Multiscale Simulations of Materials and Structures

Lecture 1.
Molecular Dynamics I

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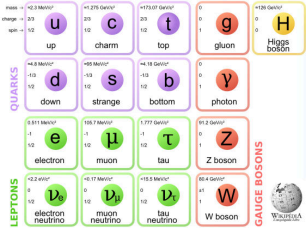
@ Centre des Matériaux (virtually)
February 16, 2021

Outline

Matter constituents

Standard Model



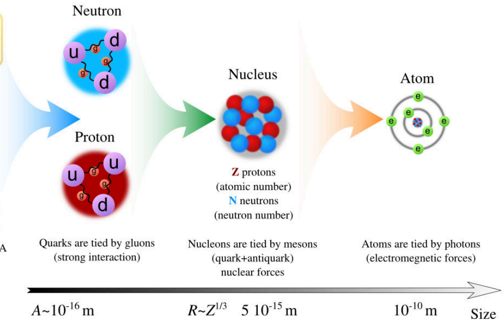
mass → charge → spin →	≈2.3 MeV/c^2 2/3 1/2 u up	≈1.275 GeV/c^2 2/3 1/2 c charm	≈173.07 GeV/c^2 2/3 1/2 t top	0 0 1 g gluon	≈126 GeV/c^2 0 0 H Higgs boson
QUARKS	≈4.8 MeV/c^2 -1/3 1/2 d down	≈95 MeV/c^2 -1/3 1/2 s strange	≈4.18 GeV/c^2 -1/3 1/2 b bottom	0 0 1 γ photon	
	0.511 MeV/c^2 -1 1/2 e electron	105.7 MeV/c^2 -1 1/2 μ muon	1.777 GeV/c^2 -1 1/2 τ tau	91.2 GeV/c^2 0 1 Z Z boson	
LEPTONS	<2.2 eV/c^2 0 1/2 ν_e electron neutrino	<0.17 MeV/c^2 0 1/2 ν_μ muon neutrino	<15.5 MeV/c^2 0 1/2 ν_τ tau neutrino	80.4 GeV/c^2 ±1 1 W W boson	GAUGE BOSONS

Table from WikipediA

QCD

Nuclear physics

Chemistry (QED)



Neutron

Proton

Nucleus

Z protons
(atomic number)
N neutrons
(neutron number)

Atom

Quarks are tied by gluons
(strong interaction)

Nucleons are tied by mesons
(quark+antiquark)
nuclear forces

Atoms are tied by photons
(electromegnetic forces)

$A \sim 10^{-16}$ m

$R \sim Z^{1/3}$ $5\ 10^{-15}$ m

10^{-10} m

Size

Chemical bonds

Nature of bonds :

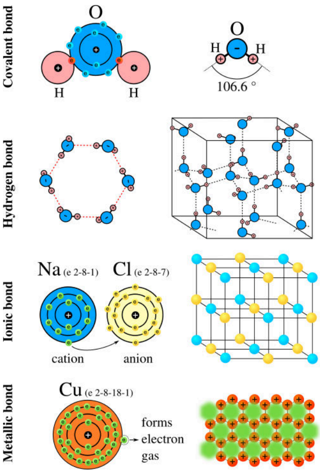
- Electrostatic force
- Electrons sharing mechanism

Strength of bonds :

- Strong (ionic, covalent)
- Weak (hydrogen, van der Waals)

Examples :

- Covalent (H_2O, H_2)
- Hydrogen (H_2O–H_2O, DNA)
- Ionic (NaCl, NaF)
- Metallic (all metals)
- Van der Waals (dipole-dipole e.g. HCl-HCl, induced dipoles)



Linus Pauling "The Nature of the Chemical Bond"
`http://scarc.library.oregonstate.edu/coll/pauling/bond/index.html`

Assemblies

Lattices

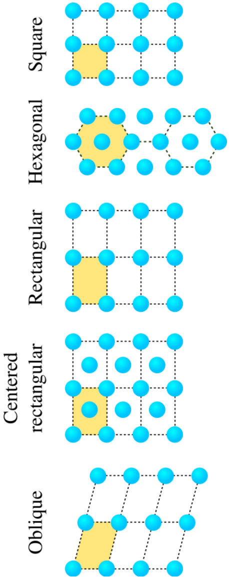
- In 2D : 5 Bravais lattices
- In 3D : 14 Bravais lattices

Molecules

- Diatomic gas (N_2, O_2)
- Ethanol (C_2H_5OH)
- Macromolecules (rubber, DNA, polyethene, protein)

Amorphous

- Silica SiO_2
- Metallic glass



Complexity

- Non-relativistic Schrödinger equation for a single particle in an electric field

$$i\hbar\frac{\partial\Psi(\boldsymbol{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(\boldsymbol{r},t)\right]\Psi(\boldsymbol{r},t),$$

  where Ψ is the wave function, V is particle's potential energy, μ is its reduced mass

- For n particles

$$i\hbar\frac{\partial\Psi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_n,t)}{\partial t} = \left[-\frac{\hbar^2}{2}\left(\frac{\nabla_1^2}{\mu_1}+\dots+\frac{\nabla_n^2}{\mu_n}\right) + V(\boldsymbol{r}_1,\dots,\boldsymbol{r}_n,t)\right]\Psi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_n,t),$$

- Time independent form :

$$E\Psi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_n) = \left[-\frac{\hbar^2}{2}\left(\frac{\nabla_1^2}{\mu_1}+\dots+\frac{\nabla_n^2}{\mu_n}\right) + V(\boldsymbol{r}_1,\dots,\boldsymbol{r}_n)\right]\Psi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_n),$$

- Modern chemistry can solve Schrödinger equation with up to 40-50 electrons (only !).

Density Functional Theory

- The DFT is the most successful approach to compute the electronic structure of matter
  (Nicely presented in `http://www.uam.es/personal_pdi/ciencias/jcuevas/Talks/JC-Cuevas-DFT.pdf`) see also E.A. Carter "Challenges in Modeling Materials Properties Without Experimental Input", Science 321 (2008)
- Applicable from nuclei to solids and fluids :
  molecular structures, vibrational frequencies, energies of atomization, ionization energies, electromagnetic properties, reaction paths, etc.
- Many-particle Schrödinger equation is reduced to minimization of an energy functional with respect to the non-universal functional V (system-dependent part of the total system energy)
- Nobel prize in Chemistry was attributed to Walter Kohn and John Pople for their developments in computational methods in quantum chemistry
  W Kohn, LJ Sham. Self-consistent equations including exchange and correlation effects, Phys Rev, 1965 (37 540 citations)

  RG Parr, W Yang. Density-functional theory of atoms and molecules. Oxford university press, 1989 (16 830 citations)
- Software : e.g. *QuantumEspresso* (`www.quantum-espresso.org`)

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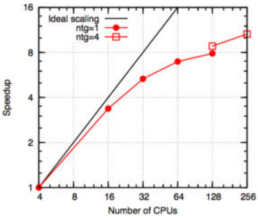
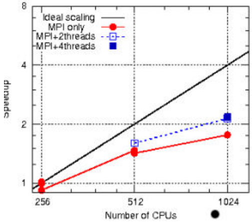


128 Water molecules (1024 electrons) in a cubic box 13.35 Å side, MPI only.



Fragment of an Aβ-peptide in water containing 838 atoms and 2312 electrons in a 22.1×22.9×19.9 $Å^3$ cell : MPI+OpenMP

Simulating bonds

Straightforward in classical mechanics (Coulomb), non-trivial in quantum one (Schrödinger, DFT)

- **Ionic bonds**

Non-trivial (Schrödinger, DFT)

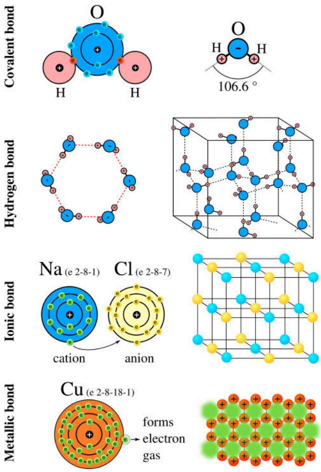
- **Covalent bonds**

If electronic structure of the molecule is well resolved (DFT) then feasible :

- **Hydrogen bonds**
- **Dipole-dipole**
- **Induced dipoles**

If electronic structure of the **lattice** *is well resolved (DFT) then feasible :*

- **Metallic bonds**



MD from the family of Particle Methods

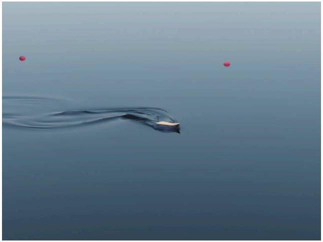
Particle methods

- **SPH**
  Smooth-particle hydrodynamics (fluids, solids)
- **DEM**
  Discrete element method (granular matter)
- Multi-body gravity methods (space scale systems)

Common algorithms

- Search and detection
- Data structure
- Parallelization

Coupled SPH and particle level-set
Losasso, Talton, Kwatra, Fedkiw. IEEE TVCG (2008).



