Challenges and Results from Simulations

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Disordered Materials in Synchrotron and XFEL X-ray light

Hamburg 18 Feb 2010

Outline

1. Numerical simulations of matter
2. Classical molecular dynamics simulations and *IMD*
3. Model potentials
4. Realistic potentials
5. Simulations of physical properties
6. Simulations of amorphous materials

1. Numerical simulations of matter

Basic equation for a solid

Many-body Schrödinger equation:

$$\left\{T_N + T_e + V_{ee}\left(\vec{r}_i\right) + V_{NN}\left(\vec{R}_l\right) + V_{eN}\left(\vec{r}_i,\vec{R}_l\right)\right\}\Psi\left(\vec{r}_i,\vec{R}_l\right) = E\Psi\left(\vec{r}_i,\vec{R}_l\right)$$

Born – Oppenheimer approximation:

$$\Psi\left(\vec{r}_i,\vec{R}_l\right) = \psi_e\left(\vec{r}_i,\vec{R}_l\right)\Psi_N\left(\vec{R}_l\right)$$

Insertion :

$$\Psi_N\left(\vec{R}_l\right)\underbrace{\left\{T_e + V_{ee}\left(\vec{r}_i\right) + V_{eN}\left(\vec{r}_i,\vec{R}_l\right)\right\}\psi_e\left(\vec{r}_i,\vec{R}_l\right)}_{\varepsilon_e\left(\vec{R}_l\right)\psi_e\left(\vec{r}_i,\vec{R}_l\right)} +$$

$$\psi_e\left(\vec{r}_i,\vec{R}_l\right)\left\{T_N + V_{NN}\left(\vec{R}_l\right)\right\}\Psi_N\left(\vec{R}_l\right) = E\psi_e\left(\vec{r}_i,\vec{R}_l\right)\Psi_N\left(\vec{R}_l\right)$$

Basic equations continued

Separation of equations:

$$\left\{T_e + V_{ee}\left(\vec{r}_i\right) + V_{eN}\left(\vec{r}_i, \vec{R}_I\right)\right\}\psi_e\left(\vec{r}_i, \vec{R}_I\right) = \varepsilon_e\left(\vec{R}_I\right)\psi_e\left(\vec{r}_i, \vec{R}_I\right)$$

$$\left\{T_N + V_{NN}\left(\vec{R}_I\right) + \varepsilon_e\left(\vec{R}_I\right)\right\}\Psi_N\left(\vec{R}_I\right) = E\Psi_N\left(\vec{R}_I\right)$$

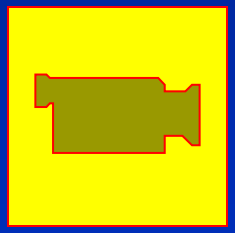
Classical approximation - Ab-initio Molecular Dynamics:

$$\frac{d\vec{P}_I}{dt} = -\nabla_I\left\{V_{NN}\left(\vec{R}_I\right) + \varepsilon_e\left(\vec{R}_I\right)\right\} = -\nabla_I V_{eff}\left(\vec{R}_I\right)$$

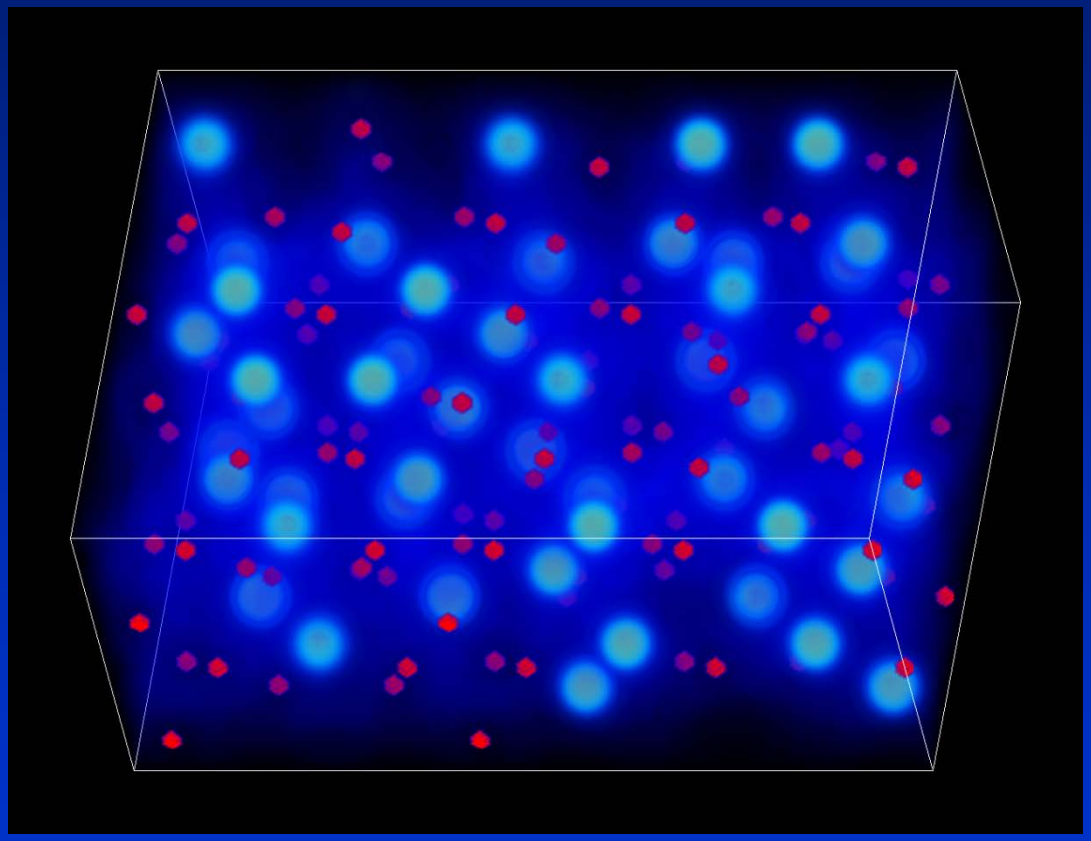
Solution of Schrödinger equation for electrons:

Local Density Approximation etc.

Ab-initio molecular dynamics



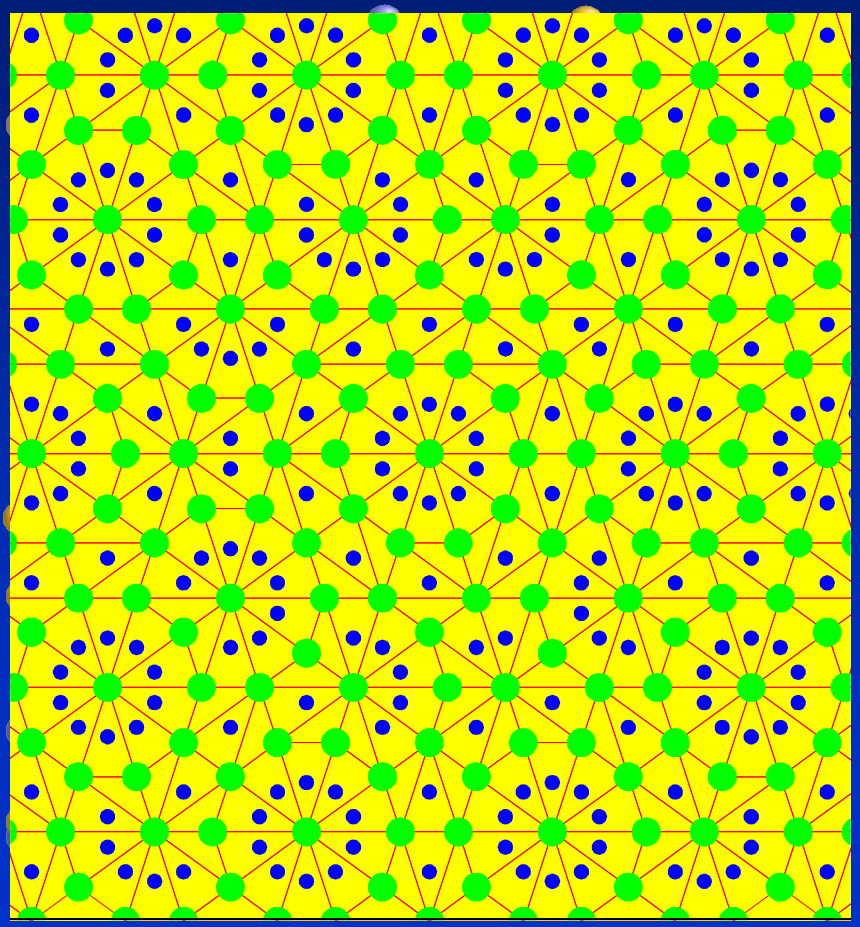
d-Al-Cu-Co



2. Classical molecular dynamics simulations and *IMD*

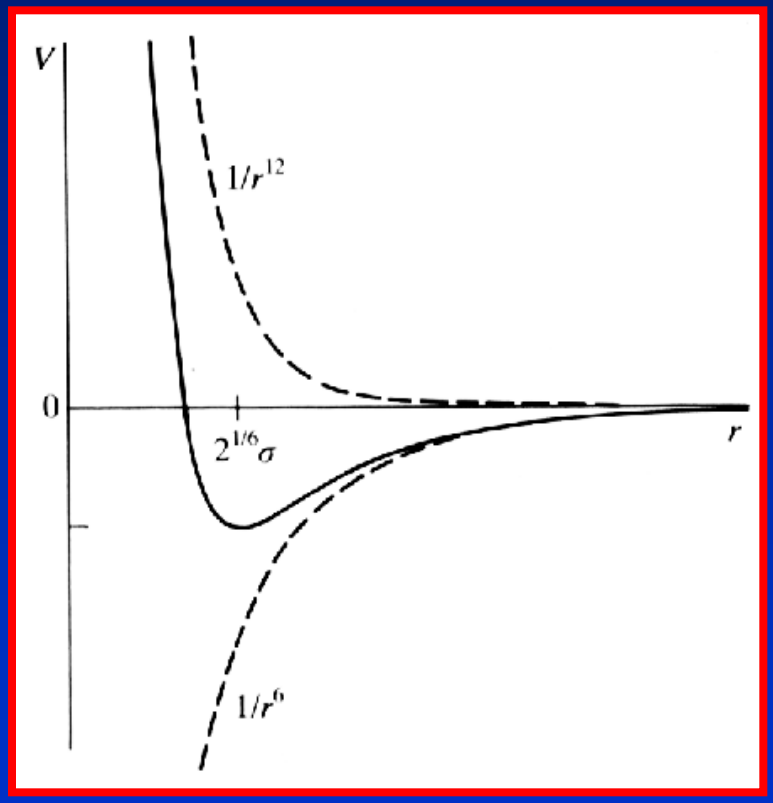
Step 1

- Fix structure in the form of particle coordinates
  - Random
  - Model structure
  - From real experiment



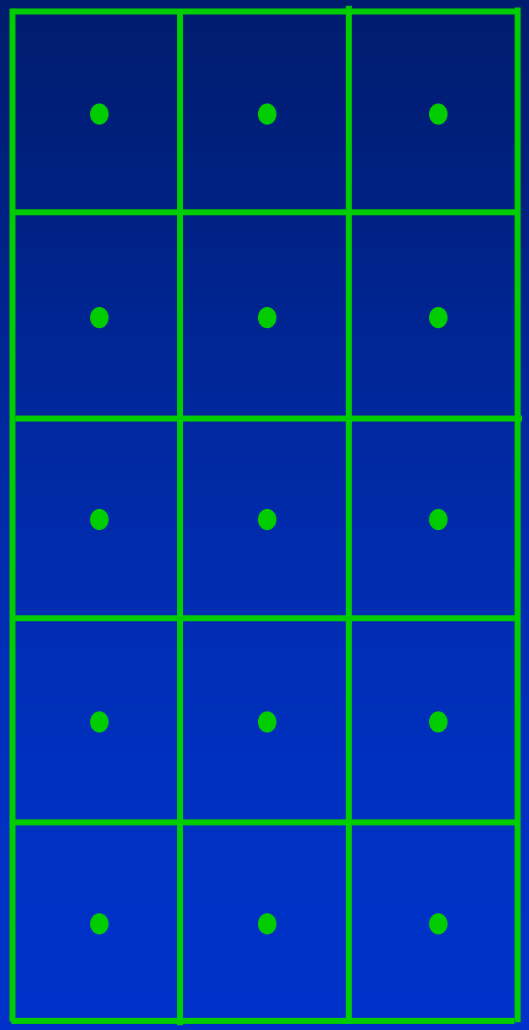
Step 2

- Determine interactions
  - From electronic structure calculations (ab-initio, force matching)
  - Model potentials
  - Potentials: two-, three-, many-body



Step 3

- Fix boundary conditions
  - Open boundaries
  - Periodic boundaries
  - Fixed boundaries
  - Other (spherical, twisted, Lees-Edwards)



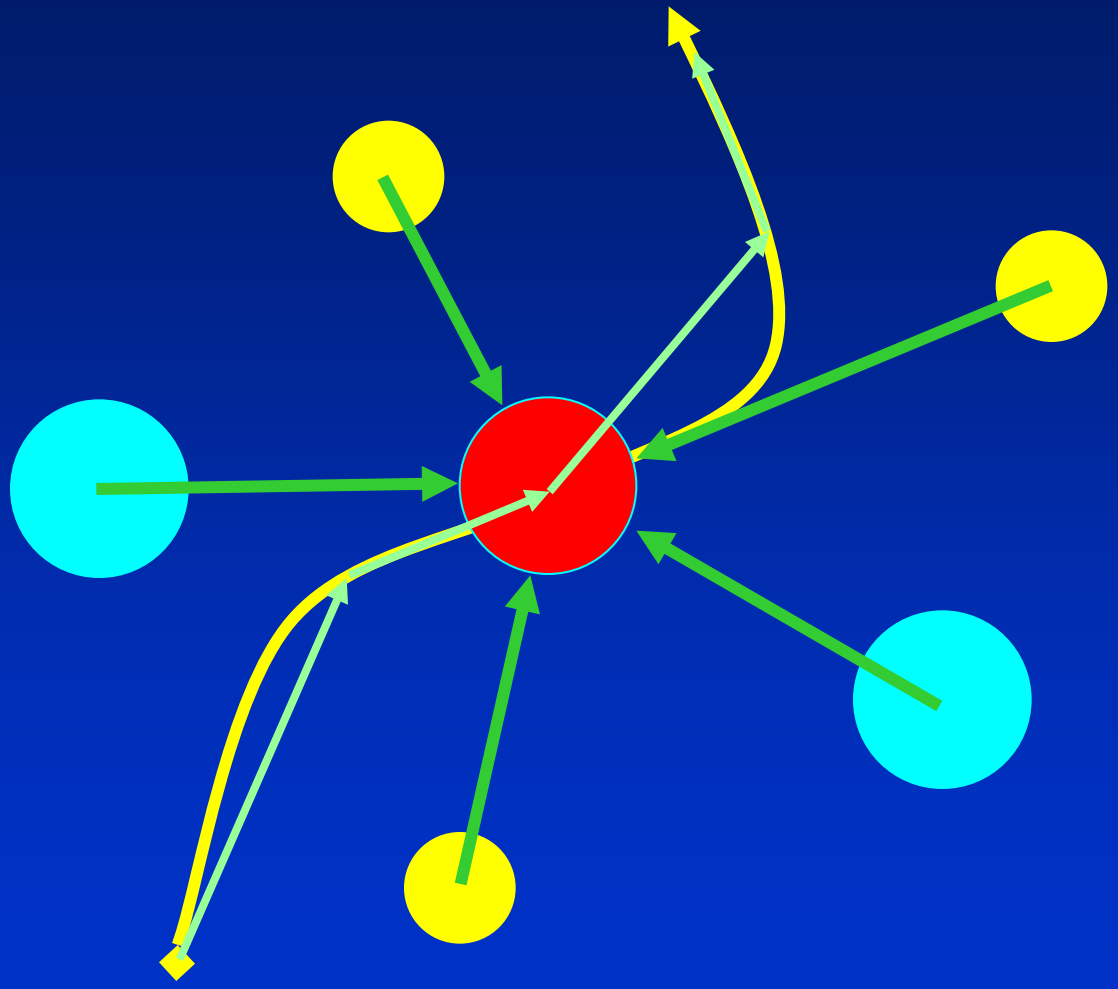
Step 4

- Solve Newton's equations
  - Discretize in time
  - Choose integrator

$$\frac{d\vec{p}_i}{dt} = -\nabla_i V\left(\vec{r}_1, \ldots, \vec{r}_N\right)$$

$$\frac{d\vec{r}_i}{dt} = \frac{\vec{p}_i(t)}{m_i}$$

Atomistic simulations



Verlet and Leap-frog algorithm

Instead of differential equations: Difference equations.

