enters from the other side
 - ▶ There are no walls and no surface particles
- ▶ Some systems inherently contains a boundary, for instance a liquid droplet, or a surface



The Minimum Image Convention

- ▶ Particles interact only with the closest periodic image of the other particles:



How to compute minimum image :

- ▶ Simple and straightforward

```
rx = xi - xj;  
if (rx > 0.5 * length)  
    rx = rx - length;  
if (rx < -0.5 * length)  
    rx = rx + length;
```

- ▶ Fortran has a function, `anint`, which returns the nearest integer

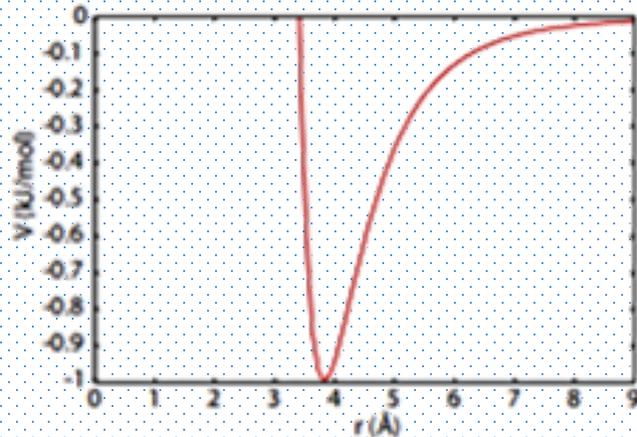
```
rx = rx - length * anint (rx/length)
```

- ▶ In C, the `floor` function can be used

```
rx = rx - length * floor (rx/length + 0.5);
```

Truncating the Potential

- ▶ The most time consuming part: Computing the nonbonded (vdw & electrostatic) energies and forces
- ▶ For a pair additive potential there are N^2 such interactions
- ▶ Consider the Lennard-Jones argon potential again:



- ▶ Spherical nonbonded cutoff

$$V'_{ij}(r_{ij}) = V_{ij}(r_{ij}) \quad r_{ij} \leq r_c$$

$$V'_{ij}(r_{ij}) = 0 \quad r_{ij} > r_c$$

- ▶ Disadvantage: Discontinuity in the energy and forces

- ▶ Switching function ($S(r_{ij})$ smoothly from 1 to 0)

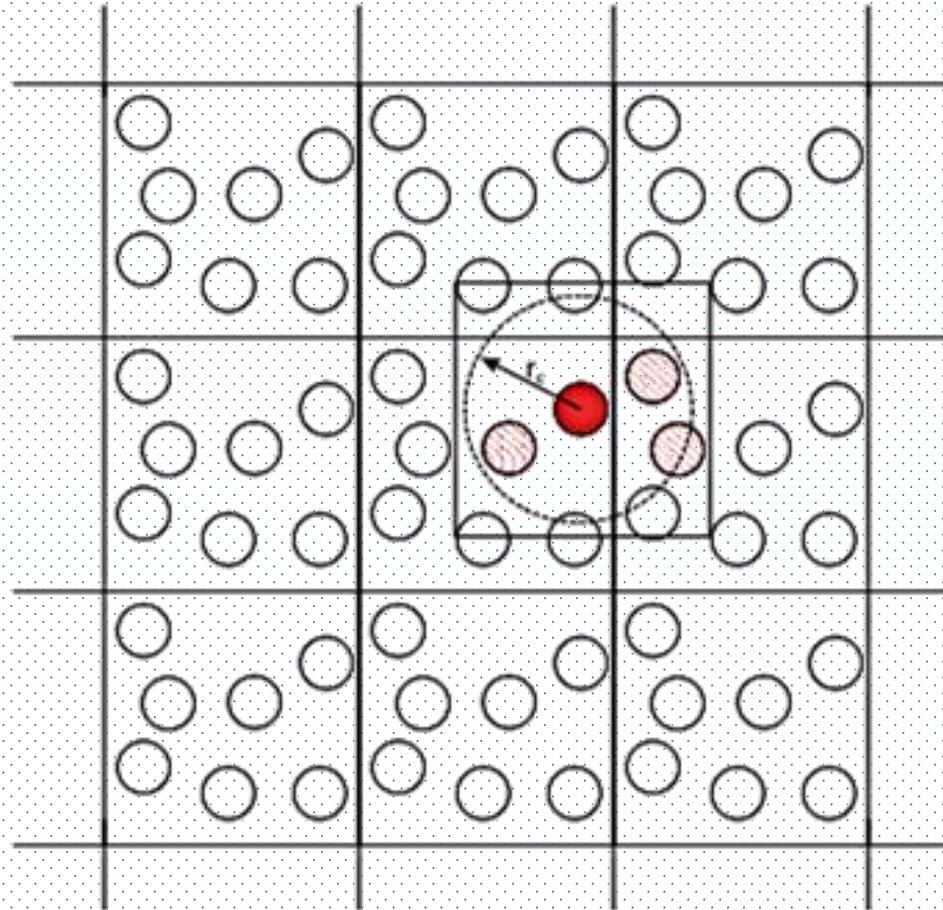
$$V'_{ij}(r_{ij}) = V_{ij}(r_{ij}) \quad r_{ij} < r_l$$

