993SM - Laboratory of Computational Physics
Unit XIV
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Maria Peressi
Università degli Studi di Trieste - Dipartimento di Fisica
Sede di Miramare (Strada Costiera 11, Trieste)
e-mail: peressi@units.it
tel.: +39 040 2240242

Modelling other random processes

- Fractals & Diffusion Limited Aggregates
- Percolation
- Monte Carlo approach for classical fluids

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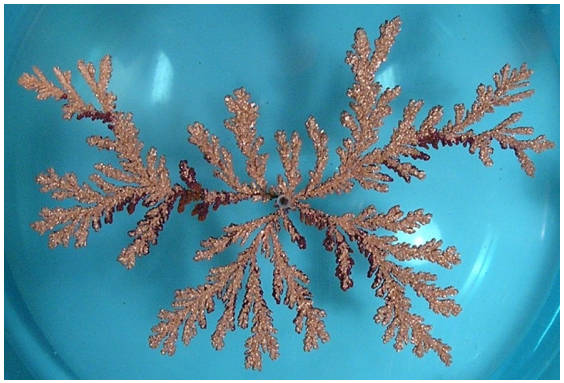
Diffusion Limited Aggregation

Several examples of formation of natural patterns showing common features:



Electrodeposition:
cluster grown from a copper sulfate solution in an electrodeposition cell

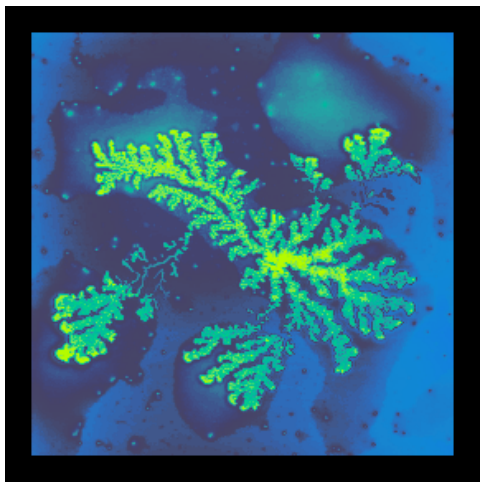
Dielectric breakdown:
High voltage dielectric breakdown within a block of plexiglas

These common features that can be captured by very simple models:

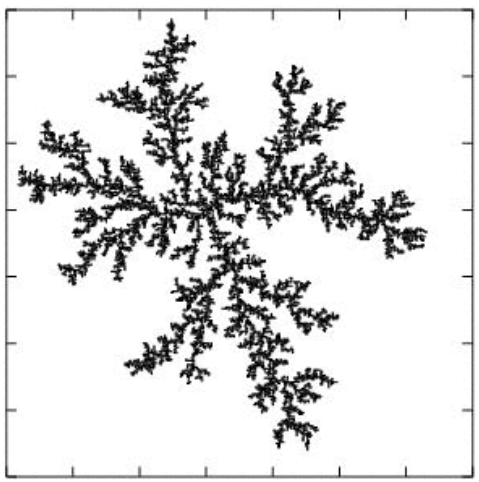
Diffusion Limited Aggregation

- simple model of FRACTALS GROWTH, initially proposed for irreversible colloidal aggregation, although it was quickly realized that the model is very widely applicable.

- by T.A. Witten and L.M. Sander, Phys. Rev. Lett. 47, 1400 (1981)



REAL IMAGE (Atomic Field Microscopy) of a gold colloid of about 15 nm over a gel substrate



SIMULATION

DLA: algorithm

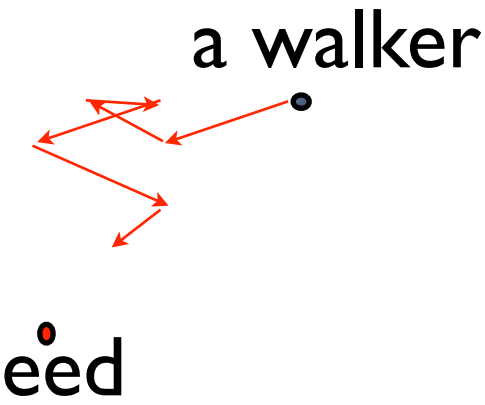
* Start with an immobile seed on the plane

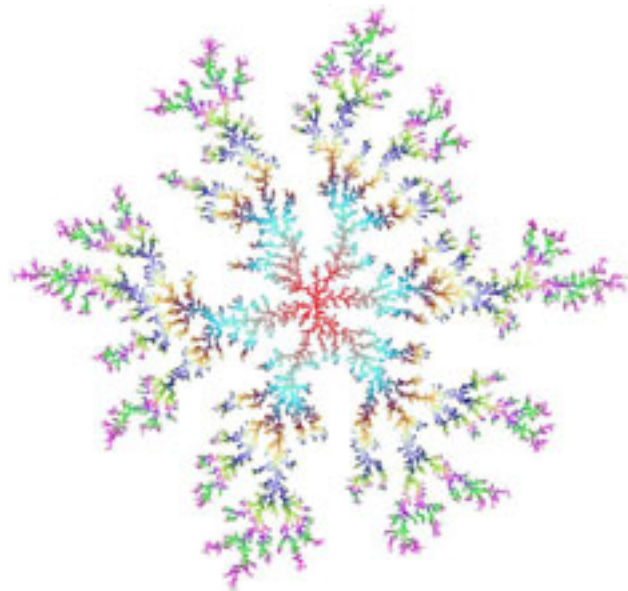
* A walker is then launched from a random position far away and is allowed to diffuse

* If it touches the seed, it is immobilized instantly and becomes part of the aggregate

* We then launch similar walkers one-by-one and each of them stops upon hitting the cluster

* After launching a few hundred particles, a cluster with intricate branch structures results

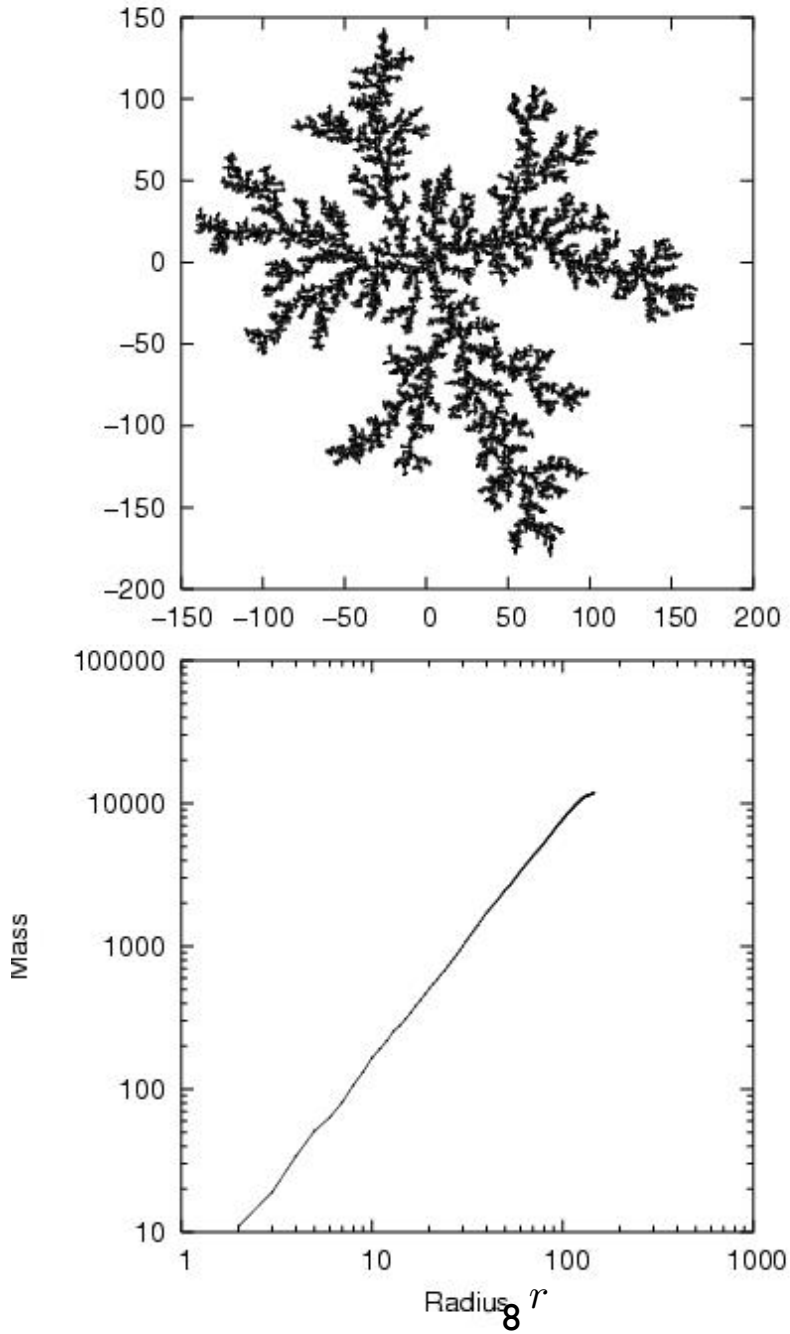




DLA: algorithm - details

- We launch walkers from a "launching circle" which inscribes the cluster
- They are discarded if they wander too far and go beyond a "killing circle"
- The diffusion is simulated by successive displacements in independent random directions
- At every step, the walker which would aggregate is checked to detect any overlapping with the particles on the cluster

DLA: results

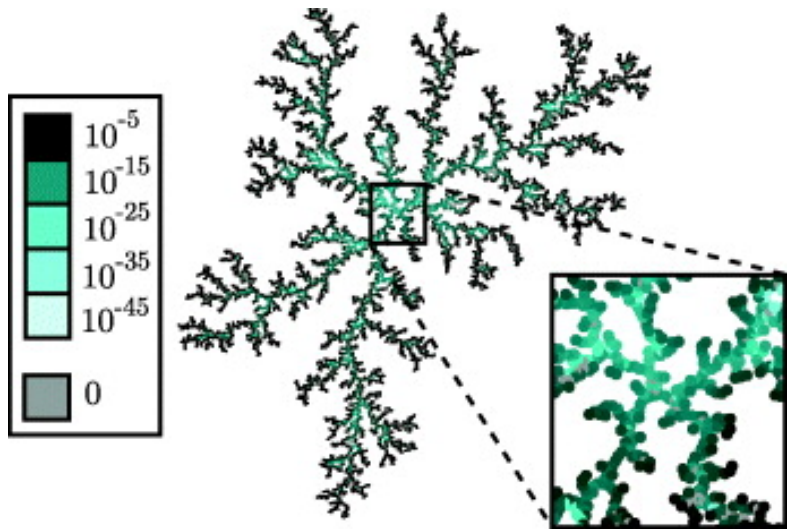


(mass M of the cluster ≡ number of particles N)

$$\ln N \propto \ln r$$
$$\Downarrow$$
$$N \propto r^k$$

DLA: interesting quantities

- in a "normal" 2D object: $N \propto r^2$
- FRACTAL DIMENSION: the number of particles N with respect to the maximum distance r of a particle of the cluster from its center of mass is $N \propto r^{D_f}$, with $1 < D_f < 2$

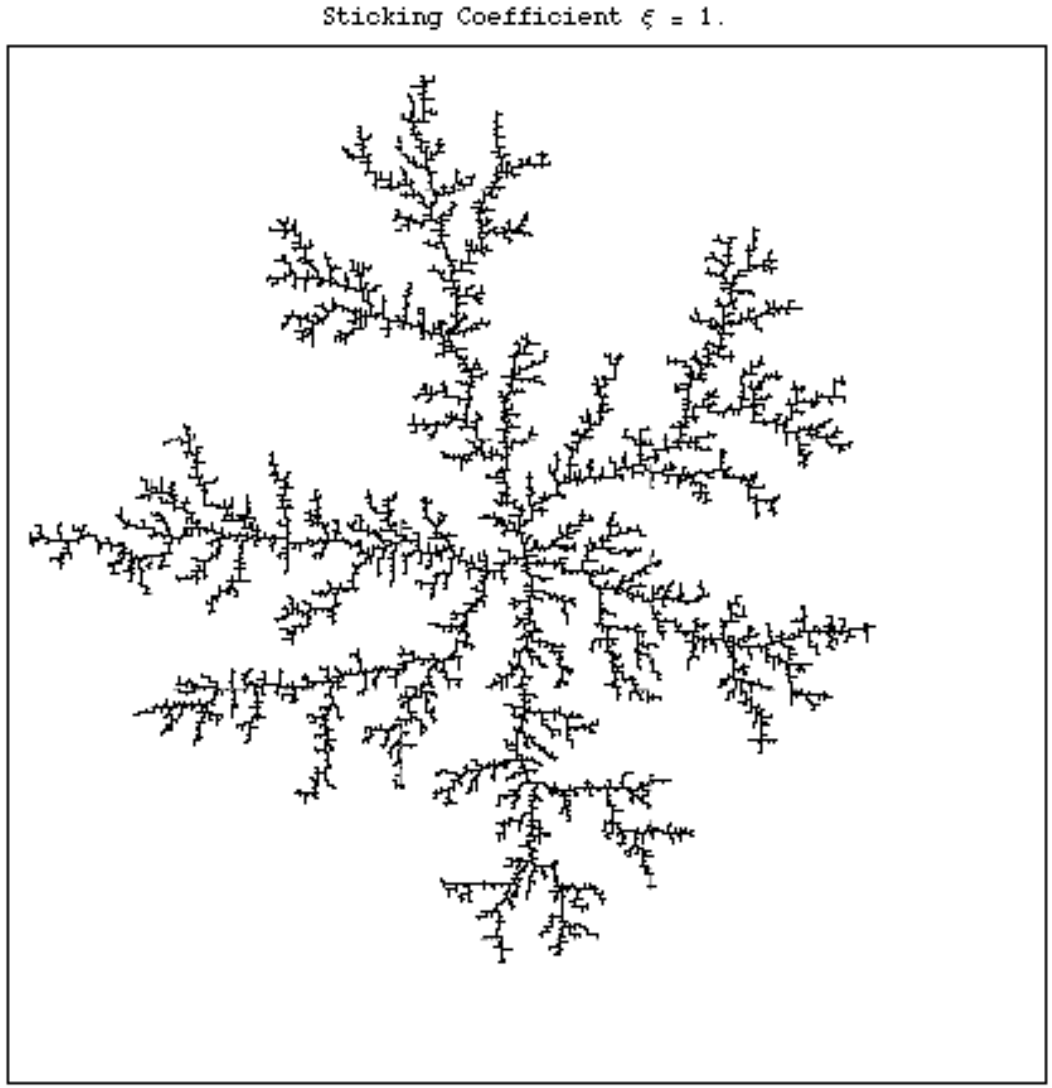


DLA: algorithm - details II

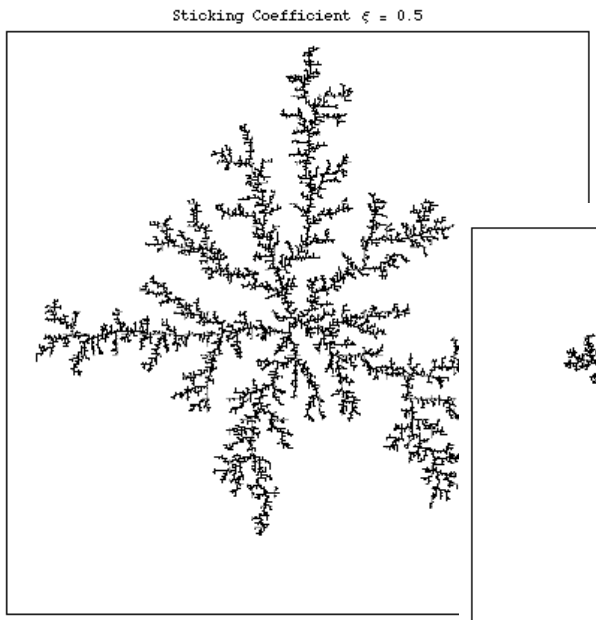
- the simplest DLA models: diffusion on a lattice. On a **square lattice**, 4 adjacent sites are available for the diffusing particle to stick
- modification: the particle will stick with certain probability (the "sticking coefficient") - to simulate somehow the surface tension
- another modification: with a sort of Brownian diffusion in the continuum