Integration e.g. by time centered "Leap-frog"-algorithm:

$$\vec{p}_i\left(t+\Delta t/2\right)=\vec{p}_i\left(t-\Delta t/2\right)+\vec{f}_i(t)\cdot\Delta t,\quad \vec{f}_i=-\nabla_i V\left(\vec{r}_1,\ldots,\vec{r}_N\right)$$

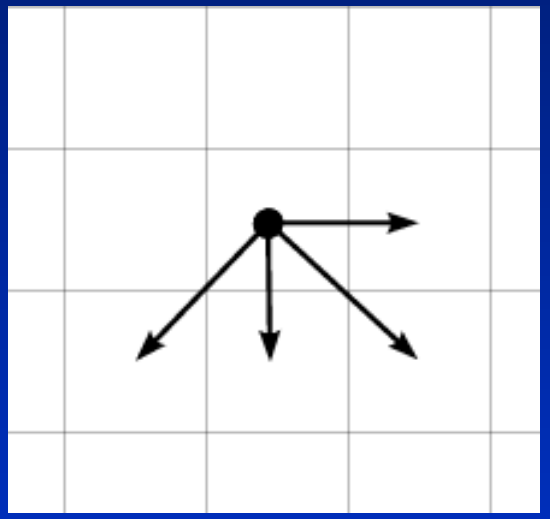
$$\vec{r}_i(t+\Delta t)=\vec{r}_i(t)+\frac{1}{m_i}\vec{p}_i\left(t+\Delta t/2\right)\cdot\Delta t$$

Reproduces differential operator for $\Delta t \to 0$

$O(\Delta t^4)$, time reversal invariant, energy conserving

Cutoff and neighbour lists

- Force calculation: $O(N^2)$, 80% runtime
- Short range potentials allow decomposition into cells
- Only atoms in adjacent cells interact
- Each cell pair only once considered
- Run time: $O(N)$



Step 5

- Influence from outside
  - Temperature (numerical thermostats)
  - Pressure (numerical barostats)
  - Stress, strain, flow
  - Shock waves, laser light

Nosé-Hoover thermostat

Instantaneous temperature:

$$\frac{3}{2}Nk_B T(t)=\sum_i \frac{\vec{p}_i^{\,2}}{2m_i}$$

Required temperature: T

Feedback regulation:

$$\dot{\vec{r}}_i=\frac{\vec{p}_i}{m_i} \qquad \dot{\vec{p}}_i=-\nabla_i V-\eta\vec{p}_i \qquad \dot{\eta}=\nu_T\left\{\frac{T(t)}{T}-1\right\}$$

Dimension of ν_T: frequency

Volume control barostat

Instantaneous pressure:

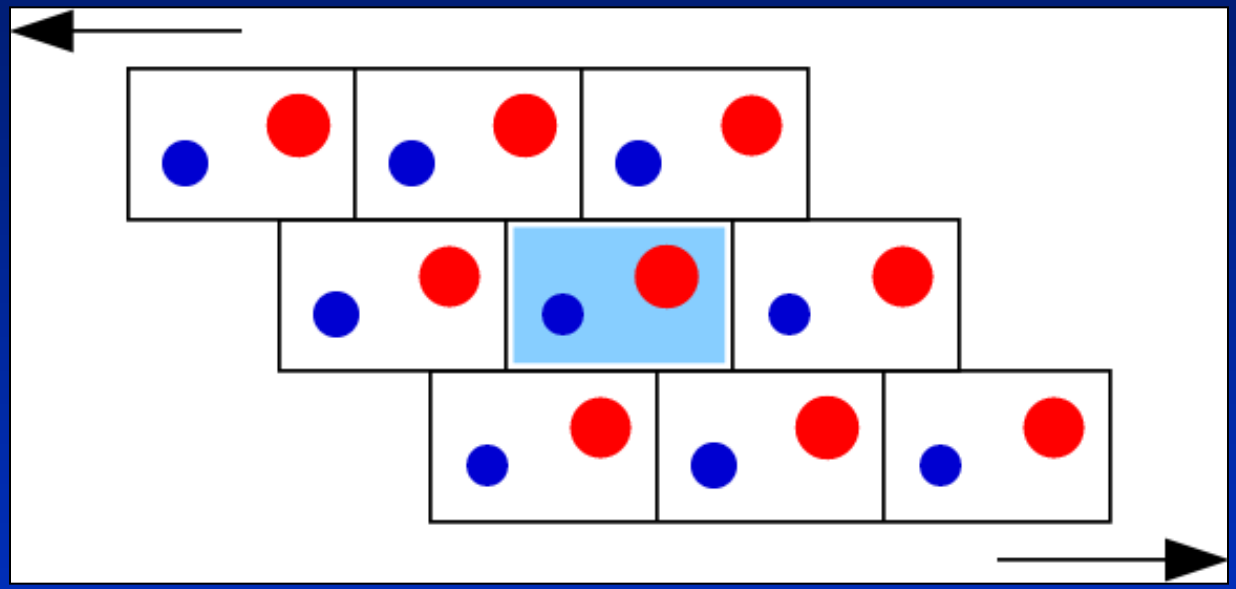
$$P(t)=\rho k_B T(t)+W/V,\quad W=\frac{1}{3}\sum_{i=1}^{N}\vec{r}_i\cdot\vec{f}_i$$

Required pressure: P

Feedback regulation:

$$\dot{\vec{r}}_i=\frac{\vec{p}_i}{m_i}+\xi\vec{r}_i \qquad \dot{\vec{p}}_i=-\nabla_i V-\xi\vec{p}_i \qquad \dot{\xi}=\frac{\nu_P V}{Nk_B T}\{P(t)-P\}$$

Lees-Edwards boundary conditions

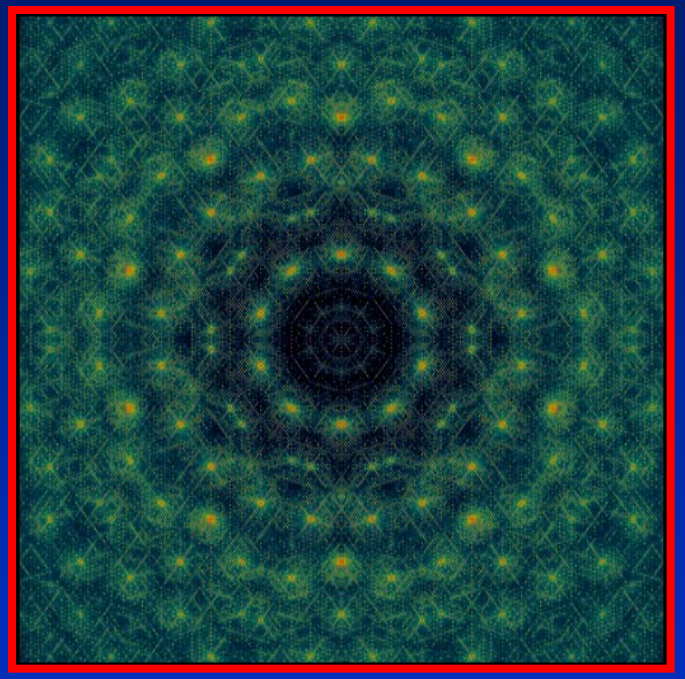


$$\dot{x}_i = \frac{p_{xi}}{m_i} - \gamma y_i \qquad \dot{y}_i = \frac{p_{yi}}{m_i}$$

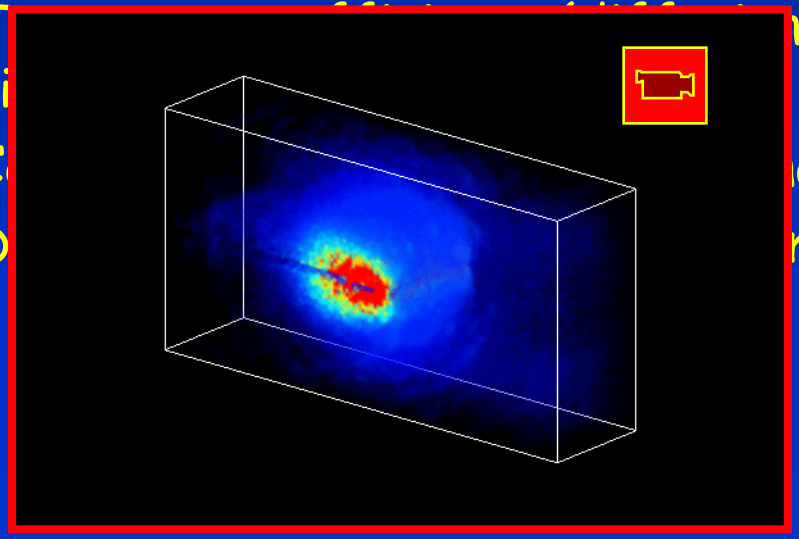
$$\dot{p}_{xi} = -\nabla_{xi} V + m\gamma \dot{y}_i \qquad \dot{p}_{yi} = -\nabla_{yi} V$$

Step 6

- Extract data

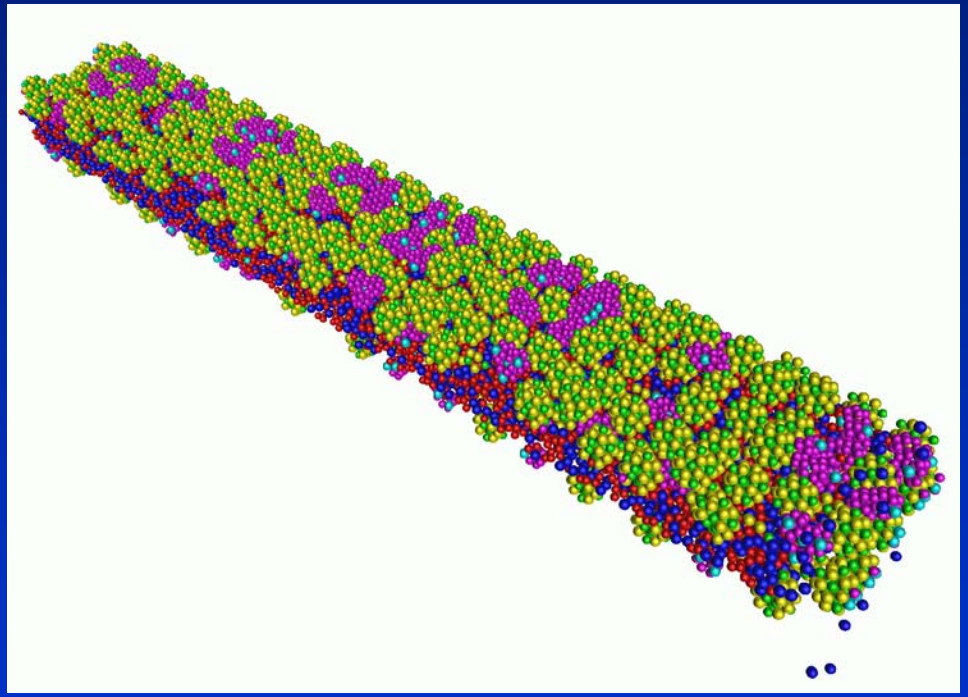


- Potential energy, kinetic energy, total energy
- Free energy
- Total and local stress
- Displacement fields
- Elastic coefficients
- T , heat, vi
- C amic)
- D mic)



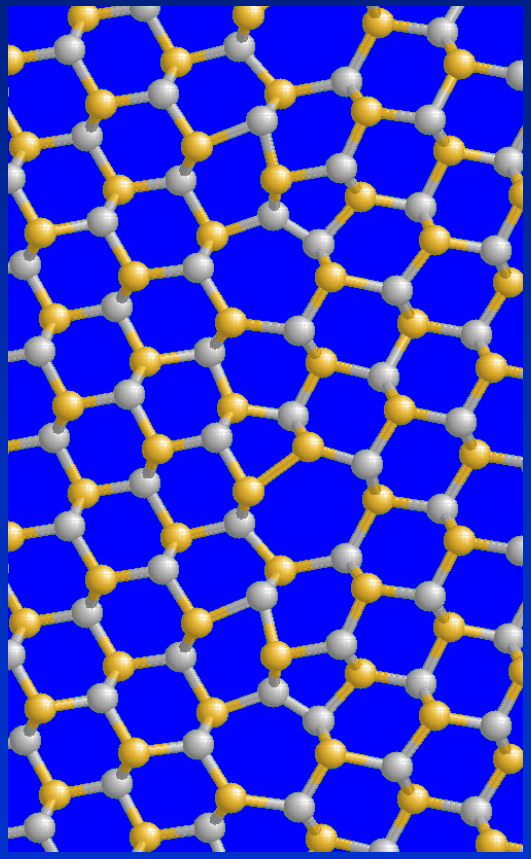
Step 7

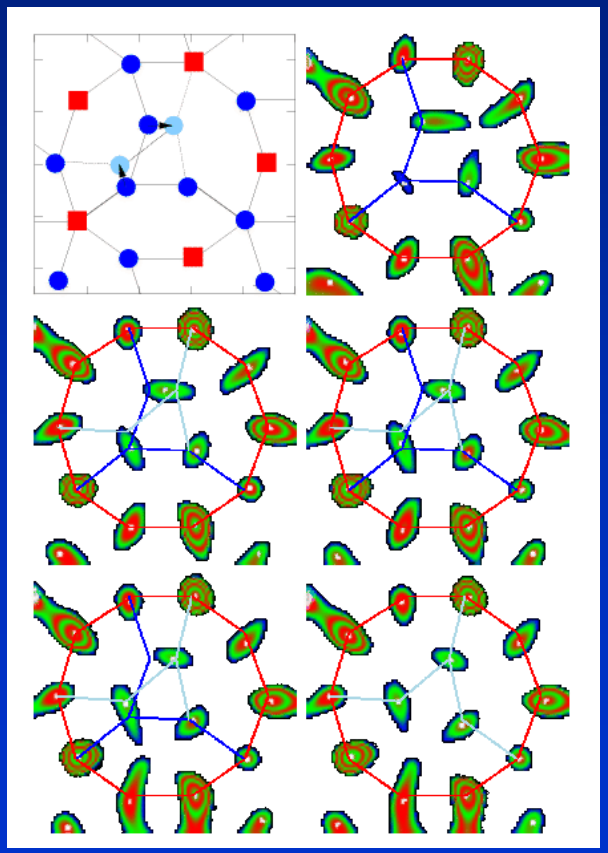
- Visualize data
  - Direct plot of atoms
  - Color code for observables
  - Selective visualization in 3d
  - Animations