$$V'_{ij}(r_{ij}) = S(r_{ij})V_{ij}(r_{ij}) \quad r_l \leq r_{ij} \leq r_c$$

$$V'_{ij}(r_{ij}) = 0 \quad r_{ij} > r_c$$

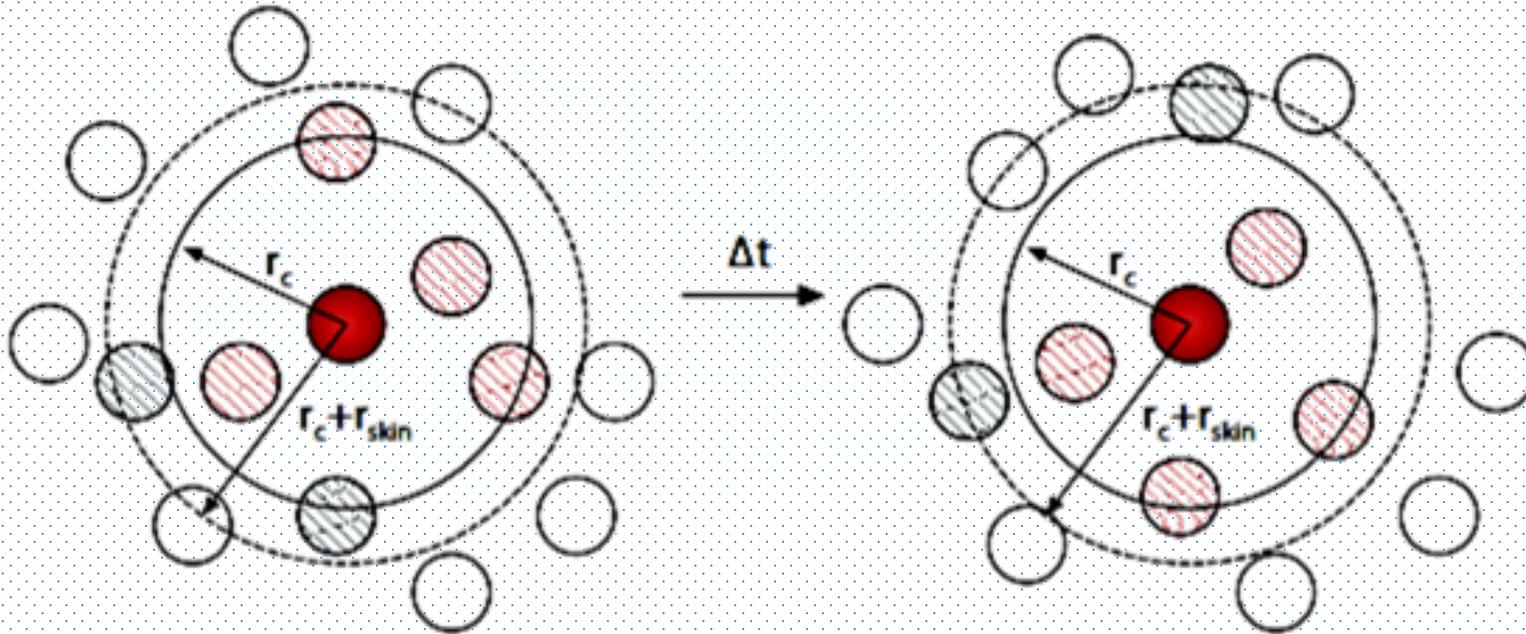
Minimum Image and Spherical Cutoff

- ▶ Very commonly minimum images and spherical cutoffs are used together



Searching for Neighbors

- ▶ The search loop is a double loop over all particles (n). Execution time for the loop is proportional to n^2
- ▶ The Verlet neighbor list: Maintain list of neighbor pairs closer than the radius (r_c) plus a buffer (r_{skin})



- ▶ Update list from time to time (about once every 25 timesteps, but this can be automated)

Equilibration

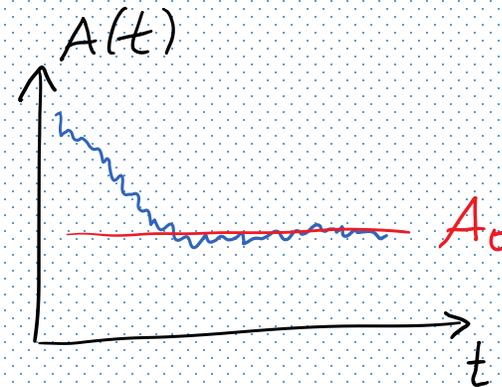
- After initial setup or after change of parameters, system is out of equilibrium. i.e. its properties will not be stationary but drift, relax towards new equilibrium state
→ if we are interested in equilibrium, must wait for a number of time steps to reach equilibrium before measuring observables

Normally, observable $A(t)$ approaches equilibrium value A_0 as

$$A(t) = A_0 + C e^{-t/\tau_{eq}}$$

$A(t)$ short time average to eliminate fluctuations)

What is τ_{eq} , i.e. how long do we have to wait? Hard to know a priori.



2-Simple Observables

1. Looking at the atoms

Simplest analysis, reveals a lot about simulation

Looking at trajectories $\vec{r}_i(t)$ or $x_i(y_i), x_i(z_i)$ gives information:

- How far does atom move during run?
- Are there collisions?

Looking at configuration of all atoms at fixed time (snapshot) gives info about structure (random vs ordered...)