Coupling grid+particle
Zheng, Zhu, Kim, Fedkiw, J. Comp. Phys. (2015)

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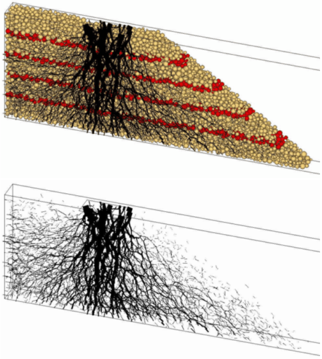


DEM simulation
Fabio Gabrieli (University of Padova)
`geotechlab.wordpress.com`

Examples of simple pair potentials

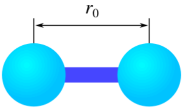
- **Short-range potentials (possible cut-off, fast)**
  - Lennard-Jones potential $U(r_{ij}) = \alpha\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^n - \left(\frac{\sigma}{r_{ij}}\right)^m\right], \quad m < n$
  - Morse potential $U(r_{ij}) = \alpha\left[1 - \exp(-\beta(r_{ij} - r_0)\right]^2$
  - Van der Waals potential $U(r_{ij}) = -\alpha\varepsilon\left(\frac{\sigma}{r_{ij}}\right)^6$
- **Long-range potentials (cut-off prohibited, slow)**
  - Gravitational potential $U(r_{ij}) = -G\frac{m_1m_2}{r_{ij}}$
  - Electrostatic (Coulomb) potential : $U(r_{ij}) = -\frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{r_{ij}}$
  - Elastic (harmonic) potential : $U(r_{ij}) = \frac{k}{2}(r_{ij} - r_0)^2$
- **Regularization**

$$\frac{1}{r_{ij}} \sim \frac{1}{\sqrt{r_{ij}^2 + \varepsilon^2}}$$

Examples of simple molecular models

- Covalent bonds approximated by harmonic potential

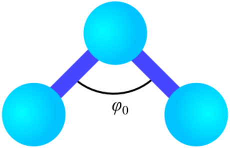
$$V_l(\boldsymbol{r}_1,\boldsymbol{r}_2) = \tfrac{k_l}{2}(|\boldsymbol{r}_1-\boldsymbol{r}_2| - r_0)^2$$



- In-plane angular potential

$$V_a(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) = \tfrac{k_a}{2}(1-\cos(\phi-\phi_0))^2$$

$$V_a(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) \approx \tfrac{k_a}{2}(\phi-\phi_0)^2$$

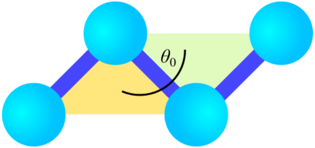


- Torsional potential

$$V_t(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\boldsymbol{r}_4) \approx \tfrac{k_t}{2}(\theta-\theta_0)^2$$

- Intra-molecular potential

$$V_m(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\ldots,\boldsymbol{r}_n) =$$
$$\tfrac{1}{2}\left(\textstyle\sum_{i=1}^{n-1} V_l(r^i) + \sum_{i=1}^{n-2} V_a(\phi^i) + \sum_{i=1}^{n-3} V_t(\theta^i)\right)$$



- **Total potential is complemented by an interaction potential with other molecules**

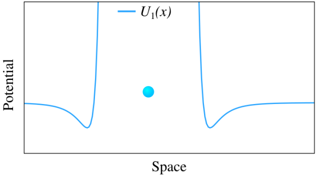
$$V(\boldsymbol{r}) = \sum_{\text{molecules}} V_m(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_n) + V_i(\boldsymbol{r})$$

Potentials in LAMMPS

- **pairwise potentials** : Lennard-Jones, Buckingham, Morse, Born-Mayer-Huggins, Yukawa, soft, class 2 (COMPASS), hydrogen bond, tabulated
- **charged pairwise potentials :** Coulombic, point-dipole
- **many-body potentials :** EAM, Finnis/Sinclair EAM, modified EAM (MEAM), embedded ion method (EIM), EDIP, ADP, Stillinger-Weber, Tersoff, REBO, AIREBO, ReaxFF, COMB, SNAP, Streitz-Mintmire, 3-body polymorphic
- **long-range interactions for charge, point-dipoles, and LJ dispersion :** Ewald, Wolf, PPPM (similar to particle-mesh Ewald)
- **polarization models :** QEq, core/shell model, Drude dipole model
- **coarse-grained potentials :** DPD, GayBerne, REsquared, colloidal, DLVO
- **mesoscopic potentials :** granular, Peridynamics, SPH
- **electron force field :** eFF, AWPMD
- **bond potentials :** harmonic, FENE, Morse, nonlinear, class 2, quartic (breakable)
- **angle potentials :** harmonic, CHARMM, cosine, cosine/squared, cosine/periodic, class 2 (COMPASS)
- **dihedral potentials :** harmonic, CHARMM, multi-harmonic, helix, class 2 (COMPASS), OPLS
- **improper potentials :** harmonic, cvff, umbrella, class 2 (COMPASS)
- **polymer potentials :** all-atom, united-atom, bead-spring, breakable
- **water potentials :** TIP3P, TIP4P, SPC
- **implicit solvent potentials :** hydrodynamic lubrication, Debye
- **hybrid potentials :** multiple pair, bond, angle, dihedral, improper potentials can be used in one simulation
- **overlaid potentials :** superposition of multiple pair potentials

Many-body Hamiltonian system

General algorithm



- Potential :
  $U(r_{ij})$
- System pair potential :
  $$V(\boldsymbol{r}) = \sum_{\forall i,j:\, i<j} U(|\boldsymbol{r}_i - \boldsymbol{r}_j|)$$
- Compute force $\boldsymbol{f}_0$ on particle $\boldsymbol{r}_0$:
  $\boldsymbol{F}_0 = -\nabla_{\boldsymbol{r}_0} V(\boldsymbol{r}) = -\sum_{j\neq 0} \nabla_{\boldsymbol{r}_0} U(|\boldsymbol{r}_0 - \boldsymbol{r}_j|)$
- 2^{nd} Newton's law :
  $\ddot{\boldsymbol{r}}_0 = \frac{1}{m_0}\boldsymbol{F}_0$
- Integrate in time :
  $\boldsymbol{r}_0(t) \to \boldsymbol{r}_0(t+\Delta t)$

Properties :

- Energy conservation
  $$E = \underbrace{\frac{1}{2}\sum_i m_i \dot{\boldsymbol{r}}_i^2}_{Kinetic} + \underbrace{V(\boldsymbol{r})}_{Potential}$$

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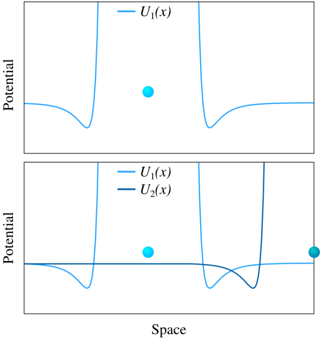

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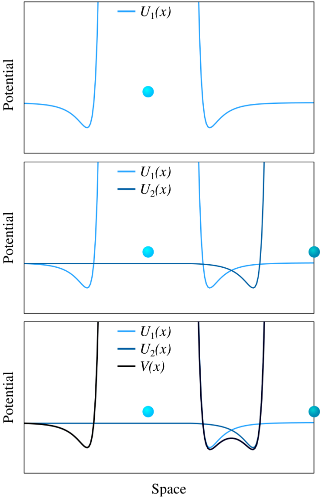

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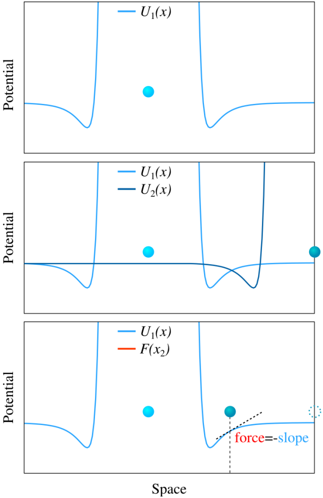

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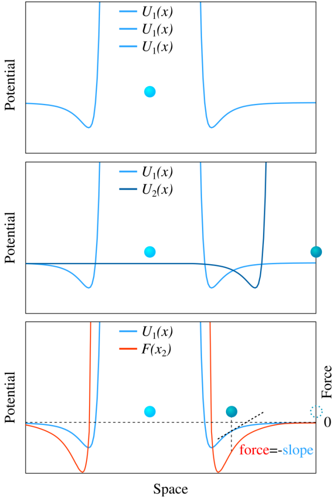

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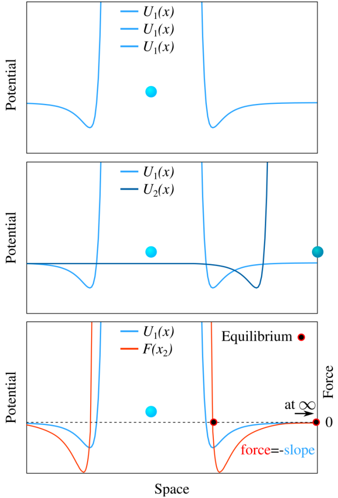


