# *Repetitia mater studiorum*

## 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

## The basic MD algorithm

**0.** Set initial conditions $\boldsymbol{r}_i(t_0)$ and $\boldsymbol{v}_i(t_0)$

**1.** If necessary, calculate new neighbour list

**2.** Solve equations of motion over a short time step Δt (predictor phase)

$$\boldsymbol{r}_i(t_n) \to \boldsymbol{r}_i^{pred}(t_{n+1})$$
$$\boldsymbol{v}_i(t_n) \to \boldsymbol{v}_i^{pred}(t_{n+1})$$

**3.** Calculate new forces $\boldsymbol{F}_i(\boldsymbol{r}_i^{pred})$

**4.** Solve equations of motion over a short time step Δt (corrector phase)

$$\boldsymbol{r}_i^{pred}(t_{n+1}) \to \boldsymbol{r}_i(t_{n+1})$$
$$\boldsymbol{v}_i^{pred}(t_{n+1}) \to \boldsymbol{v}_i(t_{n+1})$$

**5.** Do temperature or pressure scaling, if appropriate

**6.** Calculate desired physical quantities

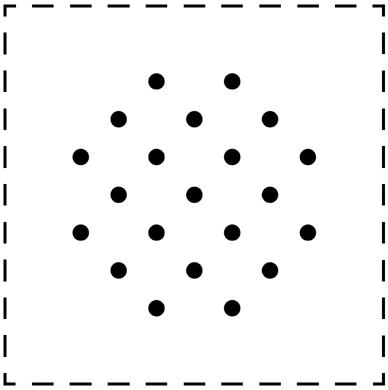
**7.** Set $t = t + \Delta t,\ n=n+1$

**8.** If $t < t_{\max}$, return to phase **1.**

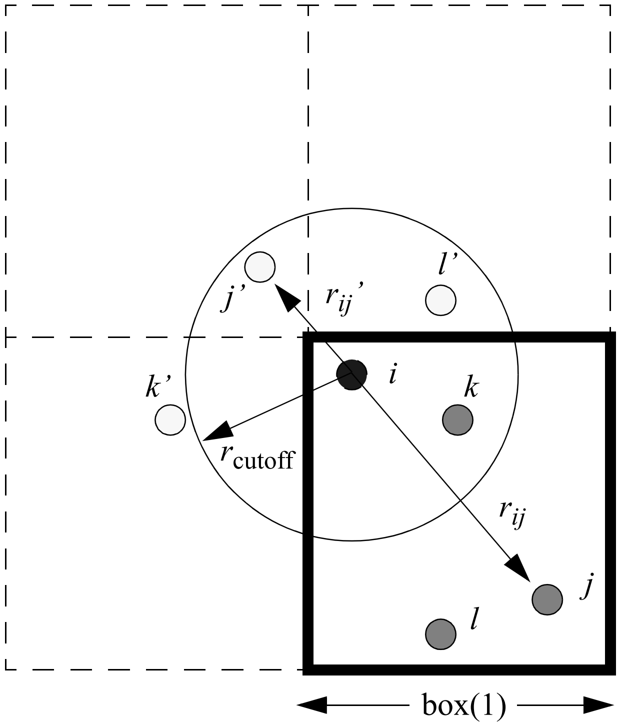
**9.** Calculate final results and end simulation