2. Statistical Quantities

$$A(t) = f(\vec{r}_i(t), \vec{v}_i(t))$$

- $A(t)$ will fluctuate with t . Fluctuations are the stronger the smaller the system
- Thermodynamic behavior is represented by average:

$$\langle A \rangle = \frac{1}{N_\tau} \sum_{n=1}^{N_\tau} A(t_n) \quad t_n = n\tau$$

- Measurement can only be started **after** equilibration

a) **Potential energy**

$$E_{pot}(t) = \frac{1}{2} \sum_{i \neq j} V(\vec{r}_i - \vec{r}_j)$$

b) **Kinetic energy**

$$E_{kin}(t) = \frac{1}{2} \sum m_i \vec{v}_i(t)^2$$

c) **Total energy**

$$E(t) = E_{kin}(t) + E_{pot}(t)$$

- Should be conserved in Newton's dynamics
- Energy conservation is a good check of the time integration
- Typically relative fluctuations of, say, $\sim 10^{-4}$ are OK

→ Choice of **time step** τ :

small enough to conserve energy to accuracy 10^{-4} ,

but large enough to allow for a sufficiently long simulation time

d) **Temperature:** derived quantity in MD simulation
in microcanonical (NVE) ensemble

$$\langle E_{kin} \rangle = \frac{3}{2} N k_B T \quad \Rightarrow \quad T = \frac{2 \langle E_{kin} \rangle}{3 N k_B}$$

e) **Caloric curve** $E(T)$, specific heat $c_v = \frac{\partial E}{\partial T}$

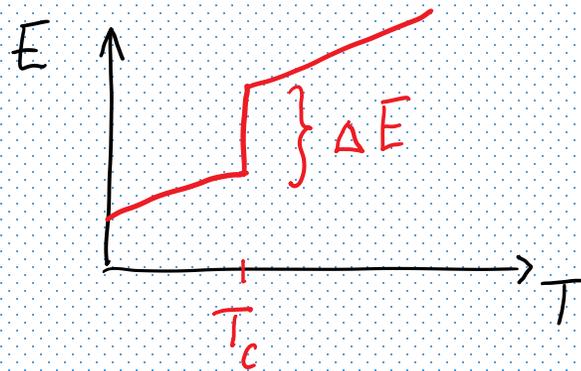
$E(T)$ will have features at a phase transition

- $E(T)$ has jump

1st order phase transition

ΔE **latent heat**

Examples: melting of ice,
liquid water \rightarrow vapor



OR:

- $E(T)$ is continuous (**no latent heat**), but $\frac{\partial E}{\partial T}$ is discontinuous:

\rightarrow **continuous phase transition (2nd order)**

Example: Curie point of iron

f) Mean-square displacement

$$\langle \Delta r^2(t) \rangle = \frac{1}{N} \sum_i \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle$$

Contains information about diffusivity,
distinguishes phases

Solid: atoms remain at positions, undergo vibrations
→ $\langle \Delta r^2 \rangle$ will saturate at a value of the order of
(lattice constant)²

Fluid: atoms can move freely
→ $\langle \Delta r^2 \rangle$ will saturate at a value of the order of
(box size)²

Distinguish two regimes:

(i) “no collisions (small box, low density)

- Mean free path λ (distance between collisions)

$$\lambda \gg L$$

- Particles move **ballistic**, $\Delta r \sim t$
- $\langle \Delta r^2 \rangle \sim t^2$ before saturation

(ii) “many collisions (large box, high density)

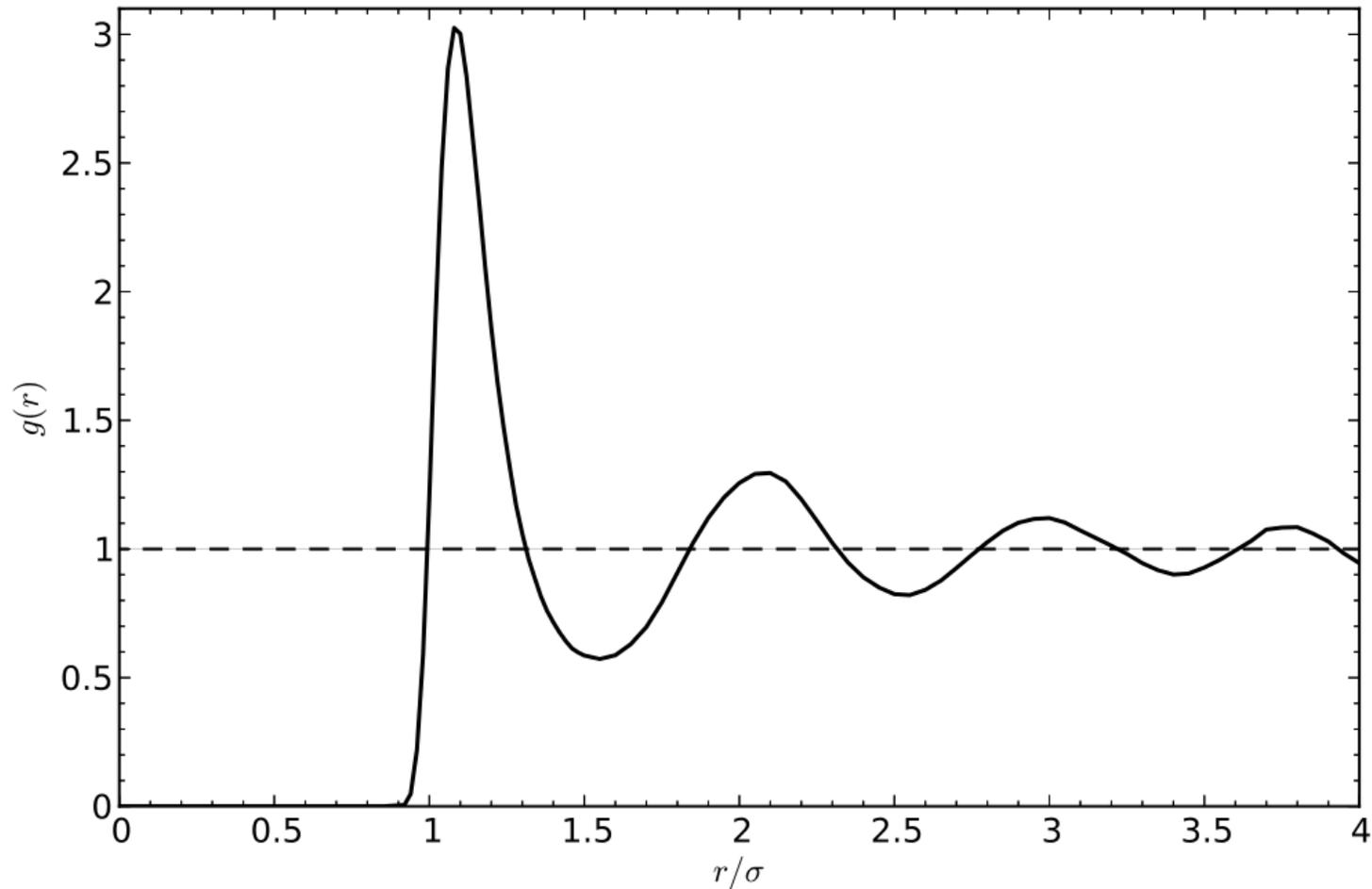
- Example: real gases at ambient conditions