Example : Lennard-Jones potential

Example :

- Lennard-Jones 6-12 (LJ 6-12) :

$$U(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

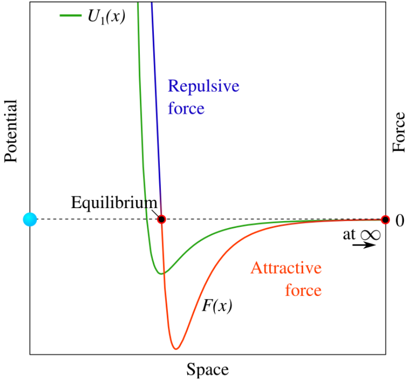
- Force :

$$\boldsymbol{F}_i(\boldsymbol{r}_i, \boldsymbol{r}_j) = -\nabla U(r_{ij}) =$$

$$= 24\varepsilon\left(\frac{\sigma}{r_{ij}}\right)^{6}\left[1 - 2\left(\frac{\sigma}{r_{ij}}\right)^{6}\right]\frac{\boldsymbol{r}_j - \boldsymbol{r}_i}{r_{ij}^2}$$

- Equilibrium :
  - At $T = 0$ K : $r^e_{ij} = 2^{1/6}\sigma$
  - At $T > 0$: $r^e_{ij}(T) > 2^{1/6}\sigma$
- Stable lattice : hcp (or fcc (111))
- Parameters :

σ - length units ~ lattice spacing
ε - energy units ~ bonding energy.



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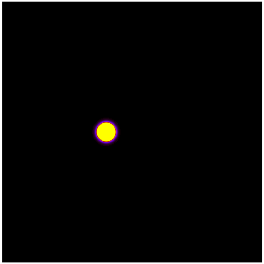
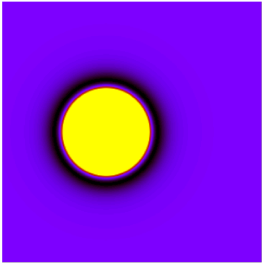
Particles



Potential



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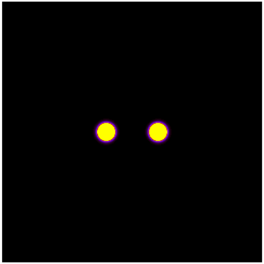
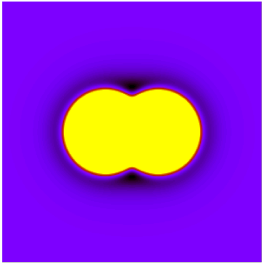


Potential



Example : Lennard-Jones potential

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- Lennard-Jones 6-12 (LJ 6-12) :

$$U(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

- Force :

$$\boldsymbol{F}_i(\boldsymbol{r}_i,\boldsymbol{r}_j) = -\nabla U(r_{ij}) =$$

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- Equilibrium :
  - At $T = 0$ K : $r^e_{ij} = 2^{1/6}\sigma$
  - At $T > 0$: $r^e_{ij}(T) > 2^{1/6}\sigma$
- Stable lattice : hcp (or fcc (111))
- Parameters :

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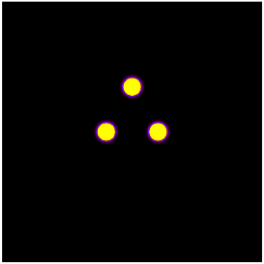

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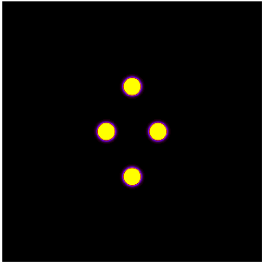

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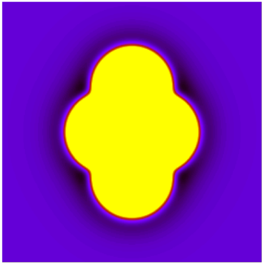

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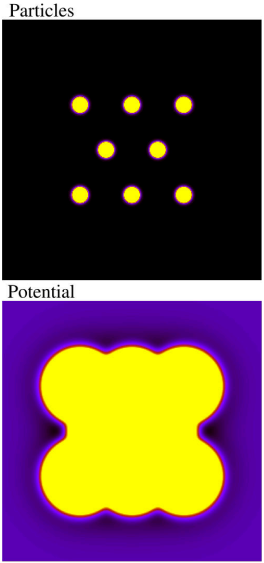

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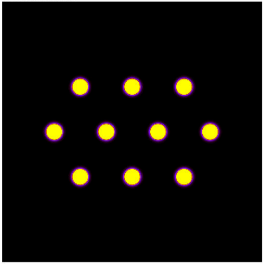

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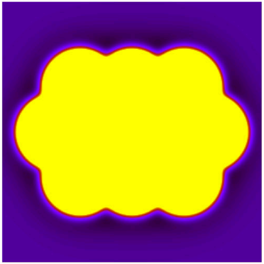

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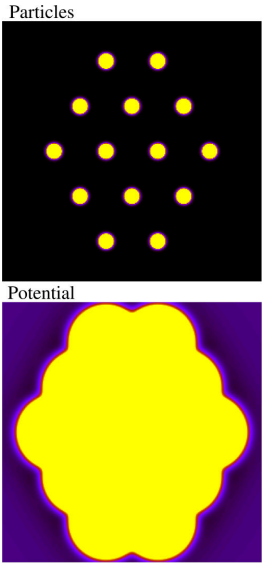


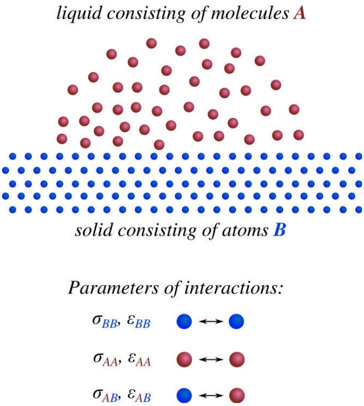
Mixing rule

- Consider a system containing 2 different atoms (molecules) : A, B
- We know ε_{AA}, σ_{AA} and ε_{BB}, σ_{BB}
- To compute energy and forces between atoms A and B we need σ_{AB} and ε_{AB}
- The classical mixing rule by Lorentz-Berthelot[1] :

$$\sigma_{AB} = \frac{1}{2}(\sigma_{AA} + \sigma_{BB})$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_{AA}\varepsilon_{BB}}$$

- From algorithmic point of view one needs to check atom types
- For a liquid drop on surface, values of σ_{AB} and ε_{AB} can be obtained from the macroscopic value of the contact angle



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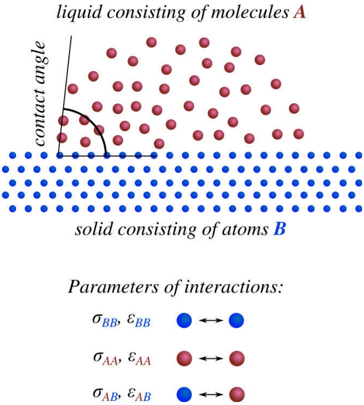


Short-range potentials and a cutoff

- Short-range potential

  $$V \sim \frac{1}{r_{ij}^{\alpha}}, \quad \alpha > \mathrm{dim}$$

- System pair potential :

  $$V(\boldsymbol{r}) = \sum_{\forall i,j:\, i<j} U(|\boldsymbol{r}_i - \boldsymbol{r}_j|)$$

- Complexity of the force evaluation : $O(N^2)$
- First simplification, for two particles :

  $$\boldsymbol{F}_{ij} = -\boldsymbol{F}_{ji}$$

- Critical simplification : **cutoff radius** r_{cut} :

  $$U(r_{ij}) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], & \text{if } r_{ij} \le r_{\mathrm{cut}} \\ 0, & \text{if } r_{ij} > r_{\mathrm{cut}} \end{cases}$$

- Cutoff value : $r_{\mathrm{cut}} > 2.5\sigma$
- Attention : truncated potential is discontinuous, additional errors are introduced.

Multi-body potentials

Example **EAM** : Embedded-Atom Model/Method

- Pair-potential does not work for defects, free surfaces and fracture surfaces, impurities (hydrogen embrittlement), etc.
- In the EAM, each atom in a solid is considered as an impurity embedded in a host made of other atoms (like in Eshelby problem and self-consistent homogenization)
- Multi-body potential EAM :

$$E_{tot} = \sum_i F(\rho_{h,i}) + \sum_{i,j,i\neq j} \phi_{ij}(R_{ij})$$

- With electron densities assumed to be $\rho_{h,i} = \sum_{j\neq i} \rho^a_j(R_{ij})$
- Force acting on atom i :

$$\boldsymbol{F}_i = -\nabla E_i = -\sum_j \frac{\partial F}{\partial \rho_j}\frac{\partial \rho_j}{\partial R_{ij}} - \sum_j \frac{\partial \phi_{ij}}{\partial R_{ij}}$$

[A] Daw, M. S., & Baskes, M. I. (1984). Embedded-atom method . . .. Phys Rev B, 29(12), 6443.