## 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
```

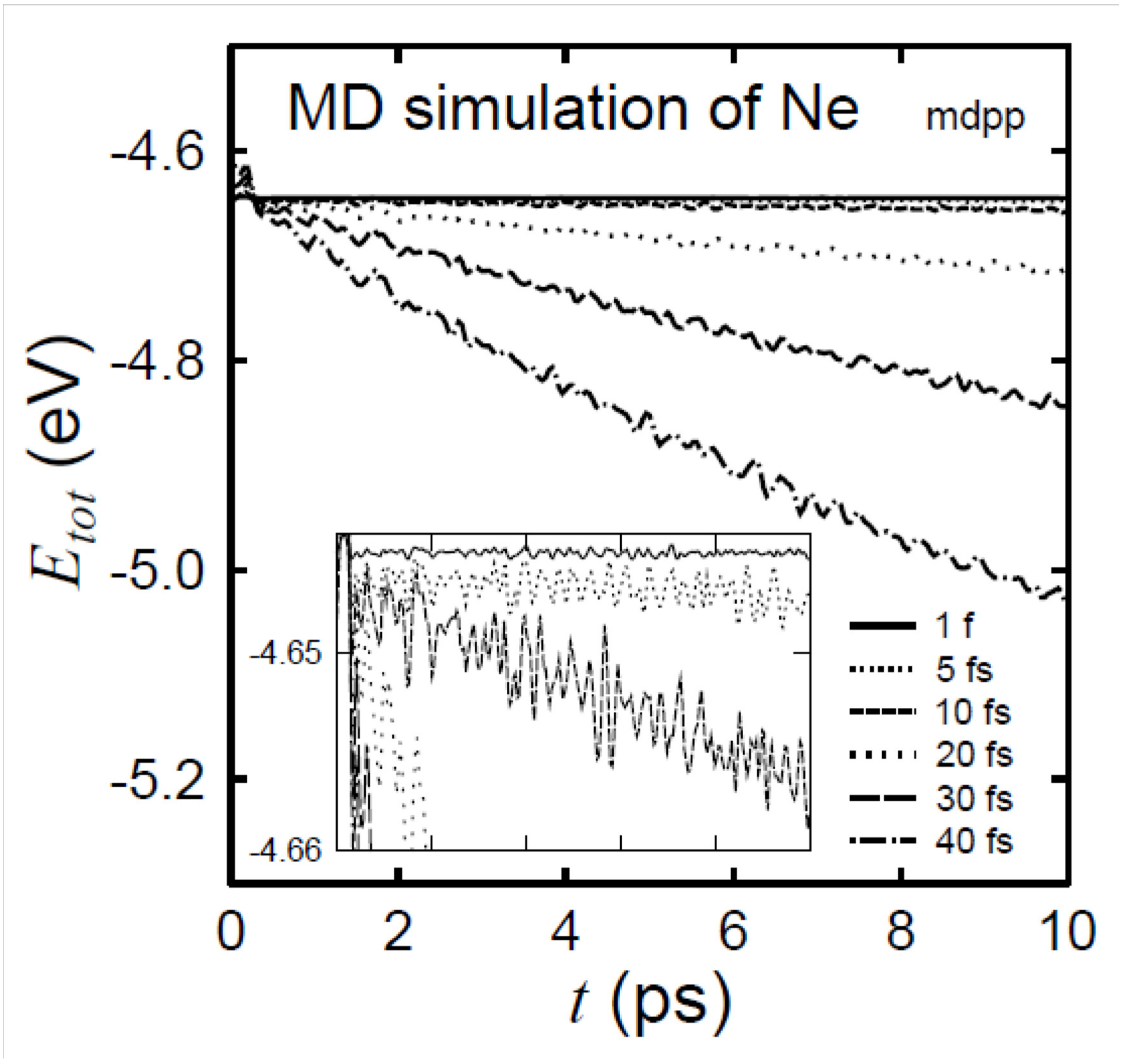
## Choice of time step

- In choosing the time step one could rule of thumb is that an atom should not move farther than ~ 1/20 of the nearest-neighbour distance during one time step

- In practice for atoms with Z > 10 or so Δt ~ $0.05 \times 10.18\sqrt{m\ (\mathrm{u})}\ \mathrm{fs}$ has been found to work well for most materials in classical simulations with the Gear V - algorithm.
    - 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

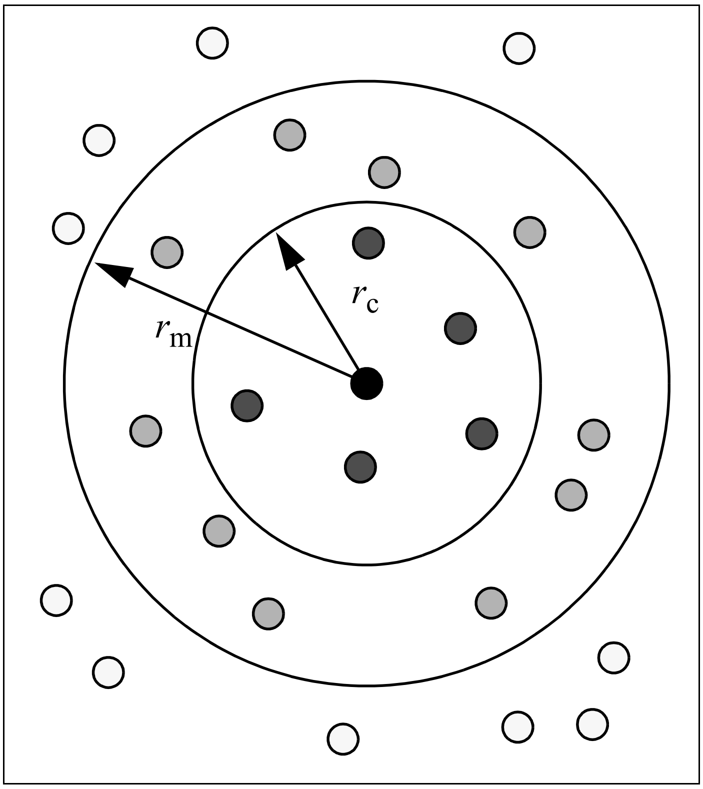
- To save time in classical MD, and often CG and MC as well, it is worth constructing a neighbour list. If there are more than ~ 1000 atoms, it is worth constructing it with a linkcell method.

- **Verlet neighbour list**

  - $r_\mathrm{c}$ is the potential cutoff radius

  - Construct a list which contains the atom indices for all neighbours within $r_\mathrm{m} > r_c$.

  - The list should be updated as soon as two atoms may have moved further than $r_\mathrm{m} - r_c$



- **Cellular method**

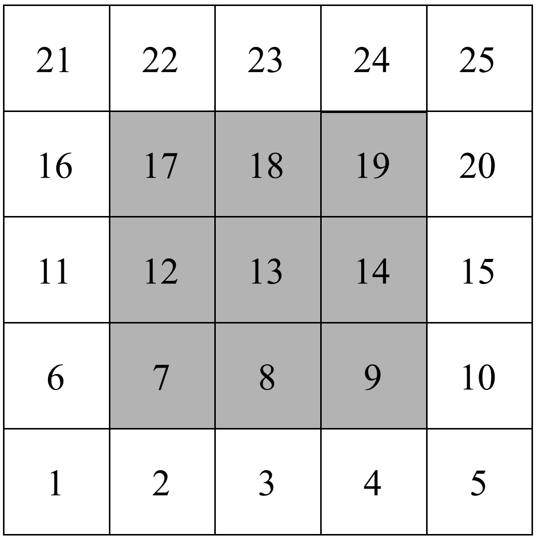
  - Divide the MD simulation cell into $M \times M \times M$ subcells

  - 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

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

  where $L$ = the size of the whole MD cell.



| | | | | |
|---|---|---|---|---|
| 21 | 22 | 23 | 24 | 25 |
| 16 | 17 | 18 | 19 | 20 |
| 11 | 12 | 13 | 14 | 15 |
| 6 | 7 | 8 | 9 | 10 |
| 1 | 2 | 3 | 4 | 5 |

## 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:

$$
\begin{aligned}
a(t) &= \nabla V(r(t)) \\
r(t+\Delta t) &= r(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2 \\
v(t+\Delta t) &= a(t)\Delta t
\end{aligned}
$$

  but these equations are very inaccurate. A good general algorithm is velocity Verlet

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