- $\lambda \ll L$

- Particles move **diffusive**
- $\langle \Delta r^2 \rangle \sim t$ before saturation

g. Correlation functions:

- Relate the particle positions to each other
- Important quantities conceptually
- Directly related to scattering experiments



Describes probability for finding particle at position \vec{r} if another particle is at 0 (relative to uniform distribution).

$$g(\vec{r}) = \frac{1}{\int} \frac{1}{N} \sum_i \sum_{j \neq i} \langle \delta(\vec{r} - \vec{r}_{ij}) \rangle \quad g = \frac{N}{V}$$

Particles independent, uniformly distributed:

$$\langle \delta(\vec{r} - \vec{r}_{ij}) \rangle = \frac{1}{V} \int d^3 r_{ij} \delta(\vec{r} - \vec{r}_{ij}) = \frac{1}{V}$$

$$g(\vec{r}) = \frac{V}{N} \frac{1}{N} \sum_i \sum_{j \neq i} \frac{1}{V} = \frac{1}{N} N(N-1) \rightarrow 1$$

Any deviation from 1 describes correlations between particles!

3-MD as a minimization method

- So far, we have viewed molecular dynamics as a tool to simulate **thermodynamic equilibrium**
- Equilibration needs to be finished before measurements can begin

Now:

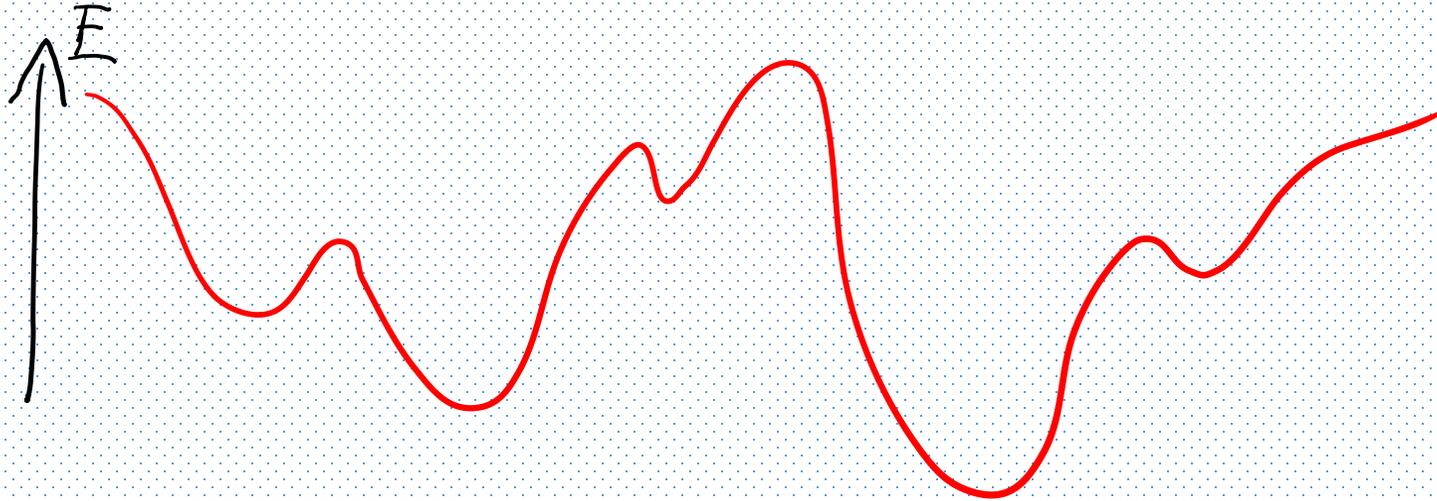
- Look at equilibration for its own sake
- Can be used as an **optimization algorithm**

Minimization methods

- Energy Minimisation
 - Calculate Lowest Energy Structure
 - Gives structural, mechanical and dielectric properties
- Molecular Dynamics
 - Calculates the effect of Temperature
 - Gives dynamics e.g. diffusivity
- Monte Carlo
 - Calculates a range of structures
 - Gives the thermally averaged properties
- Genetic Algorithms
 - Calculates a range of structures
 - Efficient search for global minimum

- At **low temperatures**, equilibration means finding states with the lowest energies
- Nontrivial problem, even for small particle numbers (see project 5)

Why?