Equilibrium problems

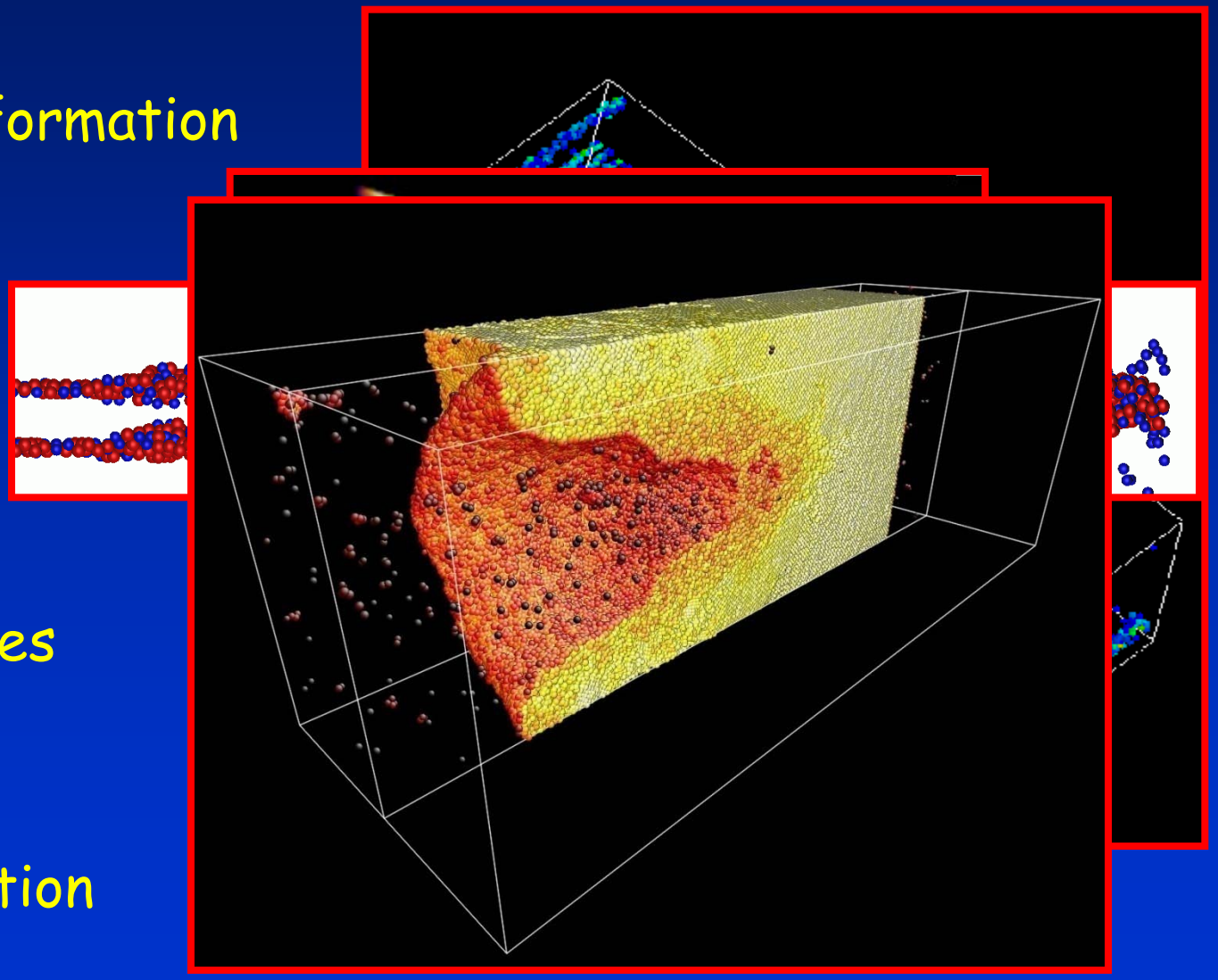
- Grain boundary structures
- Phason dynamics





Nonequilibrium problems

- Plastic deformation
- Fracture
- Shock waves
- Laser ablation

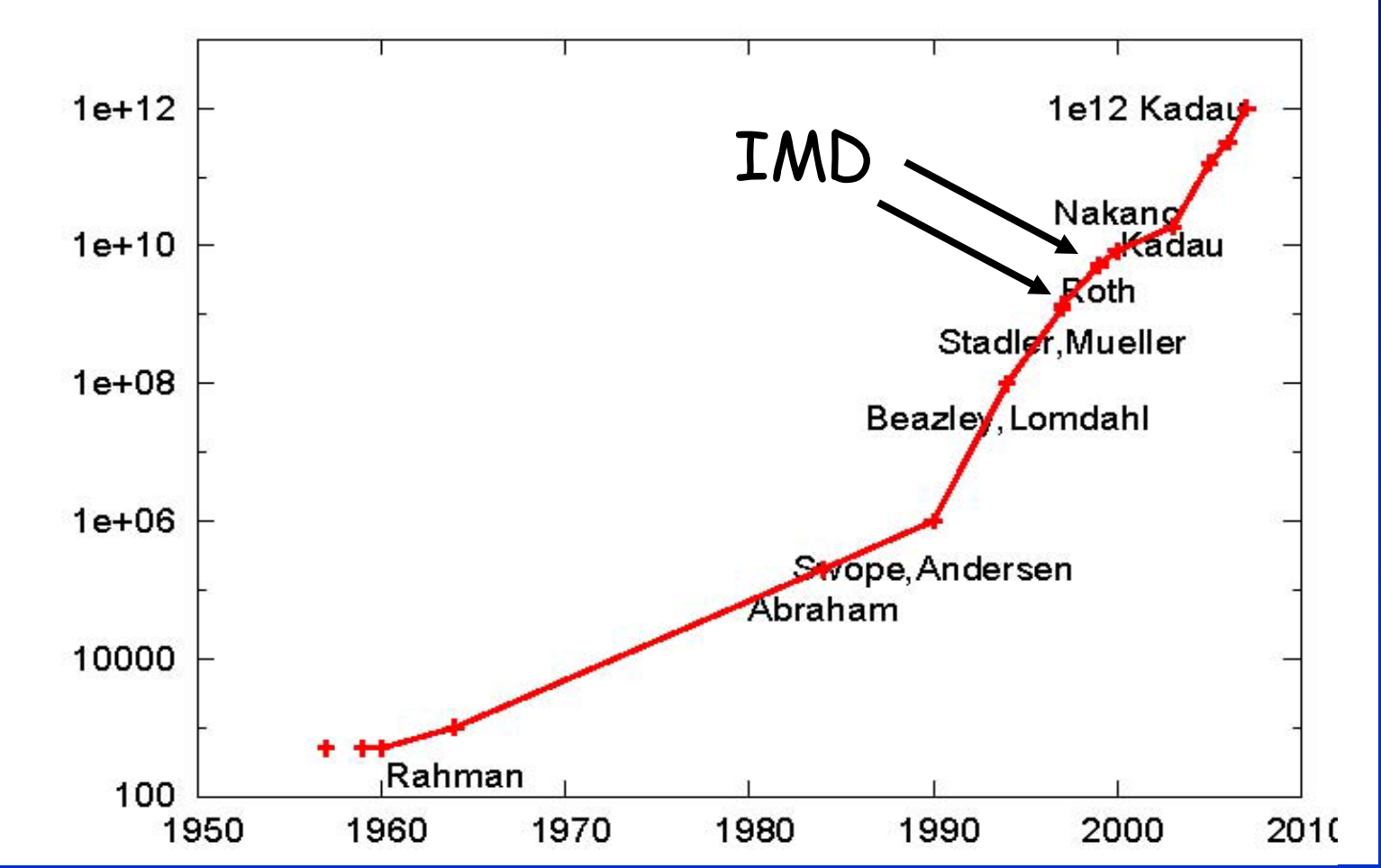


IMD (ITAP Molecular Dynamics)

- Molecular dynamics program package
- Established 1996, continuously improved and extended since
- Easily portable and extendable
- Workstations, clusters, massively parallel supercomputers
- Parallelized with Message Passing Interface
- Many effective potentials applicable
- Simple integrators (Verlet, Leap-frog) with energy stability over long times
- Timesteps: a few fs, computation time: a few µs for each time step and atom
- Scalable up to hundred thousands of CPUs
- Available at:

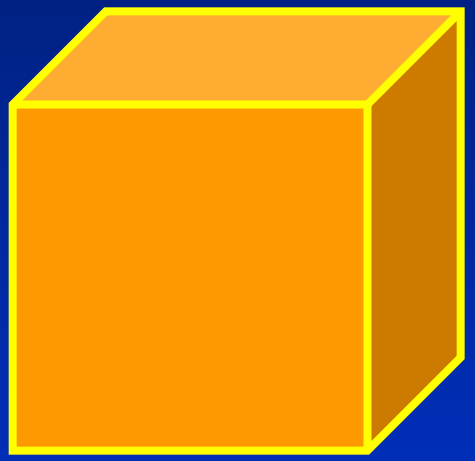
  http://www.itap.physik.uni-stuttgart.de/~imd

World records in particle numbers



World records in particle numbers

1964	1.000	Rahman
1984	200.000	Abraham
1990	1.000.000	Swope, Anderson
1994	100.000.000	Beazley, Lomdahl
14.03.1997	1.213.857.792	Stadler
15.11.1997	1.399.440.000	Müller
28.10.1999	5.180.116.000	Roth
2000	8.500.000.000	Vashishta
08.08.2003	19.000.416.964	Kadau, Germann, Lomdahl
16.04.2005	160.000.000.000	Kadau, Germann, Lomdahl
2006	320.000.000.000	Kadau, Germann, Lomdahl



15.11.2007 1.000.000.000.000 Germann, Kadau

IBM BlueGene/L, 212992 nodes with IBM PowerPC 440 processors, 360 Tflop/s

Time scales

How long lasts a time step(Δt)?

Characteristic time for an oscillating system:

$$T = \sqrt{\frac{m\sigma^2}{\varepsilon \approx mv^2}}$$

E.g. earth in gravitational field of sun, $\varepsilon = \frac{m_{\text{sun}} m}{\sigma} G$:

$$T = 60 \text{ days}$$

Iron atoms: $m = 10^{-22}$ g, $\sigma = 2.5 \cdot 10^{-8}$ cm, $\varepsilon = 10^{-12}$ g cm^2 s^{-2}

$$T = 0.25 \cdot 10^{-12} \text{ s}$$

Total simulation times: up to several μs

3. Model potentials

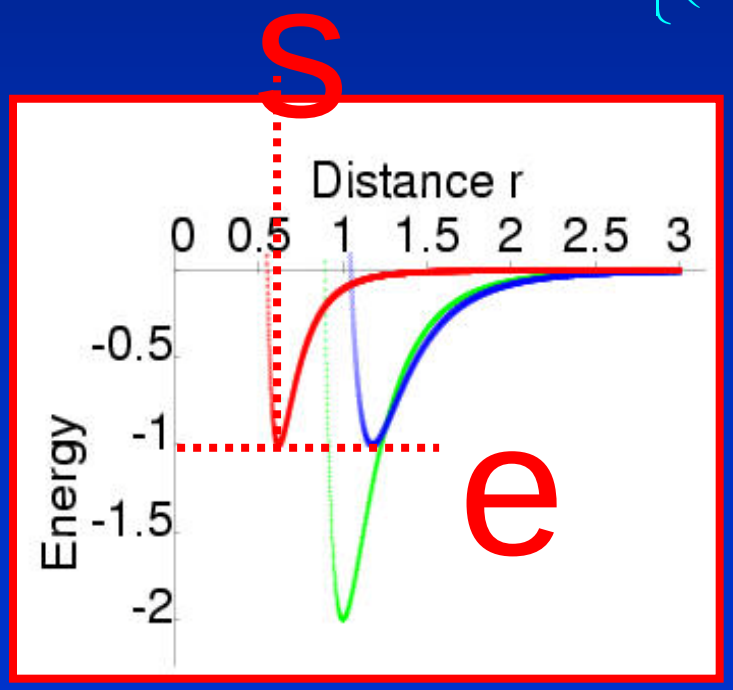
a) Lennard-Jones potential
b) Dzugutov potential
c) Lennard-Jones-Gauss potential

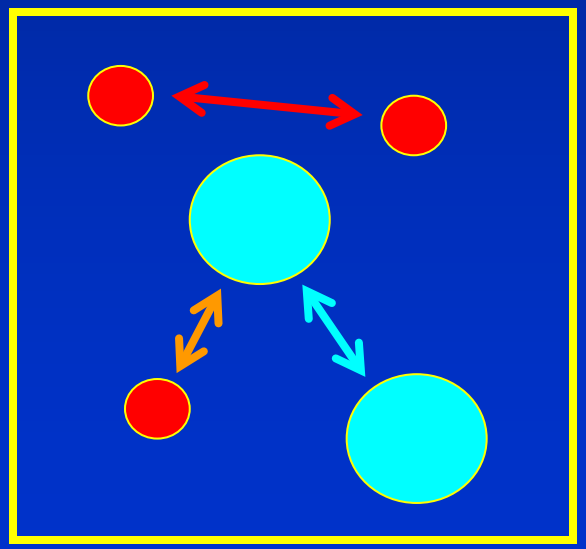
Lennard-Jones pair potential

Total potential

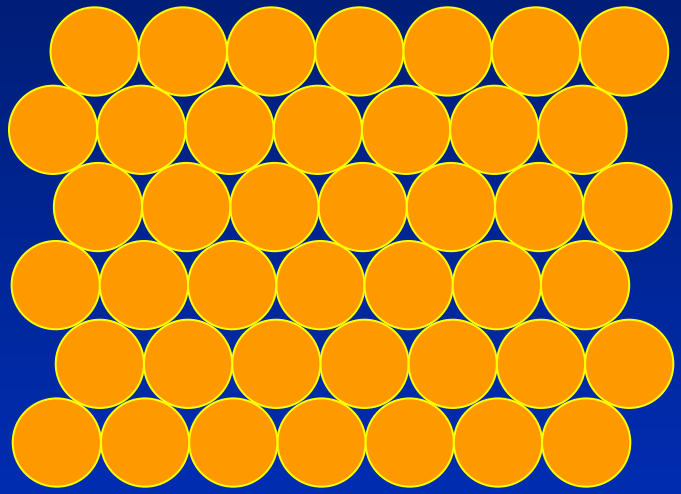
$$V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) = \sum_{i<j=1}^{n} \Phi_{ij}\left(\left|\vec{r}_i - \vec{r}_j\right|\right)$$

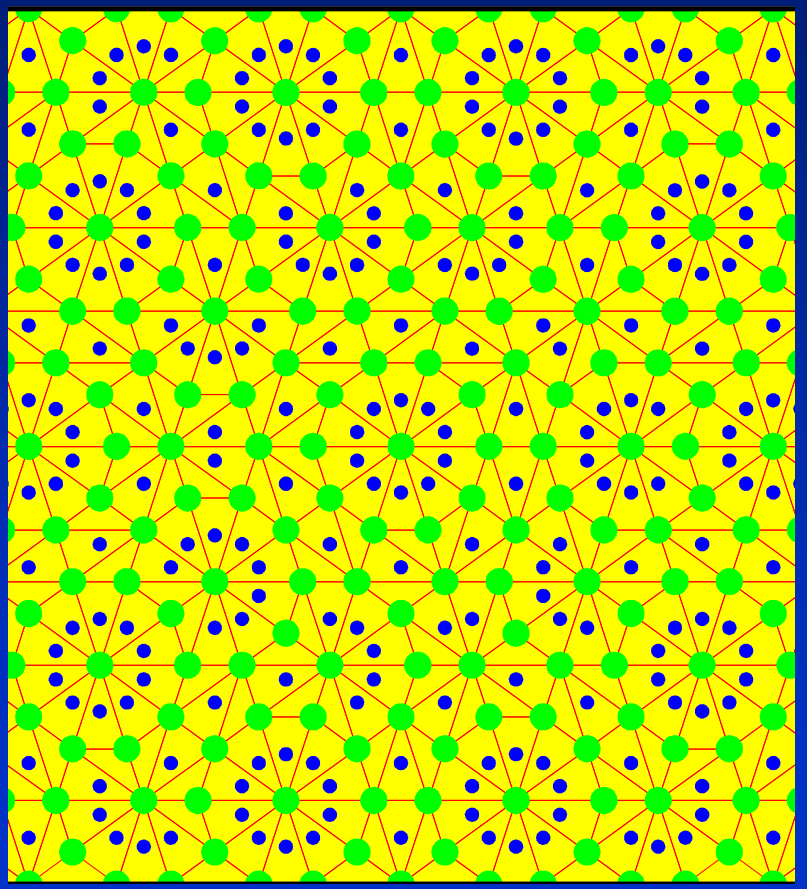
$$\Phi_{ij}(r) = 4\varepsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right\} f^{ij}{}_{cut}(r)$$