- A highly accurate algorithm for small time steps is 5th order Gear:

Denote $\mathbf{r}_i = \dfrac{\mathbf{r}^{(i)}(\delta t)^i}{i!}$

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

correction: $\mathbf{r}_n = \mathbf{r}_n^{\mathrm{P}} + \alpha\delta\mathbf{R}_2$ where $\alpha = \begin{bmatrix} 3/16 \\ 251/360 \\ 1 \\ 11/18 \\ 1/6 \\ 1/60 \end{bmatrix}$

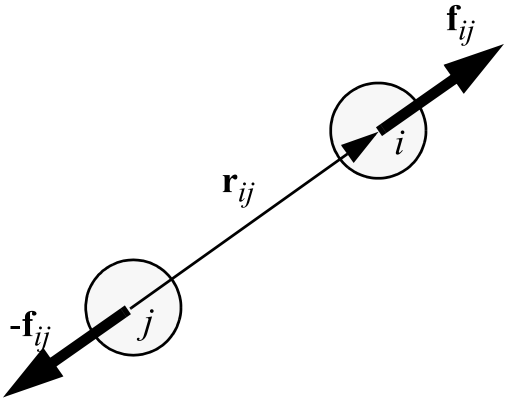
## Force calculations

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

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

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, $V_3 = V_3\,(r_{ij}\,,\,r_{ik}\,,\,\theta_{\mathrm{ijk}})$

- **Force calculation for a pair potential:**



Say we have a pair potential $V(r_{ij})$. The force acting from atom $i$ on atom $j$ is

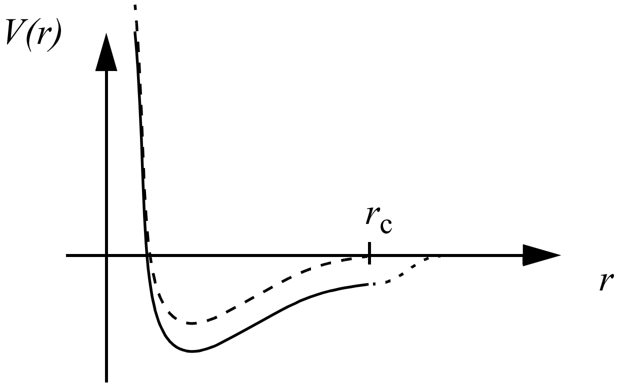
$$\mathbf{f}_{ij} = -\nabla_{\mathbf{r}_i} V(r_{ij}) = -\nabla_{\mathbf{r}_{ij}} V(r_{ij})$$

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$$

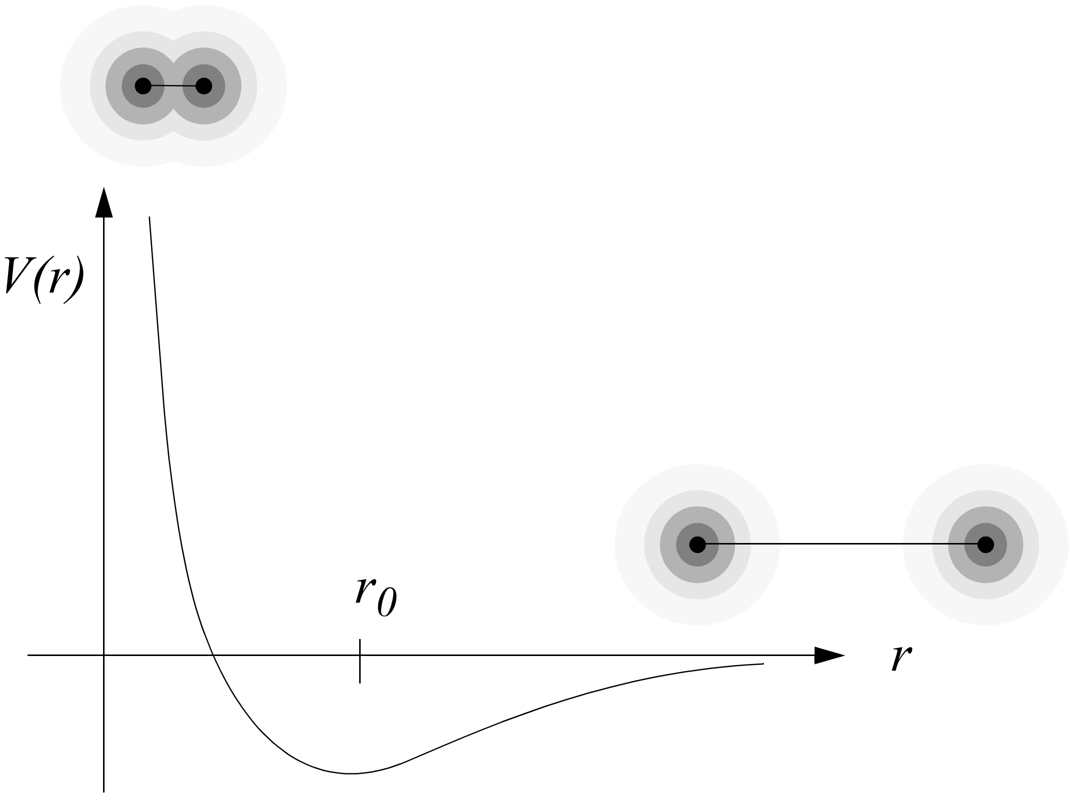
$$\mathbf{f}_{ij} = -\left[\frac{dV}{dr}\right]_{r = r_{ij}} \times \frac{\mathbf{r}_{ij}}{r_{ij}}$$

- The potentials usually have a cut-off radius $r_\mathrm{c}$. Atoms separated by a distance $> r_\mathrm{c}$ do not interact. Usually $r_\mathrm{c} \approx$ a few Å .

  In a good potential both $V$ and all its derivatives go continuously to zero when $r = r_\mathrm{c}$(dashed lines in figure).



## 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 $r_0$.

## 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 positions |
| Elastic constants $c_{\rho\sigma}$ | Long-wavelength acoustic vibrations<br>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 $\varepsilon_\infty$ | Electronic polarizability |
| Dielectric constant $\varepsilon_0$ | 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.

