Summary

Atomistic simulation types

- Molecular dynamics (MD)
 - Simulates atom motion as a function of real time based on some interaction model
- Monte Carlo (MC)
 - Atomistic Monte Carlo: calculate thermodynamic averages by letting particles move randomly according to certain rules.
 - Metropolis algorithm for NVT ensemble
 - Metropolis-based algorithms for NVE, NPT, µVT

Energy minimization

- · Conjugate gradient energy minimization
 - Efficient way to find a local minimum
- · Genetic algorithms for atoms
 - Possibly efficient way to find a global minimum
- Minimum energy path determination
 - Find the 'easiest' path from one local energy minimum to another.
 - Nudged elastic band

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Summary



Most common boundary conditions in MD

· Free boundaries: simulate matter in empty space



· Periodic boundaries: describes a continuous medium



Because here $r_{ij} > r_{ij}$, the vector r_{ij} is used for the distance between atoms *i* and *j* (minimum image convention)

```
if (periodic(1)) then
    dx = x(j) - x(i)
    if (dx > box(1)/2.0)    dx=dx-box(1)
    if (dx <= -box(1)/2.0)    dx=dx+box(1)
endif
```

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Summary

3

Choice of time step

- In choosing the time step one could rule of thumb is that an atom should not move farther than about 1/20 of the nearestneighbour distance during one time step
- In practice for atoms with Z > 10 or so $\Delta t \sim 0.5 \sqrt{m(u)}$ fs has been found to work well for most materials in classical simulations with the Gear V algorithm at room temperature.
 - For very hard materials (Pt, W) slightly smaller time steps may be needed
- The choice of time step should still be checked by checking the conservation of energy (in NVE) for every new type of system or interaction model.
- If Δt is too large, energy is not conserved:



Construction of a neighbour list

- To save time in classical MD, and often CG and MC as well, it is worth constructing a neighbour list. If there are more than
 ~ 1000 atoms, it is worth constructing it with a linkcell method.
- · Verlet neighbour list
 - r_c is the potential cutoff radius
 - Construct a list which contains the atom indices for all neighbours within $r_{\rm m} > r_c$. The list should be updated as soon as two atoms may have moved further than $r_{\rm m} - r_c$
- · Linkcell method
 - Divide the MD simulation cell into $M \times M \times M$ subcells
 - Neighbours for an atom in cell 13 is looked for only in the darker subcells.
 - The size of the subcells *l* is chosen such that

$$l = \frac{L}{M} > r_{\rm m}$$

where L = the size of the whole MD cell.





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Solving the MD equations of motion

- The basic idea of MD is to solve the motion of N atoms by numerical integration over a short time step Δt
 - The basic idea is:

$$a(t) = \frac{-\nabla V(r(t))}{m}$$
$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^{2}$$
$$v(t + \Delta t) = a(t)\Delta t$$

- These equations are very inaccurate. A good general algorithm is velocity Verlet

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

Summary

• A highly accurate algorithm for small time steps is 5th order Gear: Denote $\mathbf{r}_i = \frac{\mathbf{r}^{(i)}(\delta t)^i}{i!}$

The the predictor is:
$$\begin{bmatrix} \mathbf{r}_{0}^{P}(t+\delta t) \\ \mathbf{r}_{1}^{P}(t+\delta t) \\ \mathbf{r}_{2}^{P}(t+\delta t) \\ \mathbf{r}_{3}^{P}(t+\delta t) \\ \mathbf{r}_{4}^{P}(t+\delta t) \\ \mathbf{r}_{5}^{P}(t+\delta t) \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & 1 & 2 & 3 & 4 & 5 \\ 0 & 0 & 1 & 3 & 6 & 10 \\ 0 & 0 & 0 & 1 & 4 & 10 \\ 0 & 0 & 0 & 0 & 1 & 5 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{r}_{0}(t) \\ \mathbf{r}_{1}(t) \\ \mathbf{r}_{2}(t) \\ \mathbf{r}_{3}(t) \\ \mathbf{r}_{4}(t) \\ \mathbf{r}_{5}(t) \end{bmatrix}$$

and the corrector:

error term $\delta \mathbf{R}_2 = \mathbf{a} - \mathbf{a}^p$

correction:
$$\mathbf{r}_{n} = \mathbf{r}_{n}^{P} + \alpha \delta \mathbf{R}_{2}$$
 where $\alpha = \begin{bmatrix} 3/16\\ 251/360\\ 1\\ 11/18\\ 1/6\\ 1/60 \end{bmatrix}$