Structures with LJ potentials



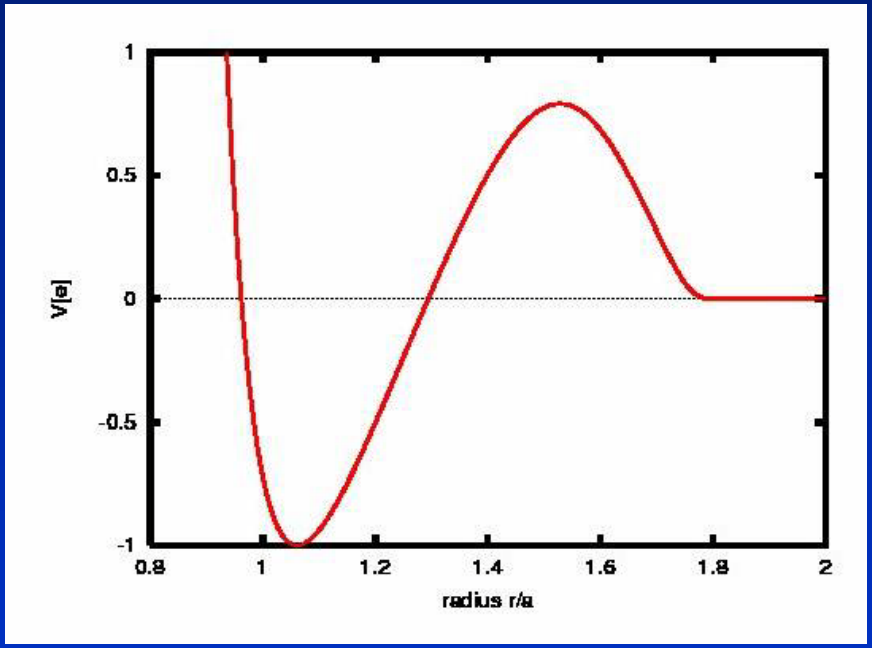


Dzugutov potential

$$\Phi(r) = \Phi_1(r) + \Phi_2(r)$$

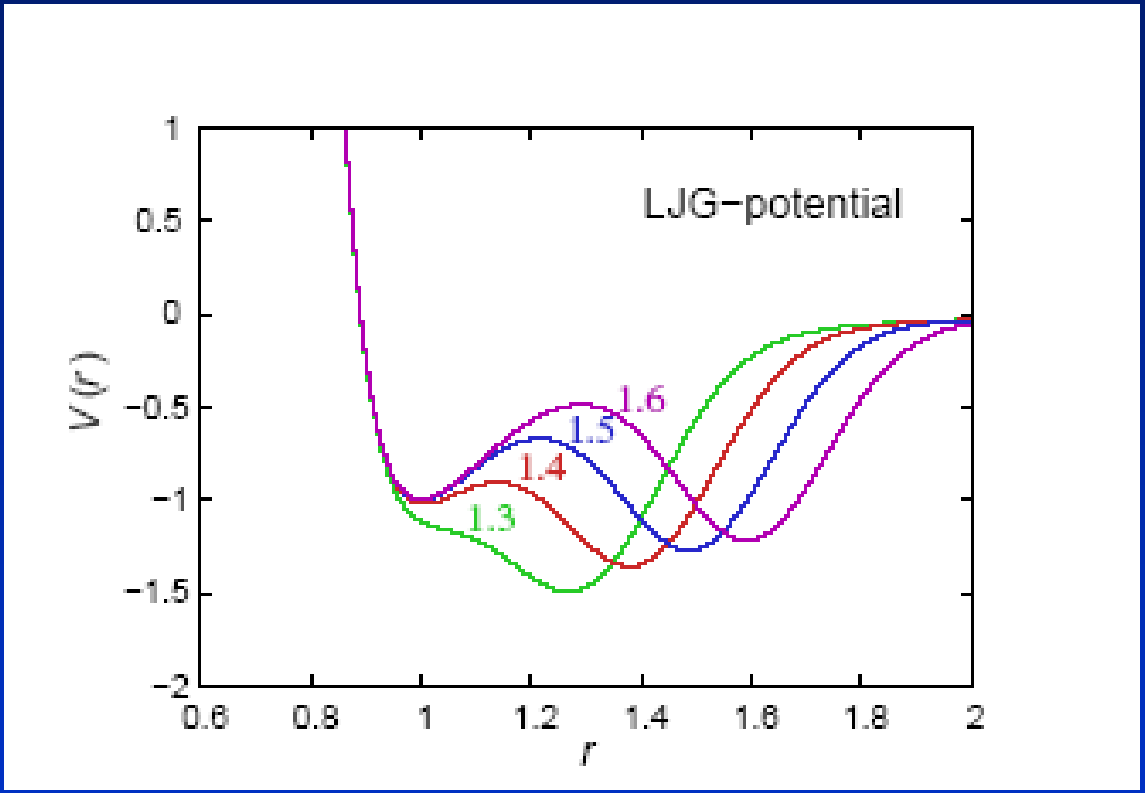
$$\Phi_1(r) = \begin{cases} A\left(r^{-m} - B\right)\exp\left(\dfrac{c}{r-a}\right), & r < a \\ 0, & r \geq a \end{cases}$$

$$\Phi_2(r) = \begin{cases} B\exp\left(\dfrac{d}{r-b}\right), & r < b \\ 0, & r \geq b \end{cases}$$



bcc – fcc – σ-phase – dodecagonal qc - glass

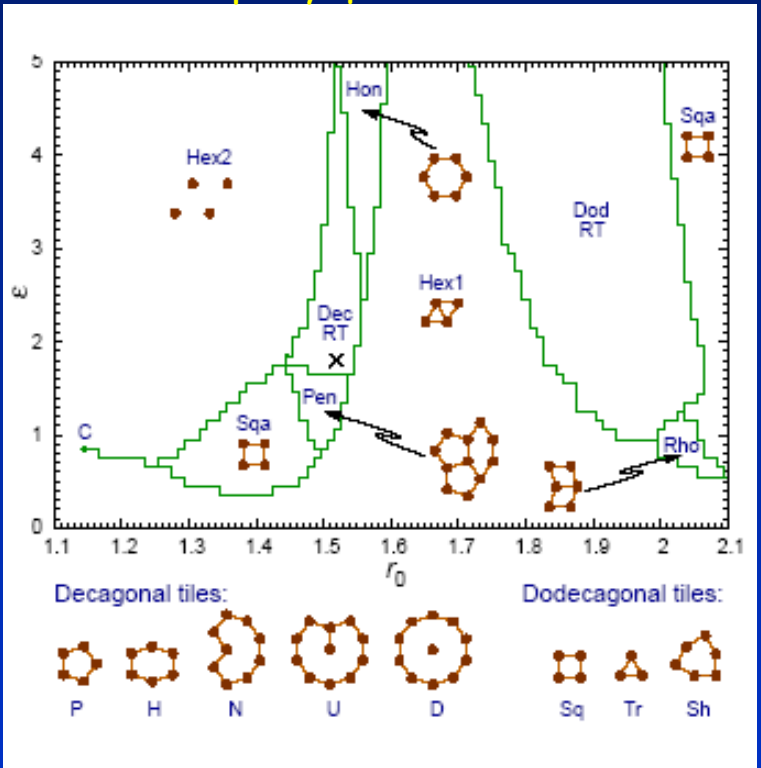
Lennard-Jones-Gauss potential



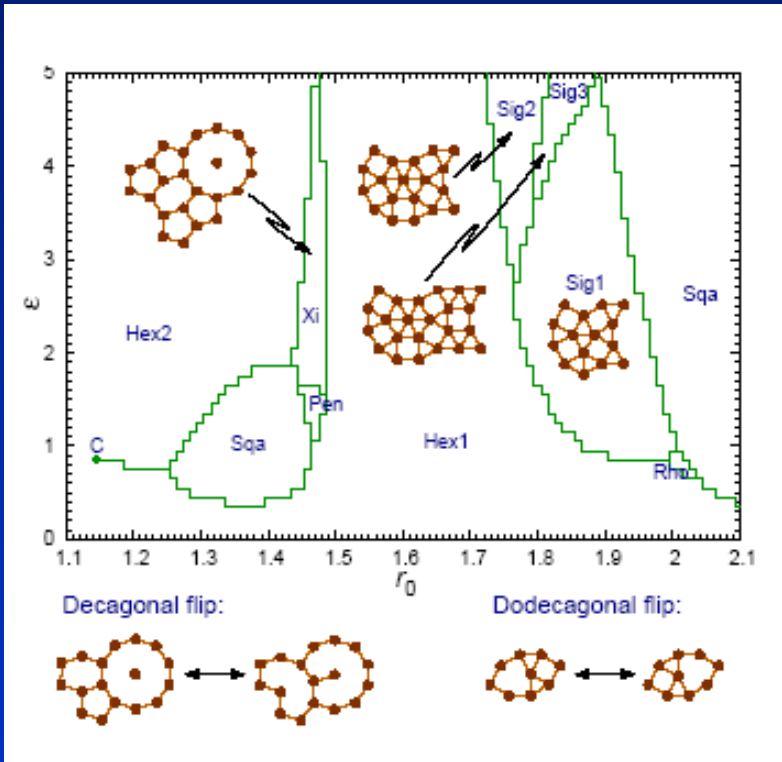
$$V(r) = \frac{1}{r^{12}} - \frac{2}{r^6} - \epsilon \exp\left(-\frac{(r-r_0)^2}{2\sigma^2}\right)$$

Phase diagram with LJG potential in two dimensions

rapidly quenched



relaxed T=0



M. Engel and H-RT 2007
Self-Assembly of Monatomic Complex Crystals and Quasicrystals with a Double-Well Interaction Potential
Phys.Rev.Lett **98** 225505

4. Realistic potentials

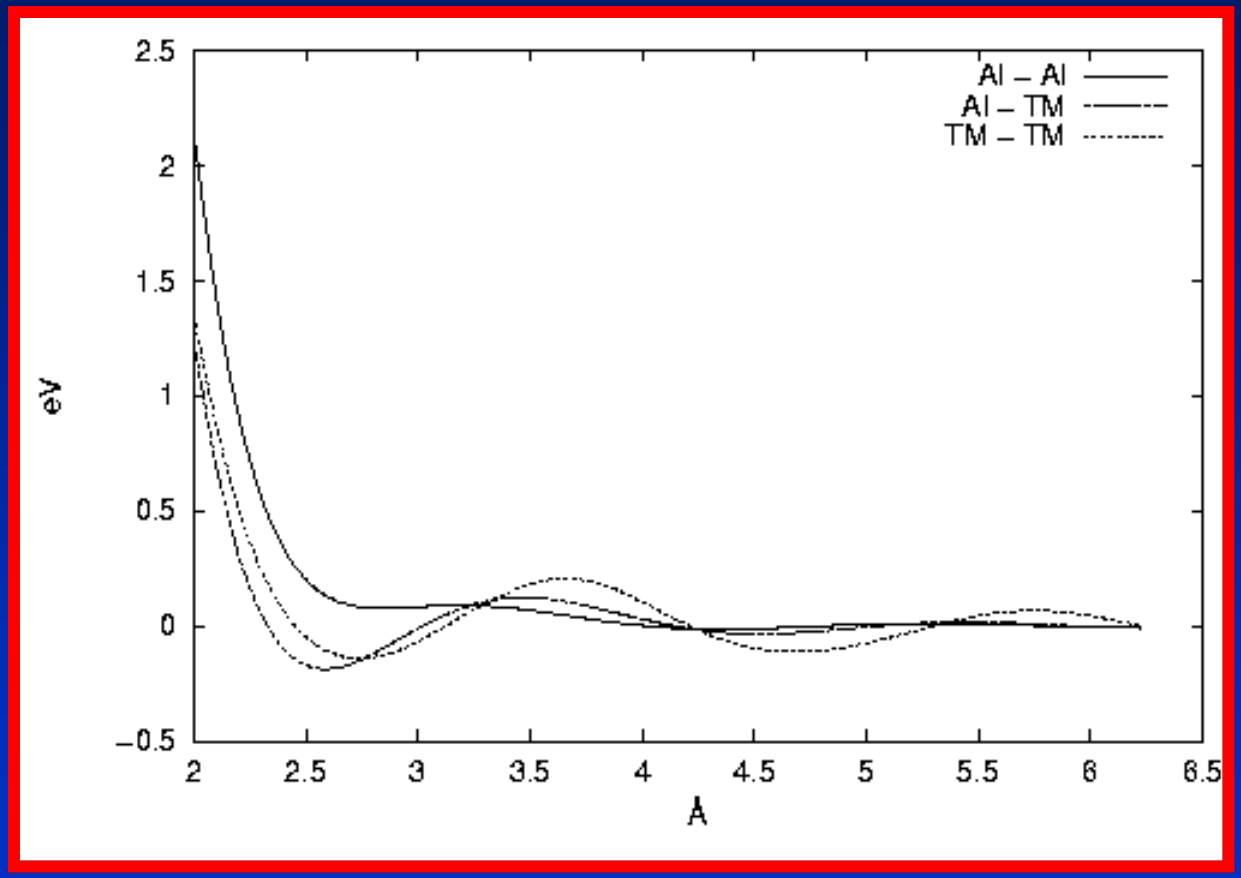
Metals, alloys
a) Advanced pair potentials
b) Embedded atom potentials

Kovalent materials
c) Stillinger-Weber potentials
d) Tersoff potentials

Oxids, water
e) Long-range interactions

Advanced two-body potentials

Effective pair potential



Fit to ab-initio calculations with *potfit*

Embedded-atom potentials (EAM)

$$V = \sum_i F_i\left(\sum_{j\neq i} f_j\left(r_{ij}\right)\right) + \sum_{i<j} \Phi_{ij}\left(r_{ij}\right)$$

Embedding energy

Electron transfer function

Pair potential

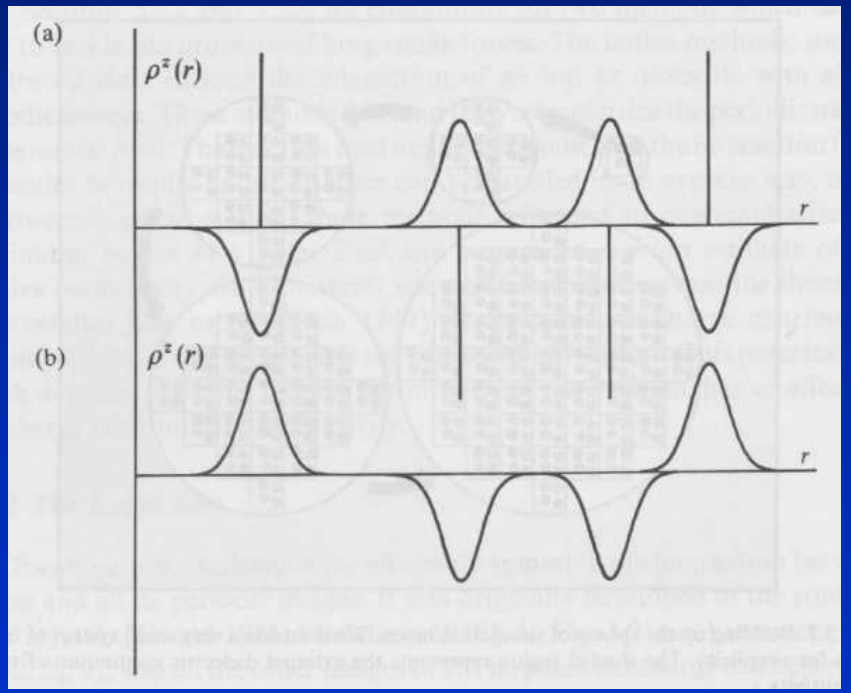
Examples

$$F(s) = \sqrt{s} \qquad f_j(r) = \left(\frac{a_j}{r}\right)^m$$

Long-range interactions (Coulomb- and polar)

- Ewald sum method $O(N^{3/2})$
  first part: real space
  second part: reciprocal space