- Energy landscape is complicated, with many local minima
- Conventional methods (e.g., steepest descent) get stuck in side minimum

Simulated annealing:

- Computational algorithm that mimics annealing of a system
 1. Start from a random configuration of particles and a kinetic energy larger than the typical barriers
 2. Perform MD simulation, but slightly reduce kinetic energy after each time step (multiply velocities by factor $a < 1$)
 3. Repeat until kinetic energy (temperature) is below some threshold
 4. The resulting configuration is (close to) the minimum energy configuration

In lammps: **fix** 1 water npt temp 300.0 0.01 100.0 iso 0.0 0.0 1000.0

Remarks:

- Finding the **global** minimum is not guaranteed
- You need to **cool very slowly** to give the system time to explore the configuration space and find the deepest and broadest minima
- If you cool too quickly, system will end up in the closest local minimum rather than the global one
- velocity scaling factor a needs to be close to unity, e.g., $a=0.999$

3-MD prediction for 2D-ice structure vs ab-initio result

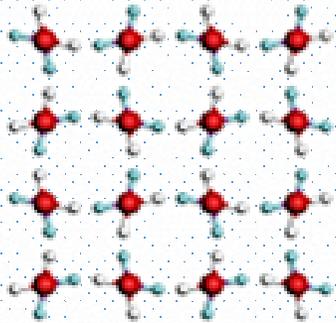
Two dimensional Ice!

LETTER

doi:10.1038/nature14295

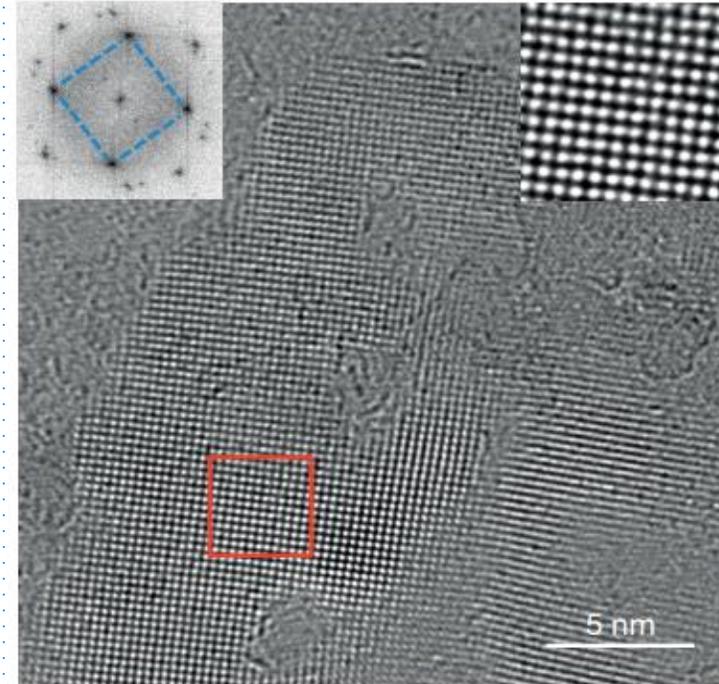
Square ice in graphene nanocapillaries

G. Algara-Siller¹, O. Lehtinen¹, F. C. Wang², R. R. Nair³, U. Kaiser¹, H. A. Wu², A. K. Geim³ & I. V. Grigorieva³



.... In contrast, the few-layer ice we report here corresponds to 90° hydrogen bonding both within and between layers.

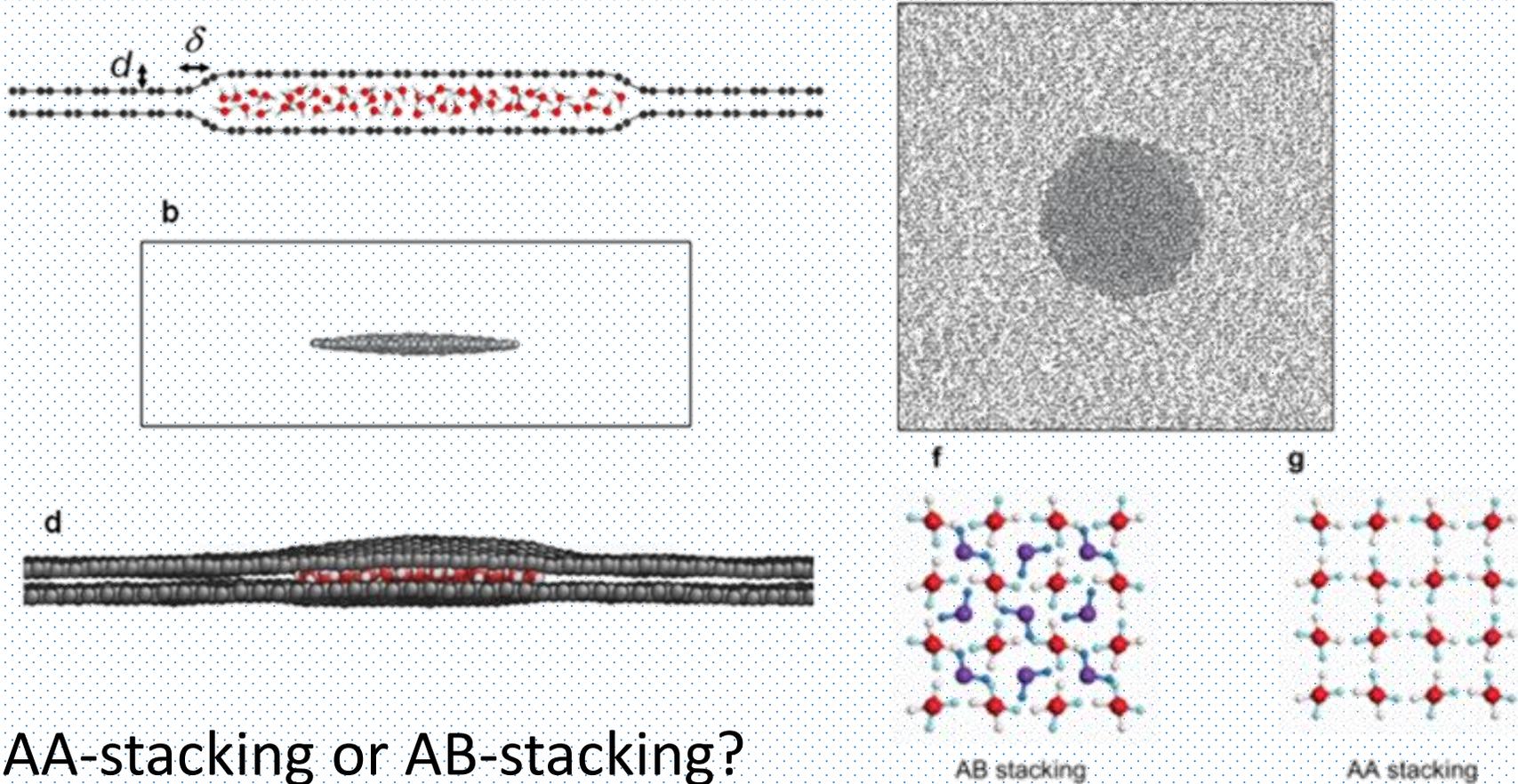
Central Facility for Electron Microscopy, Group of Electron Microscopy of Materials Science, University of Ulm, 89081 Ulm, Germany