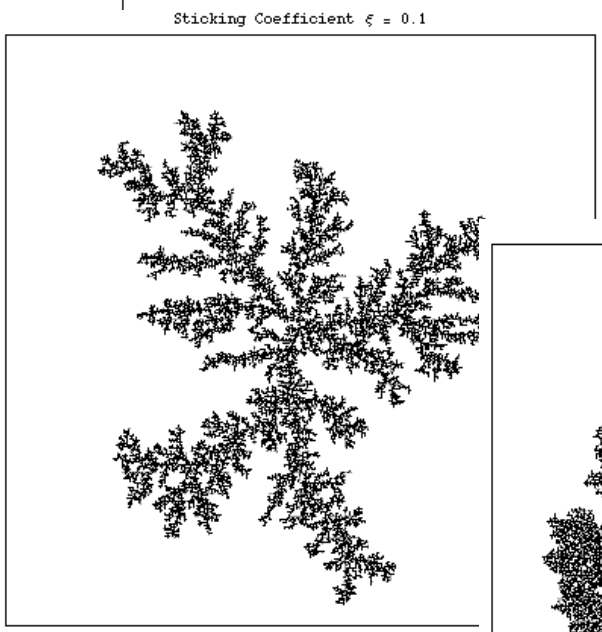
DLA: results

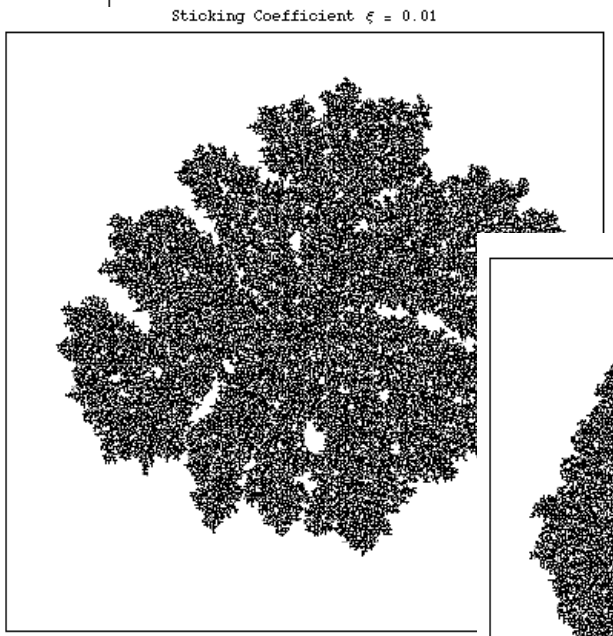
$$1 < D_f = 1.6 < 2$$

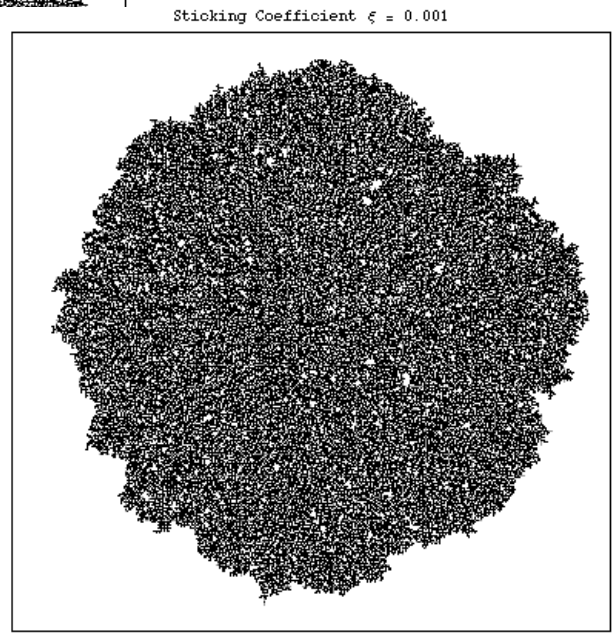


DLA: results





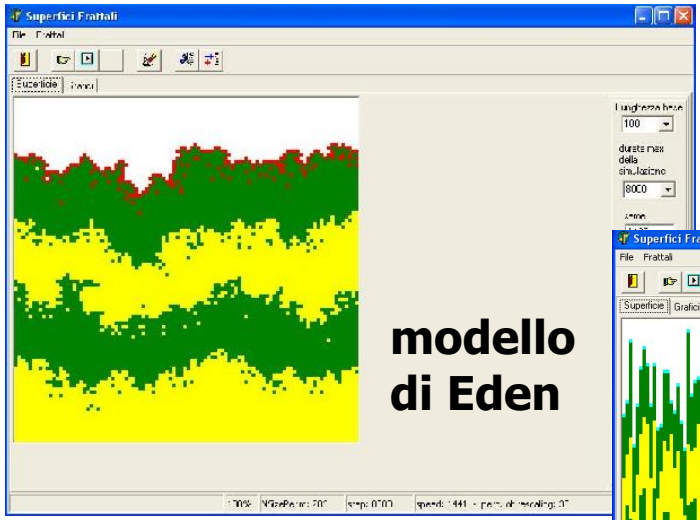




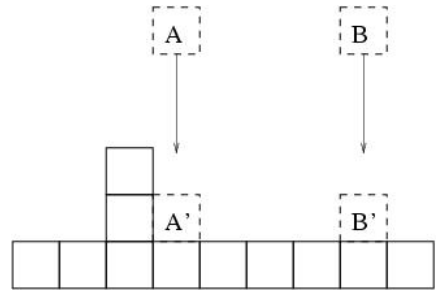
$$D_f \to 2$$

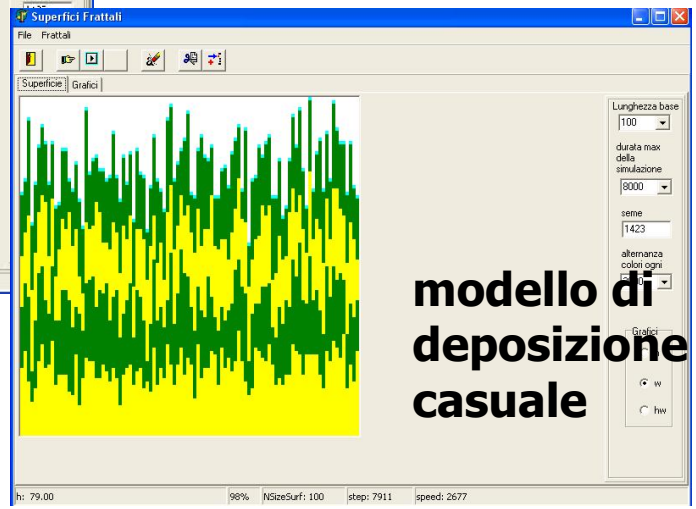
as the sticking coeff. $\to 0$

Models of surface growth

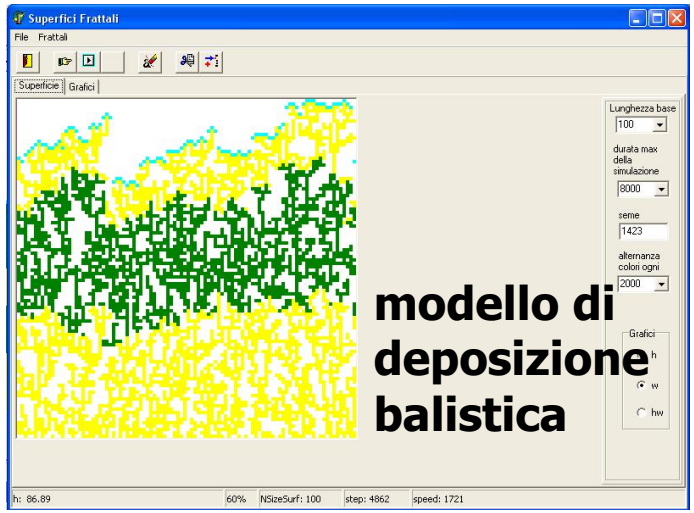


modello di Eden

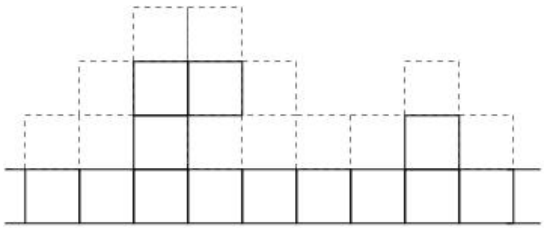


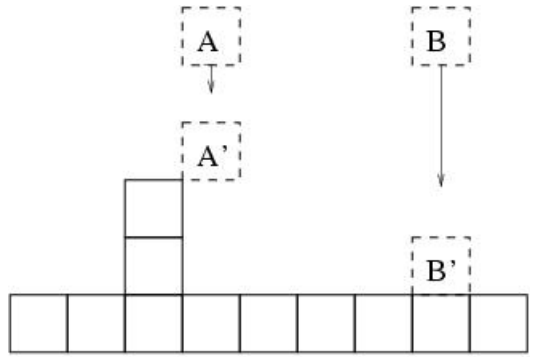


modello di deposizione casuale



modello di deposizione balistica





see e.g. Barabasi & Stanley, ***Fractal concepts in surface growth***, Cambridge University Press

Models of surface growth

The Eden model - algorithm:

(a) choose randomly a lattice site and occupy it. The *nearest neighbor sites* of the occupied site (i.e. 4 sites in case of a square lattice) are the *perimetral sites*.

(b) choose randomly a *perimetral site* and occupy it. When occupied, it is no longer a *perimetral site*: update the list of *perimetral sites* with the new ones. Repeat from (1).

Interesting quantities:

Average height: $$\bar{h} = \frac{1}{N_s} \sum_{i=1}^{N_s} h_i$$

Roughness: $$w^2 = \frac{1}{N_s} \sum_{i=1}^{N_s} (h_i - \bar{h})^2,$$

Modelling other random processes

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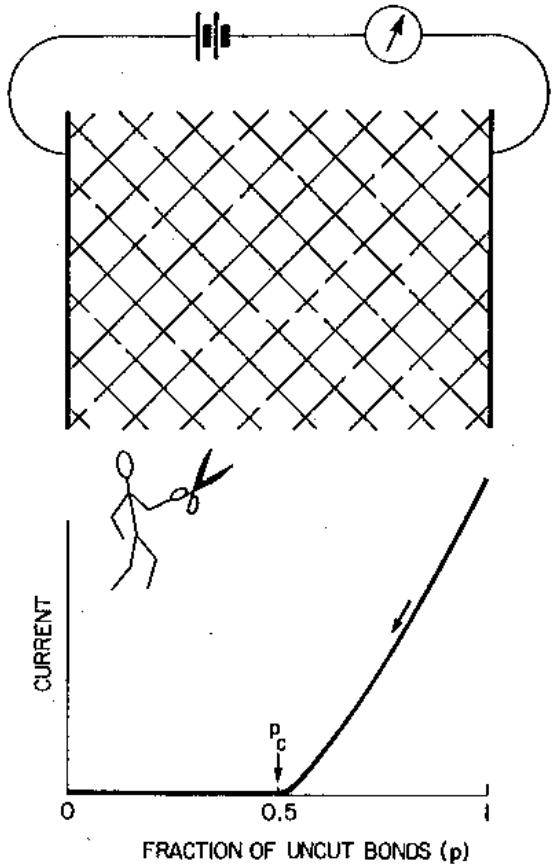
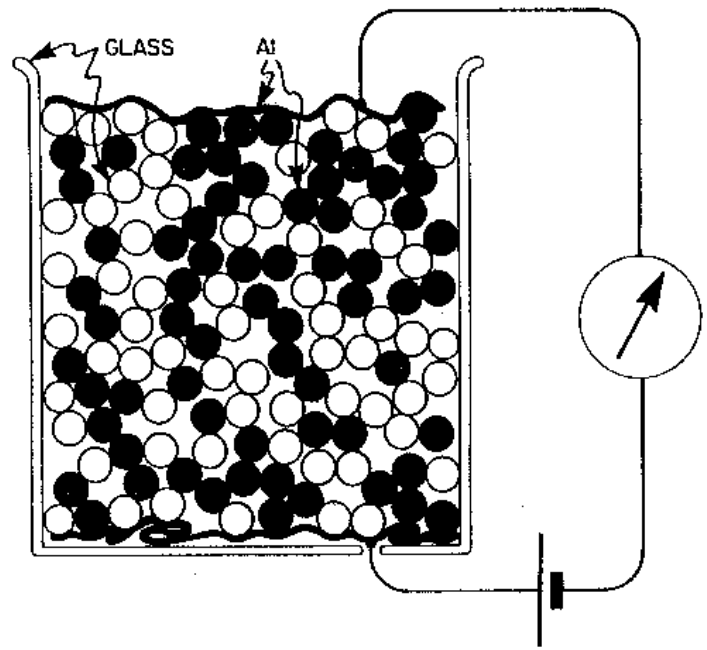
- Percolation
- Monte Carlo approach for classical fluids

Percolation

geometric connectivity in a stochastic system; modeling threshold and transition phenomena



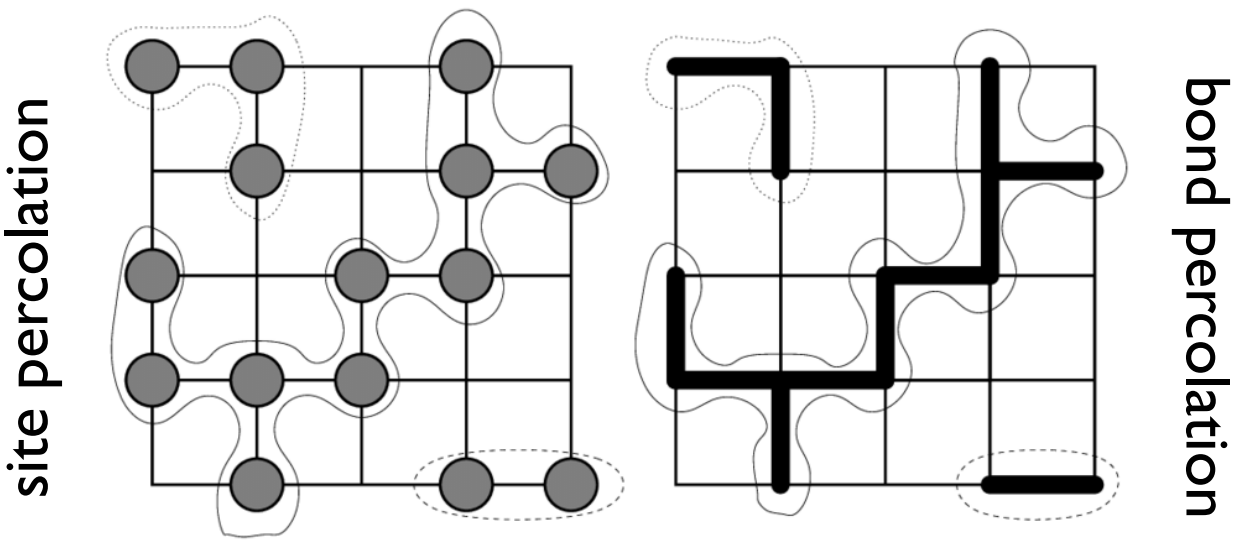


existence of a critical occupation fraction P_c above which spanning clusters occur (in nature: mixtures of conducting/insulating spheres...; resistor networks..)

Percolation

- metal/insulator threshold behavior in resistor networks (discrete percolation) and in alloys (continuous percolation)

Other examples:
- fluid adsorption in a porous medium
- spreading of a disease in a population
- spreading of a forest fire...
- liquid/glass transition...
- ...



By Rudolf A. Römer

Percolation

Definitions:

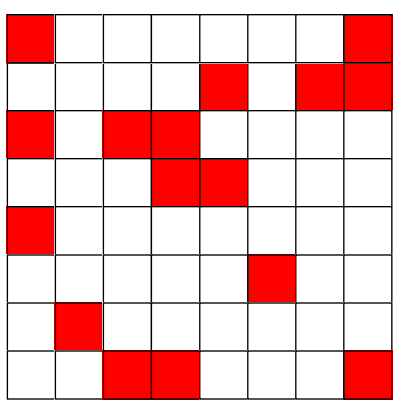
p: occupation probability of each identity (site, bond)

Cluster: group of identities (sites, bonds,...) connected by nearest neighboring bonds

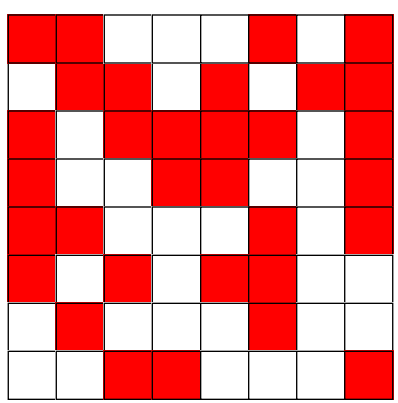
Percolating clusters: connecting two boundaries

which is the critical percolation threshold p_c ?

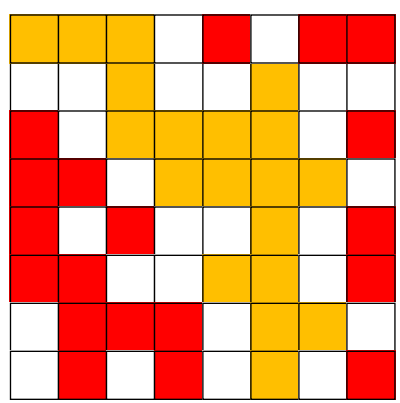
Example of site percolation on a lattice:



L = 8 p = 0.25



L = 8 p = 0.50

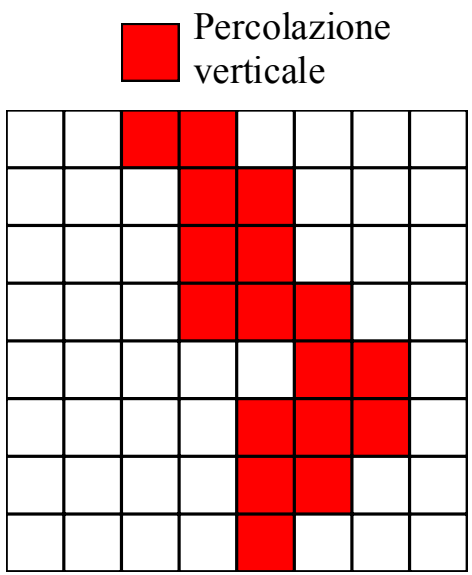


L = 8 p = 0.60

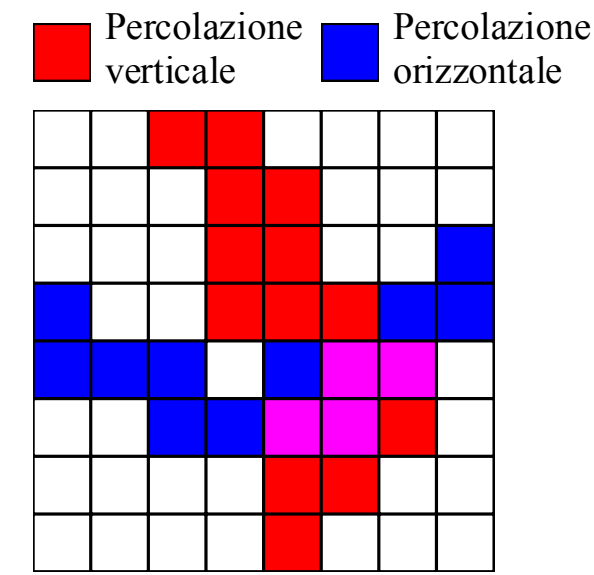
Percolation threshold

p_c depends on the criteria (different possibilities):

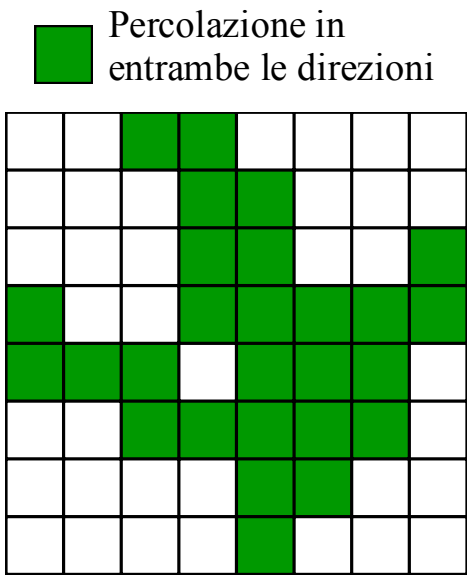
Connection along one fixed direction



Connection along one (any, horizontal or vertical) direction



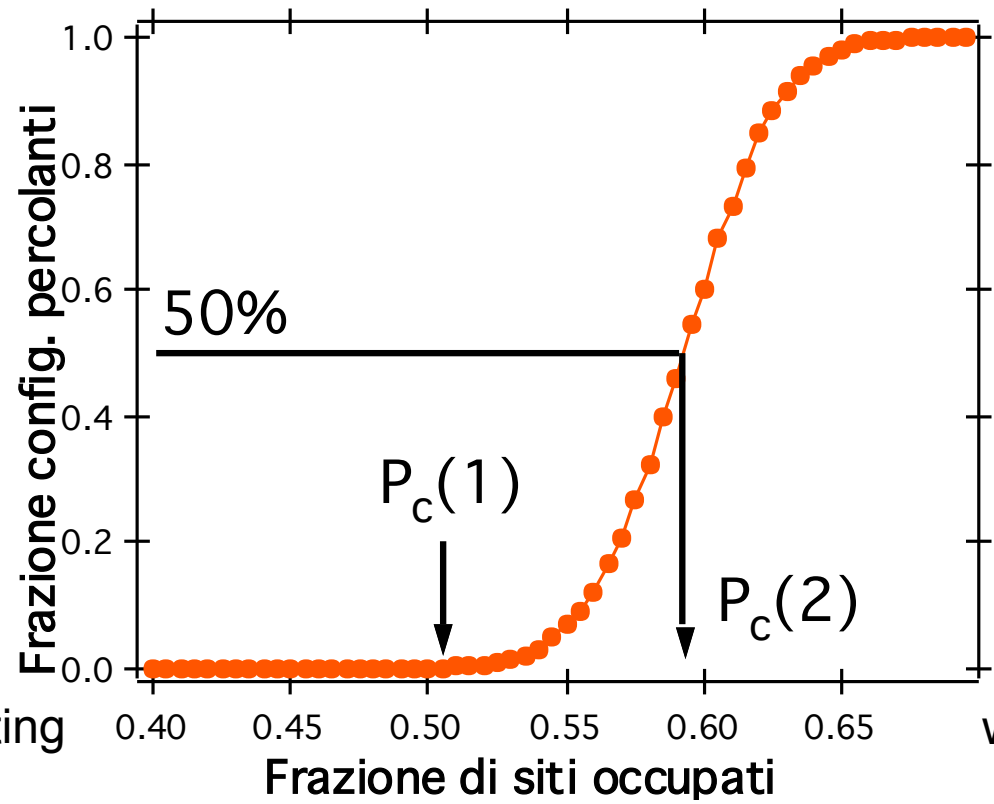
Connection in all directions



Percolation threshold

p_c depends on the criteria (different possible):

$P_c(1)$:
fraction of occupied sites when the first percolating cluster is established



$P_c(2)$:
fraction of occupied sites when 50% of the clusters are percolating

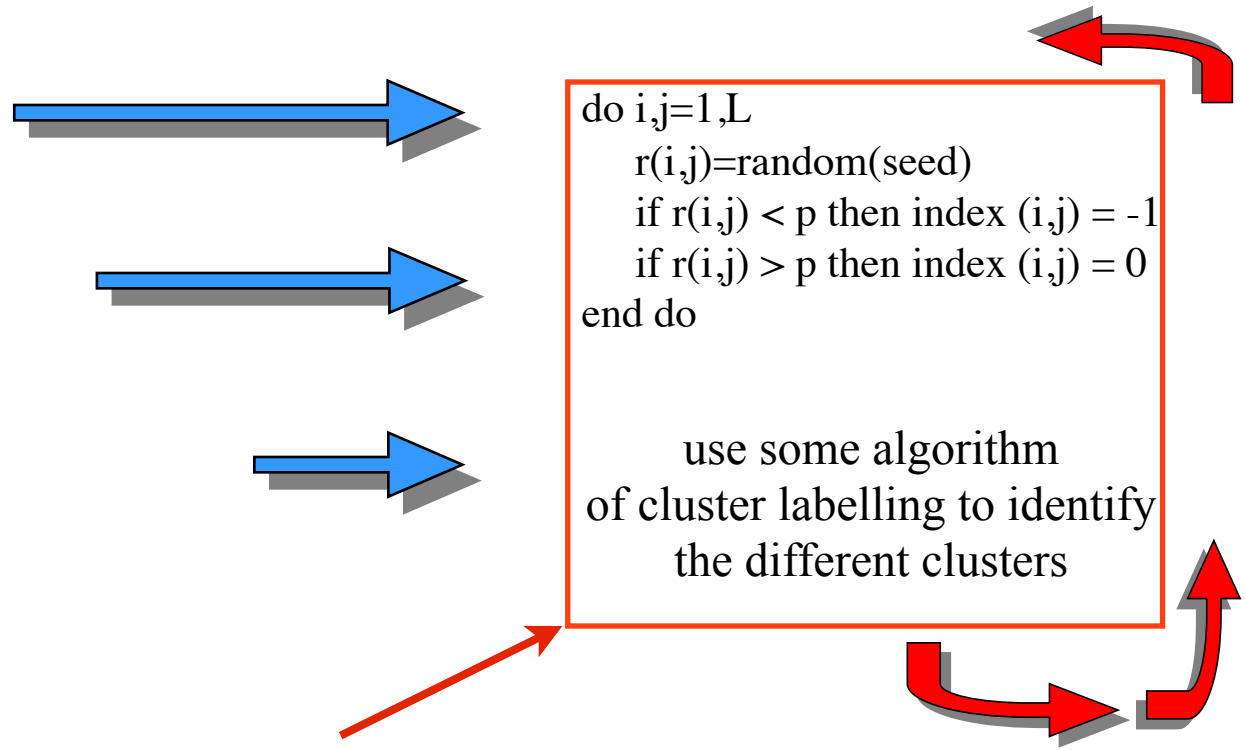
$$P_C(1) \equiv P_C(2) \qquad \text{for} \qquad L \to \infty$$

Monte Carlo approach

fix **L** => Lattice description

fix **p** => Site (or bond) filling accordingly

Identification and characterization of the clusters



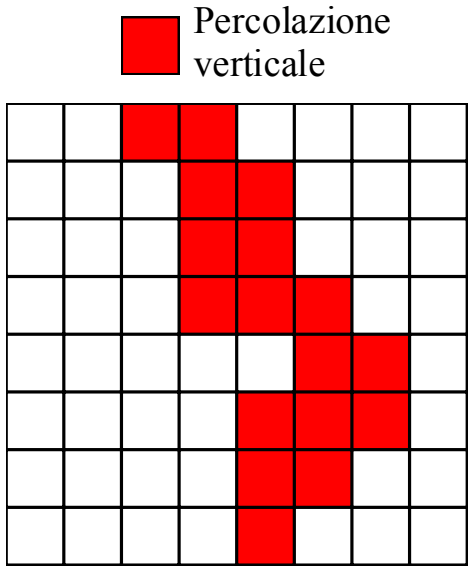
generation of many configurations for each **p**

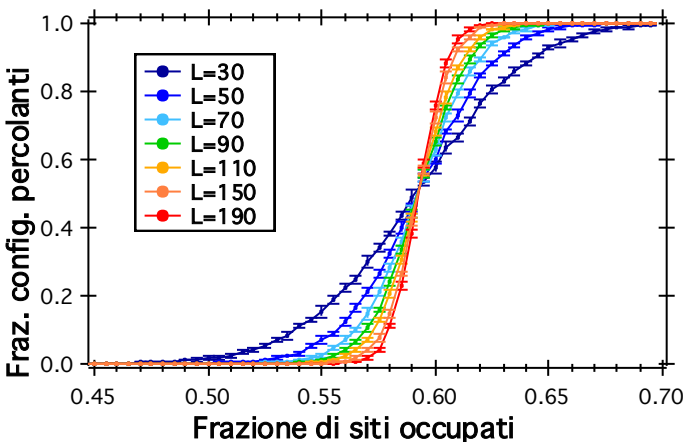
data analysis;
account for size effect (vary **L**)!