[B] Foiles, S. M., Baskes, M. I., & Daw, M. S. (1986). Embedded-atom-method functions . . .. Phys Rev B, 33(12), 7983.

Multi-body potentials II

Define functions $F(\rho), \rho(R), \phi(R)$

- Functions are defined in top-bottom fashion, to fit macroscopic quantities
- The lattice constants are

  $$A_{ij} = -F'(\bar\rho)V_{ij}, V_{ij} = \sum_m \rho'_m a_i^m a_j^m / a^m, A_{ij} = 0.5 \sum_m \phi'_m a_i^m a_j^m / a^m$$

  where a^m are distances between atoms and a_i^m is the ith-component of the vector-distance
- Elastic constants

  $$C_{ijkl} = (B_{ijkl} + F'(\bar\rho)W_{ijkl} + F''(\bar\rho)V_{ij}V_{kl})/\Omega_0$$

  with $B_{ijkl} = 0.5 \sum_m (\phi''_m - \phi'_m / a^m) a_i^m a_j^m a_k^m a_l^m / (a^m)^2$
  $W_{ijkl} = \sum_m (\rho''_m - \rho'_m / a^m) a_i^m a_j^m a_k^m a_l^m / (a^m)^2$
- Sublimation energy

  $$E_s = -\left(F(\bar\rho) + \bar\phi/2\right)$$
- Vacancy-formation energy is

  $$E_{1V}^V = -\bar\phi/2 + \sum_m (F(\bar\rho - \rho_m) - F(\bar\rho)) + E_{relax}$$

Multi-body potentials III

- From pure metal to alloy
- Need to compute ϕ_{ij} if we know ϕ_{ii} and ϕ_{ij} as :

$$\phi_{ij}(r) = Z_i(r)Z_j(r)/r,$$

with Z being an effective charge of the atom

Testing of resulting properties[B,C]

- Fracture toughness
- Formation volume and migration density of vacancies / divacancies / self-interstitials
- Surface energies of different faces
- Segregation energy of substitutional impurities
- Phonon frequencies
- Gibbs free energy (T)
- Dislocation properties

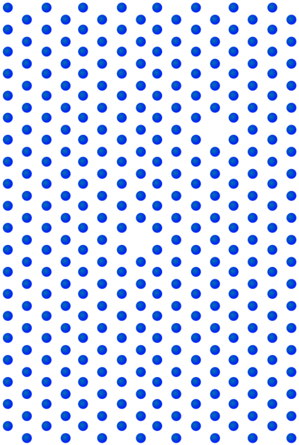
[B] Foiles, S. M., Baskes, M. I., & Daw, M. S. (1986). Embedded-atom-method functions . . .. Phys Rev B, 33(12), 7983.

[C] Daw, M. S., Foiles, S. M., & Baskes, M. I. (1993). The embedded-atom . Materials Science Reports, 9(7-8), 251-310.

Algorithm : linked-cell method

- Create a spatial grid $d \geq r_{\text{cut}}$
- Every cell contains a list of particles and a list of neighbouring cells
- Forces are evaluated in the cell and with respect to the neighbouring cells
- 3^{rd} Newton's law is used

  Instead of checking 8 neighbouring cells, we check only 4.



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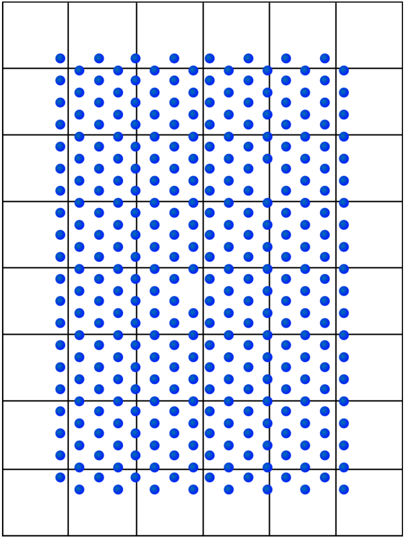

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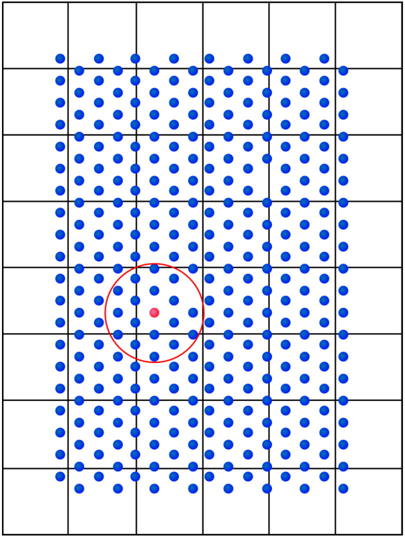

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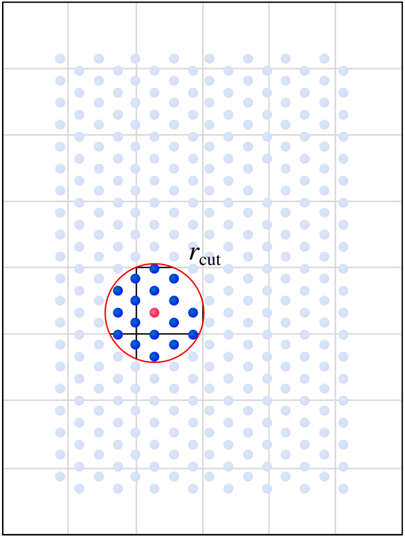

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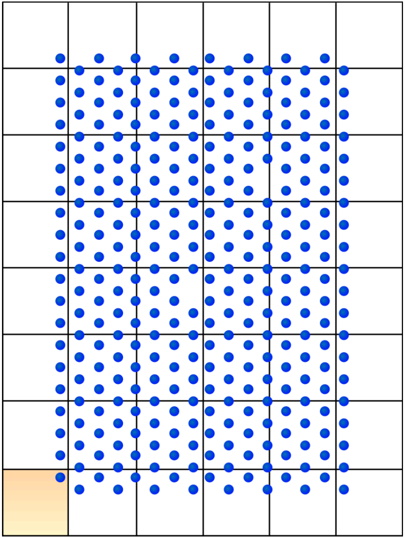

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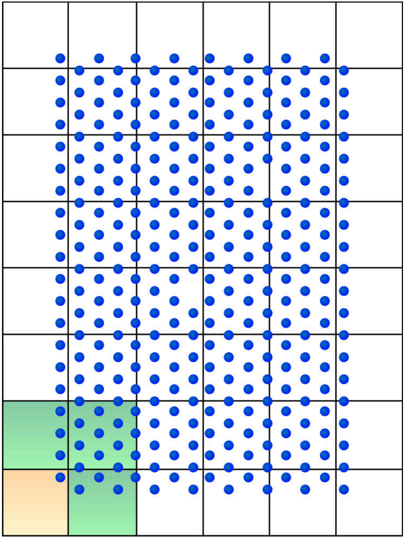

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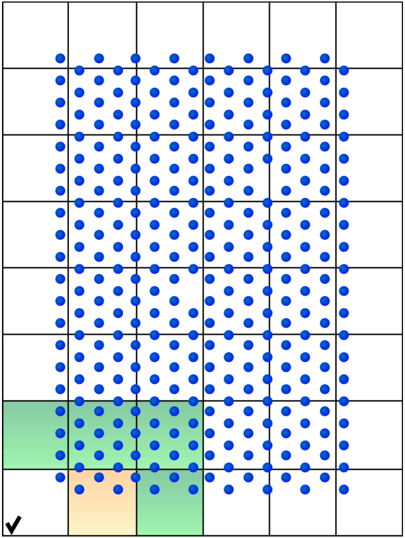

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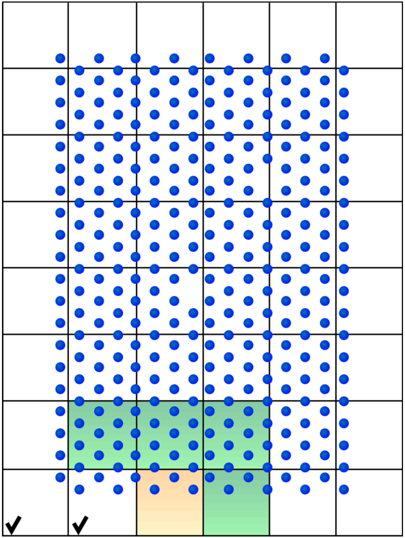

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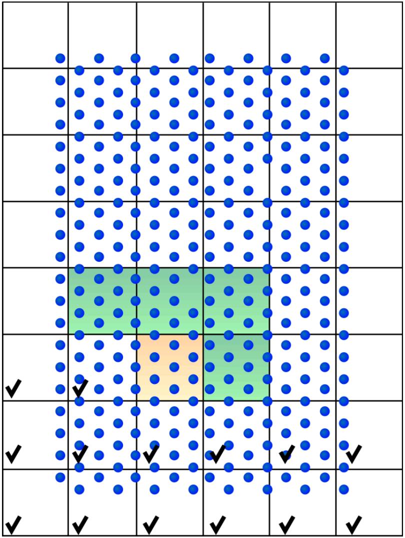