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Force calculations

· In a classical model the potential between atoms can be written as:

$$V = \sum_{i} V_1(\boldsymbol{r}_i) + \sum_{i,j} V_2(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_{i,j,k} V_3(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k) + \dots$$

where V_2 is a pair potential which only depends on the distance between atoms r_{ij} and V_3 is a three-body potential which may have an angular dependence, $V_3 = V_3(r_{ij}, r_{ik}, \theta_{ijk})$

- Force calculation for a pair potential *V*(*r*):
 - The force acting from atom *i* on atom *j* is

$$\begin{aligned} \mathbf{f}_{ij} &= -\nabla_{\mathbf{r}_i} V(r_{ij}) = -\nabla_{\mathbf{r}_{ij}} V(r_{ij}) \quad , \quad \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \\ \mathbf{f}_{ij} &= -\left[\frac{\mathrm{d}V}{\mathrm{d}r}\right]_{r = r_{ij}} \times \frac{\mathbf{r}_{ij}}{r_{ij}} \end{aligned}$$

- The potentials usually have a cutoff radius $r_{\rm c}$: atoms separated by a distance >
 - $r_{\rm c}$ do not interact. Usually $r_{\rm c} \approx {\rm a~few~\AA}$.

- In a good potential both V and all its derivatives go continuously to zero when $r = r_c$ (dashed lines in figure).



r_{ij}

Summary

General form of the interaction

• At small separations there is a repulsive force due to the overlapping of electron shells (Pauli rule and electron-electron Coulomb repulsion) and at very small distances due to the Coulomb repulsion between the charges of the nuclei.



- At larger distances there may be an attractive interaction, which may have several different causes: van der Waals, Coulomb, metallic bonding, covalent bonding, hydrogen bonding
- Potential minimum is at a distance r_0 .

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Summary

9

Fitting of potential parameters.

· Important parameters to which a potential can be fit:

Physical property	Atom-level property	
Crystal structure	Balance of atomic forces.	
Cohesive energy	Potential energy at the equilibrium atom posi- tions	
Elastic constants $c_{\rho\sigma}$	Long-wavelength acoustic vibrations. Elastic distortions of unit cell.	
Equation of state $P(V)$	Compression or expansion of material	
Neutron scattering	Phonon $\omega(\mathbf{k})$ in the Brillouin zone.	
Dielectric constant ε_{∞}	Electronic polarizability.	
Dielectric constant [£] 0	Polarization of electrons and lattice; long- wavelength optical vibration modes.	
Infrared absorption	Long-wavelength vibrations with a dipole moment.	
Raman scattering	Long-wavelength vibrations which change the polarizability.	

- Out of these, the four first ones are usually the most important in solids.
- In addition, it is also possible to fit potentials to or even derive potentials from data obtained from (hopefully) realistic quantum mechanical calculations.

Pair potentials

• Taylor expansions

$$V(r) = K_2(r - r_0)^2 + K_3(r - r_0)^3 + K_4(r - r_0)^4$$

- No physical motivation whatsoever, but can work close to equilibrium separation r_0 since any smooth function can be approximated with a Taylor series.
- Lennard-Jones (LJ)

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

- The attractive $1/r^6$ term can be derived by considering the induced dipole-dipole interaction of two electrically neutral spheres, or for quantum mechanical oscillators. It is also known as a Van der Waals or London interaction.
- The LJ potential describes well at least interactions between noble gases or dipole-dipole interactions between molecules.
- Morse potential

$$V(r) = De^{-2\alpha(r-r_0)} - 2De^{-\alpha(r-r_0)}$$

- Can describe fairly realistically chemical bonds and the breaking of chemical bonds.
- Parameters available e.g. for most metals in the solid state.