## 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

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

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

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

- 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).

## 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

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

where

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

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

$F_i$ is the embedding function and

$V_{ij}$ is a repulsive potential

- In Finnis-Sinclair and Rosato models $F_i(x) = \sqrt{x}$

- In glue models the functional form is the same as in EAM, but $V_{ij}$ 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

$$C_{13} - C_{44} > 0 \text{ and } 1/2\ (3\ C_{12} - C_{11}) > C_{13} - C_{44}$$

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

## 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 sp$^3$ bond hydridization, i.e. for the diamond crystal structure.

  - Describes well melting 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 $f_\mathrm{R}$ is the repulsive and $f_\mathrm{A}$ the attractive pair potential part. $b_{ij}$ 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.

- **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.

## Molecular interaction models (classical force fields)

- The total energy of a molecule can be written as

$$E = E_{bond} + E_{angle} + E_{torsion} + E_{oop} + E_{cross} + E_{nonbond}$$

$E_{bond}$ 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.

$E_{oop}$ describes “out-of-plane” interactions, i.e. the energy change when one part of a molecule is out of the plane with another

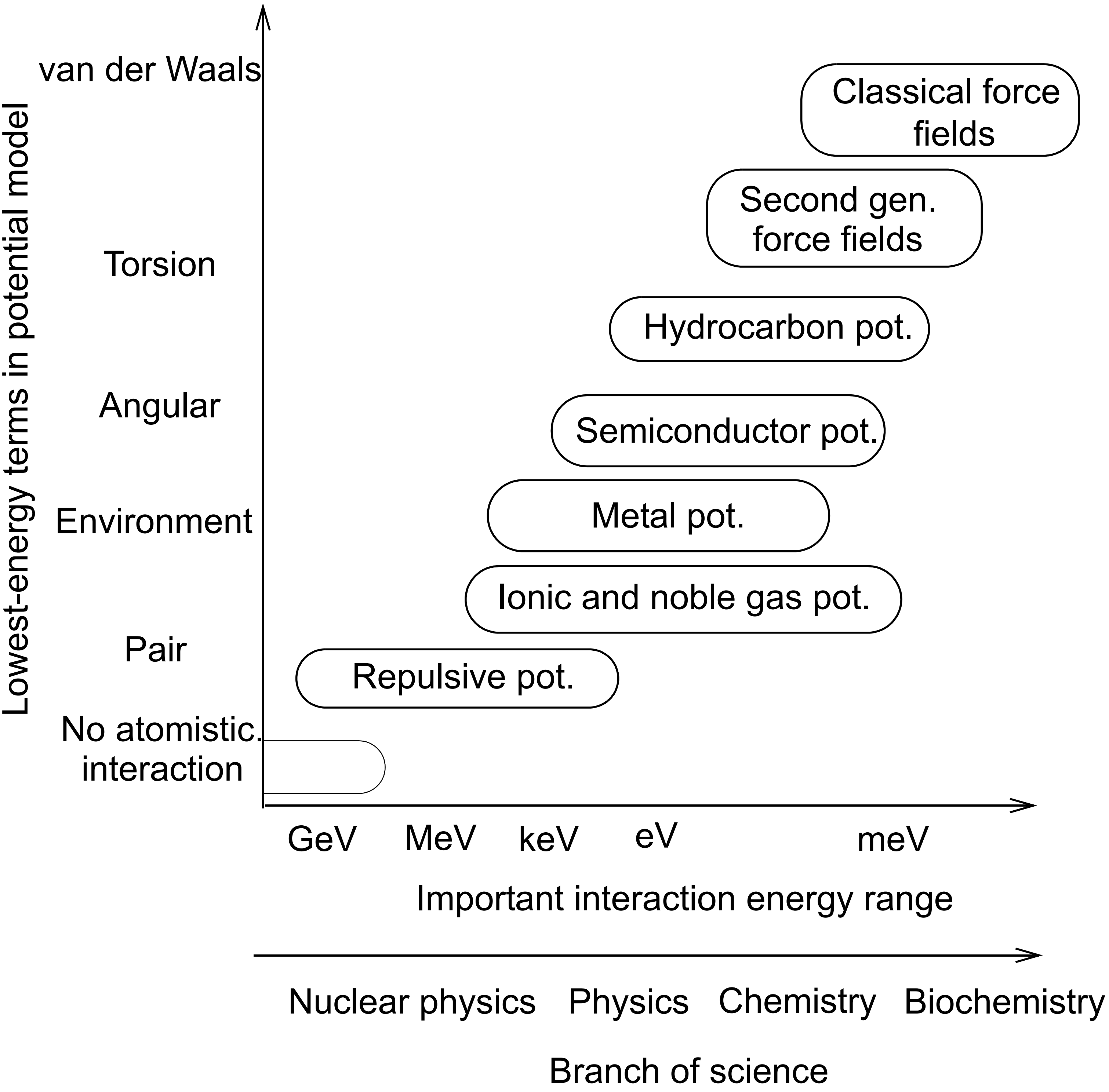
$E_{cross}$ - are cross terms between the other interaction terms.

$E_{nonbond}$ 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:

$$\begin{aligned}
V(R) = {} & \overbrace{\sum_b D_b[1-\exp(-a(b-b_0))]^2}^{E_{bond}} + \overbrace{\sum_\theta H_\theta(\theta-\theta_0)^2}^{E_{angle}} + \overbrace{\sum_\phi H_\phi[1+s\cos(n\phi)]}^{E_{torsion}} \\
E_{oop} \quad & \boxed{+\sum_\chi H_\chi \chi^2} + \sum_b\sum_{b'} F_{bb'}(b-b_0)(b'-b'_0) + \sum_\theta\sum_{\theta'} F_{\theta\theta'}(\theta-\theta_0)(\theta'-\theta'_0) \\
& + \sum_b\sum_\theta F_{b\theta}(b-b_0)(\theta-\theta_0) + \sum_\theta\sum_{\theta'} F_{\theta\theta'\phi}(\theta-\theta_0)(\theta'-\theta'_0)\cos\phi \quad E_{cross} \\
& + \sum_\chi\sum_{\chi'} F_{\chi\chi'}\chi\chi' + \sum_i\sum_{j>i}\left[\underbrace{\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}}}_{E_{vdW}} + \underbrace{\frac{q_iq_j}{r_{ij}}}_{E_{Coulomb}}\right]
\end{aligned}$$

## Overview of classical interatomic force models as a function of the branch of science



## Quantum mechanical models

- In the Schrödinger equation (7.1) the computationally most complicated part is the electron-electron interaction

  $$V_{ee} = \sum_i \sum_j \frac{e^2}{|\mathbf{r}_{ij}|^2}$$

  which is a sum from all electrons to all electrons. This can not be directly evaluated except for the very smallest system.

- The basic solution in both Hartree-Fock (HF) and density functional theory (DFT) is to create some sort of an “average” electron density, with which every electron interacts separately.
-
- HF- and DFT methods are much better motivated than classical models. Unfortunately they are also very much slower. The limit for common HF methods is maybe 50 atoms, and for DFT calculations maybe 200 atoms on ordinary computers.

- In the DFT method the so called **LDA-approximation** is often applied. In this approximation the electron exchange and correlation energy is calculated for small density elements as if the density were constant in this element.