- Wolf summation $O(N)$:
  choose cutoff such that second part vanishes

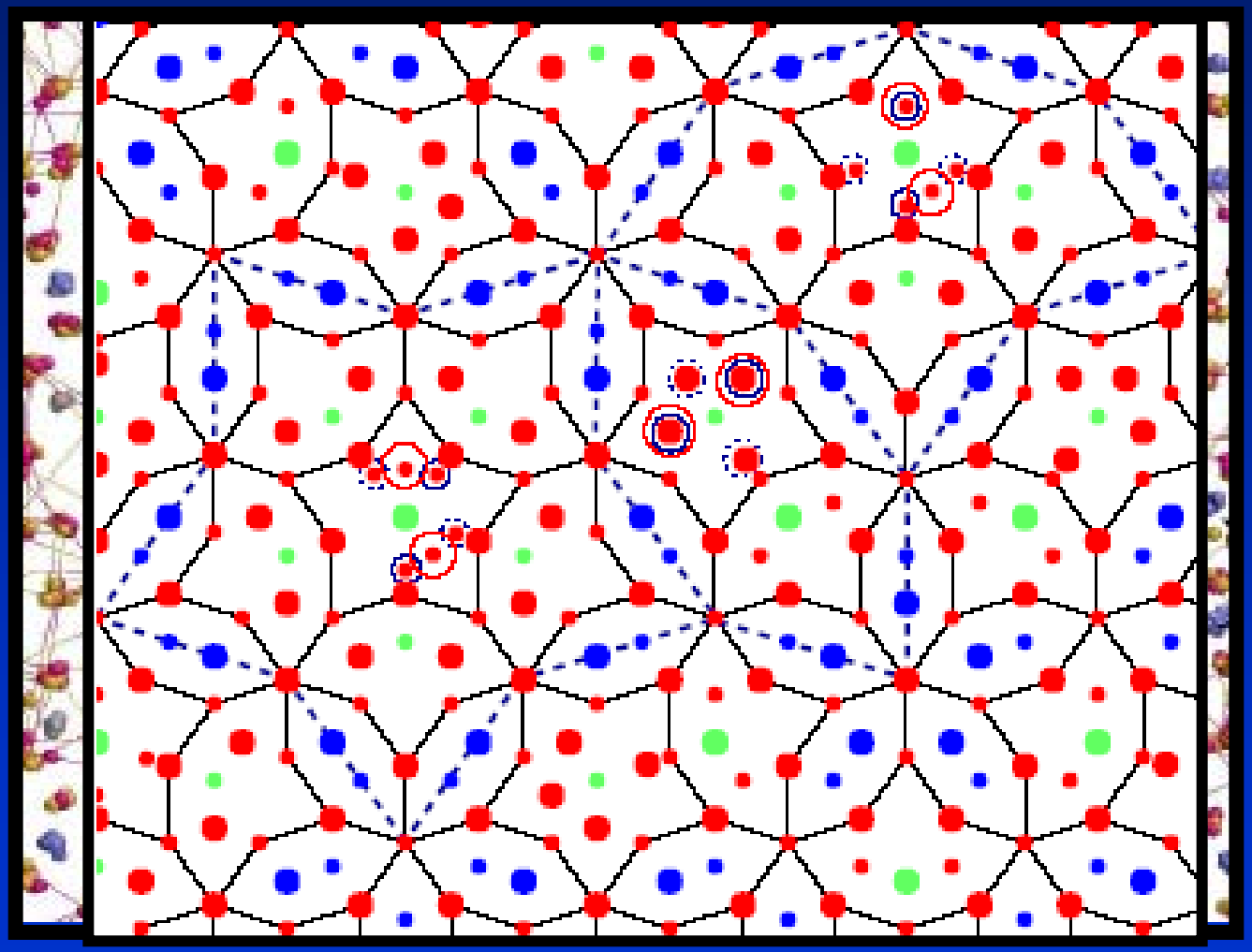


Boosts simulation by 1-2 orders of magnitude

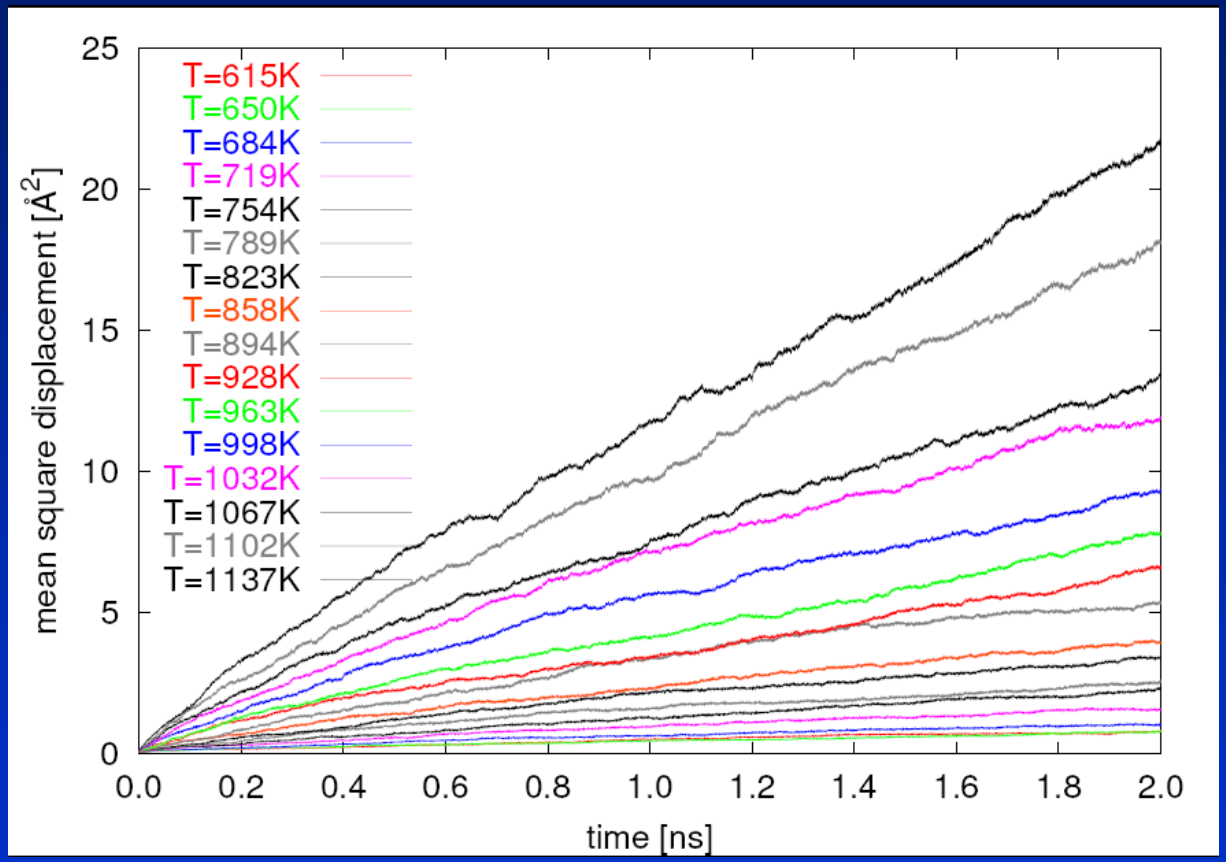
5. Simulations of physical properties

a) Diffusion in d-Al-Ni-Co
b) Dynamical structure factor for Zn_2Mg
c) Cracks in $NbCr_2$

i) Diffusion in d-AlNiCo

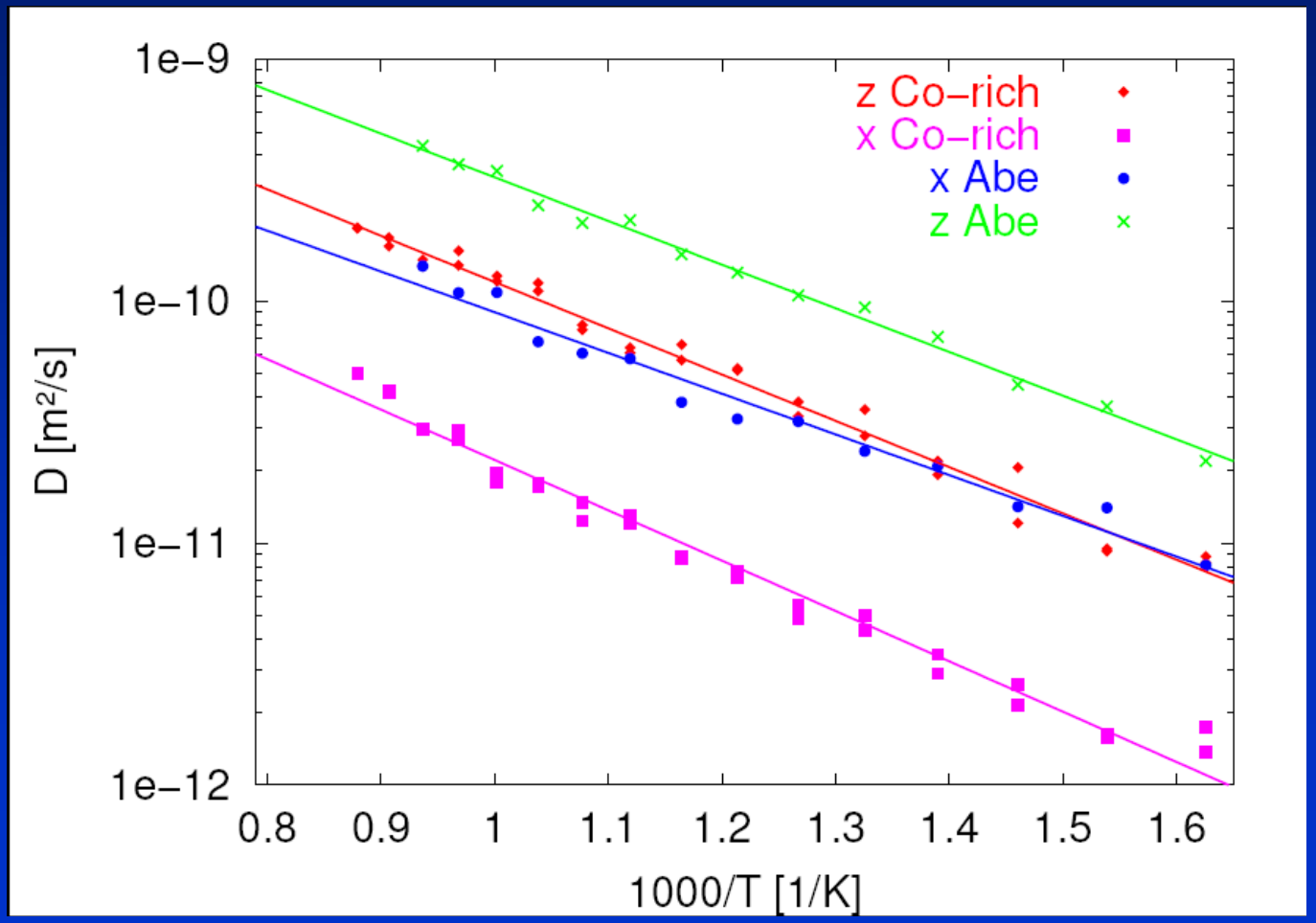


Diffusion in d-Al-Ni-Co

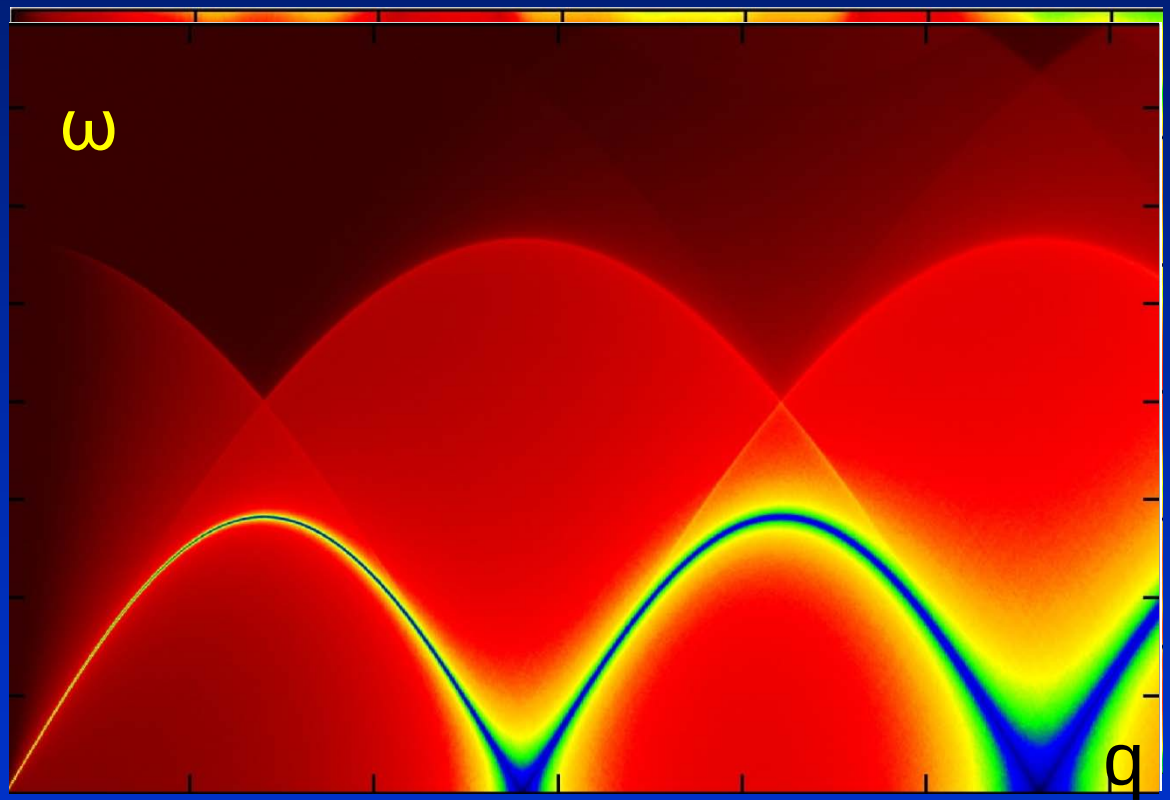


S. Hocker and F. Gähler 2004
Aluminium Diffusion in Decagonal Quasicrystals
Phys. Rev. Lett. **93** 075901

Arrhenius diagram d-Al-Ni-Co



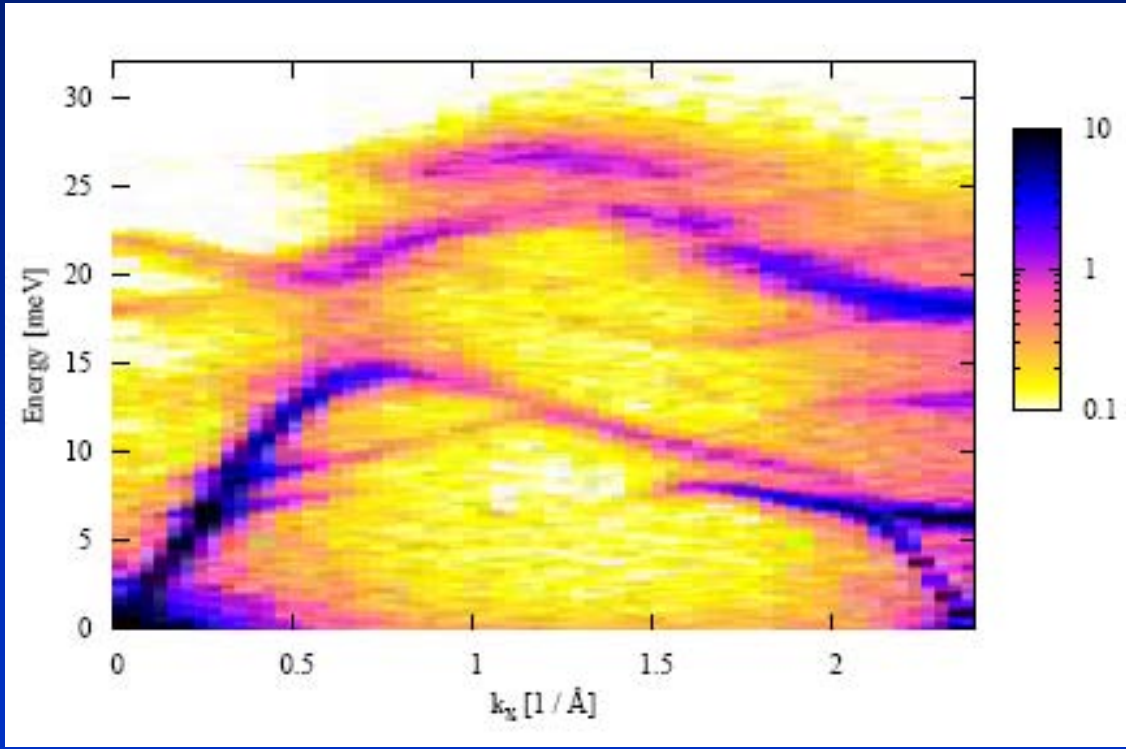
Dynamical structure factor from MD model calculations



Harmonic Fibonacci chain with bias

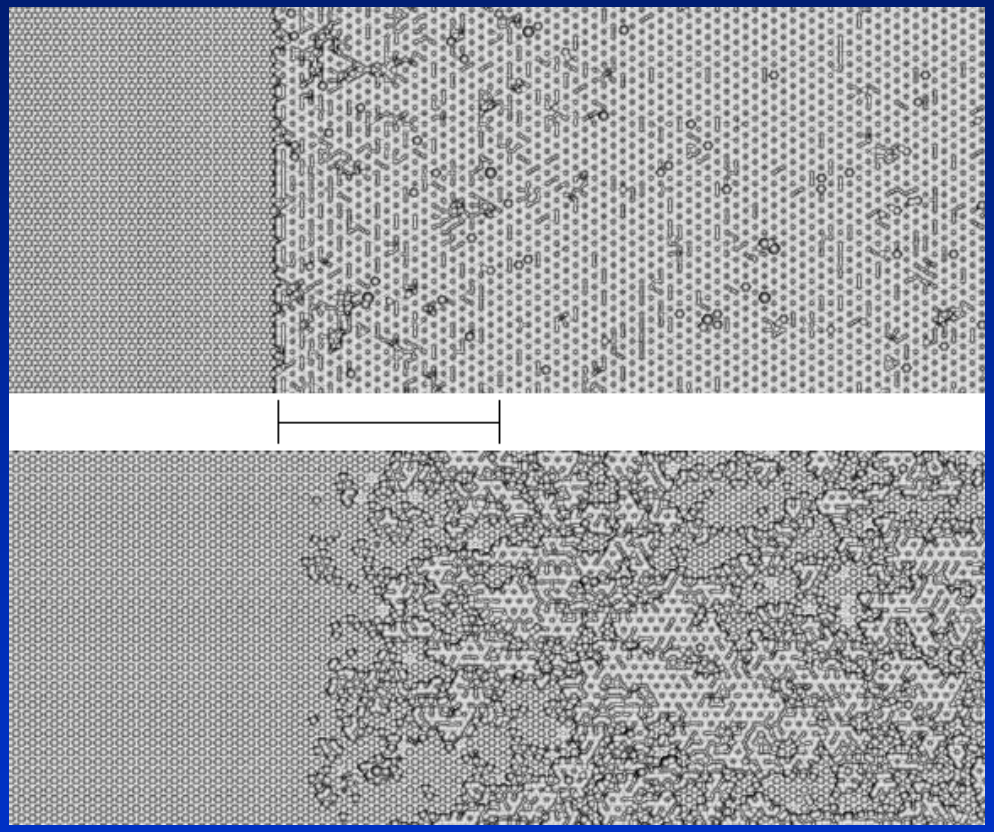
Harmonic periodic chain

ii) Dynamical structure factor Zn_2Mg



Longitudinal phonons in the hexagonal plane

iii) Crack propagation $NbCr_2$



[2-1-1]