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Potentials for ionic compounds

- The interactions between ions can of course be described with Coulomb interactions. To get a sensible short-range interaction one has to add a separate short-range potential.
- · This gives a potential of the form

$$V(r_{ij}) = V_{SR}(r_{ij}) + \frac{z_1 z_2 e^2}{4\pi \varepsilon_0 r_{ij}}$$
; z_i = ionic charges

The short.-range potential V_{SR} can be e.g.

$$V_{\rm SR}(r) = Ae^{-r/\rho} - \frac{C}{r^6}$$

• In modelling ionic compounds, the sum over neighbours does not converge automatically. Then it is best to use some special algorithms to form the sum efficiently. For small numbers of atoms the Ewald sum or Ewald mesh methods are probably fastest, for large number of atoms there are the truly O(N) scaling fast multipole algorithms (FMA's).

Summary

Metal interaction models

- Metals can be described well by considering the atoms as positively charges ions which are embedded into a surrounding free electron gas. The density of the electron gas depends on the local environment.
- These models can be derived from effective medium theory (EMT).
- · Most models used now are given in the Embedded Atom Method (EAM) functional form.
- · In EAM the total energy is given as

$$E_{\text{tot}} = \sum_{i} F_i(\rho_i) + \frac{1}{2} \sum_{ij} V_{ij}(r_{ij})$$

where

$$\rho_i = \sum_{j \neq i} \rho_j^{a}(r_{ij})$$
 is the electron density at atom i ,

 $\rho_i^{a}(r)$ is the electron density distribution of atom *j*,

 F_i is the embedding function and

V_{ii} is a repulsive potential

- In Finnis-Sinclair and Rosato models $F_i(x) \propto \sqrt{x}$
- In glue models the functional form is the same as in EAM, but V_{ii} is not purely repulsive.
- EAM-models can describe quite well the basic mechanical and thermodynamic properties of most pure FCC metals, fairly
 well most BCC metals and fairly well those HCP metals for which

$$c_{13} - c_{44} > 0$$
 and $\frac{1}{2}(3c_{12} - c_{11}) > c_{13} - c_{44}$

· Also many metal alloys can be described well with EAM models.

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Semiconductor and carbon potentials

- · For Si at least three good potentials exist:
- Stillinger-Weber (SW)
 - The potential has a pair term V_2 and a three-body term V_3 . The three-body term has an explicit minimum when the angles between the bonds correspond to ideal sp³ bond hydridization, i.e. for the diamond crystal structure.
 - Describes well melting, surfaces and surprisingly many other properties as well.
- EDIP

- An SW-like formulation which is also environment dependent. Probably the best potential for bulk Si now.

Tersoff

- The form of the potential is

$$V_{ij} = f_{\mathrm{C}}(r_{ij})[a_{ij}f_{\mathrm{R}}(r_{ij}) + b_{ij}f_{\mathrm{A}}(r_{ij})]$$

where $f_{\rm R}$ is the repulsive and $f_{\rm A}$ the attractive pair potential part. Bond order term b_{ij} modifies the strength of the pair interaction depending on the local environment and angles between bonds.

- The Tersoff potential can also describe reasonably non-tetrahedral bonding configurations.
- Two parametrizations, out of which Tersoff C or III best in non-equilibrium applications.

Summary

- · Ge:
 - Two SW parametrizations, but terrible description of melting.
 - Also a Tersoff-parametrization, but also with bad description of melting.
- For C in the bulk states (graphite and diamond) as well as fullerenes several parametrizations exist.
 - Tersoff works fairly well in all of these.
- The Brenner potential (based on the Tersoff formalism) also describes conjugated bonds and small hydrocarbon molecules well. But it is clearly slower than Tersoff.