Results

for different percolation criteria and different size

Connection along one fixed direction





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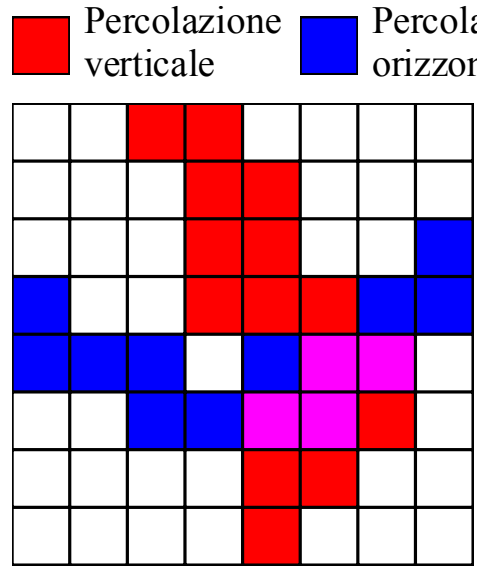
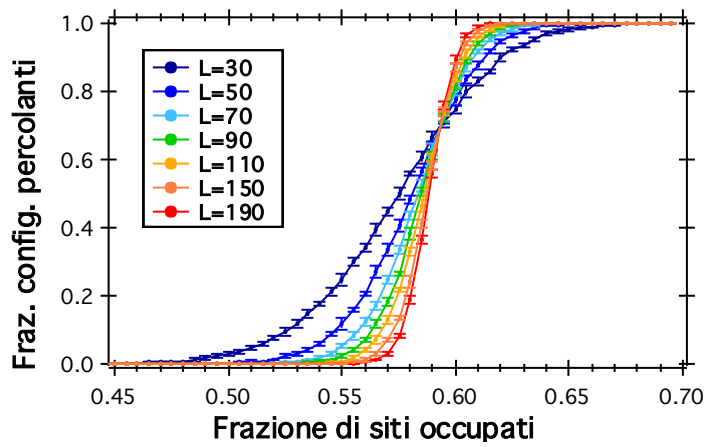
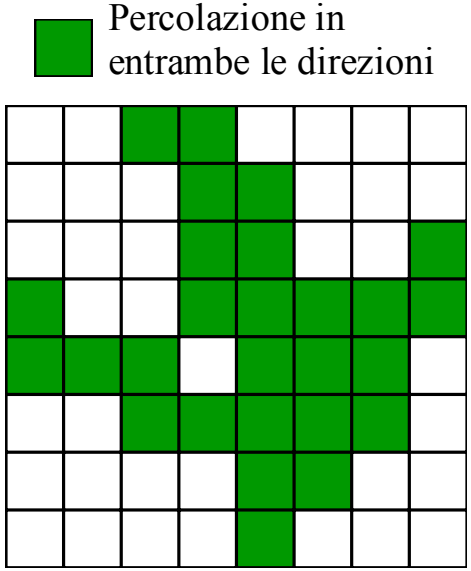
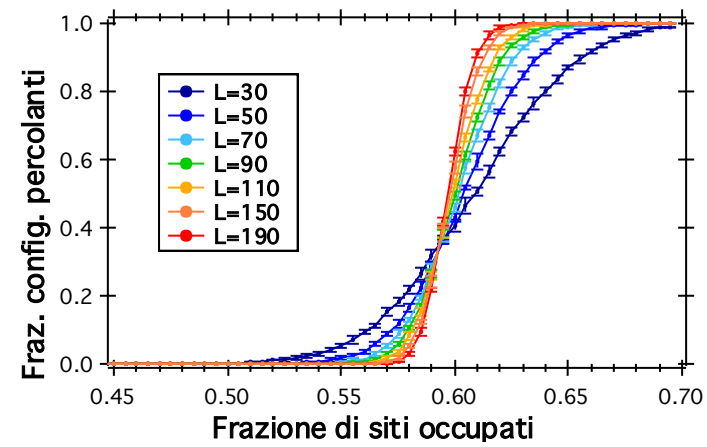




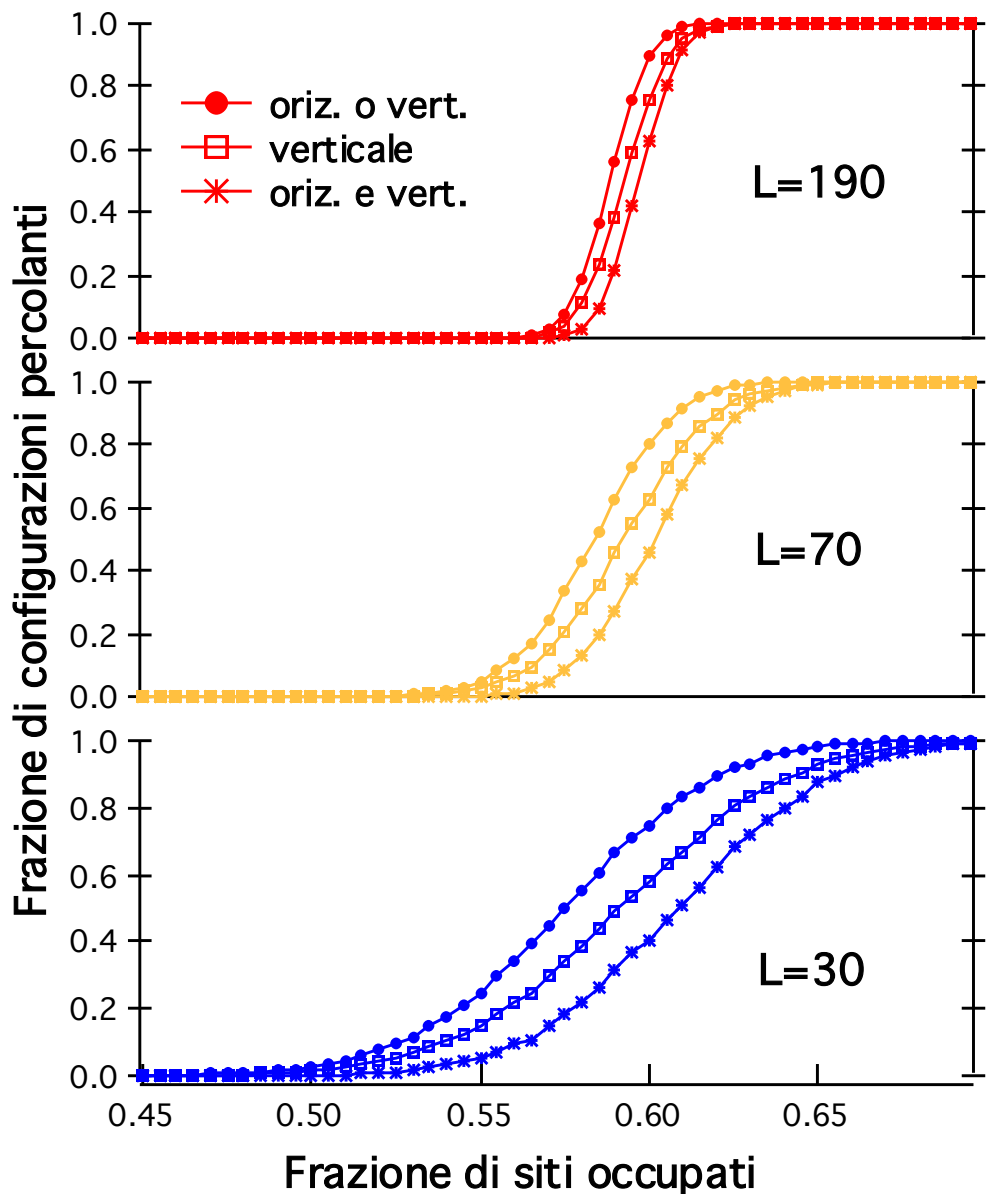
Connection in all directions





Results

for different percolation criteria and different size



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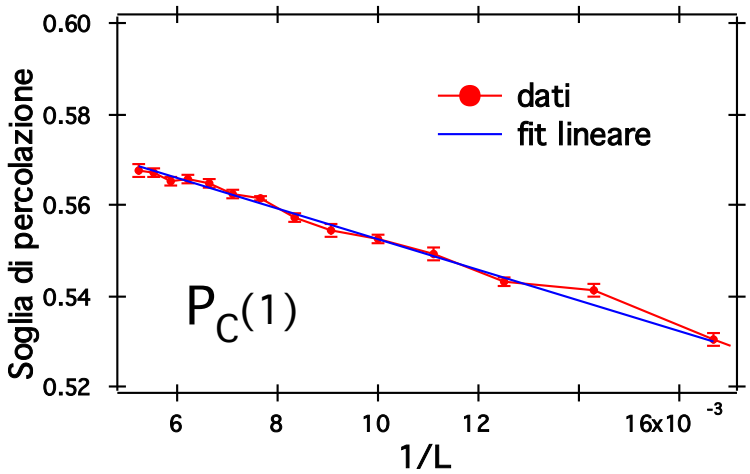
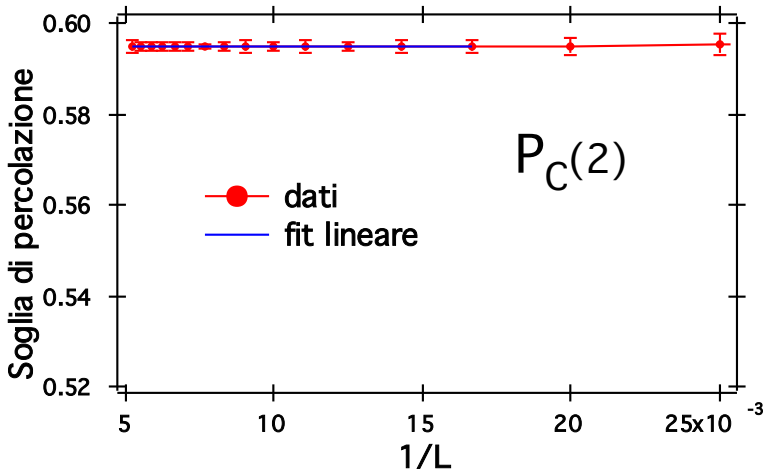


extrapolate the behavior for

$$L \to \infty$$

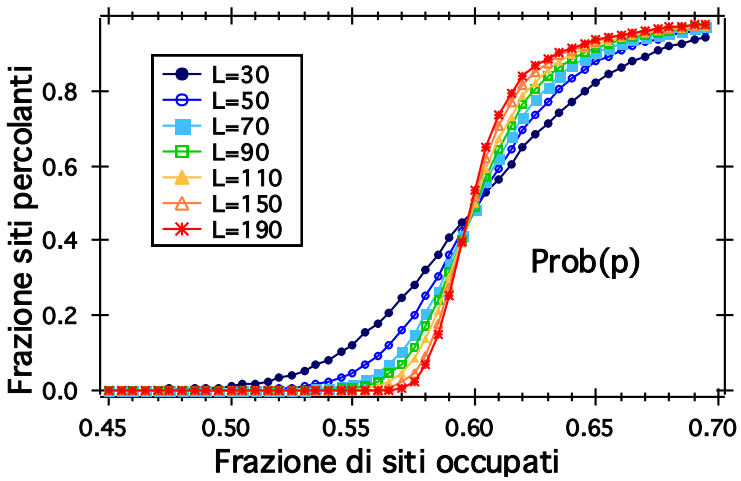
$$1/L \to 0$$



$$P_C^{\infty}(1) = P_C^{\infty}(2) = 0.59 \pm 0.05$$

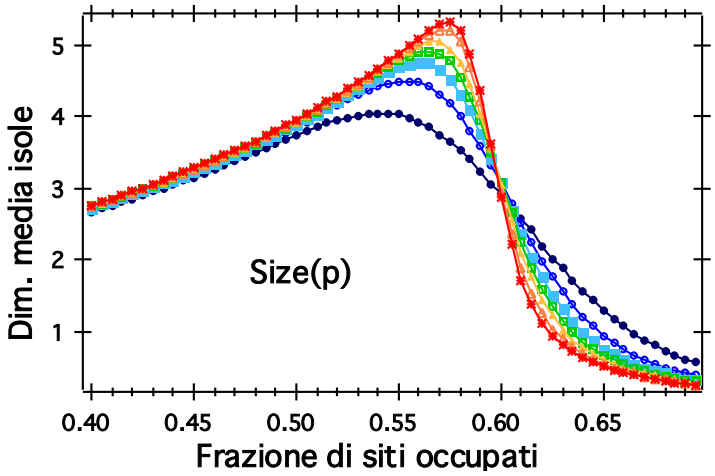
Results

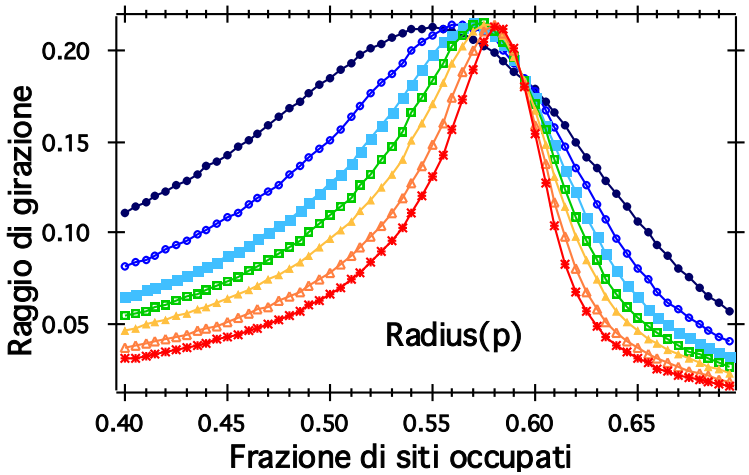
other interesting quantities



probability Prob(p) for a site to be included in a percolating cluster

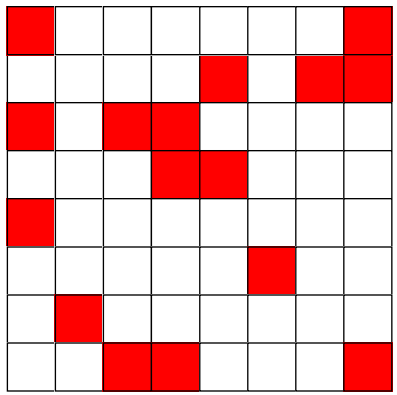
average size Size(p) of a non-percolating cluster



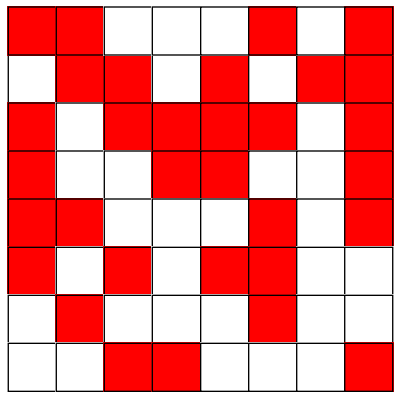


radius of gyration Radius(p) = $\sqrt{\frac{\sum_i^N (\vec{r}_i - \vec{r}_{cm})^2}{N}}$

Cluster labelling



L = 8 p = 0.25



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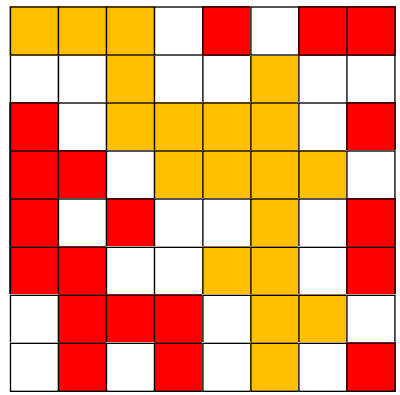
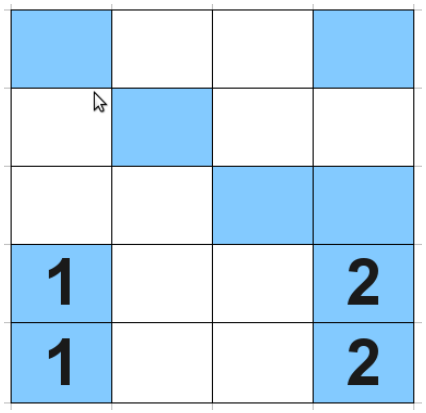


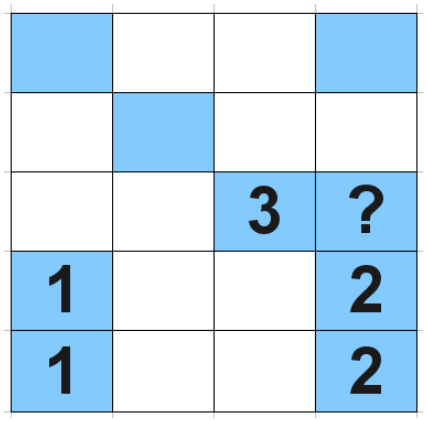
L = 8 p = 0.60

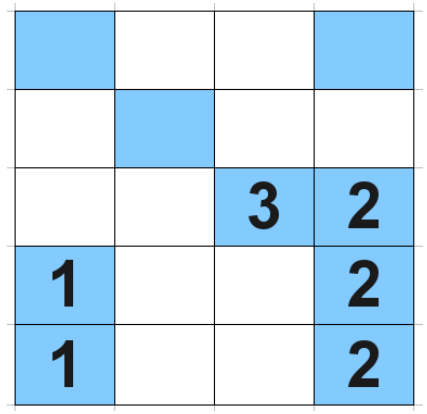
The (non trivial) part of the model:
choose a smart algorithm to identify and label the clusters made of adjacent occupied sites

Cluster labelling

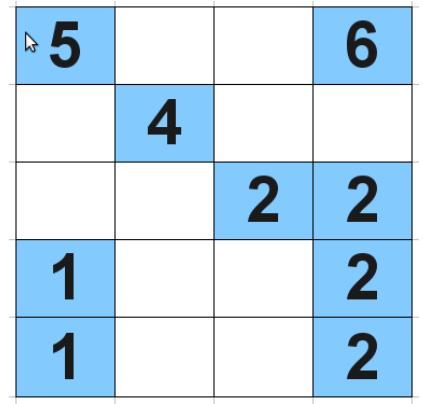


(1): span all the cells (here: left => right and bottom => up) and start labeling





(2): attribute the minimum cluster label to cells neighboring to different clusters



(3): refine labeling

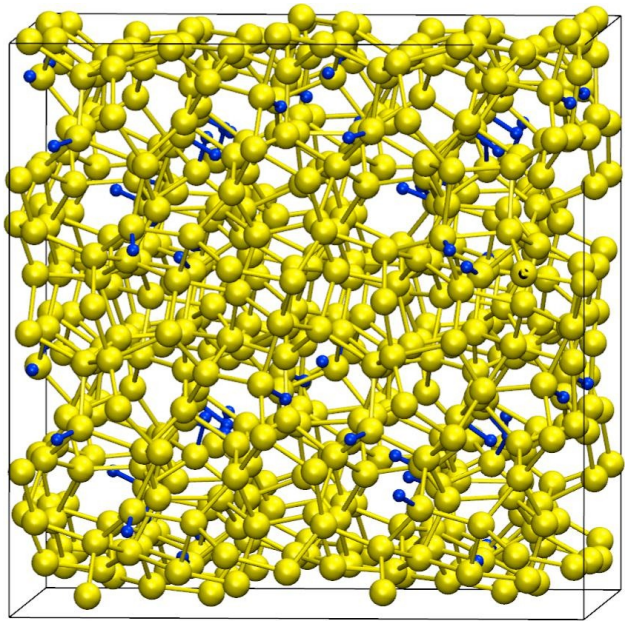
Hoshen- Kopelman algorithm for clusters labelling

Example of application in solid state physics

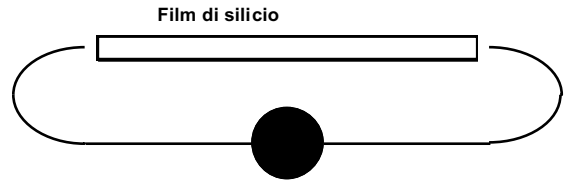
Dynamical Percolation Model of Conductance Fluctuations in Hydrogenated Amorphous Silicon

L.M. Lust e J. Kakalios, Phys. Rev. Lett. ***75****, 11 (1995)*

Fluttuazioni di conduttività nel silicio amorfo idrogenato *(a*-Si:H*)* sono simulate utilizzando un modello dinamico di diffusione di resistenze in un reticolo in condizioni di soglia di percolazione. Una frazione di siti di reticolo è designata come una trappola tale per cui quando un resistore diffonde in una di esse, rimane localizzato per un periodo finito di tempo.