Experimentalists from Ulm and Manchester team dropped one microlitre of water on to a sheet of graphene, and then placed a second graphene wafer on top, all at room temperature. As the water slowly evaporated, the graphene sheets were squeezed together until they were less than one nanometre apart, trapping pockets of water in the sandwich.

Transmission electron microscopy revealed that these pockets contained square ice. But in a layer of square ice, all the atoms lie in a flat plane with a right angle between each oxygen–hydrogen bond. Geim's patches of square ice contained one, two or three of these layers, with oxygen atoms in adjacent layers sitting directly on top of one another!!

Pressure is in the order of GPa_c



AA-stacking or AB-stacking?

One can easily calculate that when the graphene sheets are separated by distances of less than 1 nm (as used in the experiment), then the van der Waals forces can easily generate pressures as high as 1 GPa. They also reported AA stacking (rather than AB-stacking) for the layers on top of each other where oxygen atoms in adjacent layers sitting directly on top of one another. This picture is bubble containing a droplet of water which has been shrunk down to this size.

The observation of square ice in graphene questioned

ARISING FROM G. Algara-Siller *et al.* *Nature* **519**, 443–445 (2015); doi:10.1038/519443a

Algara-Siller *et al.*¹ reported the observation of a new phase of water—‘square ice’—sandwiched between two graphene layers at room temperature. Their key evidence consists of transmission electron microscope (TEM) images of a square lattice from small encapsulated crystals, the detection of oxygen from relatively large regions containing such crystals and molecular dynamics (MD) simulations indicating ‘square ice’ formation inside hydrophobic nanochannels. Here we propose that the reported experimental data can be better explained by salt (for example, NaCl) contaminants precipitating as nanocrystals in the dried-out graphene liquid cells² and common oxide contaminants in graphene. Consequently, we question the observation of room-temperature ‘square ice’. There is a Reply to this Brief Communication

Ute Kaiser · 2 years ago

With reference to the previous Comment and Brief Communication arising, we feel it is necessary to inform the readers that our further efforts to prepare and visualize square ice have been unsuccessful. This strengthens concerns that the observed square crystals could be due to accidental contamination as suggested by Zhou *et al.* We strongly believe that the envisaged square-like ice should exist as shown in our molecular dynamics simulations and confirmed by several other groups. Visualization of such ice may however require cryogenic temperatures to avoid rapid movements of water molecules. We are further pursuing this line of enquiry.

Ute Kaiser on behalf of all the authors

^ | v · Reply · Share ›

Other experimentalists proposed that the reported data can be better [explained by NaCl contaminants precipitating as nanocrystals in the dried out graphene](#) and common oxide contaminants in graphene (i.e. SiO₂).

Later experimentalists also confirmed that they can not repeat the first experiment and probably the idea of NaCl contaminants is correct.