- In the so called **Plane wave** methods the outermost electron wave function are written as the sum of periodic plane waves.

  $$\psi = \sum_l f_l(\boldsymbol{K}) e^{-i\boldsymbol{K} \cdot \boldsymbol{r}}$$

  These methods are well suited for describing periodic systems, i.e. bulk matter.

## Tight binding-methods

- Tight-binding (TB) models are so called minimal quantum mechanical models. They are usually semi-empirical, and the quality of the results varies a lot. In the TB method the total electron energy *E* is

$$E = \sum_{i=1}^{N} \varepsilon_i + \frac{1}{2}\sum_i \sum_j U(r_{ij})$$

where U is a repulsive pair potential acting between atoms, and the $\varepsilon_i$ are the eigenvalues of some Schrödinger-like equation

$$\hat{H}\psi_i(r) = \left[-\frac{1}{2}\nabla^2 + V(r)\right]\psi_i(r) = \varepsilon_i(r)$$

The TB-Schrödinger is solved in some set of basis functions $\{\phi_\alpha\}$ which only includes the outermost valence electrons.

## Efficiency of different force models.

- Crucial in selecting a model is to find one which is efficient enough to do what you want, yet realistic enough to describe the essential physics in your problem correctly. Below is a summary of the situation today:

| Model | Type | Scaling | $N_{\max}$[1] |
|---|---|---|---|
| HF (Hartee-Fock) | quantum mechanical,<br>ab initio | $O(N^{4\text{-}8})$ | 50 |
| DFT (density functional theory | quantum mechanical | $O(N^3)$ | 200 |
| TB (Tight-binding) | quantum mechanical<br>(often semiempirical) | $O(N^3)$/<br>$O(N)$ | 1000<br>10000 |
| Many-body potential | classical, semiempirical | $O(N)$ | $10^7$ |
| Pair potential | classical, semiempirical | $O(N)$ | $10^7$ |

[1] This is a rough estimate of how many atoms can be simulated in a reasonable time, i.e. a week or so, on a single-processor machine.

- Hence, typical application areas:

  - The number of atoms of quantum mechanical models (HF and DFT) ~ 100 is enough to simulate e.g. small molecules, bulk properties of common phases, and point defect properties. HF and DFT can give information on the electronic structure of the material.

  - Tight-binding is a “minimal quantum mechanical” model which works well in a few materials (e.g. C, Si, Ge) but is problematic in many others. The O(N) tight-bonding works only in a very limited set of applications, such as a-Si.

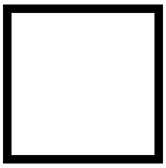
  - With classical models it is nowadays possible to simulate even very large systems, such as large protein molecules, 2- and 3-dimensional defects, whole nanoclusters, surface growth, grain boundaries etc. etc. The main limitation is that they do not usually directly give information on the electronic properties of the material.

## MD Simulation of different ensembles

- Ensembles are denoted by the thermodynamical quantities which are conserved in them. N=number of atoms, V=volume, E=energy, P=pressure, T=temperature

- **microcanonical: NVE** (isolated)

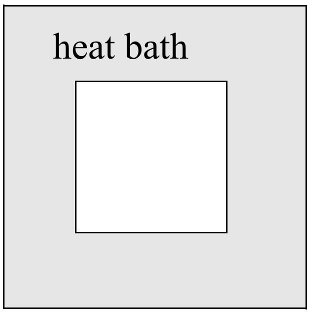
  - Algorithm: direct solution of equations of motion



- **canonical: NVT** (closed)

  - Algorithm: Berendsen “quick and dirty”, not true NVT ensemble.

    True NVT: Nosé-Hoover, or N-H chain or massive N-H chain.



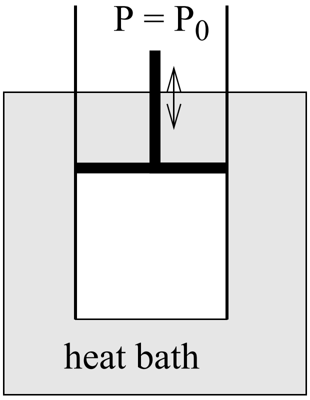
- **isothermal-isobaric: NPT**

  - 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

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

- Berendsen pressure scaling: scale atom position and the box size every time step with a factor $\mu = \sqrt[3]{1 - \frac{\beta \Delta t}{\tau_P}(P_0 - P)}$ , where $P_0$ is the desired pressure and $\beta = 1/B$