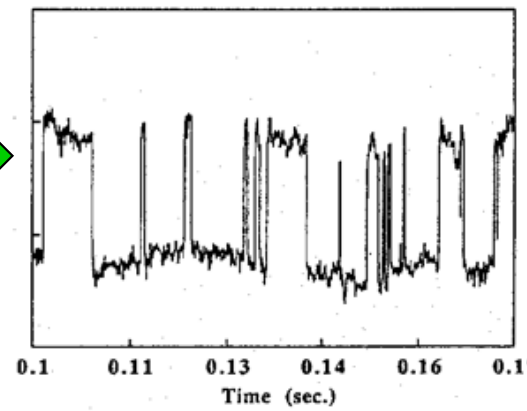


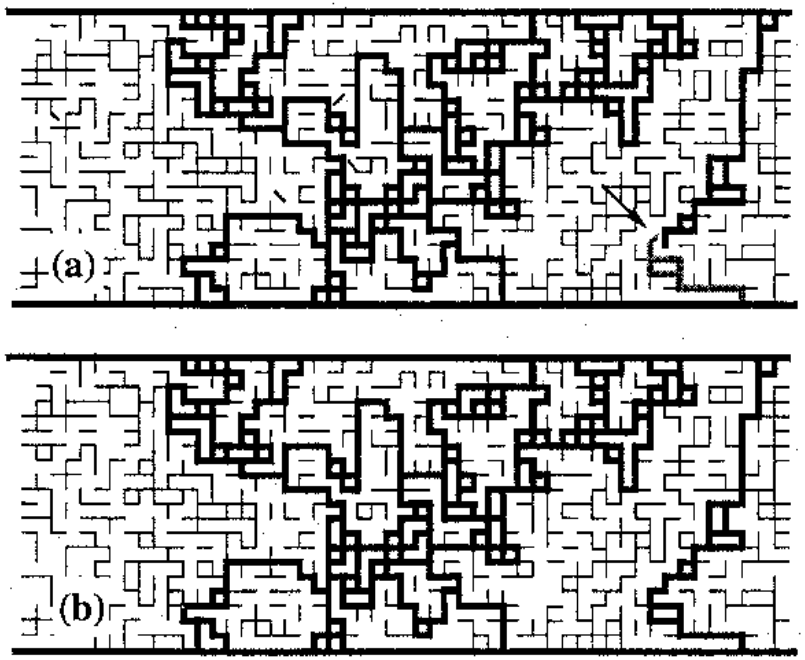
A model of a-Si:H from
https://doi.org/10.1016/j.commatsci.2018.08.027



Fluttuazioni di tipo “telegrafico”

Fluttuazioni di conduttività misurate sperimentalmente

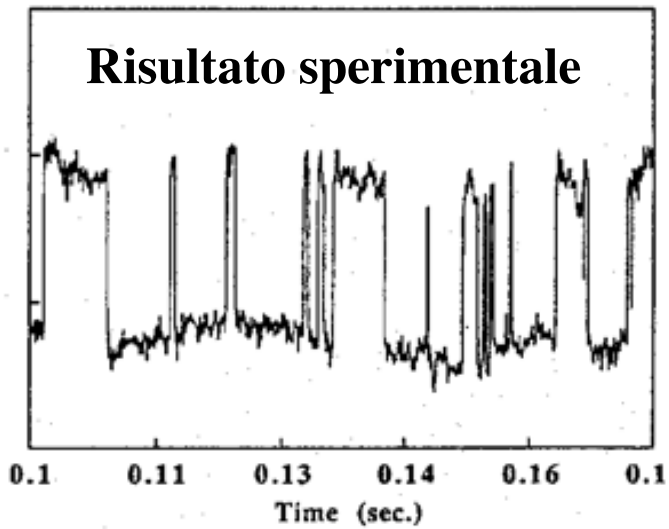


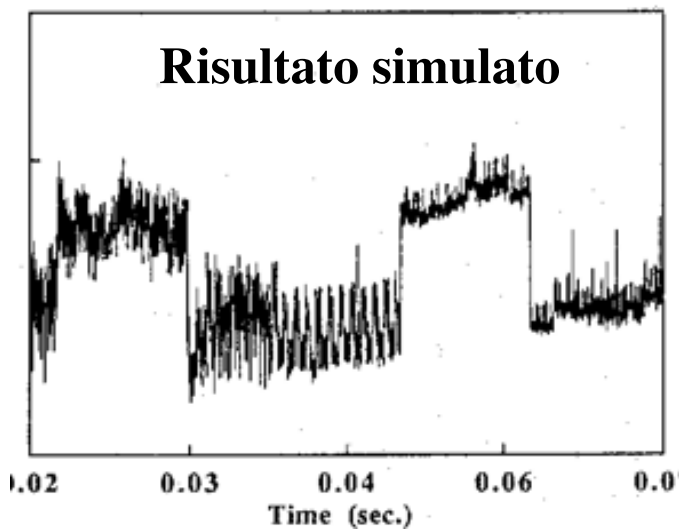


Rete casuale di resistenze con $P \sim P_C$ (fisso)

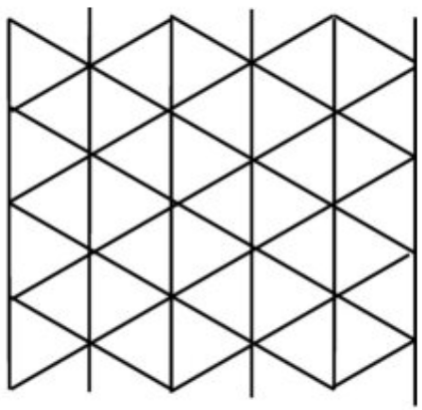
Configurazione dopo un riarrangiamento casuale dei legami

Diffusione H: Creazione/distruzione canali di conduttività





Percolation on different lattices

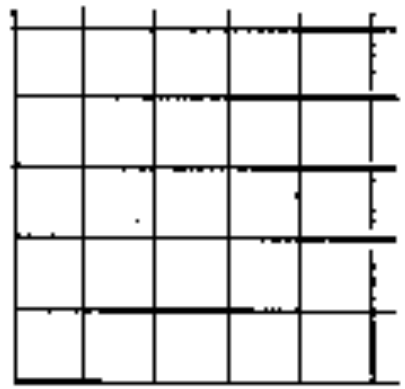


TRIANGULAR

$z = 6$

$p_c^{BOND} = 0.3473$

$p_c^{SITE} = 0.5000$

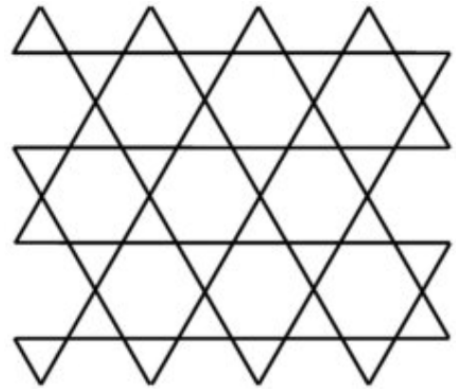


SQUARE

$z = 4$

$p_c^{BOND} = 0.5000$

$p_c^{SITE} = 0.593$

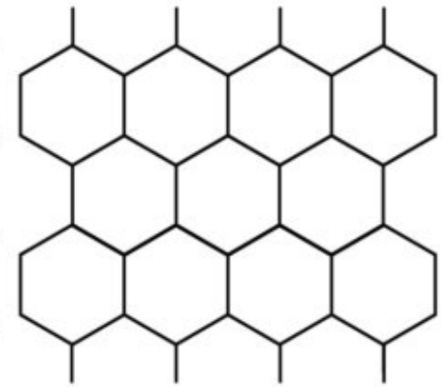


KAGOME'

$z = 4$

$p_c^{BOND} = 0.45$

$p_c^{SITE} = 0.6527$



HONEYCOMB

$z = 3$

$p_c^{BOND} = 0.6527$

$p_c^{SITE} = 0.70$

Modelling other random processes

- Fractals & Diffusion Limited Aggregates
- Percolation
- Monte Carlo approach for classical fluids

Classical fluids

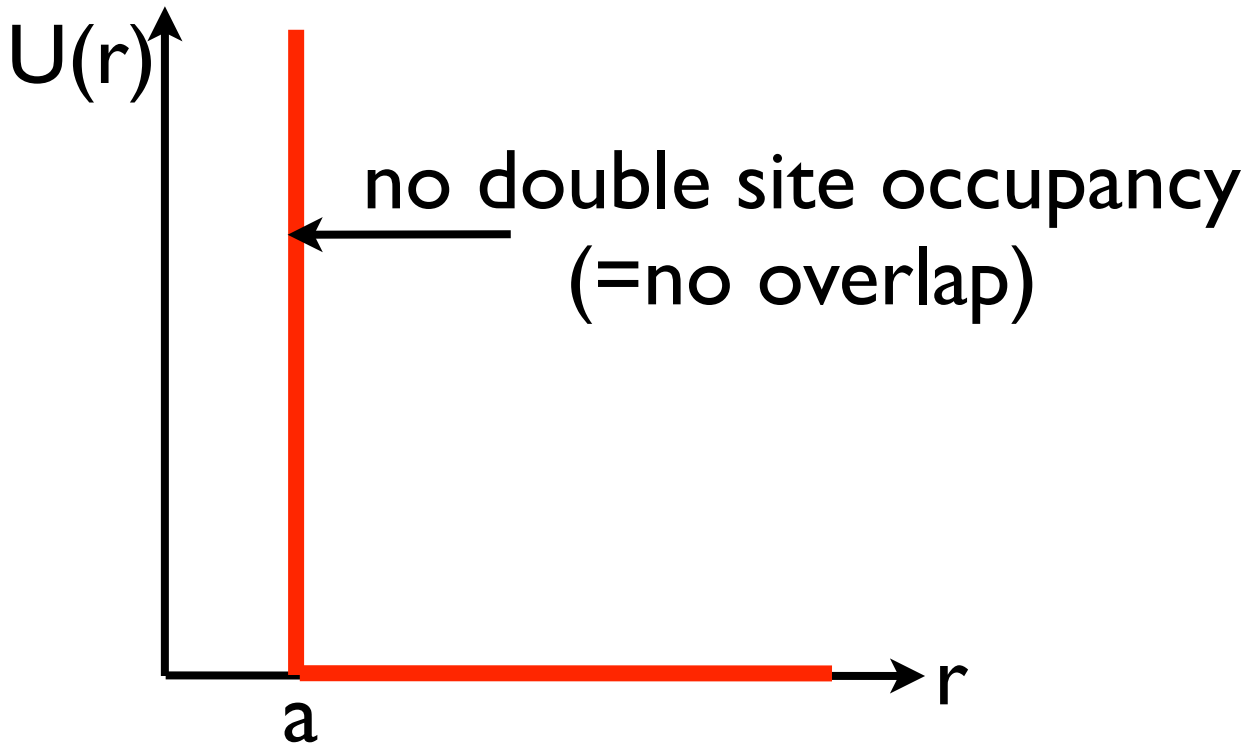
- Interactions
- Measurable and interesting physical quantities
- Metropolis Monte Carlo approach (mainly)
- Molecular dynamics

(here: several slides; but today only few basic concepts will be discussed)

Interactions

A very simple interaction

The lattice gas model :



but in general: ...

Interactions

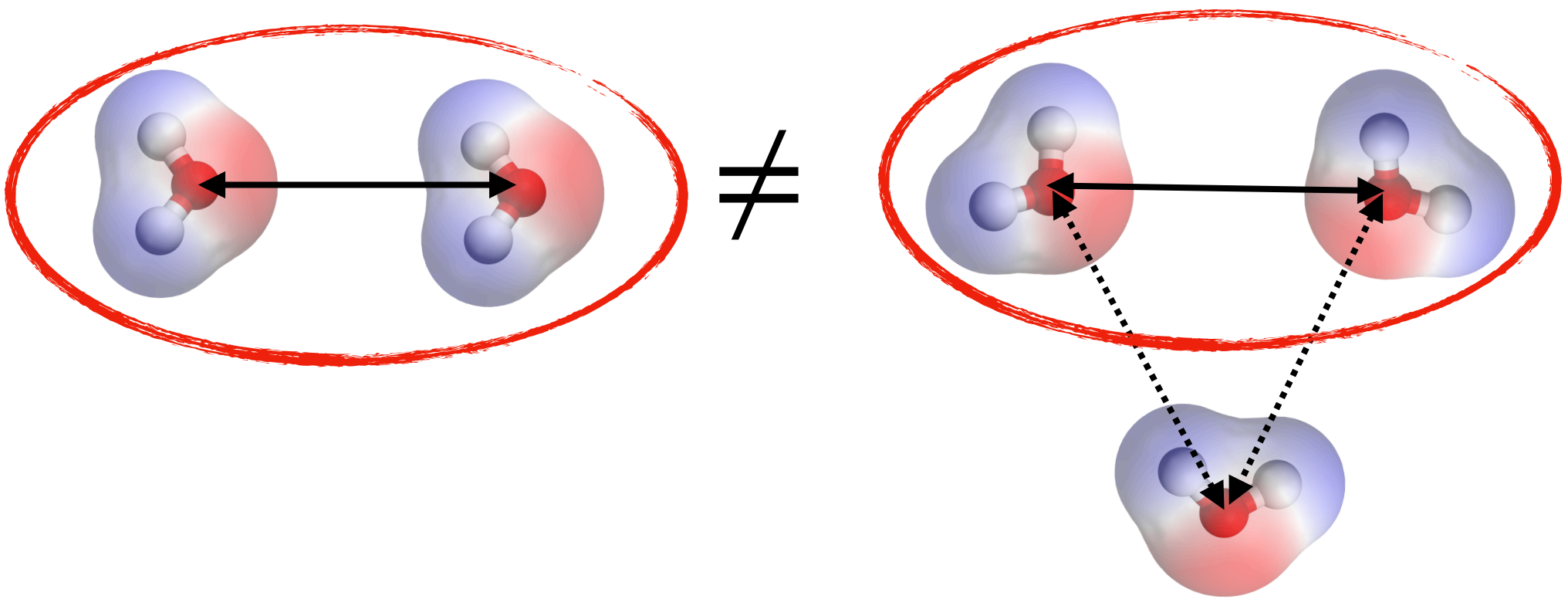
assume that the force between any pair of molecules (or atoms) depends only on the distance

($u(r_{ij})$ depends only on the magnitude of the distance $\mathbf{r}_{ij}$ between particles i and j)

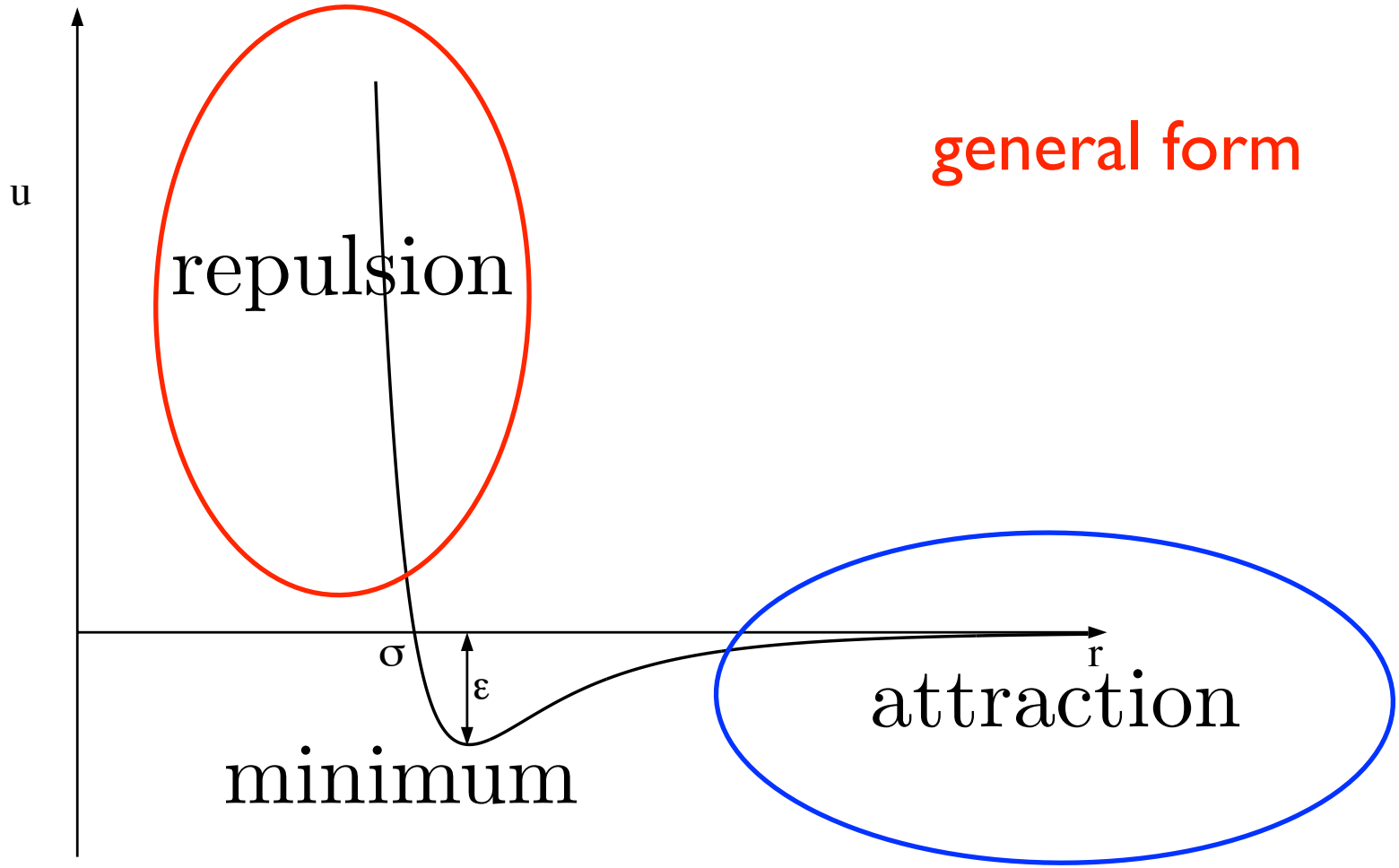
the total potential energy U is a sum of two-particle interactions:

$$U = u(r_{12}) + u(r_{13}) + \cdots + u(r_{23}) + \cdots = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij})$$

REMARK:
this is an effective interaction, a simple phenomenological form for *u(r)*
(it is an approximation, since in general, 3-, 4- ... many-body terms are present)



A typical 2-body effective potential



a strong repulsion for small r and a weak attraction at large r.