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Summary

15

Molecular interaction models (classical force fields)

- · The total energy of a molecule can be written as
 - $E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{oop}} + E_{\text{cross}} + E_{\text{nonbond}}$

 $E_{\rm bond}$ describes the energy change related to a change of bond length, and thus is simply a pair potential V_2

 E_{angle} describes the energy change associated with a change in the bond angle, i.e. is a three-body potential V_3

- E_{torsion} describes the torsion, i.e. energy associated with the rotation between two parts of a molecule relative to each other.
- $E_{\rm oop}$ describes "out-of-plane" interactions, i.e. the energy change when one part of a molecule is out of the plane with another

 $E_{\rm cross}$ are cross terms between the other interaction terms.

 $E_{\rm nonbond}$ describes interaction energies which are not associated with covalent bonding. Can be ionic, hydrogen bonding or van der Waals terms.

• An example of a real molecular potential:

$$\begin{split} E_{bond} & E_{angle} & E_{torston} \\ V(R) &= \sum_{b} D_{b} \left[1 - \exp(-a(b - b_{0})) \right]^{2} + \sum_{\theta} H_{\theta} (\theta - \theta_{0})^{2} + \sum_{\phi} H_{\phi} \left[1 + s \cos(n\phi) \right] \\ E_{oop} &+ \sum_{\chi} H_{\chi} \chi^{2} + \sum_{b} \sum_{b'} F_{bb'} (b - b_{0}) (b' - b'_{0}) + \sum_{\theta} \sum_{\theta'} F_{\theta\theta'} (\theta - \theta_{0}) (\theta' - \theta'_{0}) \\ &+ \sum_{b} \sum_{\theta} F_{b\theta} (b - b_{0}) (\theta - \theta_{0}) + \sum_{\theta} \sum_{\theta'} F_{\theta\theta'\phi} (\theta - \theta_{0}) (\theta' - \theta'_{0}) \cos\phi \\ &+ \sum_{\chi} \sum_{\chi'} F_{\chi\chi'} \chi\chi' + \sum_{i} \sum_{j>i} \left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{q_{i}q_{j}}{r_{ij}} \right] \\ &= E_{vdW} \quad E_{Coulomb} \end{split}$$



MD Simulation of different ensembles

- Ensembles are denoted by the constant thermodynamical quantities. N=number of atoms, V=volume, E=energy, P=pressure, T=temperature
- microcanonical: NVE (isolated)
 - Algorithm: direct solution of equations of motion
- canonical: NVT (closed)
 - Algorithm: Berendsen "quick and dirty",
 - not true NVT ensemble.
 - True NVT: Nosé-Hoover, or Nosé-Hoover chain.

· isothermal-isobaric: NPT

- Heat control as above, pressure control:
 - Berendsen "quick and dirty", not true NPT
 - Andersén pressure control if pressure is hydrostatic (e.g. in liquid)
 - Parrinello-Rahman pressure control for non-hydrostatic stress (e.g. in crystals)
- Berendsen temperature scaling: scale velocities every time step with

 $\lambda = \sqrt{1 + \frac{\Delta t}{\tau_T} (\frac{T_0}{T} - 1)}$, where T_0 is the desired T.

- Berendsen pressure scaling: scale atom positions and the box size every time step with a factor

$$\mu = \sqrt[3]{1 - \frac{\beta \Delta t}{\tau_P}} (P_0 - P), \text{ where } P_0 \text{ is the desired pressure and } \beta = 1/B$$

Introduction to atomistic simulations 200	8
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Energy minimization techniques.

There are at least 4 ways to approach minimizing the energy of an atom system:

1. Monte Carlo-simulation:

- May be good in looking for a global minimum, if only one very strong minimum exists
- Not very efficient in looking for a local minimum

2. MD-simulation: Do an MD simulation letting $T \rightarrow 0$ K.

- Sometimes quite efficient in finding a local minimum, especially by using the trick of setting $\mathbf{v}_i = 0$ if $\mathbf{v}_i \cdot \mathbf{F}_i < 0$.
- May sometimes be good for looking for a global minimum, but tends to get stuck if a high barrier exists.