(111) cleavage planes

[0-11]

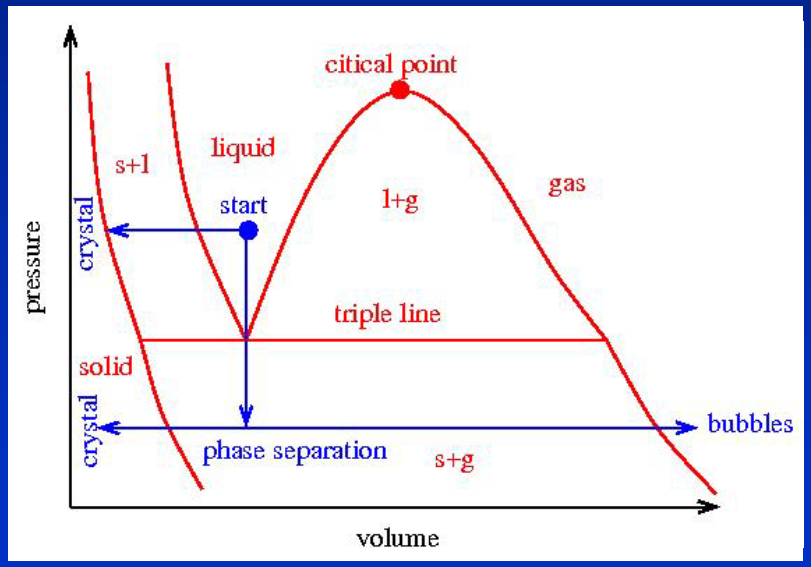
F. Rösch, H.-R. Trebin, and P. Gumbsch 2006
Interatomic potentials and the simulation of fracture: C15 $NbCr_2$
Int. J. Fracture **139**(3-4), pp. 517-526

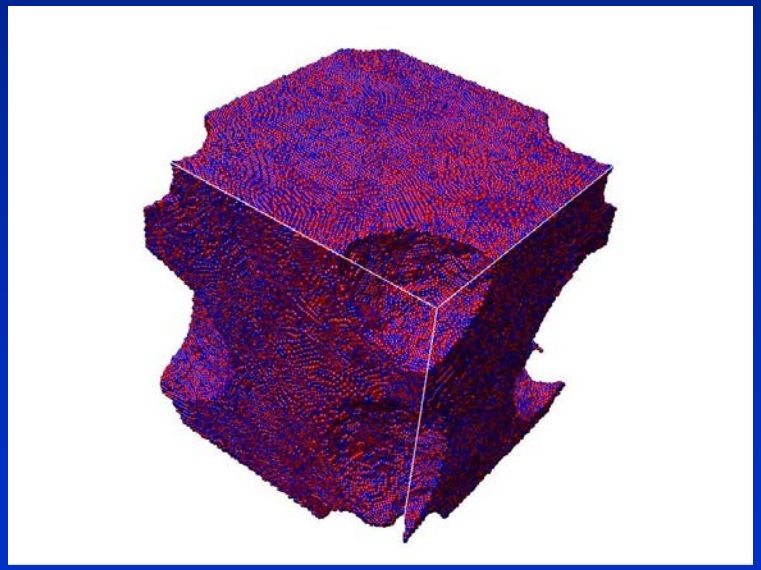
6. Simulations of amorphous materials

a) How to produce them
b) Shock waves

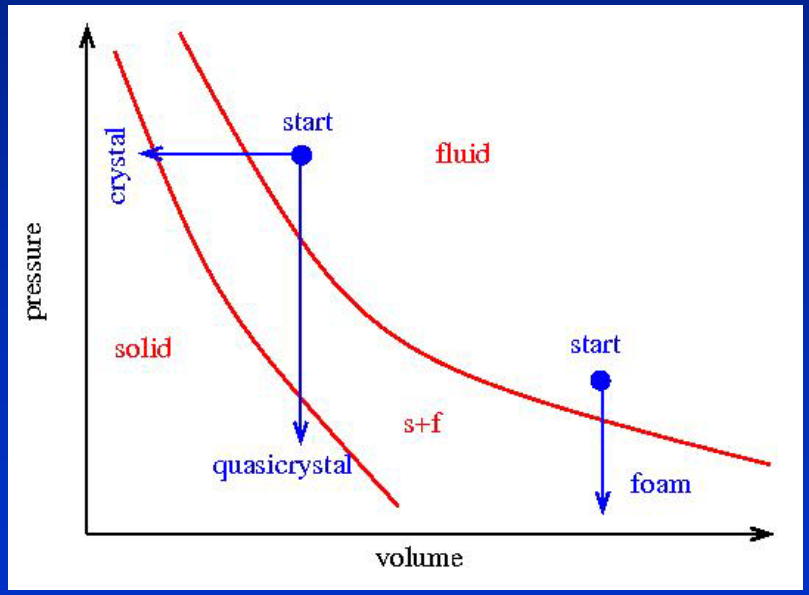
a) How to produce them

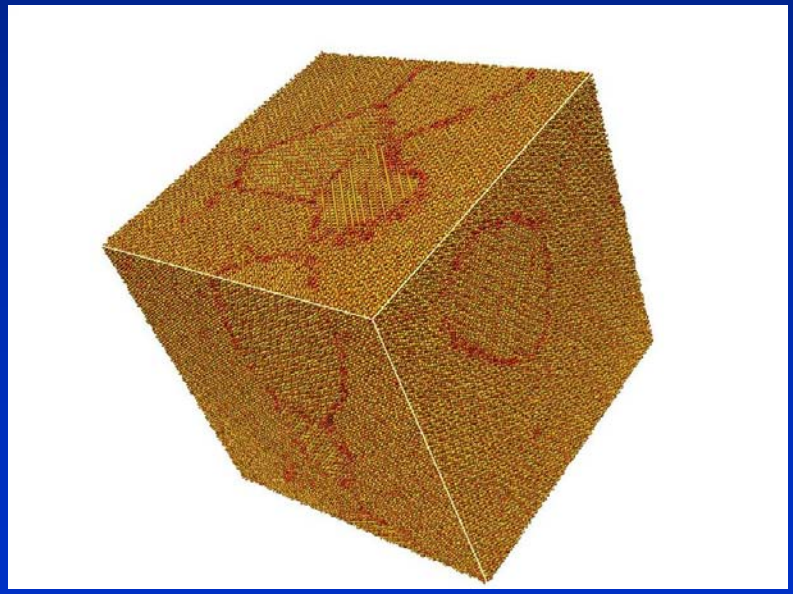
i) Lennard-Jones potential





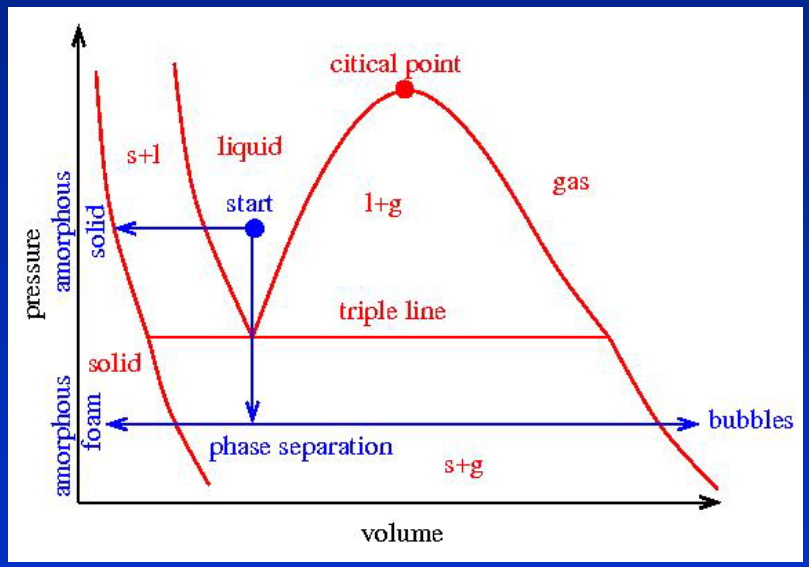
ii) Dzugutov potential

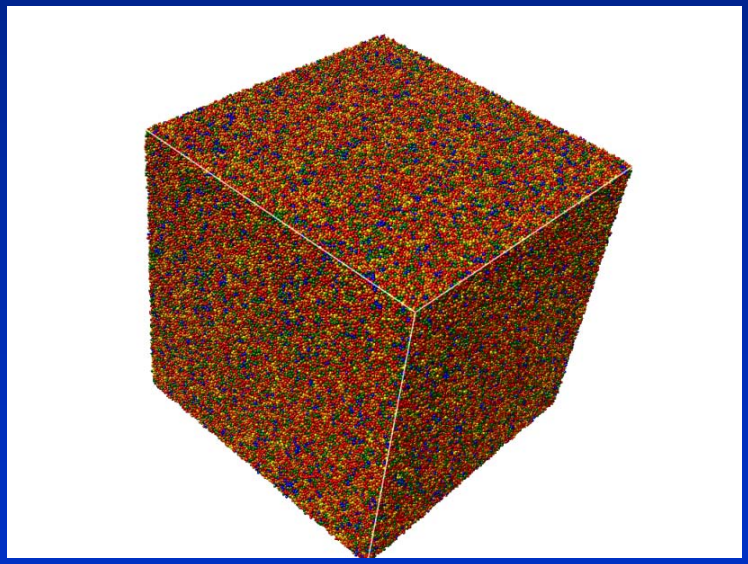




iii) Lennard-Jones-Gauss potential

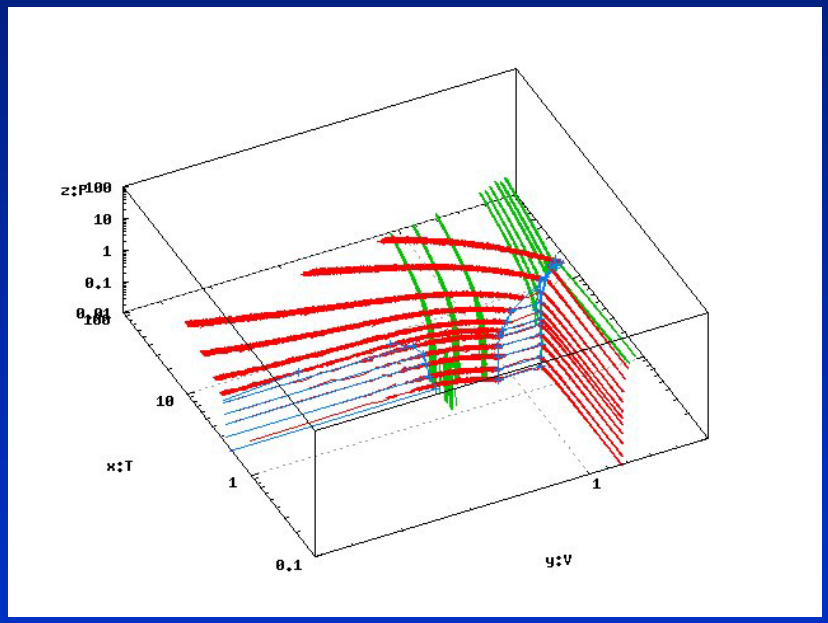
r_0=1.4, ε=1.8

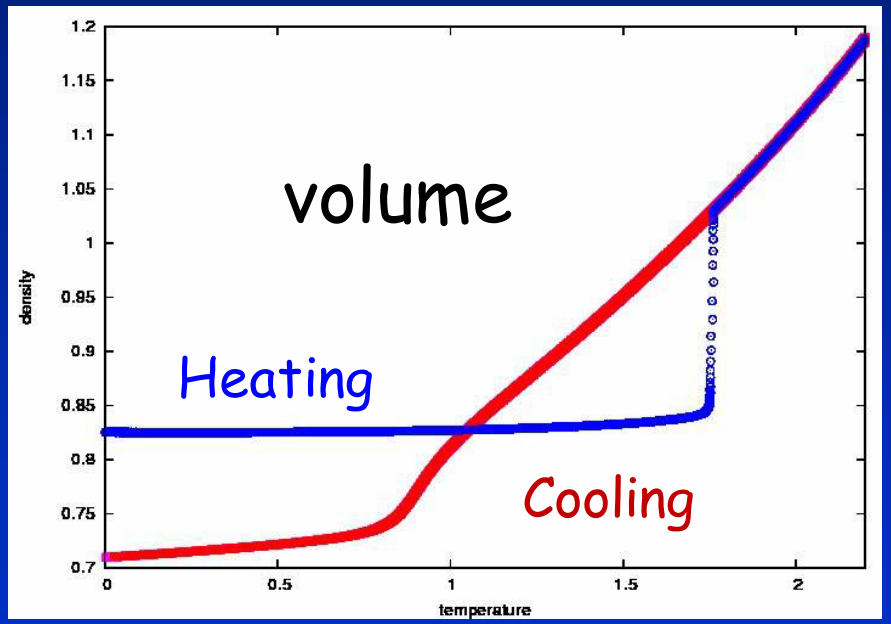




Properties of the LJG system

r_0=1.4, ε=1.8

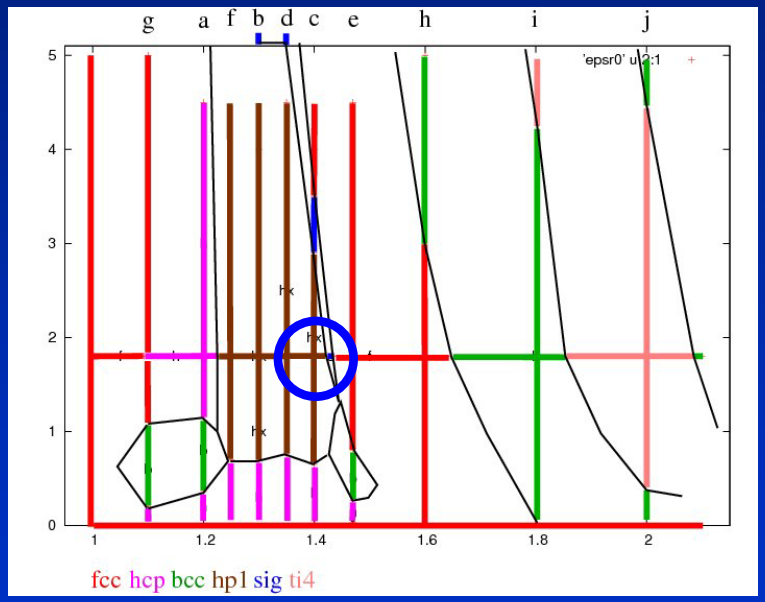


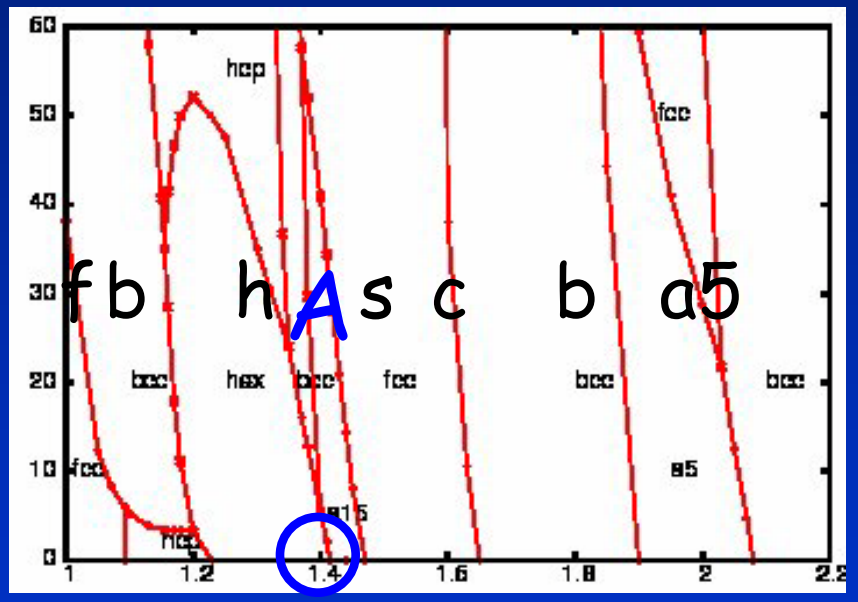


pvt diagram

density anomaly !