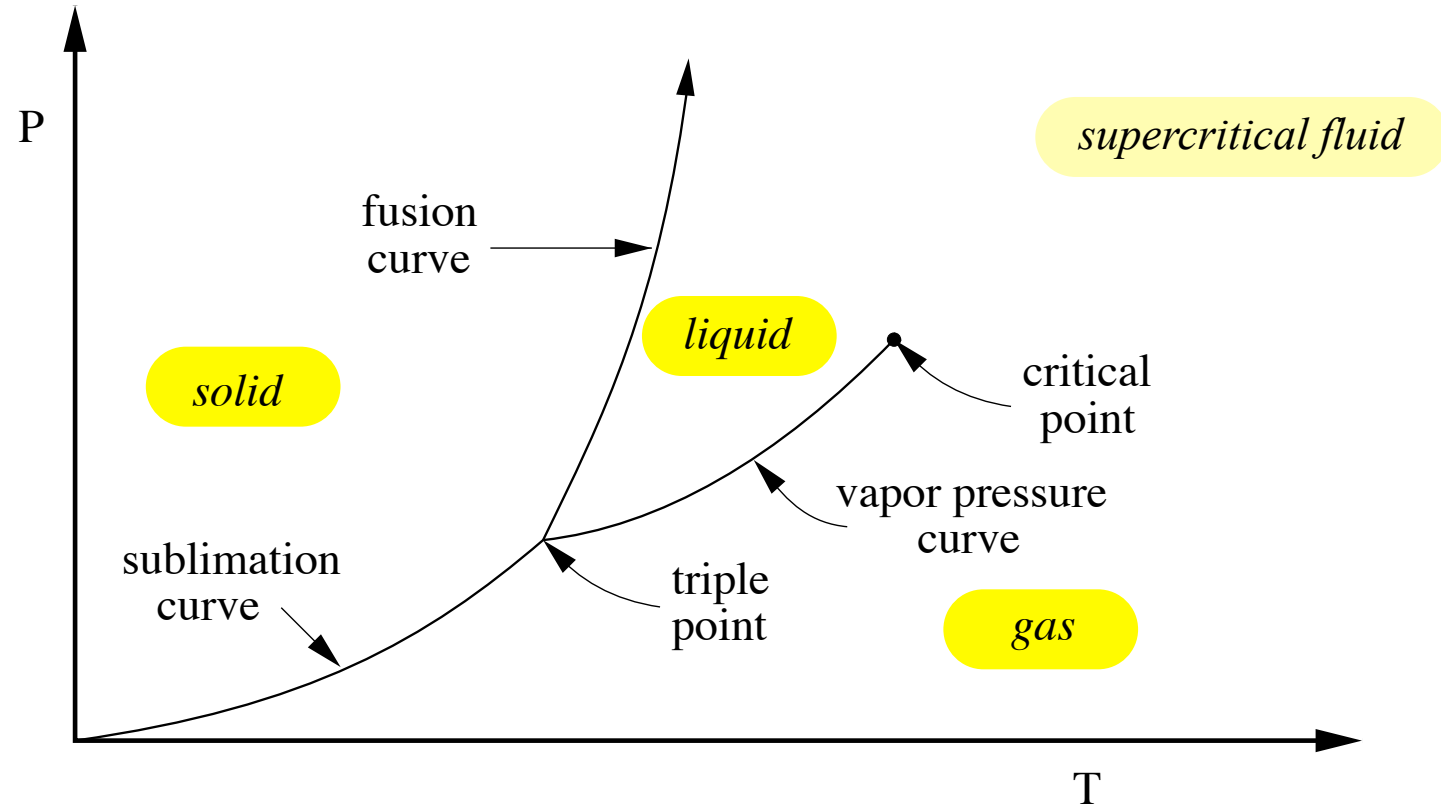
consequence of the Pauli exclusion principle

`core repulsion`

mutual polarization of each molecule

`van der Waals`

Phase diagram



A sketch of the phase diagram for a simple material.

A first goal in the study of fluids:

to gain insight into qualitative differences between different phases

Measurable and interesting physical quantities

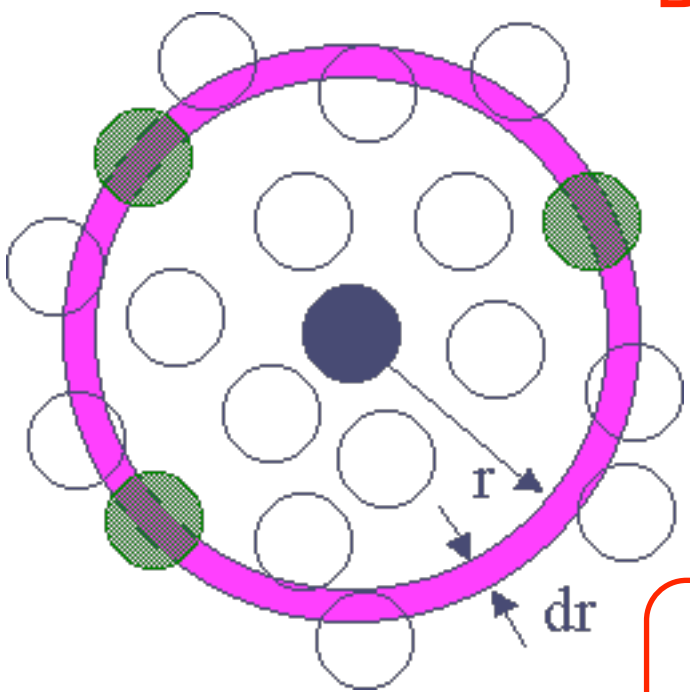
Measurable and interesting quantities

- pair correlation function $g(r)$
- energy E
- pressure p
- ...

Measurable and interesting quantities

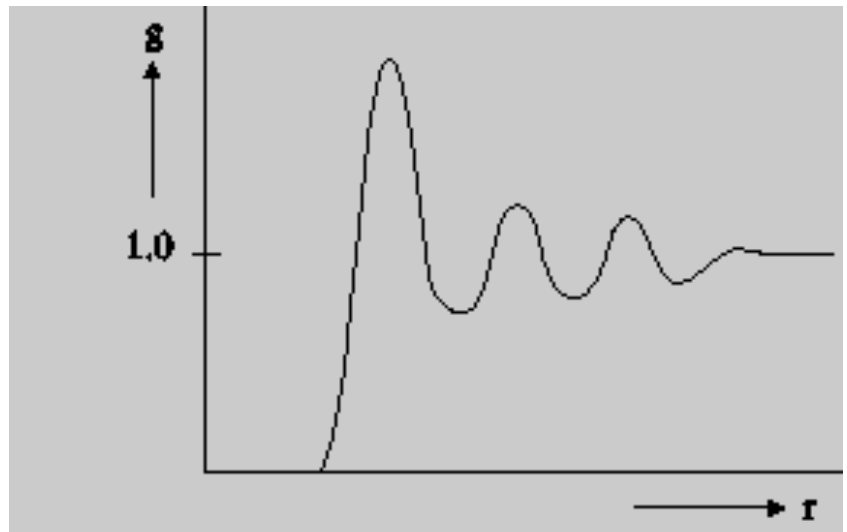
- pair correlation function $g(r)$ { concepts and qualitative features; mathematical formulation and expressions useful for computation }
- energy E
- pressure p
- ...

Radial distribution function



Definition

$g(r)$



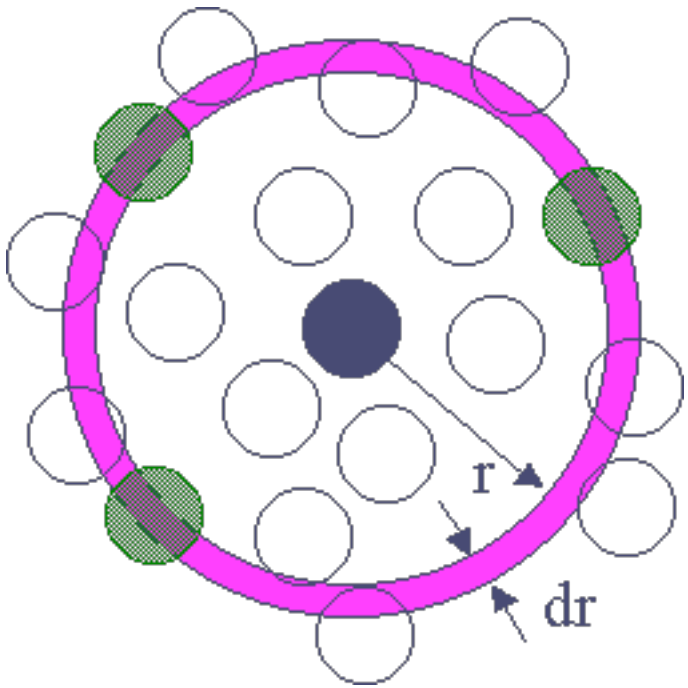
$g(r)d\mathbf{r}$ ($d\mathbf{r}$ = infinitesimal volume of the shell)

is a conditional probability (dimensionless) of finding a particle in the shell $\mathbf{r} \div \mathbf{r} + d\mathbf{r}$ given one at the origin

Consider one reference particle at the origin and count the others; then, average over the reference particles

(Here: spherically symmetric interactions assumed; g depends only on $r=|\mathbf{r}|$)

Radial distribution function



Normalization

N particles, volume V: density $\rho = N/V$

The mean number of particles in the shell with radius between r and r+dr is:

$$\rho g(r) d\mathbf{r}$$

(Reminder: spherically symmetric interactions assumed; g depends only on r=|**r**|)

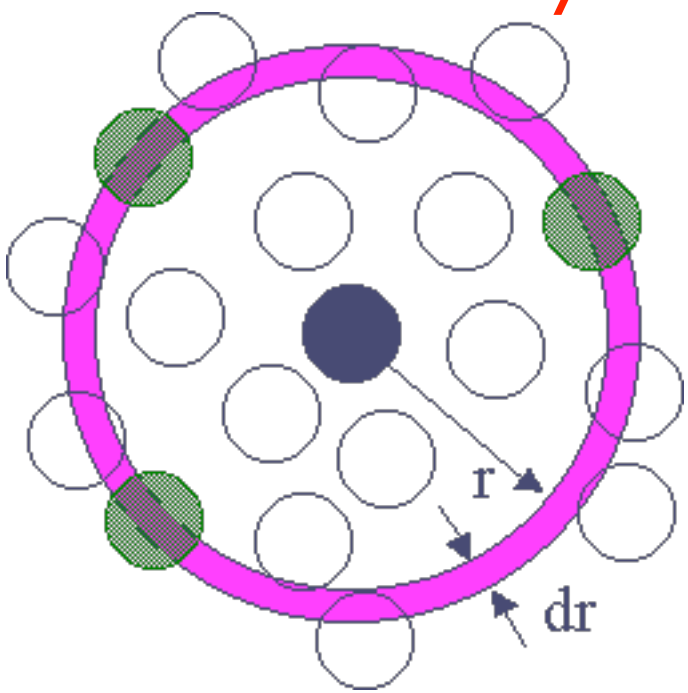
volume element $d\mathbf{r} = 4\pi r^2 dr\,(d=3),\ 2\pi r dr\,(d=2),$ or $2\,dr\,(d=1)$

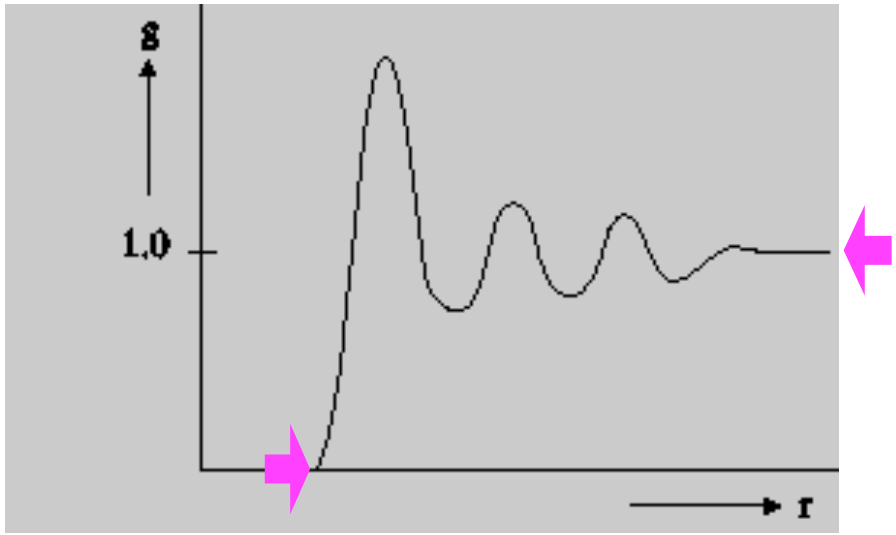
normalization condition $$\rho \int_0^\infty g(r)\, d\mathbf{r} = N - 1 \approx N$$

Radial distribution function

Physical meaning

g(r)





Gives insight into the structure of a many-body system.

General behavior at short and long distances:

repulsive interactions on short-range scale: $g(r \to 0) \to 0$

in general: $g(r) \to 1$ for $r \to \infty$

Radial distribution function

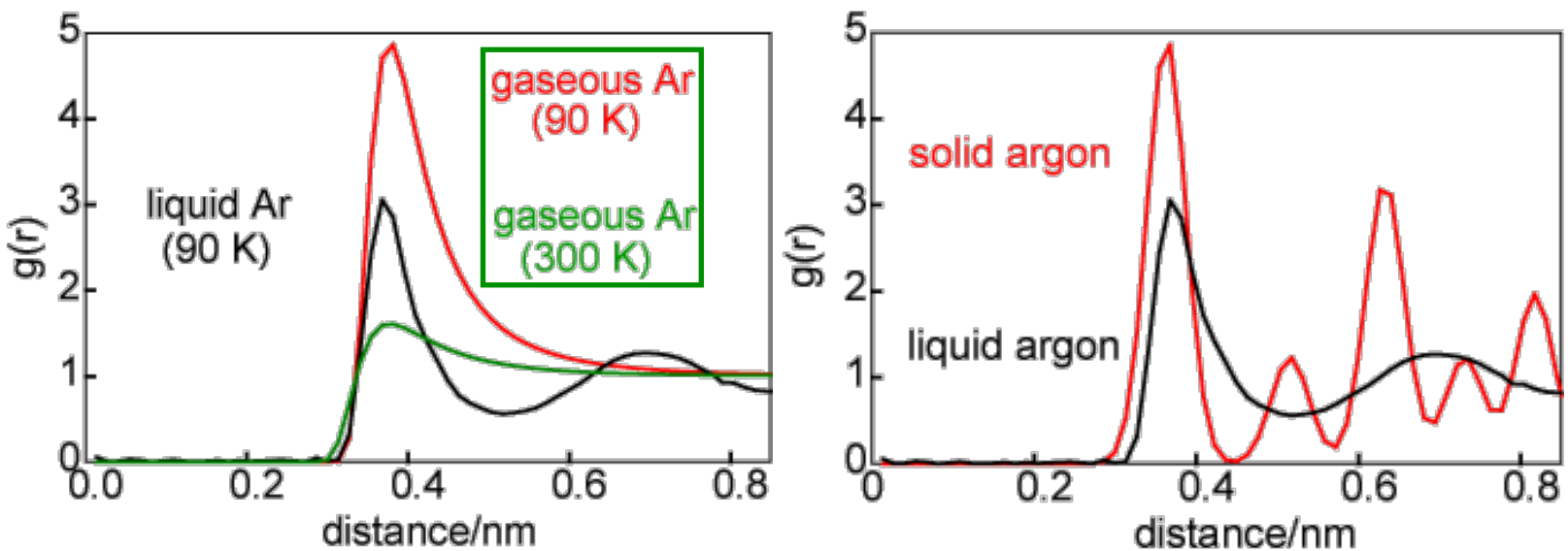
Typical features:

gas: almost structureless

(ideal gas: no interactions or correlations, $g(r) = 1$ for r large enough)

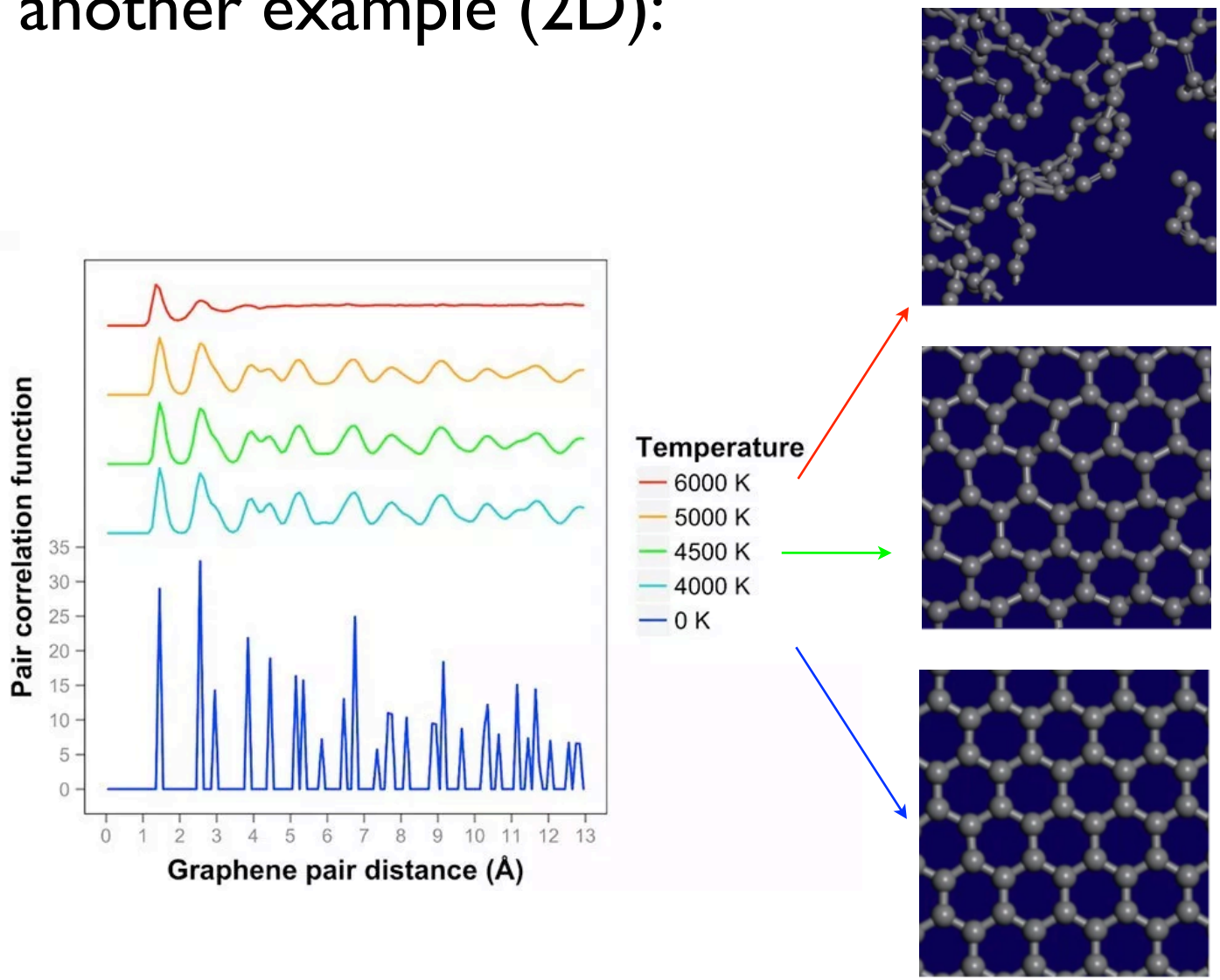
liquid: some structure with broad peaks

solid: evidence of well separated coordination shells, zero in between; broadening of the peaks depending on T



(credit to: Thomas/Penfold Group, http://rkt.chem.ox.ac.uk/)

another example (2D):



The initial stages of melting of graphene between 4000 K and 6000 K, E. Ganz et al., *Phys. Chem. Chem. Phys.*, 2017, **19**, 3756