Monolayer Ice

VOLUME 91, NUMBER 2

PHYSICAL REVIEW LETTERS

week ending
11 JULY 2003

Monolayer Ice

Ronen Zangi* and Alan E. Mark

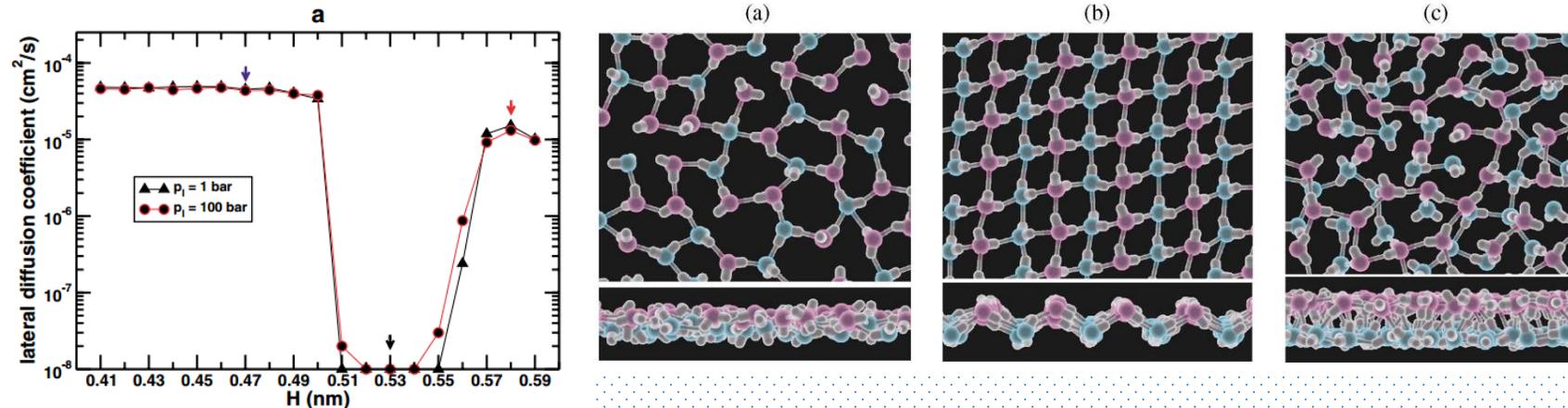
Department of Biophysical Chemistry, GBB, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received 4 October 2002; published 8 July 2003)

We report results from molecular dynamics simulations of water under confinement and at ambient conditions that predict a first-order freezing transition from a monolayer of liquid water to a monolayer of ice induced by increasing the distance between the confining parallel plates. Since a slab geometry is incompatible with a tetrahedral arrangement of the sp^3 hybridized oxygen of water, the freezing is coupled to a linear buckling transition. By exploiting the ordered out-of-plane displacement of the molecules in the buckled phase the distortion of the hydrogen bonds is minimized.

DOI: 10.1103/PhysRevLett.91.025502

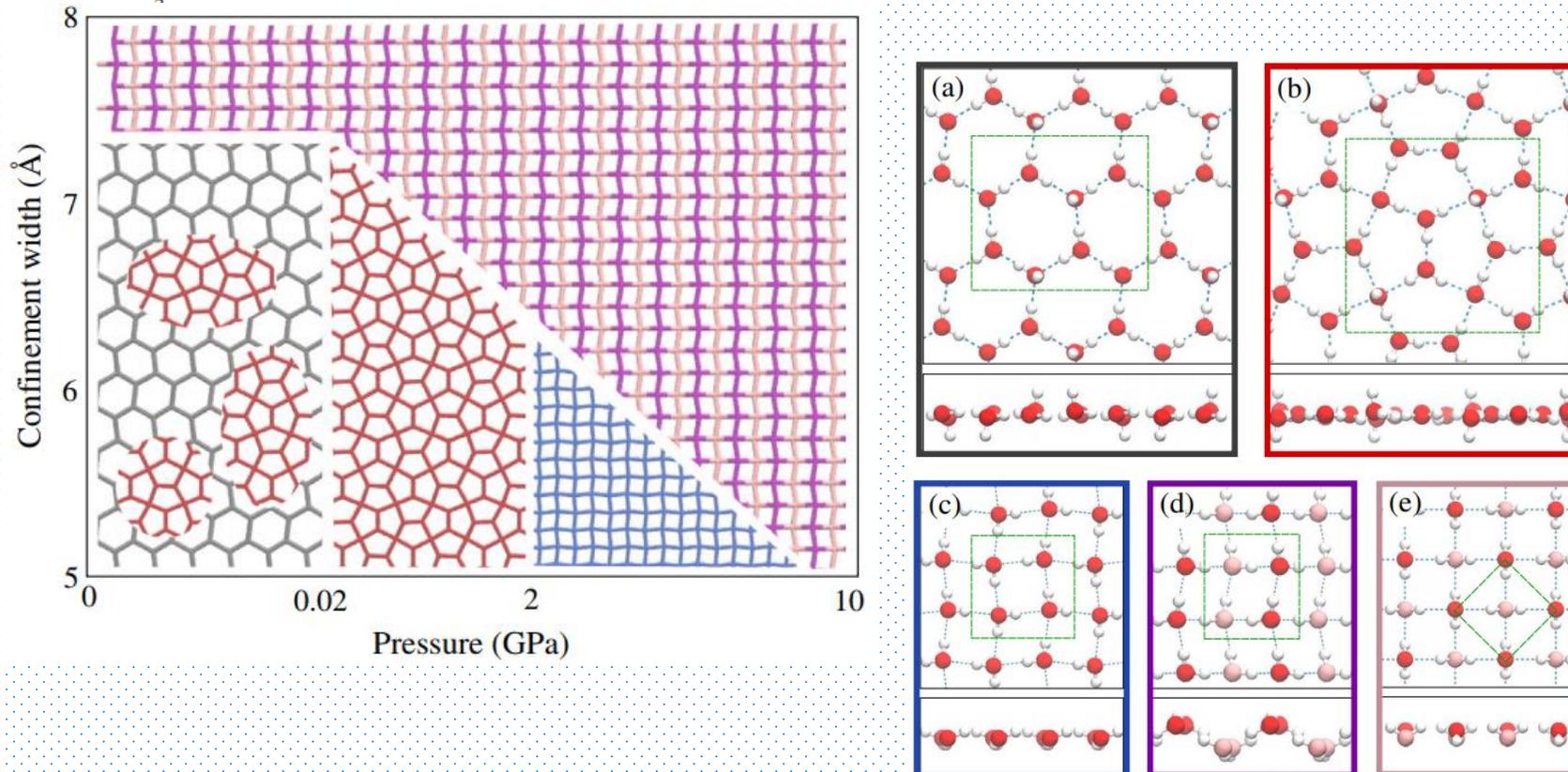
PACS numbers: 61.20.Ja, 61.46.+w, 68.15.+e



There are neuromas number of classical MD simulations and DFT simulations that confirm the ordered phase of confined water. By decreasing the distance between two slab, a phase transition from liquid water to the crystalline ice was proposed. The new ice phase has a buckled structure with rhombic lattice.