Dependency of LJG potential on parameters r_0 and ε and pressure P

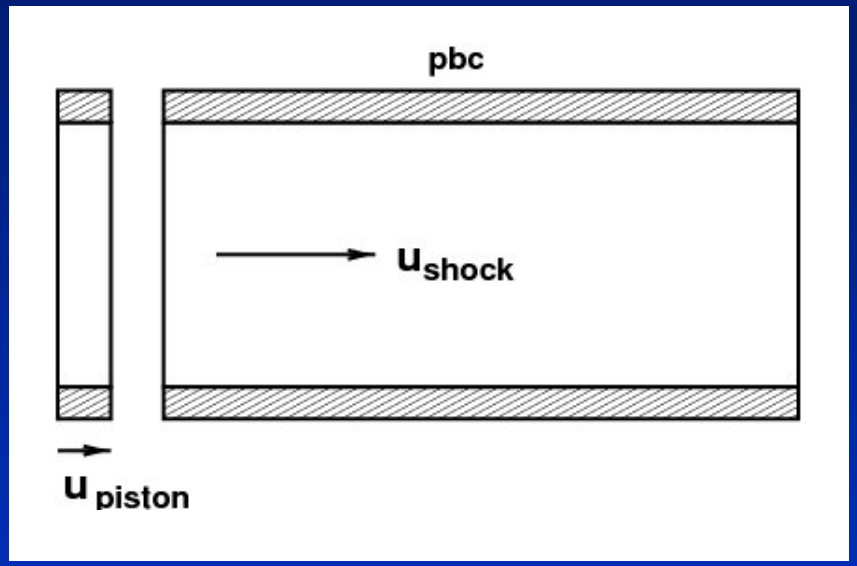




r_0-ε plane, P=0

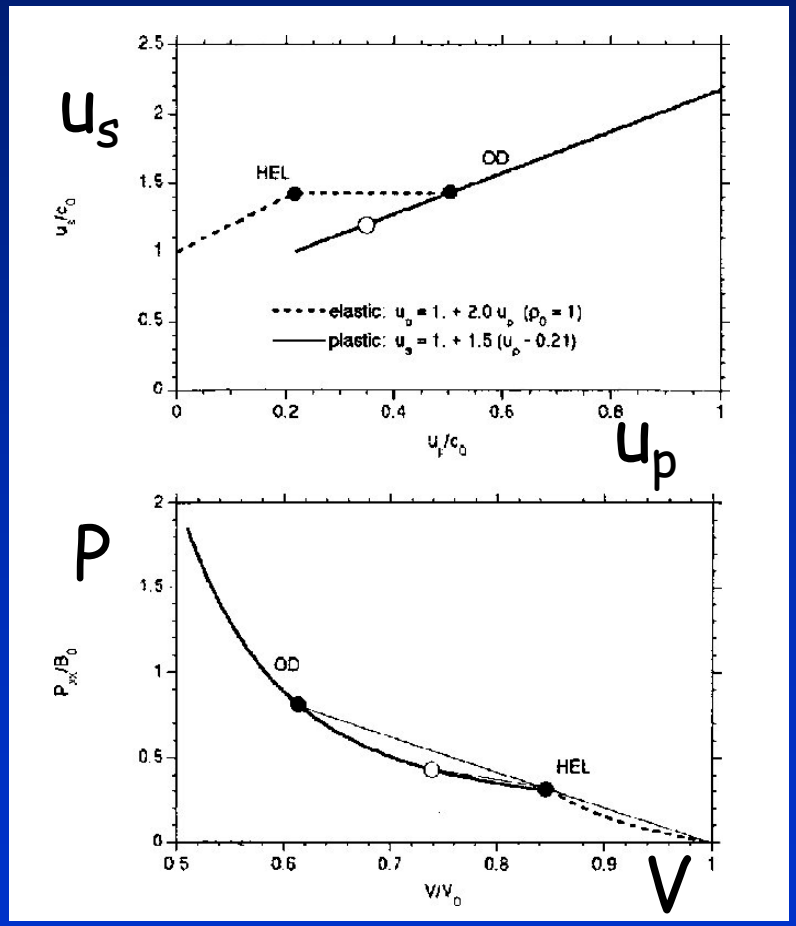
r_0-P plane, ε=1.8

b) Shock waves in amorphous materials

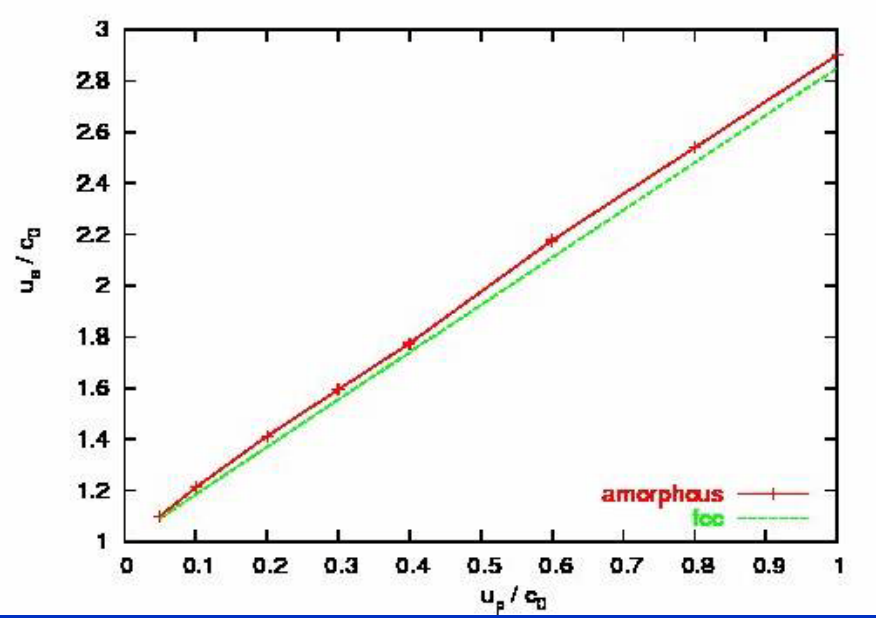


↑
generation of shock wave

measurement →



Diatomic LJ materials

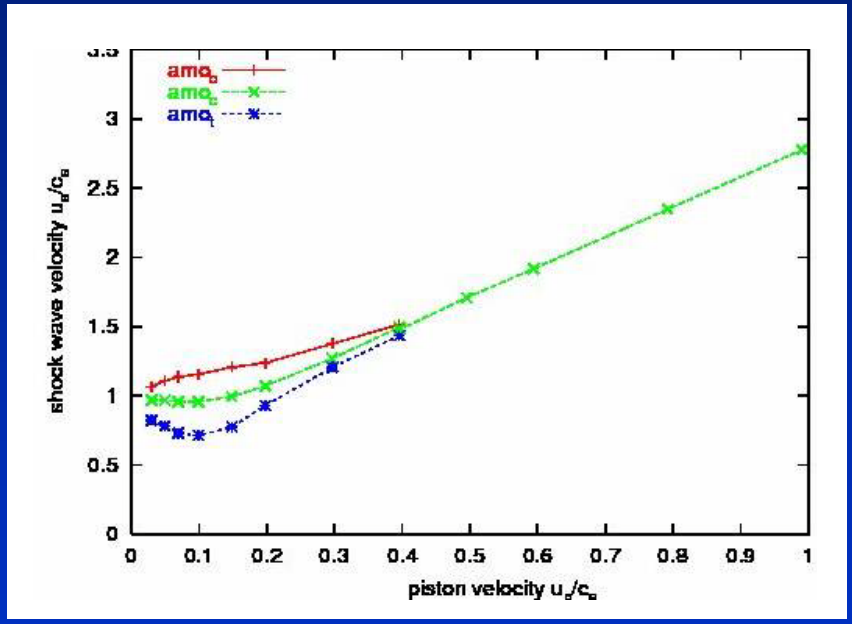


No two-phase region !

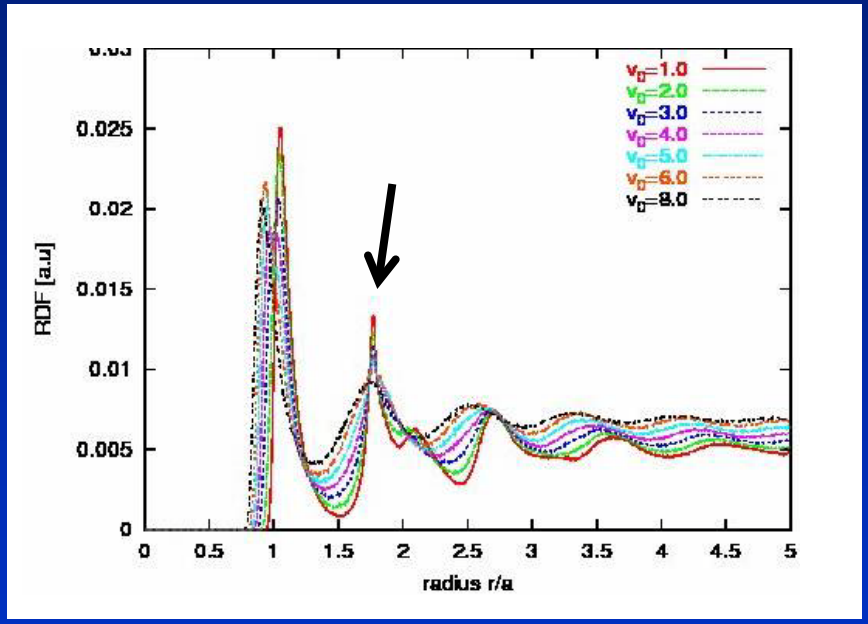
Exceptional cases:

- fcc four-fold axis
- amorphous

Dzugutov materials

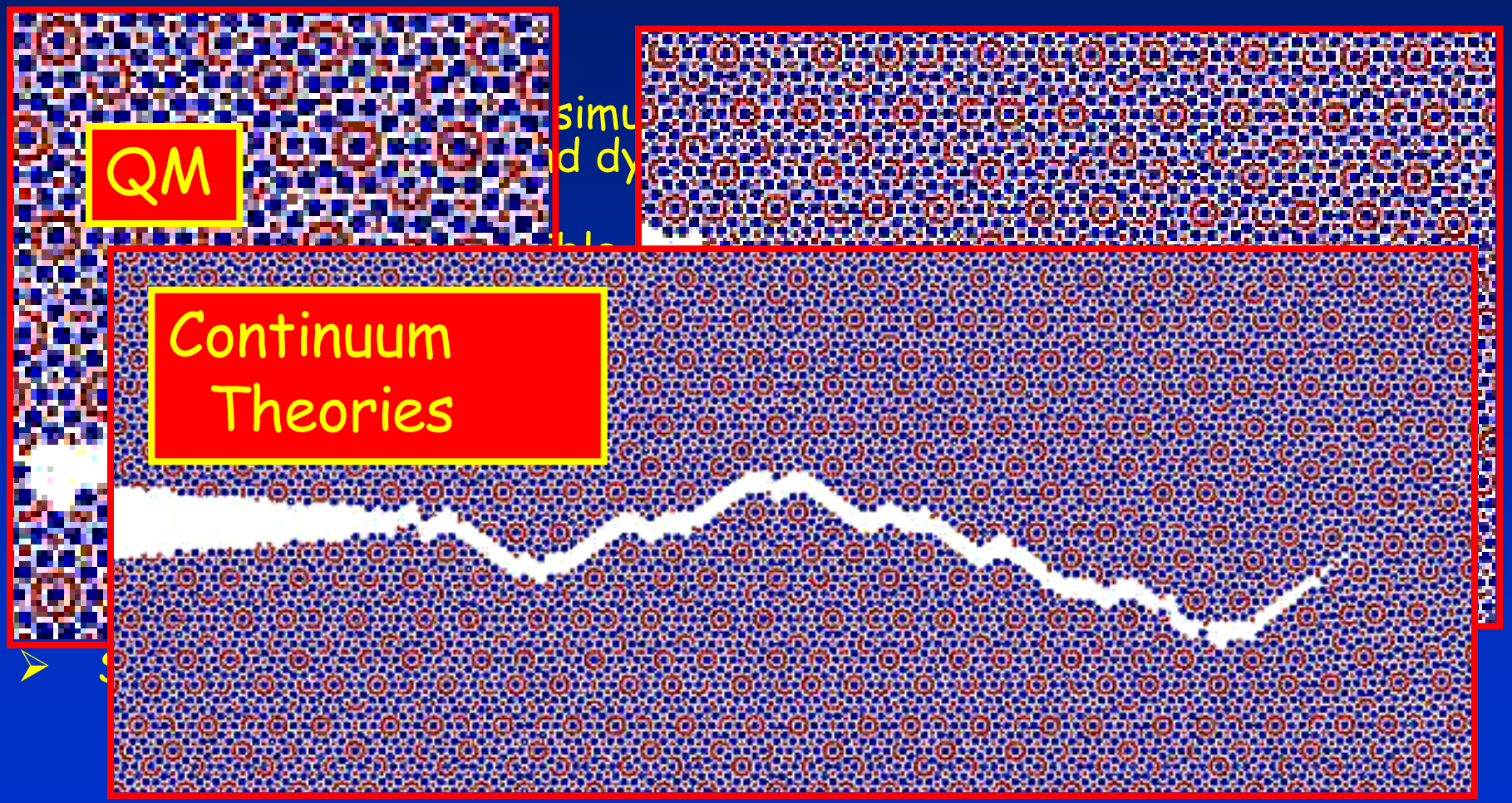


quasi-elastic region



radial distribution function

Summary



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Frohmut Rösch
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Hans-Rainer Trebin Head of Department

Integration of motion

Information about particles:

Masses m_i, positions $\vec{r}_i(t)$, momenta $\vec{p}_i(t), i = 1, \ldots, N$

From $\vec{r}_i(t)$ calculate forces $\vec{f}_i(t) = -\nabla_i V(\vec{r}_1, \ldots, \vec{r}_N)$

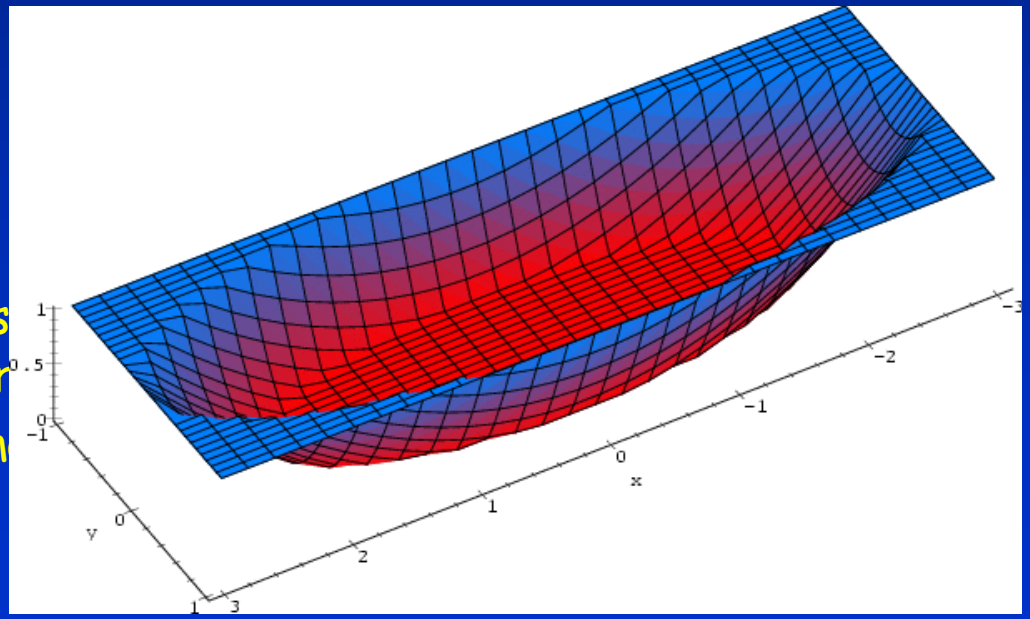
From $\vec{f}_i(t)$ calculate $\vec{p}_i(t)$ via $\frac{d\vec{p}_i}{dt} = \vec{f}_i(t)$