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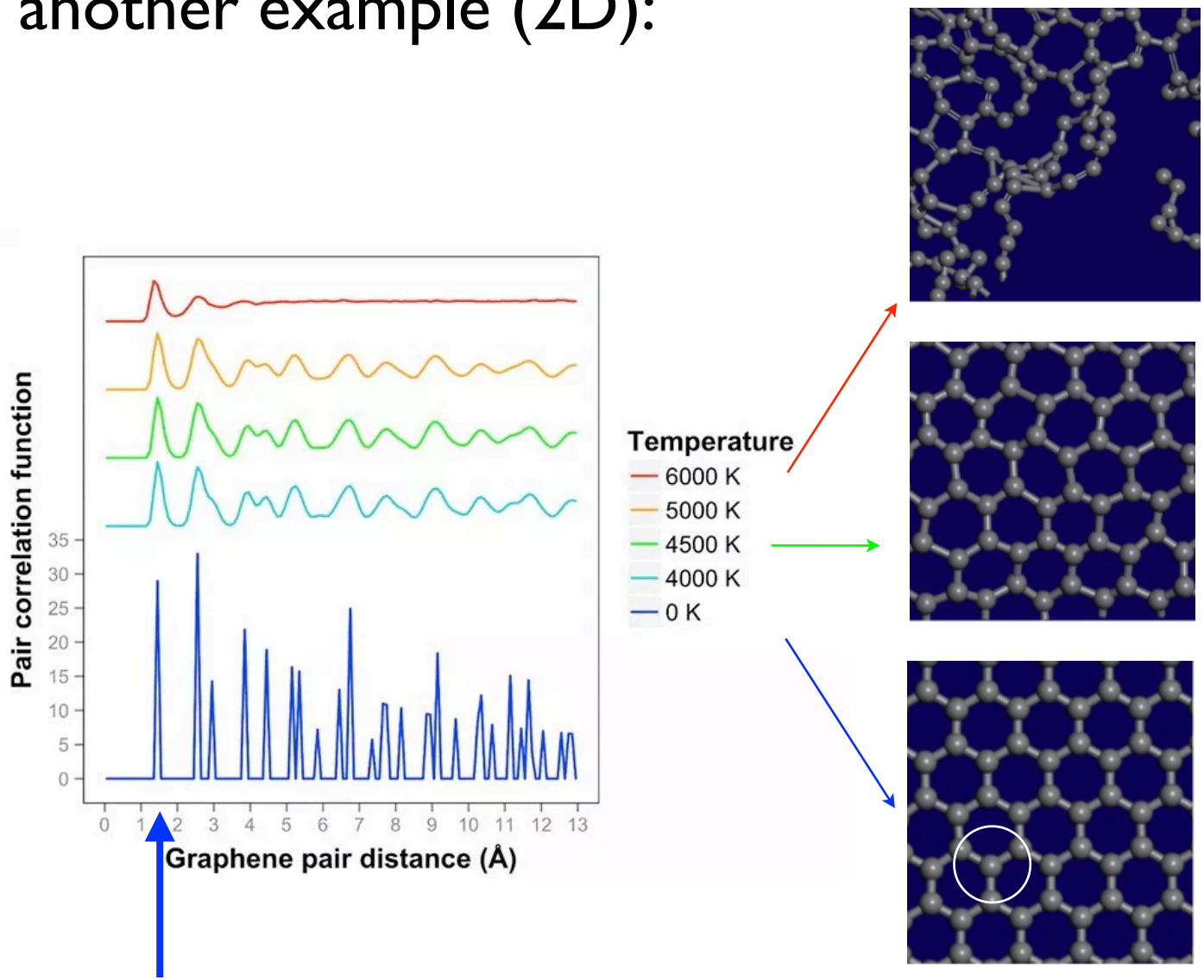

The initial stages of melting of graphene between 4000 K and 6000 K, E. Ganz et al., *Phys. Chem. Chem. Phys.*, 2017, **19**, 3756

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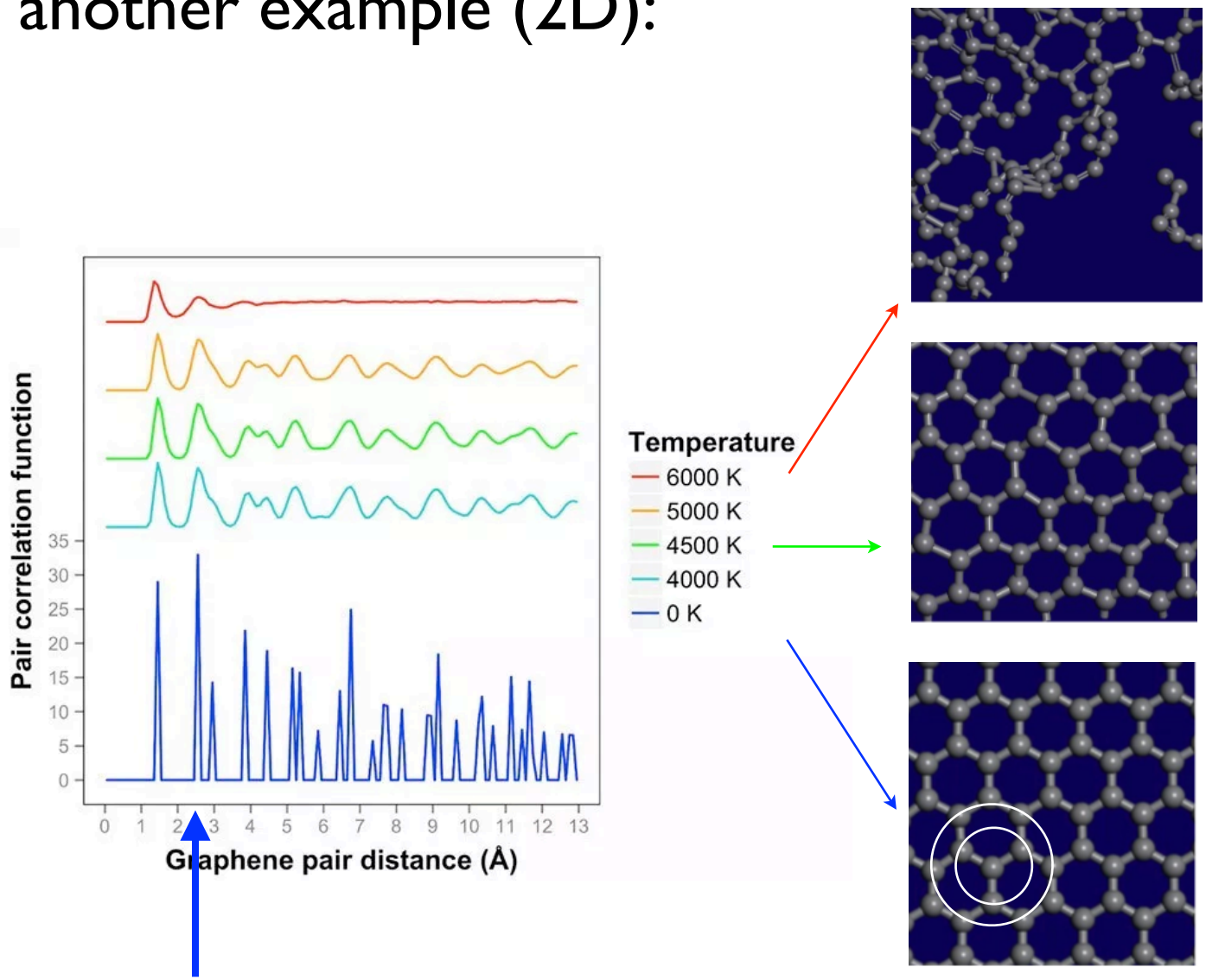

The initial stages of melting of graphene between 4000 K and 6000 K, E. Ganz et al., *Phys. Chem. Chem. Phys.*, 2017, **19**, 3756

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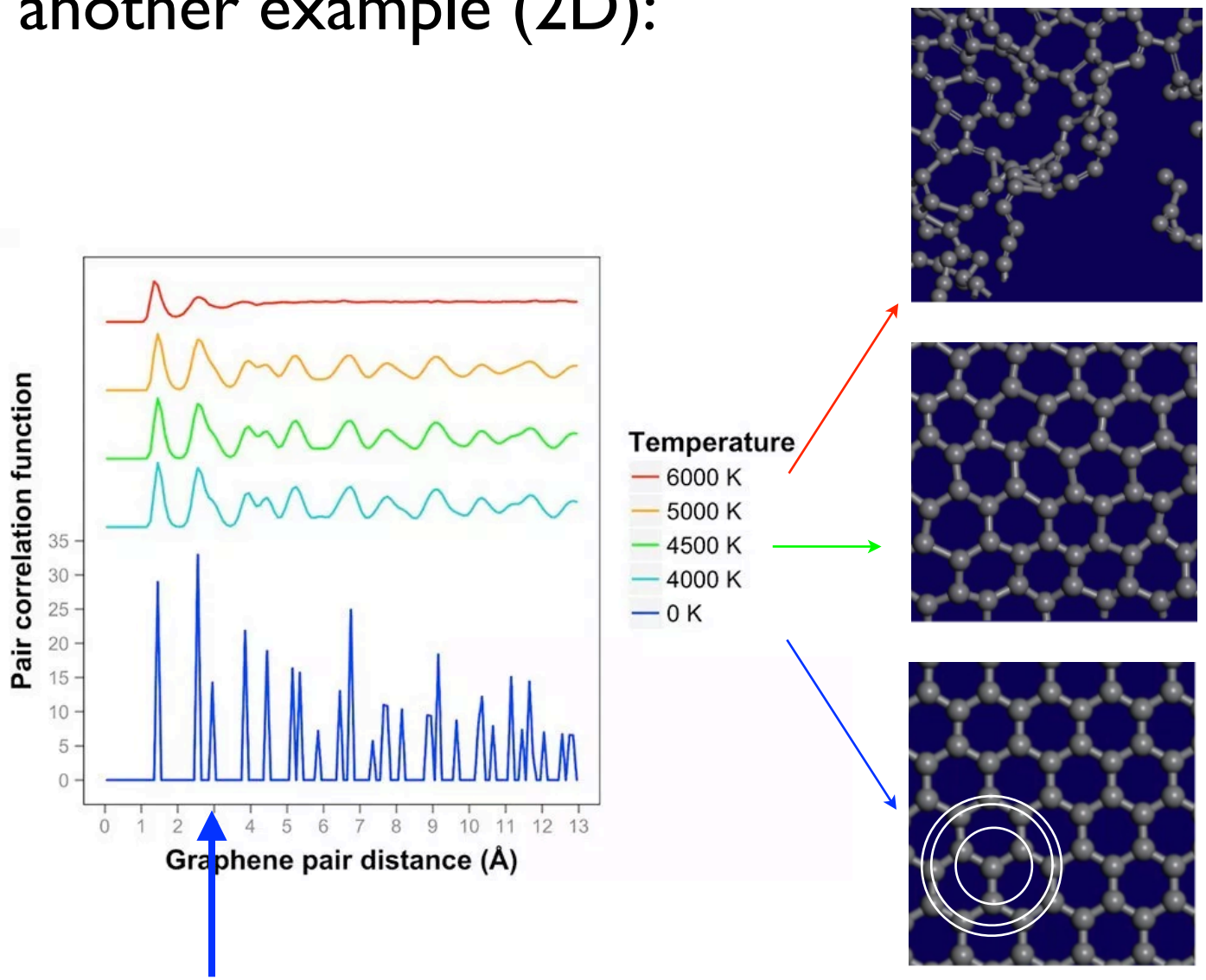


The initial stages of melting of graphene between 4000 K and 6000 K, E. Ganz et al., *Phys. Chem. Chem. Phys.*, 2017, **19**, 3756

Radial distribution function

Relevance of g(r) for other physical quantities

$\rho g(r)$: local density about a given particle

g(r) gives structural information, but
it is relevant to calculate also other ensemble averages of quantities depending on pair interactions, e.g., energy:

potential energy between this particle and others
in a volume $d\mathbf{r}$ around r: $u(r)\rho g(r)d\mathbf{r}$

average potential energy per particle: $\frac{U}{N} = \frac{\rho}{2}\int g(r)u(r)\,d\mathbf{r}$

Pressure

From the virial(see next slide) and equipartition theorems:

$$\frac{PV}{NkT} - 1 = \frac{1}{dNkT} \sum_{i<j} \overline{\mathbf{r}_{ij} \cdot \mathbf{F}_{ij}}$$

(average over particles pairs and time)
Note the additional term due to interactions with respect to the eq. of state of the ideal gas

If only two-body forces are present, the virial eq. of state can be rewritten using the radial distribution function:

$$\frac{\beta P}{\rho} = 1 - \frac{\beta \rho}{2d} \int g(r)\, r \frac{dV(r)}{dr}\, d\mathbf{r}$$

dimensionality

Virial theorem

If $\langle E_{kin} \rangle$ is the time average of the total kinetic energy and $\mathbf{F}_k$ is the force acting on the particle *k* at the position $\mathbf{r}_k$, the virial theorem states:

$$2\langle E_{kin} \rangle = -\sum_{k=1}^{N} \langle \mathbf{F}_k \cdot \mathbf{r}_k \rangle$$

If the force between any two particles of the system results from a potential energy $V(r) = \alpha r^n$ where *r* is the inter-particle distance, the virial theorem is simply:

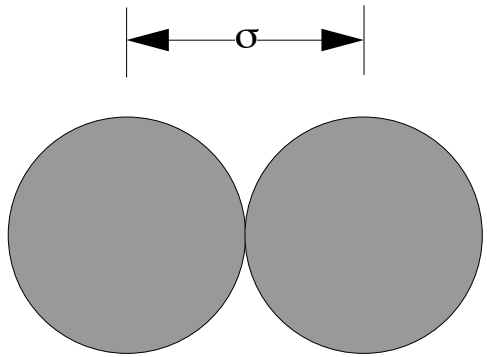
$$2\langle E_{kin} \rangle = n\langle V_{tot} \rangle$$

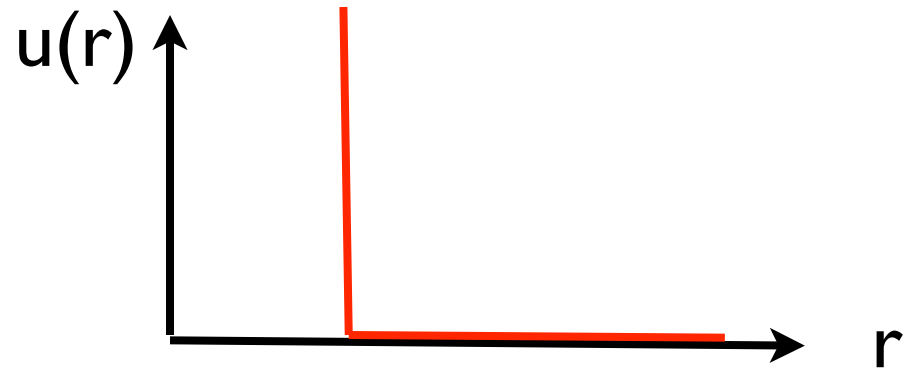
(average also over time)

Hard disks

A particular form of interacting potential

(similar to the simplest lattice gas model with no double site occupancy, but here in a continuum)





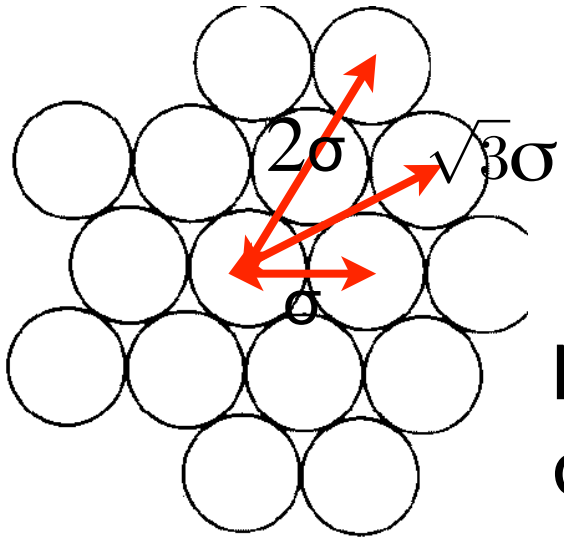
$$u(r) = \begin{cases} +\infty, & r < \sigma \\ 0, & r \geq \sigma \end{cases}$$

No minimum; check overlap!

No attractive part => no transition from gas to liquid

Hard disks

σ: diameter of the disks



Solid phase: close-packed structure (hex lattice); position of the peaks:

NN shell: σ

2NN shell: $\sqrt{3}\sigma$

3NN shell: 2σ

particle (or number) density : $\rho = \dfrac{\text{number of particles}}{\text{area}} = \dfrac{N}{A}$

max particle (or number) density : $\rho_{max} = \dfrac{2}{\sqrt{3}\sigma^2}$

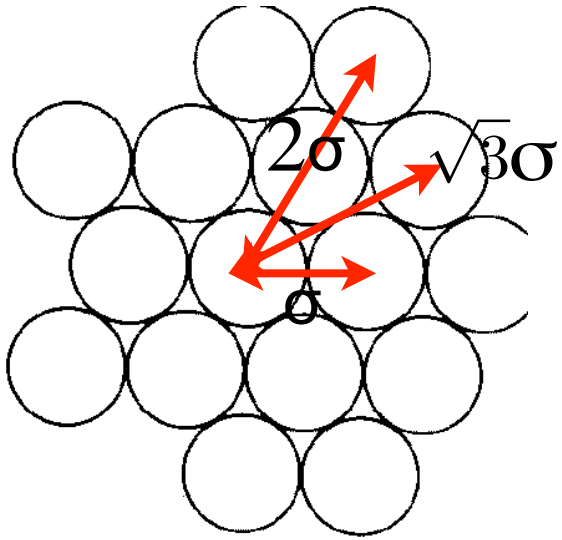
reduced density : $\rho^* = \rho\sigma^2$ (non-dimensional quantity)

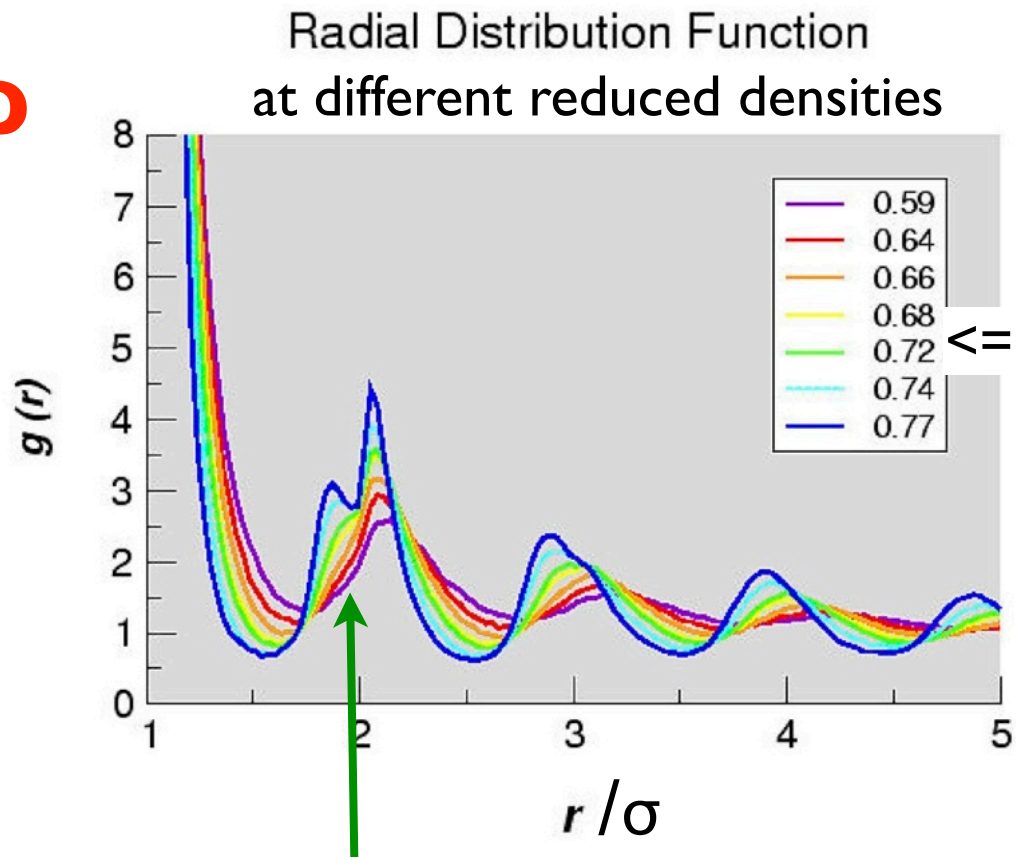
max reduced density : $\rho^*_{max} = \dfrac{2}{\sqrt{3}} = 1.1547$

max packing fraction: $f = \dfrac{area_{occupied}}{area_{available}} = \dfrac{\pi}{2\sqrt{3}} = 0.907$ $\qquad f = \dfrac{\pi}{4}\rho^*$

Radial distribution function

of **hard disks in 2D**





$$f = \frac{\pi}{4}\rho^*$$

the appearance of a double structure in the peak around 2σ
is a fingerprint of the liquid-solid transition
(high density solid: peaks at ~1.7 σ and 2 σ)

max reduced density: $\rho^*_{max} = \frac{2}{\sqrt{3}} = 1.1547$

Structural precursor to freezing in the hard-disk and hard-sphere systems

Thomas M. Truskett,[1] Salvatore Torquato,[2,3,*] Srikanth Sastry,[1] Pablo G. Debenedetti,[1] and Frank H. Stillinger[4,2]