Two Dimensional Ice from First Principles: Structures and Phase Transitions

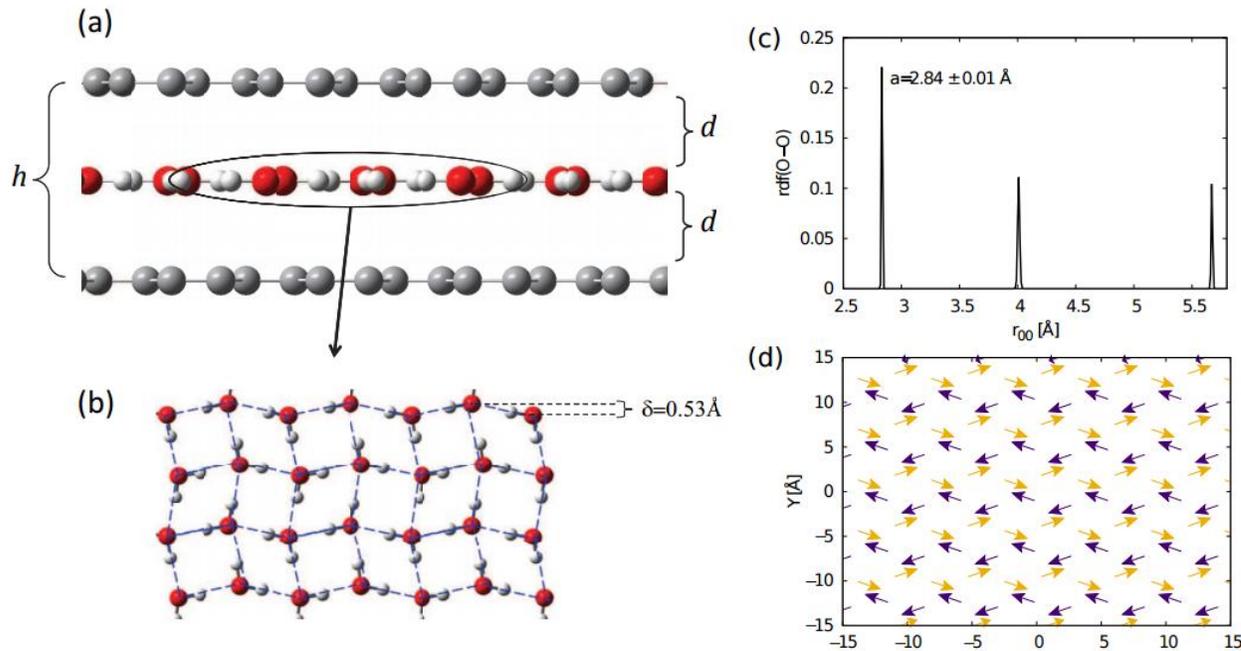
Ji Chen,^{1,2,*} Georg Schusteritsch,^{2,3,4} Chris J. Pickard,^{2,3,4} Christoph G. Salzmann,⁵ and Angelos Michaelides^{1,2,3,†}
¹London Centre for Nanotechnology, 17–19 Gordon Street, London WC1H 0AH, United Kingdom



The authors focused on the phase transitions as a function of lateral pressure and confinement width at 0 K. The stable structures identified at different pressures include a hexagonal structure, a pentagonal Cairo tiling (CT) structure, a flat square structure, and a buckled rhombic structure, all obeying the Bernal-Fowler-Pauling ice rules.

Minimum Energy Configuration

Flat, nonpolar, satisfying Ice rule , rhombic-square lattice



Using large-scale molecular dynamics simulations with the adoptable ReaxFF interatomic potential we found that flat monolayer ice with a rhombic-square structure nucleates between the graphene layers which are nonpolar and nonferroelectric.

AA-stacked bilayer square ice between graphene layers

M. Sobrino Fernandez Mario, M. Neek-Amal, and F. M. Peeters
Phys. Rev. B **92**, 245428 – Published 17 December 2015

Electric-field-induced structural changes in water confined between two graphene layers

Mario Sobrino Fernández, F. M. Peeters, and M. Neek-Amal
Phys. Rev. B **94**, 045436 – Published 27 July 2016

Reversible structural transition in nanoconfined ice

V. Satarifard, M. Mousaei, F. Hadadi, James Dix, M. Sobrino Fernandez, P. Carbone, J. Beheshtian, F. M. Peeters, and M. Neek-Amal
Phys. Rev. B **95**, 064105 – Published 15 February 2017

Electronic, dielectric, and optical properties of two-dimensional and bulk ice: A multiscale simulation study

S. Ghasemi, M. Alihosseini, F. Peymanirad, H. Jalali, S. A. Ketabi, F. Khoeini, and M. Neek-Amal
Phys. Rev. B **101**, 184202 – Published 6 May 2020

Acknowledgment:

Miguel A. Gonzalez, Institut Laue-Langevin, Grenoble, Institut Laue-Langevin, Grenoble (France)

Joo Chul Yoon, Electrical Engineering, University of Washington

https://web.mst.edu/~vojtat/class_5403/class_5403.html

<https://dasher.wustl.edu/chem430/lectures/lecture-05.pdf>

Three **postdoc position** is available in my group,
interested applicants, may send me their CV
mehdi.neekamal@gmail.com