From $\vec{p}_i(t)$ calculate $\vec{r}_i(t)$ via $\frac{d\vec{r}_i}{dt} = \frac{\vec{p}_i(t)}{m_i}$

Simulation control

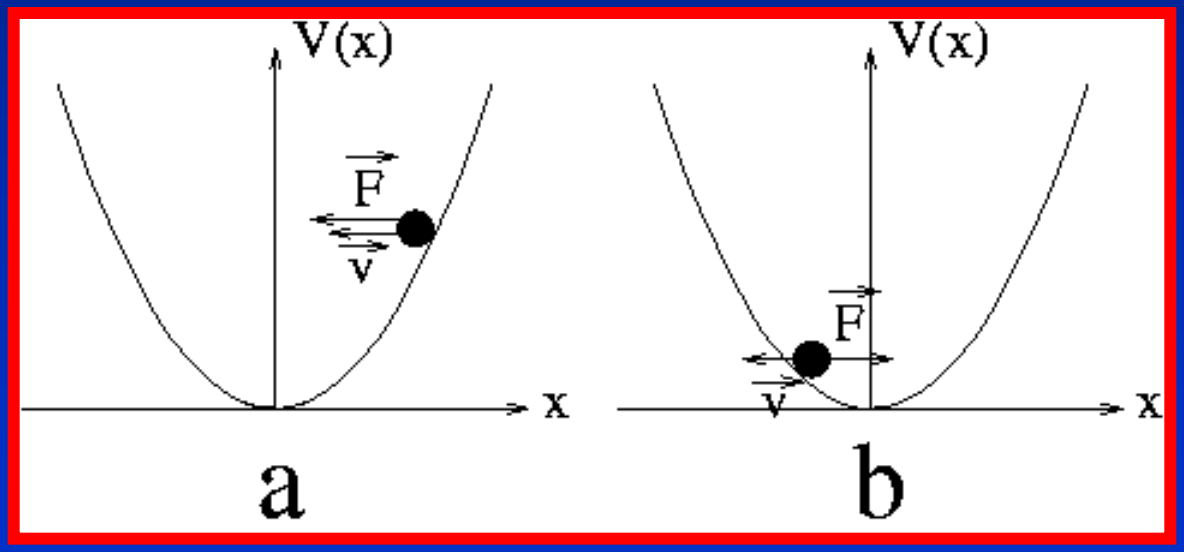
- Equilibrium ensembles: NVE, NVT, NPT
- Non-equilibrium: shear flow, expansion, plastic deformation, crack propagation with stadion-damping
- Stearing of single atoms (fixed, special forces)

- Only atoms with s
  deviation from a r
- Averages over sm

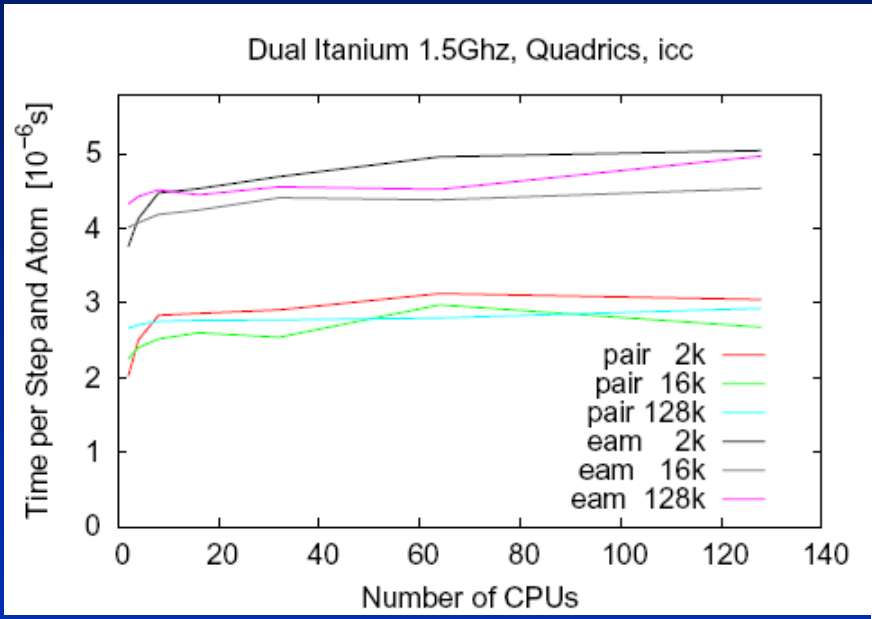


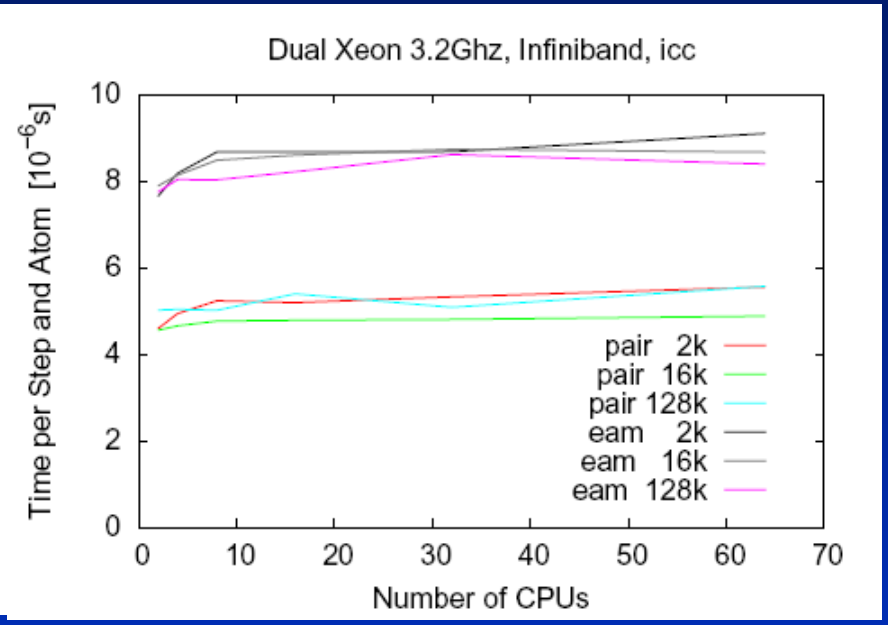
Microconvergence

- Algorithm for energy relaxation
- Rapid cooling mechanism



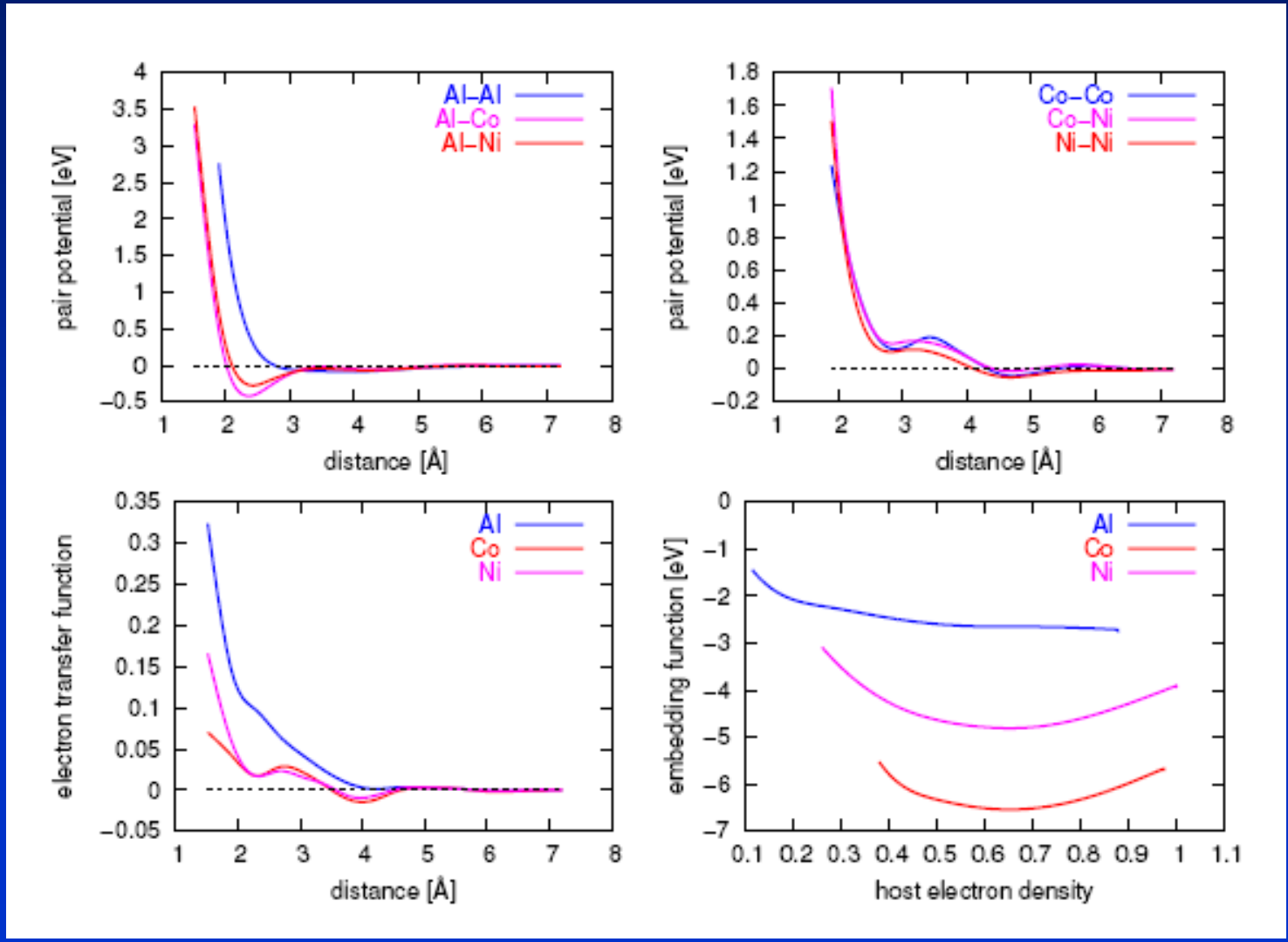
Skalierung





- Hochleistungsnetzwerk mit niedriger Latenz nötig
- Tests auf IBM BlueGene/L: Lineare Skalierung bis zu tausenden von CPUs

EAM potential for Al-Ni-Co



Stillinger-Weber potentials

$$E = \sum_{i<j} V_2(r_{ij}) + \sum_{\substack{i \neq j,k \\ j<k}} V_3(r_{ij}, r_{ik}, r_{jk})$$

$$V_3(r_{ij}, r_{ik}, r_{jk}) = Z f_c(r_{ij}) f_c(r_{ik}) \left(\cos\theta_{jik} + \frac{1}{h}\right)^2$$

Three-body Tersoff potentials

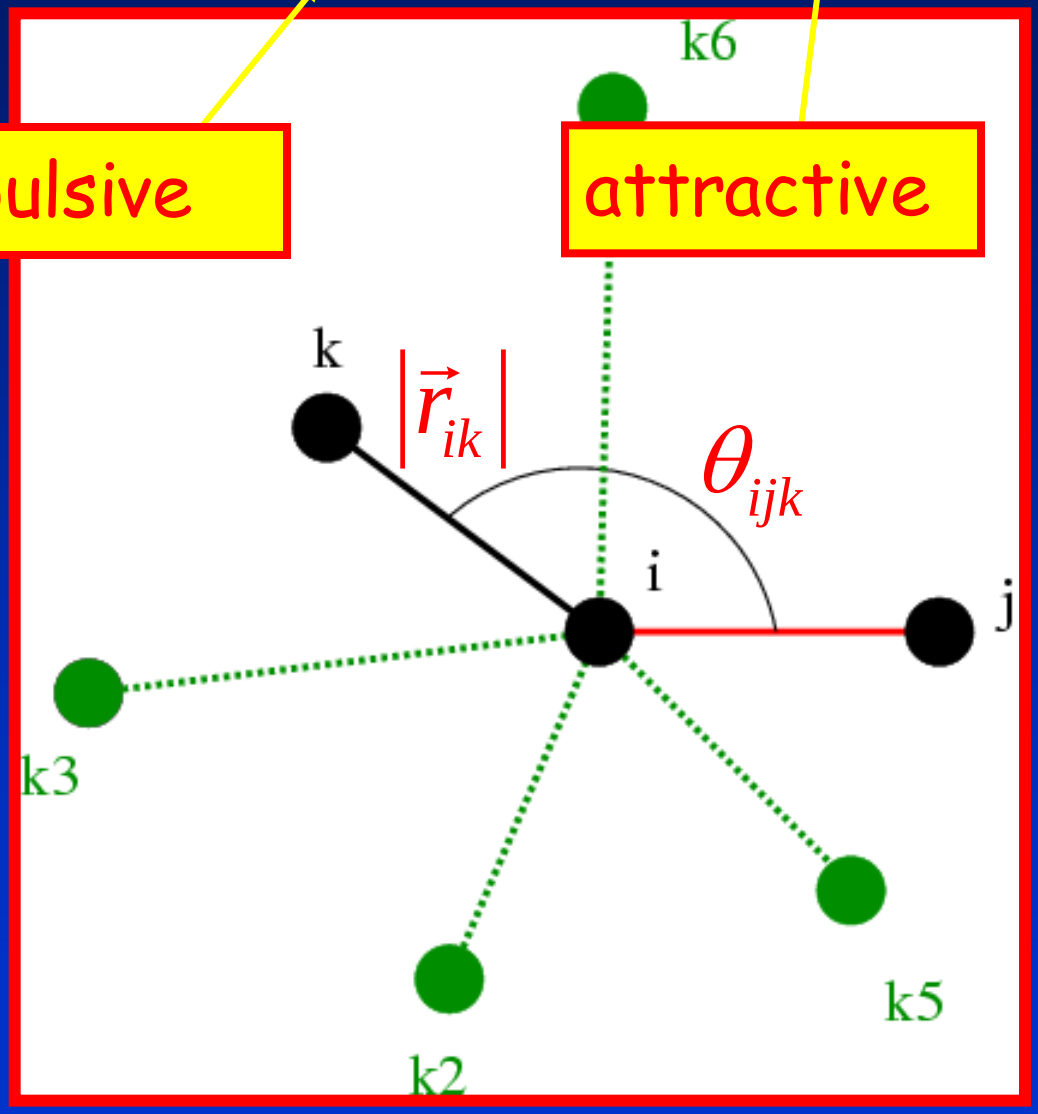
$$\Phi_{ij}\left(\{\vec{r}_n\}\right) = F_R\left(r_{ij}\right) + b_{ij}\left(\{\vec{r}_n\}\right) F_A\left(r_{ij}\right)$$

repulsive

attractive

$b_{ij}\left(\{\vec{r}_n\}\right)$:

Complicated function of number and type of k atoms



Explicit form of Tersoff-potential

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij}$$

$$V_{ij} = f_c(r_{ij}) \left(A_{ij} \exp(-\lambda_{ij} r_{ij}) - b_{ij} B_{ij} \exp(-\mu_{ij} r_{ij}) \right)$$

$$b_{ij} = \chi_{ij} \left(1 + \gamma_i^{n_i} \zeta_{ij}^{n_i} \right)^{-\frac{1}{2n_i}}$$

$$\zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) \omega_{ik} g(\theta_{kij})$$

$$g(\theta_{kij}) = 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{d_i^2 + (h_i - \cos\theta_{kij})^2}$$

$$f_c(r_{ij}) = \begin{cases} 1, r_{ij} < R_{ij} \\ \frac{1}{2} + \frac{1}{2} \cos\left(\frac{\pi (r_{ij} - R_{ij})}{S_{ij} - R_{ij}} \right), R_{ij} < r_{ij} < S_{ij} \\ 0, r_{ij} > S_{ij} \end{cases}$$

Long-range interactions (Coulomb- and polar)

- Ewald sum method
- Reaction field method
- Particle-particle/particle-mesh (PPPM)
- Fast multipole method