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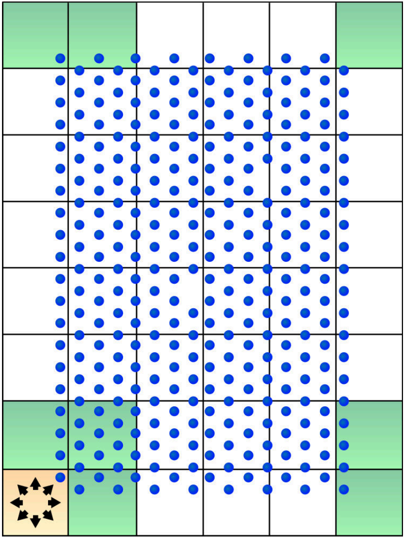
- Case of periodic BC



Time integration : explicit Euler

- Initial value problem

$$\begin{cases} M\ddot{\boldsymbol{X}}(t) = \boldsymbol{F}(\boldsymbol{X}) \\ \boldsymbol{X}(0) = \boldsymbol{X}_0, \quad \dot{\boldsymbol{X}}(0) = \dot{\boldsymbol{X}}_0 \end{cases}$$

- Straight forward approach (**explicit Euler**)

  Compute : $\boldsymbol{f}_i(\boldsymbol{x}(t))$

$$m\ddot{\boldsymbol{x}}_i = \boldsymbol{f}_i$$

$$m\frac{\dot{\boldsymbol{x}}_i(t+\Delta t)-\dot{\boldsymbol{x}}_i(t)}{\Delta t} = \boldsymbol{f}_i$$

  Compute :

$$\boxed{\dot{\boldsymbol{x}}_i(t+\Delta t) = \dot{\boldsymbol{x}}_i(t) + \frac{\Delta t}{m_i}\boldsymbol{f}_i}$$

$$\dot{\boldsymbol{x}}_i(t+\Delta t) = \frac{\boldsymbol{x}_i(t+\Delta t)-\boldsymbol{x}_i(t)}{\Delta t}$$

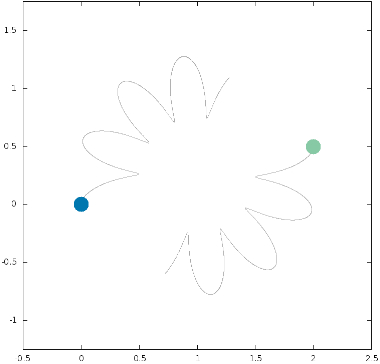
  Compute :

$$\boxed{\boldsymbol{x}_i(t+\Delta t) = \boldsymbol{x}_i(t) + \dot{\boldsymbol{x}}_i(t)\Delta t}$$

- Let's see how fast it diverges

Example : $\sigma = 1, \varepsilon = 1, m = 1, v_0 = 0.2$

$\Delta t = 0.00001$



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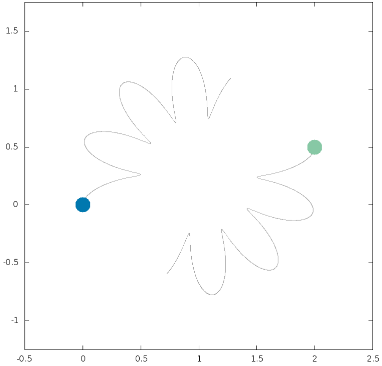
$\Delta t = 0.00005$



Time integration : explicit Euler

- Initial value problem

$$\begin{cases} M\ddot{X}(t) = F(X) \\ X(0) = X_0, \quad \dot{X}(0) = \dot{X}_0 \end{cases}$$

- Straight forward approach (**explicit Euler**)

  Compute : $f_i(x(t))$

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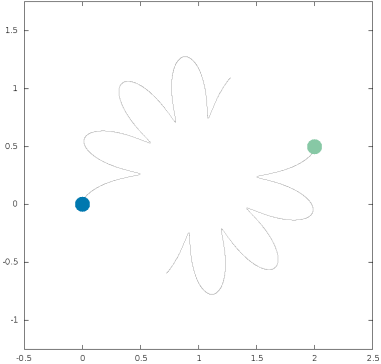

Time integration : semi-implicit Euler

- Initial value problem

$$\begin{cases} M\ddot{\boldsymbol{X}}(t) = \boldsymbol{F}(\boldsymbol{X}) \\ \boldsymbol{X}(0) = \boldsymbol{X}_0, \quad \dot{\boldsymbol{X}}(0) = \dot{\boldsymbol{X}}_0 \end{cases}$$

- **A better approach (semi-implicit Euler)**

Compute : $\boldsymbol{f}_i(\boldsymbol{x}(t))$

$$m\ddot{\boldsymbol{x}}_i = \boldsymbol{f}_i$$

$$m\frac{\dot{\boldsymbol{x}}_i(t+\Delta t)-\dot{\boldsymbol{x}}_i(t)}{\Delta t} = \boldsymbol{f}_i$$

Compute :

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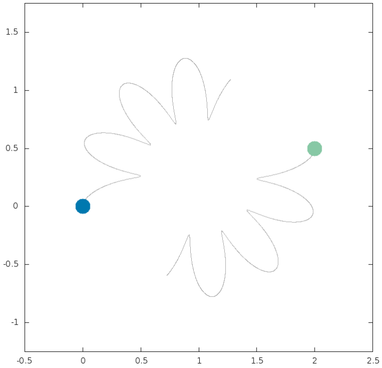
Compute :

$$\boxed{\boldsymbol{x}_i(t+\Delta t) = \boldsymbol{x}_i(t) + \dot{\boldsymbol{x}}_i(t+\Delta t)\Delta t}$$

- Symplectic integrator !
  In average it preserves the energy.

Example : $\sigma = 1, \varepsilon = 1, m = 1, v_0 = 0.2$

$\Delta t = 0.01$



Time integration : semi-implicit Euler

- Initial value problem

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- **A better approach** (**semi-implicit Euler**)

  Compute : $\boldsymbol{f}_i(\boldsymbol{x}(t))$

$$m\ddot{\boldsymbol{x}}_i = \boldsymbol{f}_i$$

$$m\frac{\dot{\boldsymbol{x}}_i(t+\Delta t)-\dot{\boldsymbol{x}}_i(t)}{\Delta t} = \boldsymbol{f}_i$$

  Compute :

$$\boxed{\dot{\boldsymbol{x}}_i(t+\Delta t) = \dot{\boldsymbol{x}}_i(t) + \frac{\Delta t}{m_i}\boldsymbol{f}_i}$$

$$\dot{\boldsymbol{x}}_i(t+\Delta t) = \frac{\boldsymbol{x}_i(t+\Delta t)-\boldsymbol{x}_i(t)}{\Delta t}$$

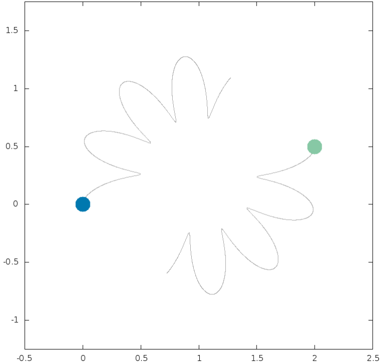
  Compute :

$$\boxed{\boldsymbol{x}_i(t+\Delta t) = \boldsymbol{x}_i(t) + \dot{\boldsymbol{x}}_i(t+\Delta t)\Delta t}$$

- Symplectic integrator ! In average it preserves the energy.

Example : $\sigma = 1, \varepsilon = 1, m = 1, v_0 = 0.2$

$\Delta t = 0.02$



Time integration : semi-implicit Euler

- Initial value problem

$$\begin{cases} M\ddot{\boldsymbol{X}}(t) = \boldsymbol{F}(\boldsymbol{X}) \\ \boldsymbol{X}(0) = \boldsymbol{X}_0, \quad \dot{\boldsymbol{X}}(0) = \dot{\boldsymbol{X}}_0 \end{cases}$$

- **A better approach** (**semi-implicit Euler**)

Compute : $\boldsymbol{f}_i(\boldsymbol{x}(t))$

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Compute :

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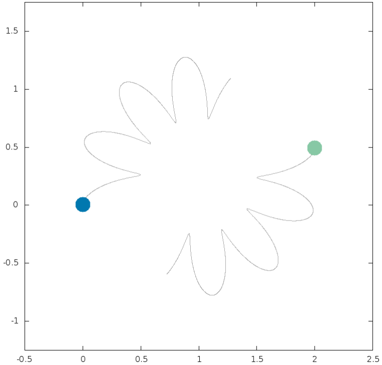
Compute :

$$\boxed{\boldsymbol{x}_i(t+\Delta t) = \boldsymbol{x}_i(t) + \dot{\boldsymbol{x}}_i(t+\Delta t)\Delta t}$$

- Symplectic integrator !
In average it preserves the energy.