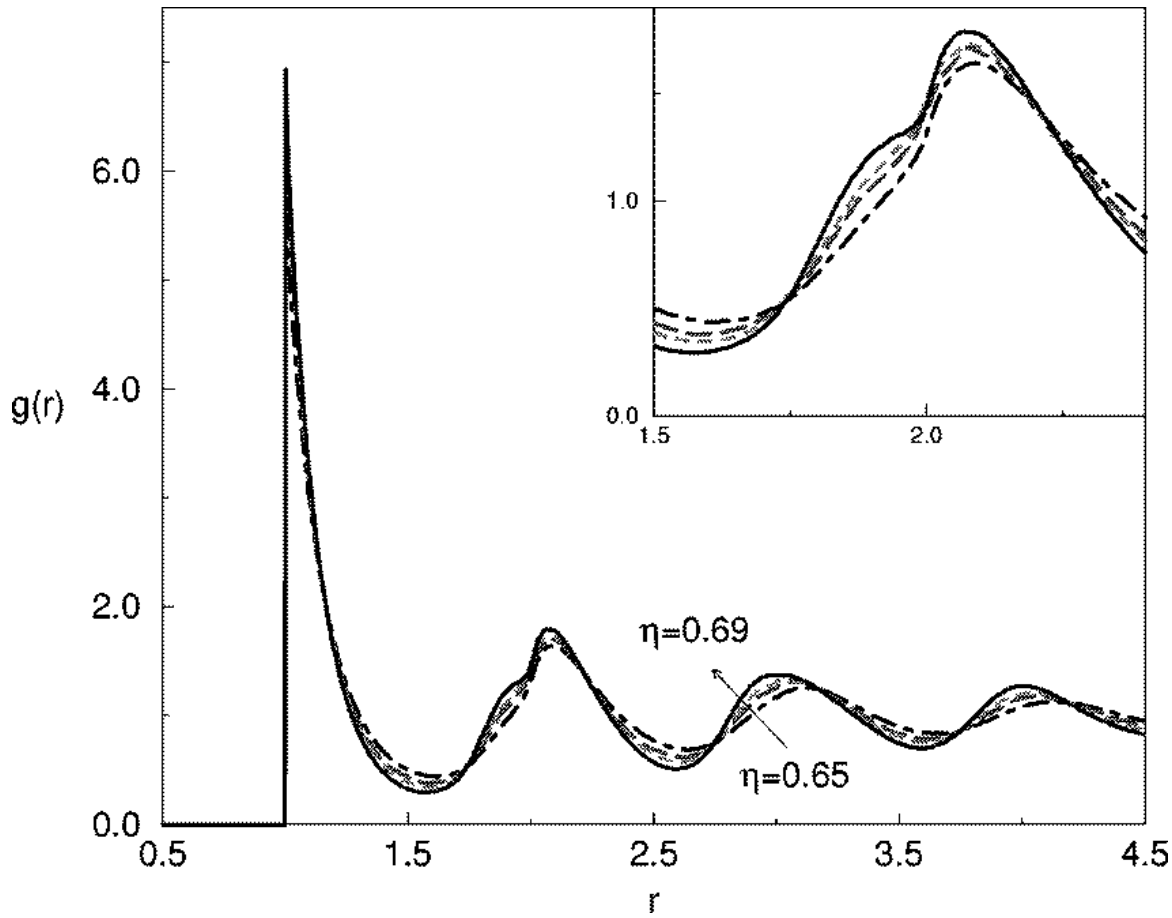


FIG. 1. Radial distribution function $g(r)$ for hard disks plotted versus distance r (in units of diameters). Curves represent the fluid phase with $\eta = 0.65$, 0.67, 0.68, and 0.69 (freezing point).

$(here : \eta \equiv \rho^*)$

Pressure

case of Hard Disks (Spheres):

Virial eq. of state

$$\frac{\beta P}{\rho} = 1 - \frac{\beta\rho}{2d}\int g(r)\, r \frac{dV(r)}{dr}\, d\mathbf{r}$$

becomes:

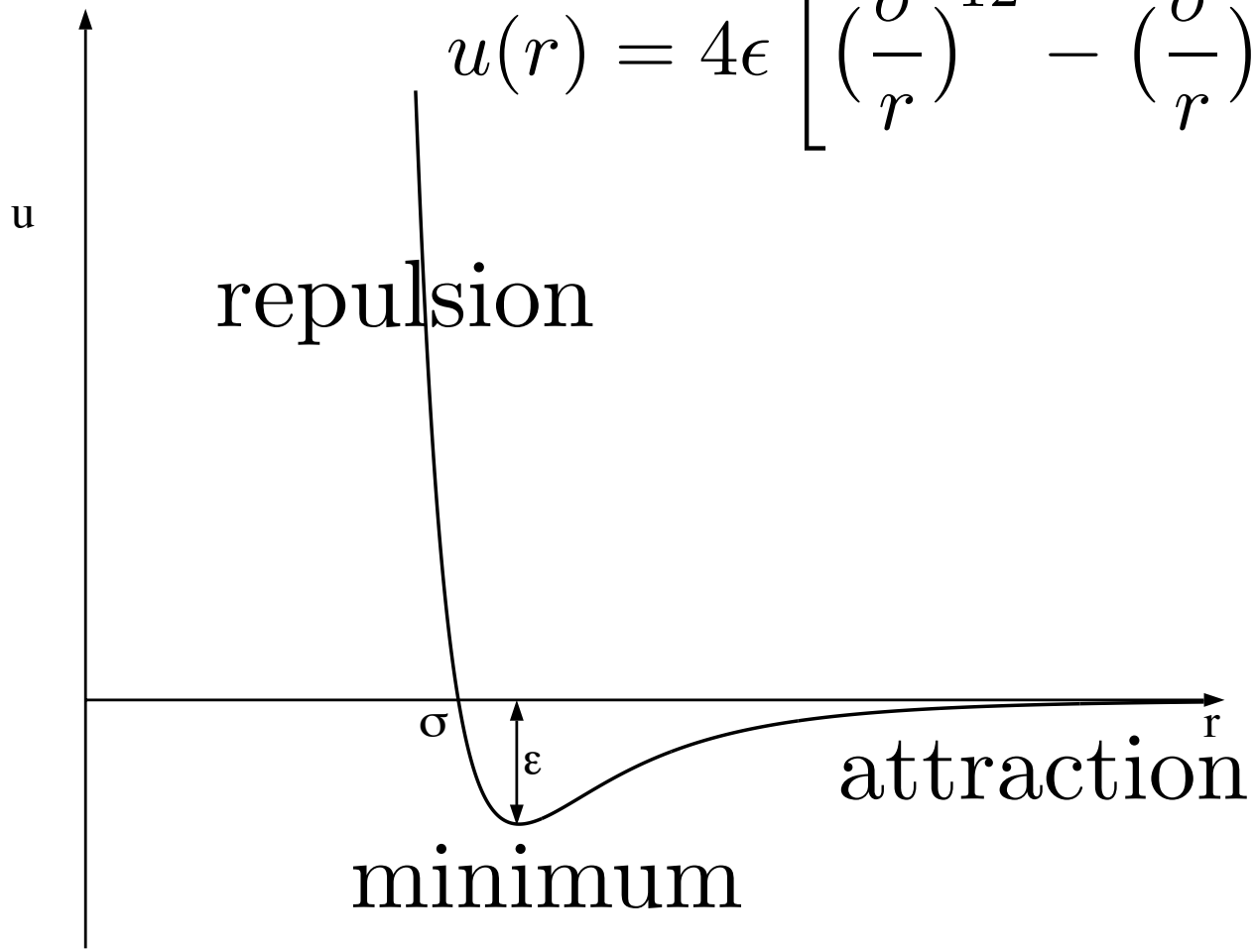
$$d\mathbf{r} = 4\pi r^2 dr \qquad \frac{\beta P}{\rho} = 1 + \frac{2}{3}\pi\rho\sigma^3 g(\sigma) \qquad (d=3)$$

$$d\mathbf{r} = 2\pi r\ dr \qquad \frac{\beta P}{\rho} = 1 + \frac{1}{2}\pi\rho\sigma^2 g(\sigma) \qquad (d=2)$$

$$d\mathbf{r} = 2\ dr \qquad \frac{\beta P}{\rho} = 1 + \rho\sigma g(\sigma) \qquad (d=1)$$

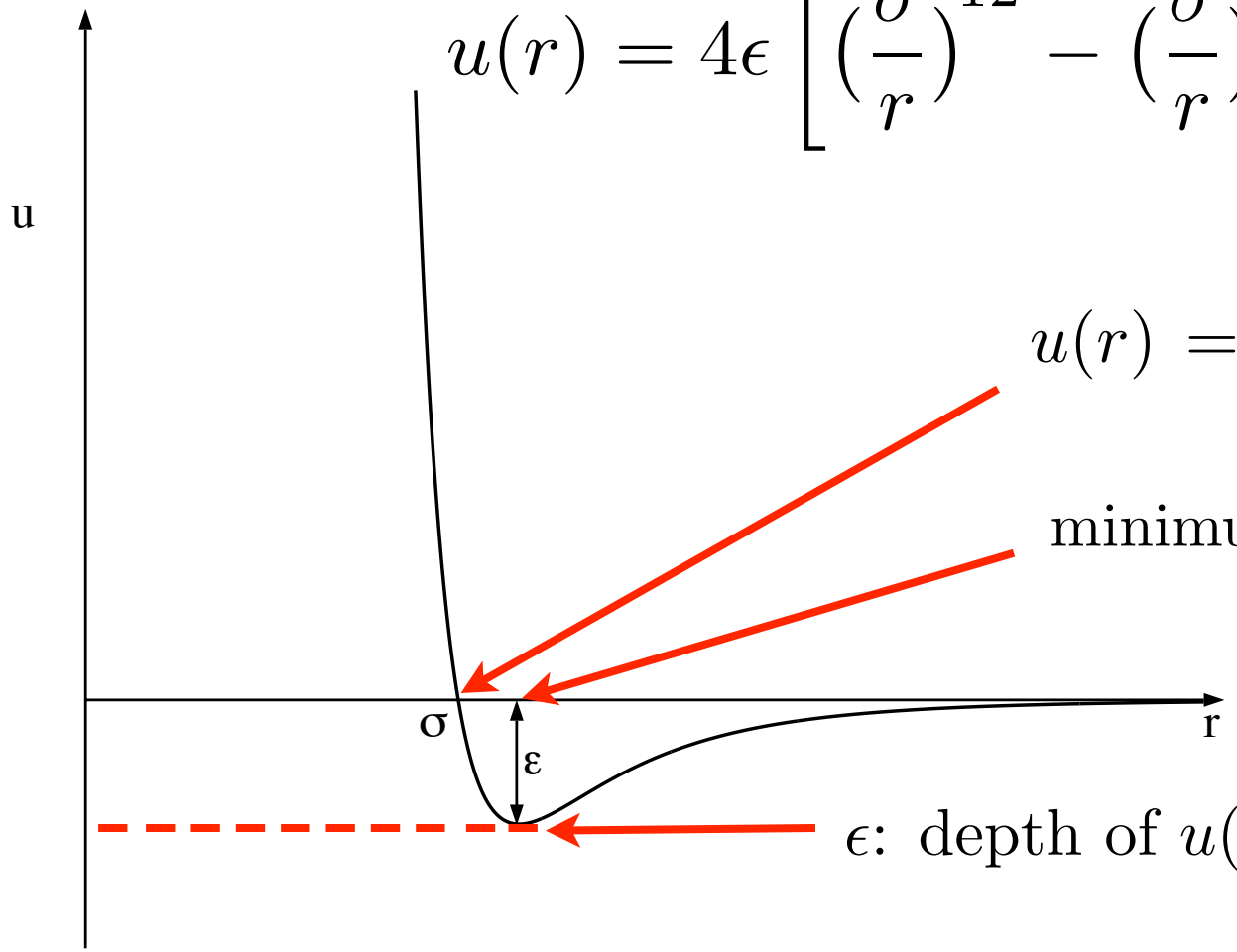
Lennard-Jones potential

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



Lennard-Jones potential

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



$u(r) = 0$ at $r = \sigma$

minimum at $r = 2^{1/6}\sigma$

ϵ: depth of $u(r)$ at the minimum

liquid argon: $\epsilon = 1.65 \times 10^{-21}$ J $\qquad \sigma = 3.4\,\mathring{A}$

Units

(d=2)

To reduce the possibility of roundoff error, it is useful to choose units so that the computed quantities are neither too small nor too large.

quantity	unit	value for argon
length	σ	$3.4 \times 10^{-10}\,\mathrm{m}$
energy	ϵ	$1.65 \times 10^{-21}\,\mathrm{J}$
mass	m	$6.69 \times 10^{-26}\,\mathrm{kg}$
time	$\sigma(m/\epsilon)^{1/2}$	$2.17 \times 10^{-12}\,\mathrm{s}$
velocity	$(\epsilon/m)^{1/2}$	$1.57 \times 10^{2}\,\mathrm{m/s}$
force	ϵ/σ	$4.85 \times 10^{-12}\,\mathrm{N}$
pressure	ϵ/σ^2	$1.43 \times 10^{-2}\,\mathrm{N \cdot m^{-1}}$
temperature	ϵ/k	$120\,\mathrm{K}$

Table 8.1: The system of units used in the molecular dynamics simulations of particles interacting via the Lennard-Jones potential. The numerical values of σ, ϵ, and m are for argon. The quantity k is Boltzmann's constant and has the value $k = 1.38 \times 10^{-23}\,\mathrm{J/K}$. The unit of pressure is for a two-dimensional system.

Unit of time is derived: e.g., for Ar: $\Delta t = 0.01 \Longrightarrow 2.17 \times 10^{-14} s$

Generalities in many-body simulations

- periodic boundary conditions
- minimum image

Periodic Boundary Conditions

for the positions

(here: in the continuum;
before: only in discretized conditions - Ising and lattice models)

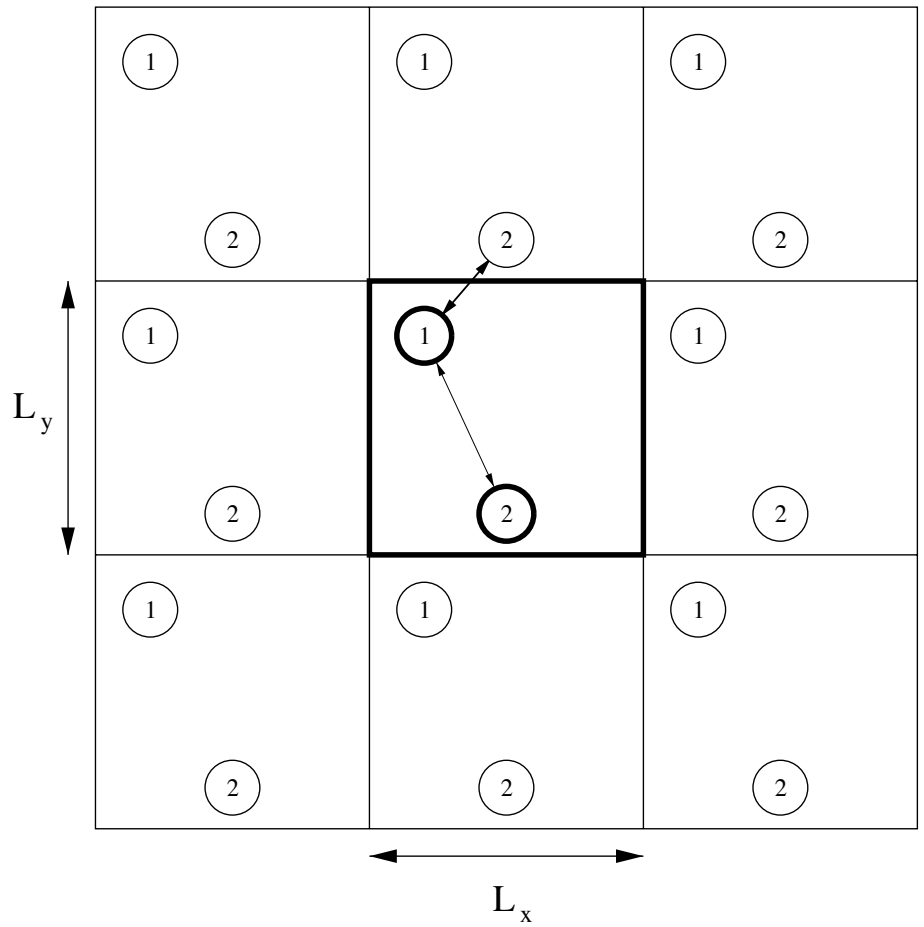
```
function pbc(pos,L) result (f_pbc)
    .......
    if (pos < 0.0) then
        f_pbc = pos + L
    else if (pos > L) then
        f_pbc = pos - L
    else
        f_pbc = pos
    end if
end function pbc
```

(OK
in the hypothesis that
-L < pos <2L)

Minimum Image convention

for the interactions

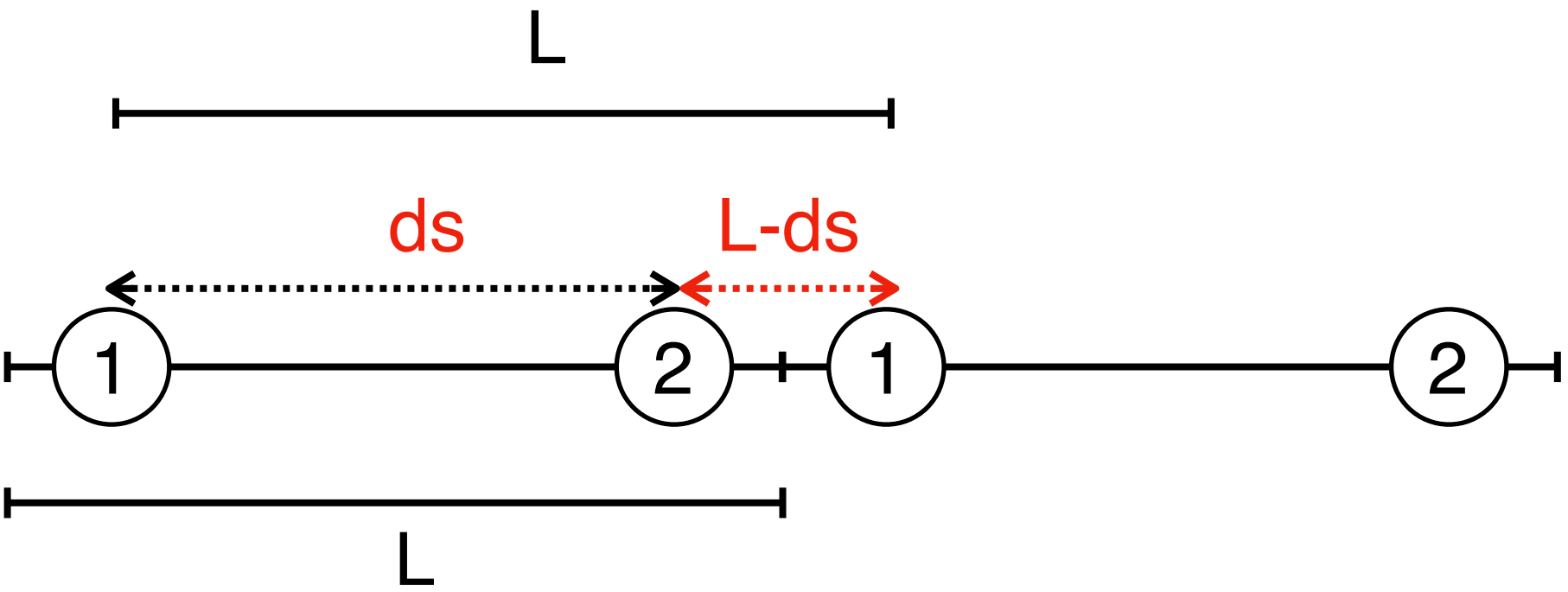
To compute the minimum distance `dx` between particles 1 and 2 at `x(1)` and `x(2)`



Only the interactions with the nearest images are considered

Minimum Image convention

for the interactions



Minimum Image convention

for the interactions

To compute the minimum distance `dx` between particles 1 and 2 at `x(1)` and `x(2)`

```
function separation(ds,L) result (separation_result)
    .......
    if (ds > 0.5*L) then
        separation_result = ds - L
    else if (ds < -0.5*L) then
        separation_result = ds + L
    else
        separation_result = ds
    end if
end function separation
```

(OK if distances do not exceed L)

(then, consider the absolute value)