**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 $\boldsymbol{v}_i = 0$ if $\boldsymbol{v}_i \bullet \boldsymbol{F}_i = 0$.
  - 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 $\boldsymbol{x}_{i+1}$ into which one moves is evaluated as

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

    $\boldsymbol{g}_{i+1} = -\boldsymbol{x}_i$ ; $\boldsymbol{h}_{i+1} = \boldsymbol{g}_{i+1} + \gamma \boldsymbol{h}_i$ and $\boldsymbol{x}_{i+1} = \boldsymbol{h}_{i+1}$

    where $\gamma = ((\boldsymbol{x}_i + \boldsymbol{g}_i) \cdot \boldsymbol{x}_i)/(\boldsymbol{g}_i \cdot \boldsymbol{g}_i)$

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

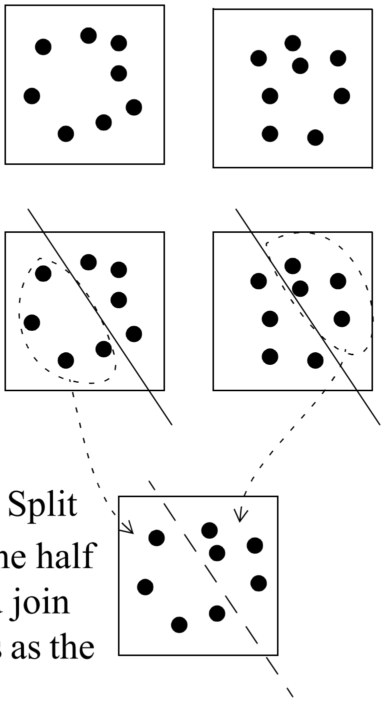
## 4. Genetic algorithms

- An efficient way to look for a global minimum in dilute systems
- Not much tested in atom systems yet.

- The basic idea comes from evolution theory; a population is formed, this is allowed to breed, and the best-adjusted species 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 $\boldsymbol{G}_i$ with the probability

$$P(\boldsymbol{G}) \propto e^{-E(\boldsymbol{G})/T_m}$$

where the mating 'temperature' $T_m$ is selected as the range of energies among the whole population $\{\boldsymbol{G}_i\}$. 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 $\mu \geq 0$ 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 $\delta E$. If this is true, include it in the population, and kill the least-well adapted parent.

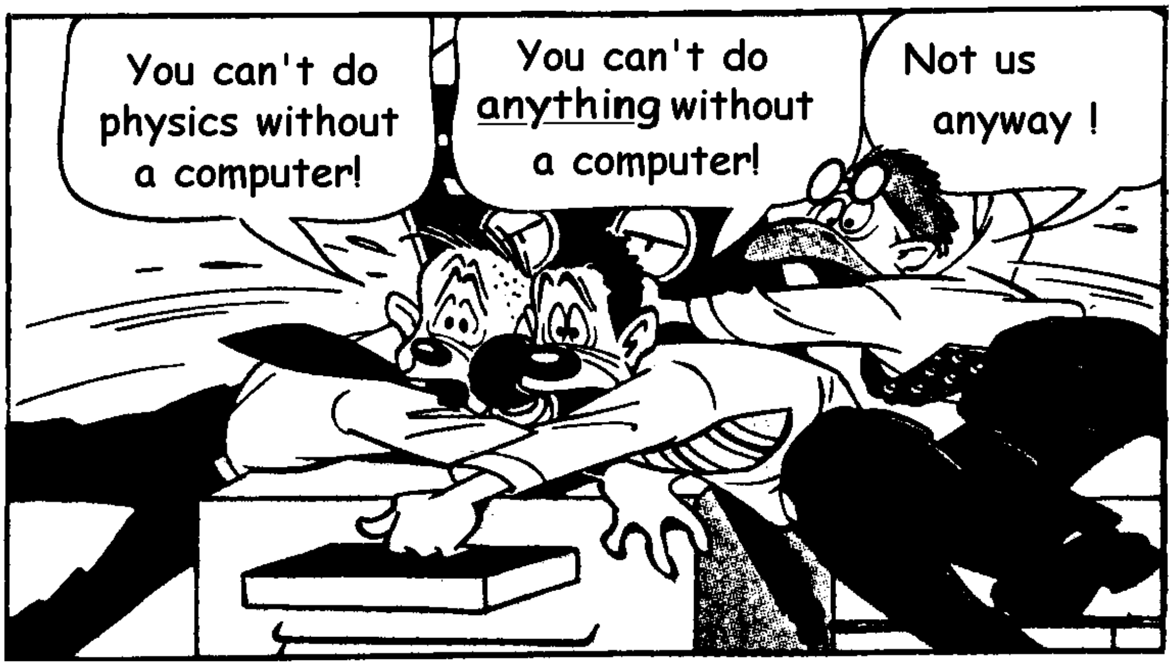
**5.** If convergence has not been reached, return to stage **1.**

## Comparison to experiments

- Atomistic data can be seldom compared directly to experiments. Most often some intermediate analysis code is needed to enable a sensible comparison.

- A special caveat should be taken with STM and TEM: in both methods, what may look like an atom may in fact be something entirely different.

# Final comment of the course



*Hope you have enjoyed the materials and have happy simulation-times !*