Example : $\sigma = 1, \varepsilon = 1, m = 1, v_0 = 0.2$

$\Delta t = 0.05$



Time integration : semi-implicit Euler

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$$\begin{cases} M\ddot{\boldsymbol{X}}(t) = \boldsymbol{F}(\boldsymbol{X}) \\ \boldsymbol{X}(0) = \boldsymbol{X}_0, \quad \dot{\boldsymbol{X}}(0) = \dot{\boldsymbol{X}}_0 \end{cases}$$

- **A better approach** (**semi-implicit Euler**)

  Compute : $\boldsymbol{f}_i(\boldsymbol{x}(t))$

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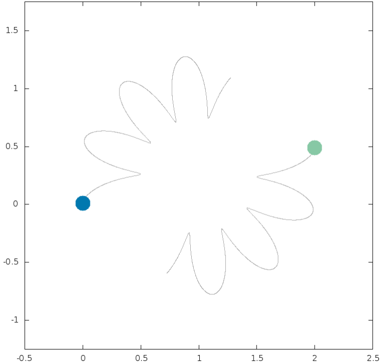
  Compute :

$$\boxed{\boldsymbol{x}_i(t+\Delta t) = \boldsymbol{x}_i(t) + \dot{\boldsymbol{x}}_i(t+\Delta t)\Delta t}$$

- Symplectic integrator ! In average it preserves the energy.

Example : $\sigma = 1, \varepsilon = 1, m = 1, v_0 = 0.2$

$\Delta t = 0.10$



Time integration : Verlet method

- Initial value problem

$$\begin{cases} M\ddot{\boldsymbol{X}}(t) = \boldsymbol{F}(\boldsymbol{X}) \\ \boldsymbol{X}(0) = \boldsymbol{X}_0, \quad \dot{\boldsymbol{X}}(0) = \dot{\boldsymbol{X}}_0 \end{cases}$$

- Velocity-Verlet method[1]

Compute : $\boxed{\boldsymbol{x}_i(t+\Delta t) = \boldsymbol{x}_i(t) + \left[\dot{\boldsymbol{x}}_i(t) + \frac{\Delta t}{2m_i}\boldsymbol{f}_i(t)\right]\Delta t}$

Store $\boldsymbol{f}_i(t)$

Compute : $\boldsymbol{f}_i(t+\Delta t) = \boldsymbol{f}_i(\boldsymbol{x}(t+\Delta t))$

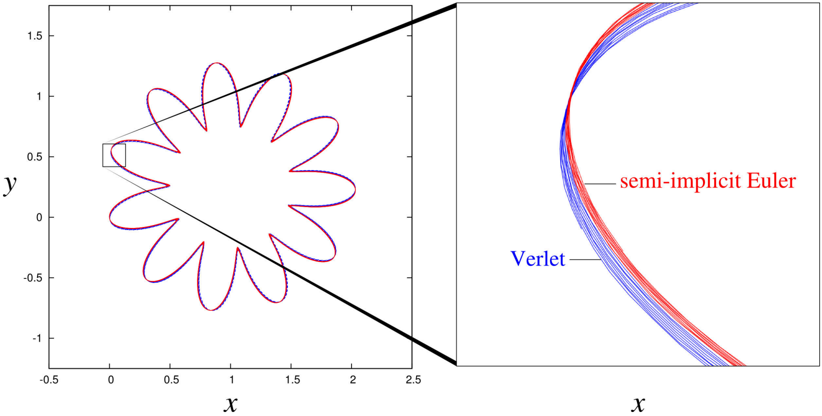
Compute : $\boxed{\dot{\boldsymbol{x}}_i(t+\Delta t) = \dot{\boldsymbol{x}}_i(t) + \frac{\Delta t}{2m_i}\left[\boldsymbol{f}_i(t) + \boldsymbol{f}_i(t+\Delta t)\right]}$

- Requires additional storage for $\boldsymbol{f}_i(t)$.
- Symplectic integrator !
  In average it preserves the energy.

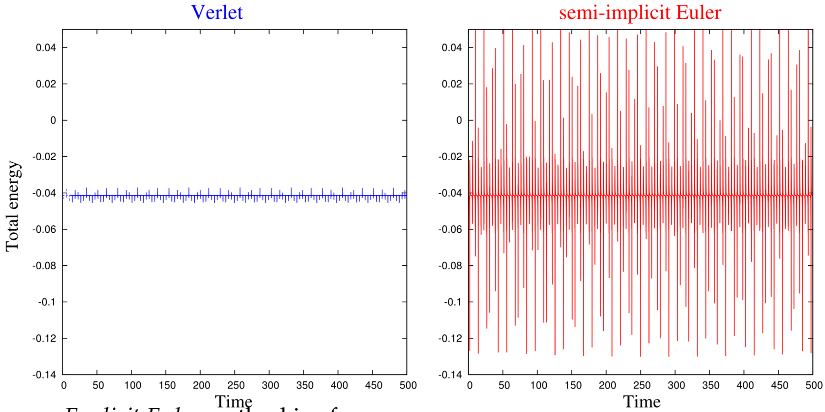
---

[1] Verlet L. “Computer Experiments on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules”. Phys Rev (1967)

Comparison Verlet vs Euler



Comparison Verlet vs Euler



- *Explicit Euler* method is of no use
- Both *Velocity-Verlet* method and *semi-implicit Euler* methods are simplectic, i.e. in average they preserve the system energy
- *Velocity-Verlet* has better energy preserving properties

General algorithm

- **Initialize :**
  1. distribute particles $x_i(0)$ for $i \in [0, N]$
  2. assign initial velocity field $\dot{x}_i(0)$
  3. assign boundary conditions
  4. evaluate forces on particles $f_i(x(0))$
- **Integrate in time (velocity Verlet method) :**
  1. $t \longrightarrow t + \Delta t$
  2. update boundary conditions
  3. compute new positions
     $$x_i(t+\Delta t) = x_i(t) + \left[\dot{x}_i(t) + \frac{\Delta t}{2m_i} f_i(t)\right]\Delta t$$
  4. store forces $f_i(t)$
  5. evaluate new forces (using, e.g., linked-cell method) $f_i(x(t+\Delta t))$
  6. compute new velocities
     $$\dot{x}_i(t+\Delta t) = \dot{x}_i(t) + \frac{\Delta t}{2m_i}\left[f_i(t) + f_i(t+\Delta t)\right]$$
  7. if needed store data and compute energies.

General algorithm

- **Initialize :**
  1. **distribute particles $x_i(0)$ for $i \in [0, N]$**
  2. assign initial velocity field $\dot{x}_i(0)$
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  6. compute new velocities

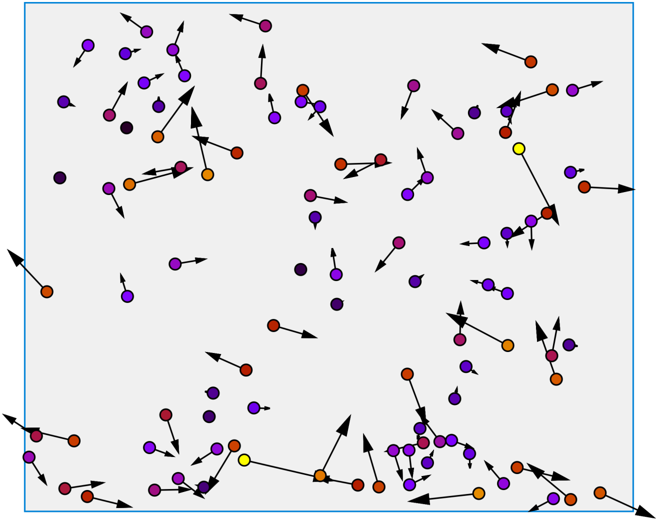
     $$\dot{x}_i(t+\Delta t) = \dot{x}_i(t) + \frac{\Delta t}{2m_i}\left[f_i(t) + f_i(t+\Delta t)\right]$$
  7. if needed store data and compute energies.