3. Conjugate gradients (CG)

- Very efficient way to reach the closest local minimum
- Works by movement down a potential well, but so that the new direction is *conjugated* with respect to the previous to prevent zig-zag motion.
- The new direction \mathbf{x}_{i+1} into which one moves is evaluated as

$$\mathbf{x}_i = -\nabla V(\mathbf{r}_{i+1}) ;$$

$$\mathbf{g}_{i+1} = \mathbf{x}_i; \quad \mathbf{h}_{i+1} = \mathbf{g}_{i+1} + \gamma \mathbf{h}_i \text{ and } \mathbf{x}_{i+1} = \mathbf{h}_{i+1}$$

where $\gamma = [(\mathbf{x}_i + \mathbf{g}_i) \cdot \mathbf{x}_i]/(\mathbf{g}_i \cdot \mathbf{g}_i)$

- In the CG method for atoms it is often even more efficient to use an adaptive step length instead of line minimization.



heat bath

Summary

4. Genetic algorithms

- An efficient way to look for a global minimum in dilute systems
- Not much tested in atom systems yet. Used e.g. in optimizing cluster geometry.
- The basic idea comes from evolution theory; a population is formed, this is allowed to breed, and the best-adjusted individuals are allowed to stay alive.
- Deaven and Ho genetic algorithm for atoms, slightly simplified.
 - **0. Start.** Create random initial positions for *p* structures, each with exactly *N* atoms.
 - **1. Mating and breeding.** Select two well-adjusted parents for breeding. This is done by selecting a given parent *i* with state **G**_{*i*} with the probability

 $P(\mathbf{G}_i) \propto e^{-E(\mathbf{G}_i)/T_{\mathrm{m}}}$

where the mating 'temperature' T_m is selected as the range of energies among the whole population $\{G_i\}$. Split the two parent structures along the same line. Take one half of one parent, and another half of another parent, and join them together. Make sure the child has as many atoms as the parents.

- **2.** Mutation. With a probability $\mu \ge 0$ perform a mutation on the child.
- 3. Minimize the energy of the child to the closest local minimum. This is done by CG or MD.
- **4. Natural selection.** If the child has lower energy than any of the parents, allow it to stay alive. Then check that its energy does not match the energy of any parent within an energy range δE . If this is true, include it in the population, and kill the least-well adapted parent.
- 5. If convergence has not been reached, return to stage 1.

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Minimum energy path determination

- · Thermally activated atomistic processes
 - If not too small probability direct MD simulation possible to determine the rate.
 - If really a rare event then the transition state theory (TST) used:
 - Rate $B_1 \rightarrow B_2$ (events/unit time) $v = v_0 e^{-E_A/k_BT}$.
 - Prefactor can be obtained from vibrational properties of the system.
 - Need to know the activation energy $E_A = E_S E_1$ because being in the exponent it has a large effect on the rate.
 - Must determine the minimum energy path (**MEP**) going from B_1 to B_2 .
- Nudged Elastic Band method or NEB:
 - Images of the system are created by interpolating the atomic coordinates between the initial and final configurations.
 - End configurations fixed.
 - Every image is connected by a spring force to its neighboring images.
 - Spring forces are applied in the direction of the tangent of the path: prevent images from all falling to local minima.
 - Potential forces $(-\nabla V)$ are applied only in the direction perpendicular to the path: find the minimum route of the path.
 - NEB run: using the abovementioned forces cool down the system (e.g. by MDcooling).



Exam

- Thursday 18.12.2006 at 12-16, room D116
- Consists of 4-6 question that can be
 - Simple calculations
 - Explanation of concepts
 - Broader essay questions: e.g. a research problem, what tools to use to solve it.
- · Main source: lecture notes
 - However, you can skip the effective medium theory (EMT), in chapter 8 and chapter on ionic interaction models (chapter 11).
 - You need not remember the exact mathematical forms of different potentials. However, the basic forms and the theoretical basis of different models should be known.
 - The same applies to integration algorithms.

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Summary