Radial distribution function

```
subroutine correl()
      ...
do i=1,N-1
   do j=i+1,N
      dx = x(i) - x(j)
      dy = y(i) - y(j)
      call separation(dx,dy)
      r2 = dx*dx + dy*dy
      ibin = int(sqrt(r2)/dr)+1
      if (ibin<=nbin) then
        gcum(ibin) = gcum(ibin) + 1
      end if
    end do
end do
```

implementation of
the counting algorithm

$$g(r) = \frac{2}{2\pi r \Delta r \cdot nN} \left\langle \sum_{i=1}^{N-1} \sum_{j>i} \delta(r - |\mathbf{r}_{ij}|) \right\rangle$$

```
xnorm = 2./(rho*nmcs*N)       ! rho : average density = N/V
 ...
      r    = ir*dr + 0.5*dr          ! r in the middle of the circular shell
      area = 2.0*pi*r*dr             ! area of the shell
      g    = gcum(ir)*xnorm/area
 ...
```

Two approaches to simulate the evolution of the system

(to sample the configuration space)

- stochastic (Metropolis Monte Carlo)
- deterministic (integration of the eq. of motion)

Programs:

on moodle2

hd-MC.f90
hd-MD.f90
LJ-MD.f90

Classical fluids: Metropolis Monte Carlo method canonical ensemble (NVT)

- calculate E_{tot}

- displace an individual particle by a small amount: calculate ΔE (variation of the interaction of that particle with all the others)

- accept/reject the new position with the usual Metropolis factor: $w = \min [1, \exp (-\Delta E/kT)]$

- iterate

- accumulate distances to calculate g(r)

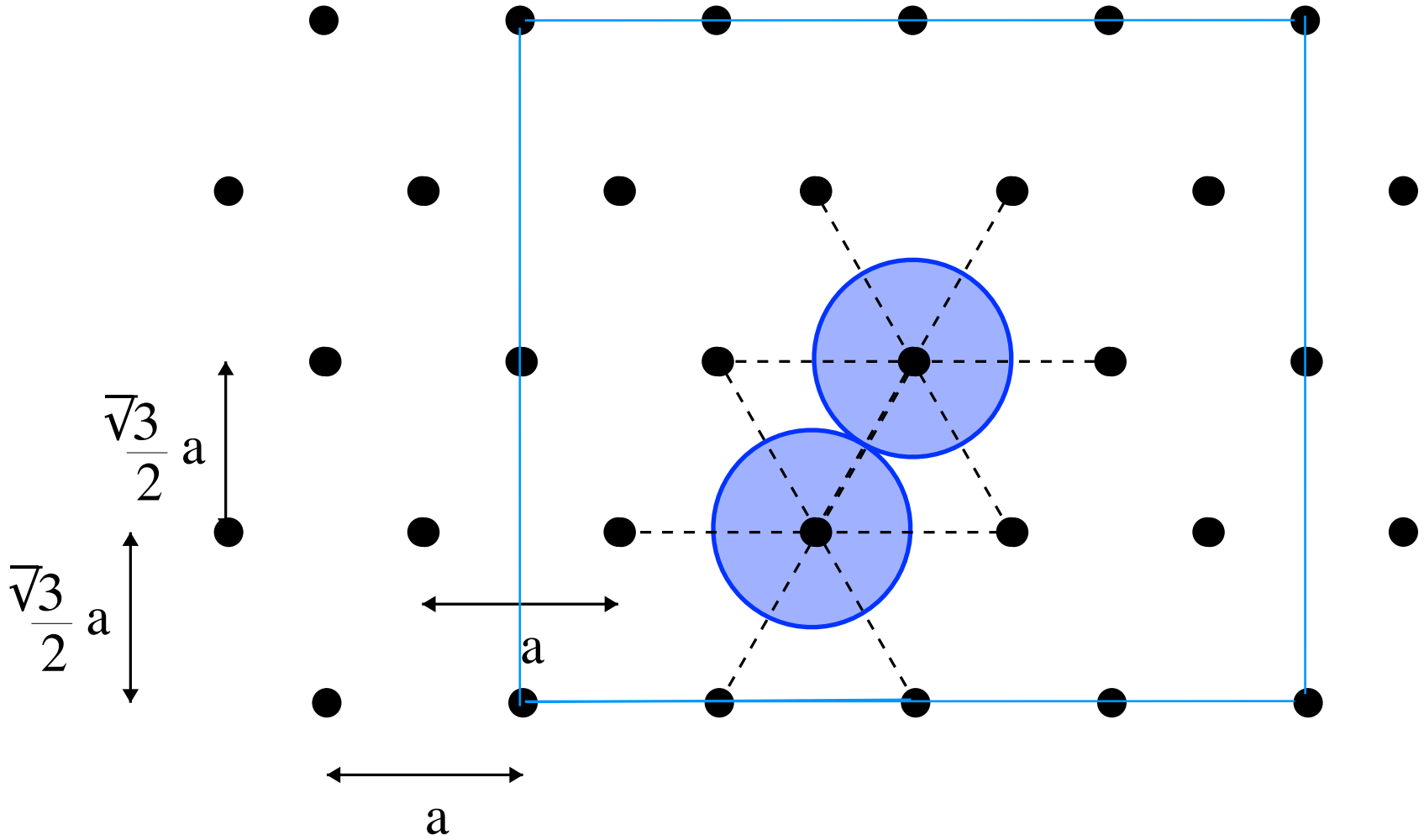
Metropolis Monte Carlo method for Hard Disks (Spheres)

displace an individual particle by a small amount:
if overlap with another particle: REJECTED
if no overlap with any other particle: ACCEPTED

-Metropolis algorithm with $\Delta E = 0 \quad or \quad \infty$

-ergodicity: obvious at low densities;
complicated at high densities

Maximum package



hexagonal lattice

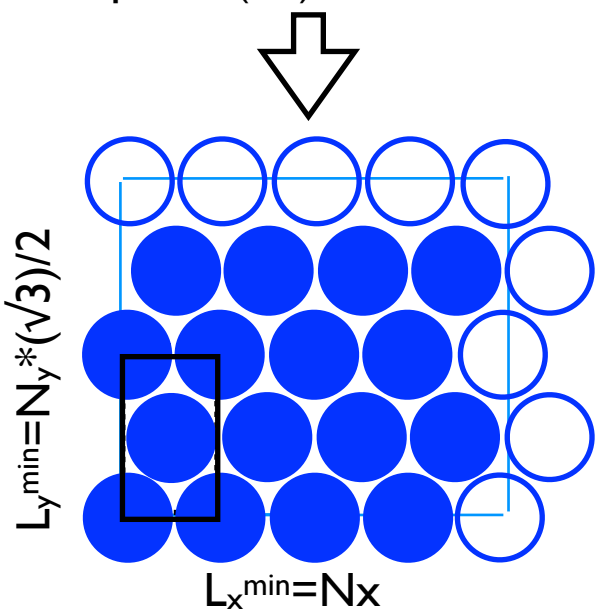
take the linear dimensions of the cell to be L_x and $L_y = \sqrt{3}L_x/2$ (here: N=16)

Initializing the positions

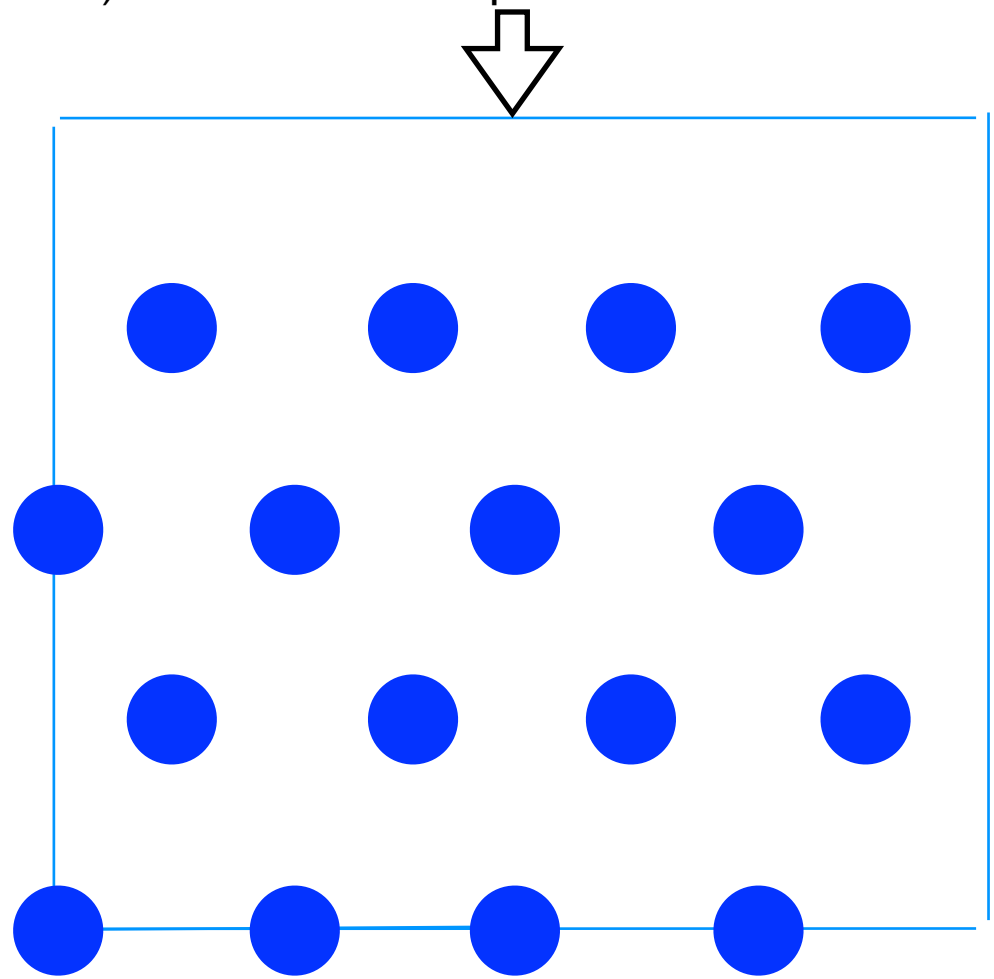
Convenient to start from maximum packing and then reduce the density:

1) choose N_x (even or odd); $L_x^{min}=N_x$
2) choose N_y even (and not too different from Ny in order to have a cell not too elongated) (here = 4); $L_y^{min}=N_y*(\sqrt{3})/2$
3) This gives the maximum packing and the maximum density ρ^{max}
4) Calculate the individual positions:

x(i)=integer/semi-integer for even/odd rows;
y(i)=multiple of $(\sqrt{3})/2$



1) choose ρ
2) Determine the new L_x and L_y by scaling: $L_x=\kappa L_x^{min}$ and $L_y=\kappa L_y^{min}$, where $k^2=\rho^{max}/\rho$
3) Rescale individual positions



some useful gnuplot commands:

set size ratio {Ly/Lx}
unset key (to avoid the label)
p [0:Lx][0:Ly] '*file_of_positions*' u 1:2:(0.5) w circles

(the radius could be given in the 3rd column; here it is set to 0.5)

Molecular dynamics

a deterministic approach to the dynamics of a system

MD generates the dynamical trajectories of a system of *N* particles by integrating Newton's equations of motion

- with suitable initial and boundary conditions
- proper interatomic potentials
- while satisfying thermodynamical (macroscopic) constraints

- and with a 'smart' algorithm for numerical integration

Molecular dynamics

and Newton's equations of motion

$$F = ma$$

But not always easy to solve… In general:

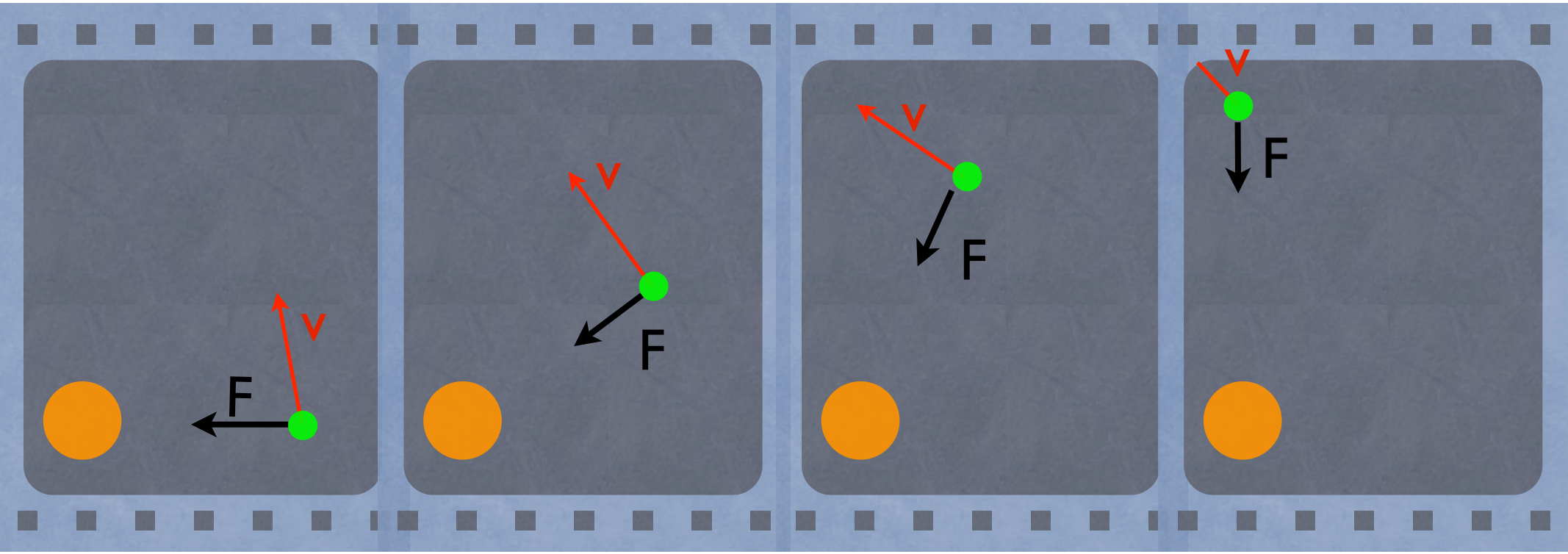
$$\frac{d^2x}{dt^2} = a(x, t, \dots) = \frac{F(x, t, \dots)}{m}$$

Analytical solution for constant forces;
but in general not always possible

=> **different possible algorithms for numerical integration of the eqs. of motion**

Basic idea: discretization - e.g. consider uniformly acc. motion

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



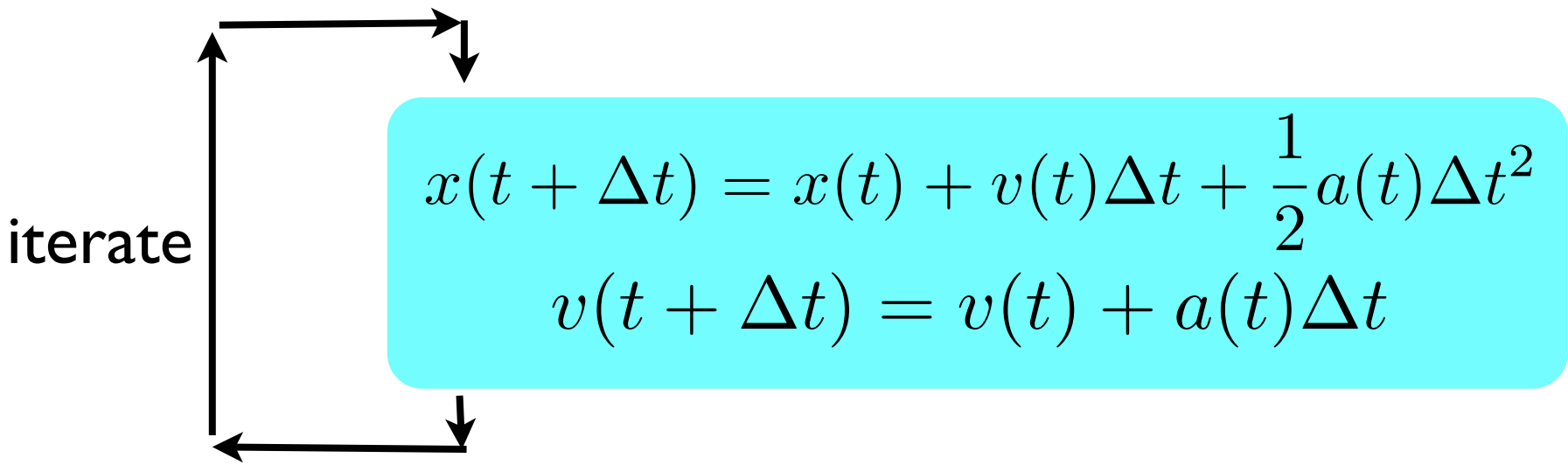
x(0) v(0) F(0) x(1) v(1) F(1) x(2) v(2) F(2) ... ...

Uniformly accelerated motion in each time interval

$t \div t + \Delta t$

then iterate!

EULER algorithm

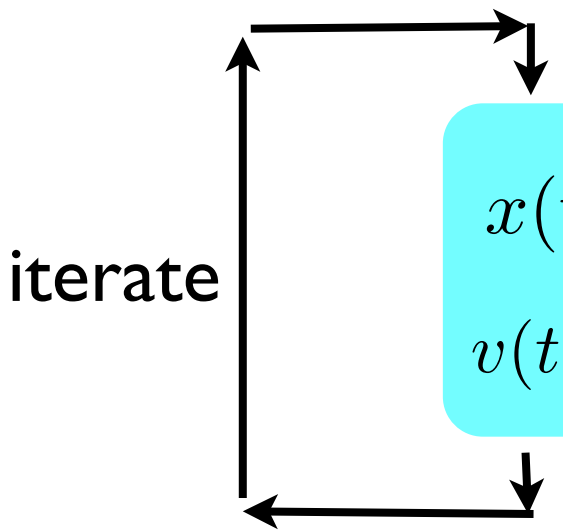


$$x(t) \Longrightarrow x(t + \Delta t) \Longrightarrow x(t + 2\Delta t) \Longrightarrow x(t + 3\Delta t) \Longrightarrow \ldots$$

$$v(t) \Longrightarrow v(t + \Delta t) \Longrightarrow v(t + 2\Delta t) \Longrightarrow v(t + 3\Delta t) \Longrightarrow \ldots$$

DO BETTER: instead of choosing the value of the **acceleration** at the beginning of each time interval, take its **average value in the interval** $t \div t + \Delta t$ for the update of the velocity

Velocity-VERLET algorithm



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

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

Remark: the new acceleration can be calculated as soon as the new position is calculated, so that the algorithm is explicit!

Choice of an integration algorithm

- **Accuracy** - does it give an accurate description of the motion?
- **Stability** - does it conserve the system energy and temperature (in case of conservative forces)? (*)
- **Simplicity** - is it easy to implement it in a computer code?
- **Speed** - does it require only few or a lot of operations?
- **Economy** - how much memory does it require?

Velocity- Verlet algorithm

a second-order algorithm allows a good energy conservation if forces are NOT dependent on velocities (*)

Thermodynamical ensemble

IF POTENTIAL ENERGY does not depend on velocities (conservative potentials), the TOTAL ENERGY of the system should be conserved!

Therefore, since Verlet's integration of the Newton's equations will:

Conserve total energy (E=const.)
Keep number of particles constant (N=const.)
Keep volume constant (V=const.)

Thus: Yields an **NVE ensemble ("microcanonical ensemble")**

Energy
in MD - NVE simulations

the TOTAL ENERGY of the system should be conserved!

TO BE CHECKED during simulations
(it may not be conserved because
of a bad integration algorithm)

It is common practice to compute it at each time step in order to check that it is indeed constant with time.
During the run energy flows back and forth between kinetic and potential: they fluctuate while their sum remains fixed.

In practice there could be small fluctuations in the total energy, tolerance ~ 1%

Temperature in MD - NVE simulations

T is related to (and therefore can be estimated from) the kinetic energy:

$$E_{kin} = \frac{1}{2} m \sum_{i}^{N} v_i^2 \quad \Rightarrow \quad T = \frac{2}{3} \frac{E_{kin}}{N k_B}$$

It is not a constant !

Pressure

It can also be calculated at each time step from kinetic energy, forces and positions (Virial theorem)

Choices of:

- Initial conditions

- time step

A good integration algorithm is not enough:

INITIAL CONDITIONS: Important in case of deterministic evolutions

TIME STEP:
too short => phase space is sampled inefficiently,
too long => energy will fluctuate wildly and simulation may become catastrophically unstable ("blow up").
Instabilities are caused e.g. by the motion of particles (atoms, planets...) being extrapolated into regions where the potential energy is prohibitively high (e.g. overlapping or too much close particles).
E.g. in atomic fluids simulations: choose time step comparable to the mean time between ionic collisions (about 5 fs for Ar at 298K) (a good rule of thumb)

MD vs MC simulations

MD has a kinetic energy contribution to the total energy, whereas **in MC the total energy is determined solely by the potential energy function**.

MD samples naturally from the microcanonical (NVE) ensemble, whereas Metropolis MC samples from the canonical (NVT) ensemble.

However, both MC and MD can be modified to sample from different ensembles.