Boundary conditions I

Animation `pbc.gif`

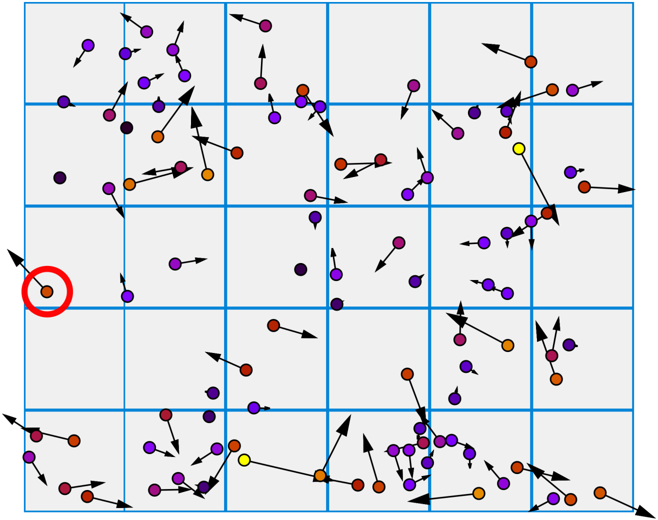
Boundary conditions I

- Periodic boundary conditions



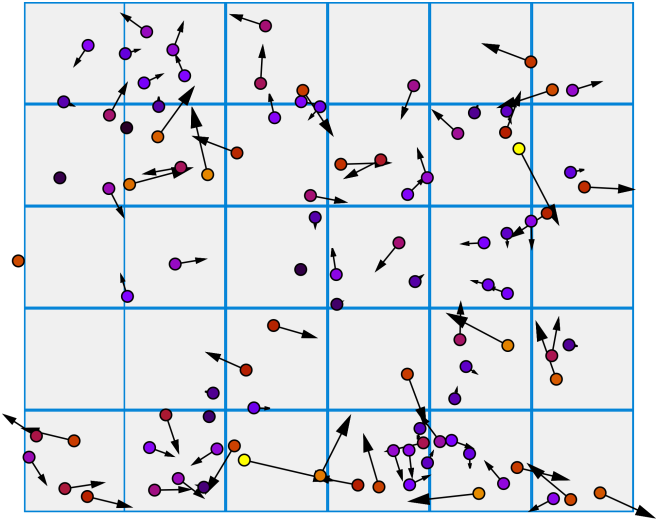
Boundary conditions I

- Periodic boundary conditions



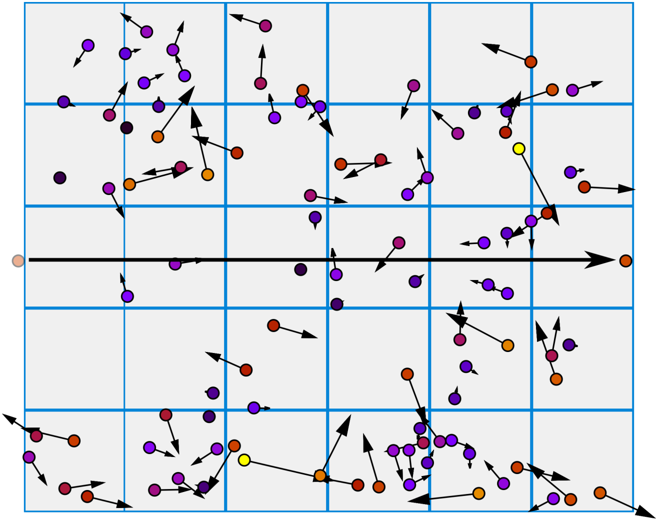
Boundary conditions I

- Periodic boundary conditions



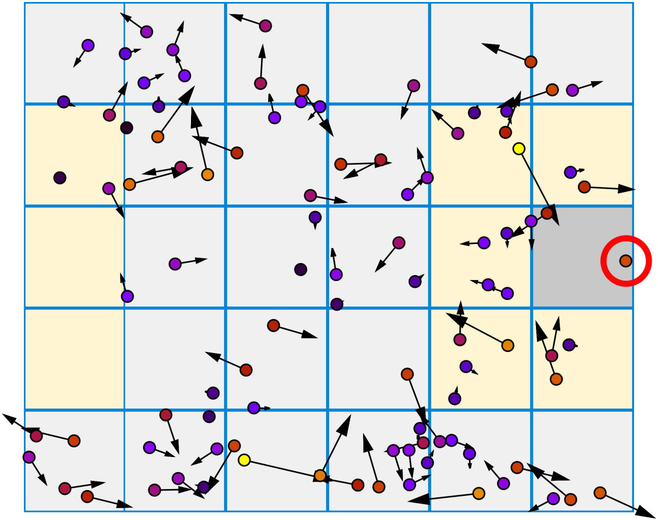
Boundary conditions I

- Periodic boundary conditions



Boundary conditions I

- Periodic boundary conditions



Boundary conditions II

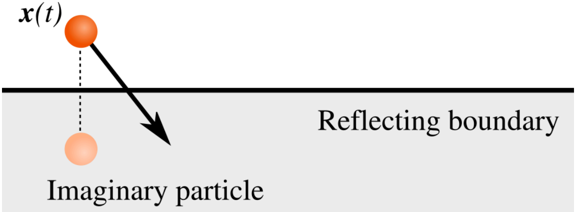
Animation `rbc.gif`

Boundary conditions II

- Reflecting boundary conditions

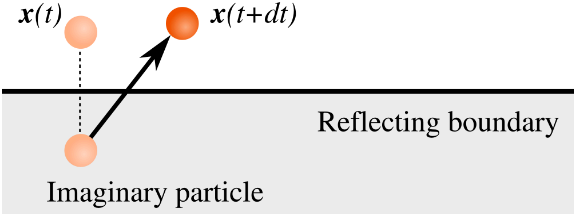
Boundary conditions II

- Reflecting boundary conditions



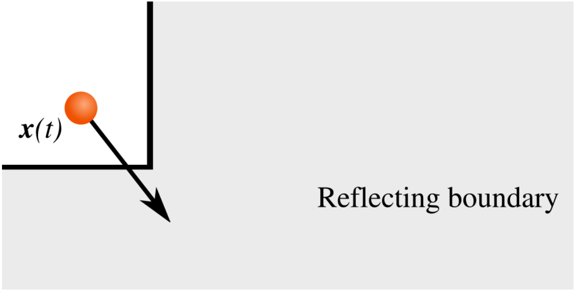
Boundary conditions II

- Reflecting boundary conditions



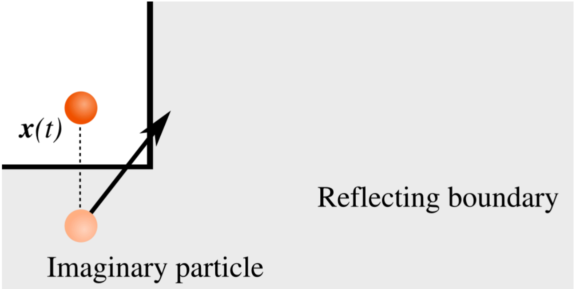
Boundary conditions II

- Reflecting boundary conditions



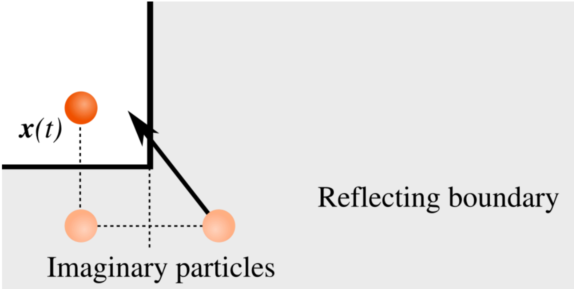
Boundary conditions II

- Reflecting boundary conditions



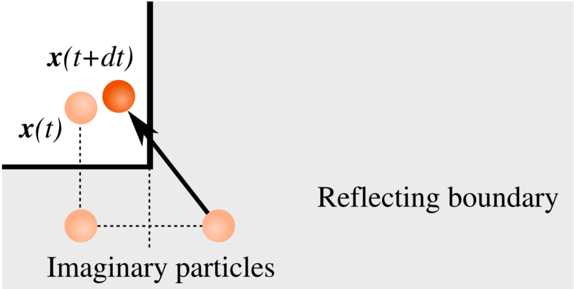
Boundary conditions II

- Reflecting boundary conditions



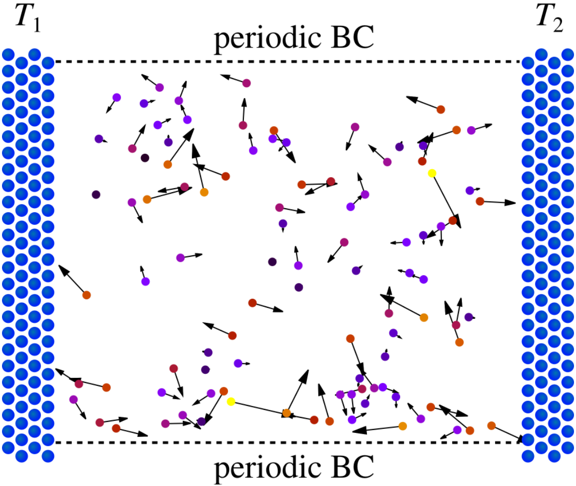
Boundary conditions II

- Reflecting boundary conditions



Boundary conditions II

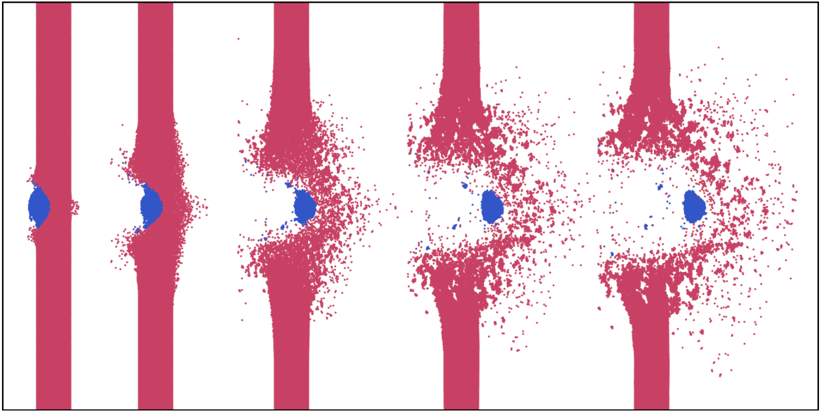
- Reflecting boundary conditions (different approach)



- Rigid walls of immobile atoms (only repulsive or combined action)
- Or walls of moving atoms at certain temperature

Boundary conditions III

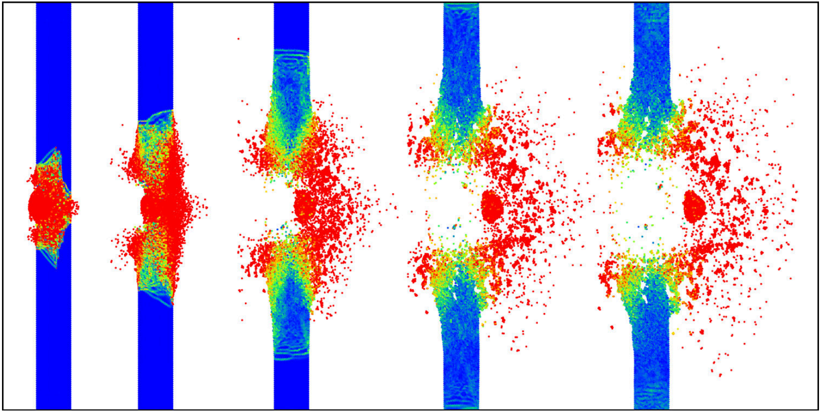
- Initial velocity (initial value problem) : impact, penetration



- Volumetric forces : gravity (additional force $F_i \mathrel{+}= m_i\mathbf{g}$)

Boundary conditions III

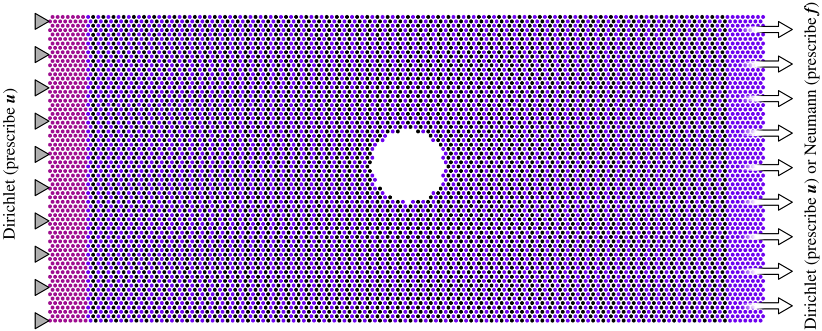
- Initial velocity (initial value problem) : impact, penetration



- Volumetric forces : gravity (additional force $F_i \mathrel{+}= m_i \mathbf{g}$)

Boundary conditions IV

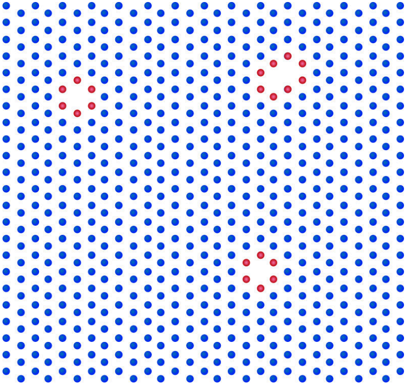
- Mechanical boundary conditions : Dirichlet and Neumann



Initial configuration

Simple configurations[*] **:**

- Gas/liquid
- Perfect crystal
- Crystal with vacancy defects
- Bi-crystals
- Stacking faults and dislocations
- Simple geometries
- Long molecules



Crystal with vacancy defects (easy to control)

---

[*] Stable initial configuration can be produced by minimization of the system potential energy.

Initial configuration

Simple configurations* **:**

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- Bi-crystals[1]
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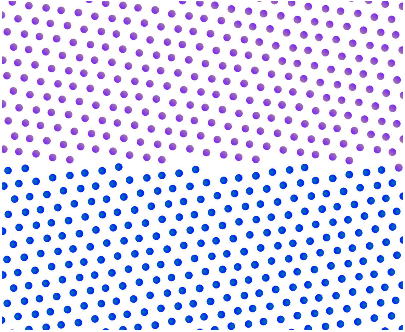

Bi-Crystal (grain boundary)

---

*Stable initial configuration can be produced by minimization of the system potential energy.

[1] Coffman & Sethna. Grain boundary energies and cohesive strength as a function of geometry. Phys Rev B 77 (2008)

Initial configuration

Simple configurations* **:**

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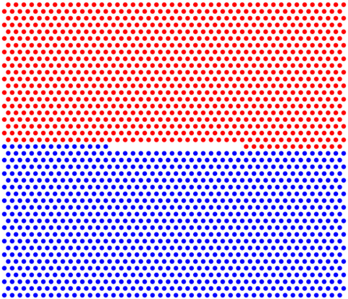

Remove several atoms

---

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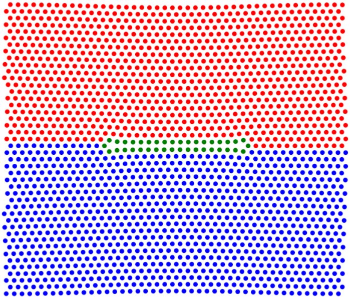

Stacking fault with partial dislocations

---

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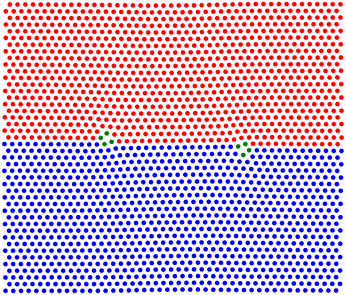

Healing stacking fault forms two perfect edge dislocations

---

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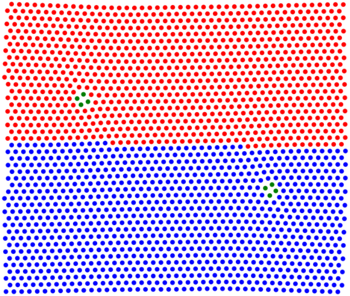

Dislocations glide

---

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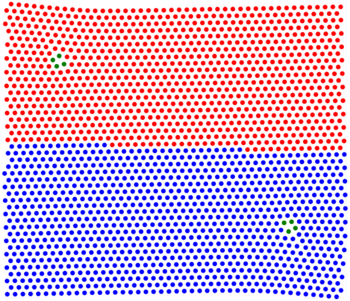

Dislocations glide

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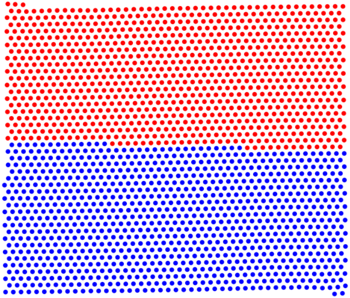

Dislocations form steps on the surface

---

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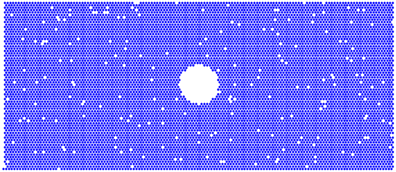


Layer with a circular hole

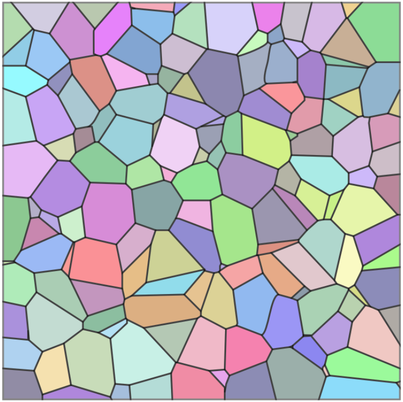
---

*Stable initial configuration can be produced by minimization of the system potential energy.

Initial configuration

Physically based configurations :

- Amorphous solid
  rapidly solidified from a liquid
- Voronoi-based polycrystal
- Polycrystalline solid
  porosity and grain size are controlled by the cooling rate
- Hight-temperature corrosion
  heat up and cool down initial configuration



Voronoi tesselation as a basis for construction of a nano-grained material
(*adapted from Wikipedia*)

Initial configuration

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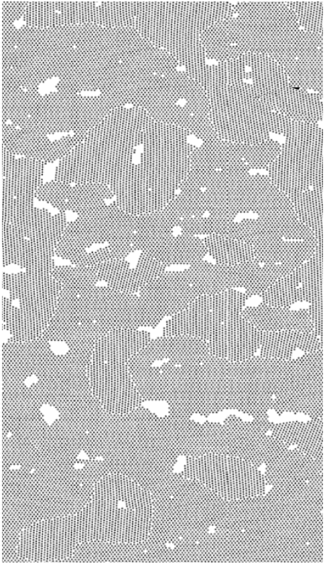

Porous polycrystal obtained from liquid state by relatively fast cooling

General algorithm

- **Initialize :**
  1. distribute particles $x_i(0)$ for $i \in [0, N]$
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  3. assign boundary conditions
  4. evaluate forces on particles $f_i(x(0))$
- **Integrate in time (velocity Verlet method) :**
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  7. if needed store data and compute energies.

End of part I

End of part I