



# 993SM - Laboratory of Computational Physics lecture XI May 18, 2022

**Maria Peressi**

Università degli Studi di Trieste - Dipartimento di Fisica

Sede di Miramare (Strada Costiera 11, Trieste)

e-mail: [peressi@units.it](mailto:peressi@units.it)

tel.: +39 040 2240242

# Classical fluids

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

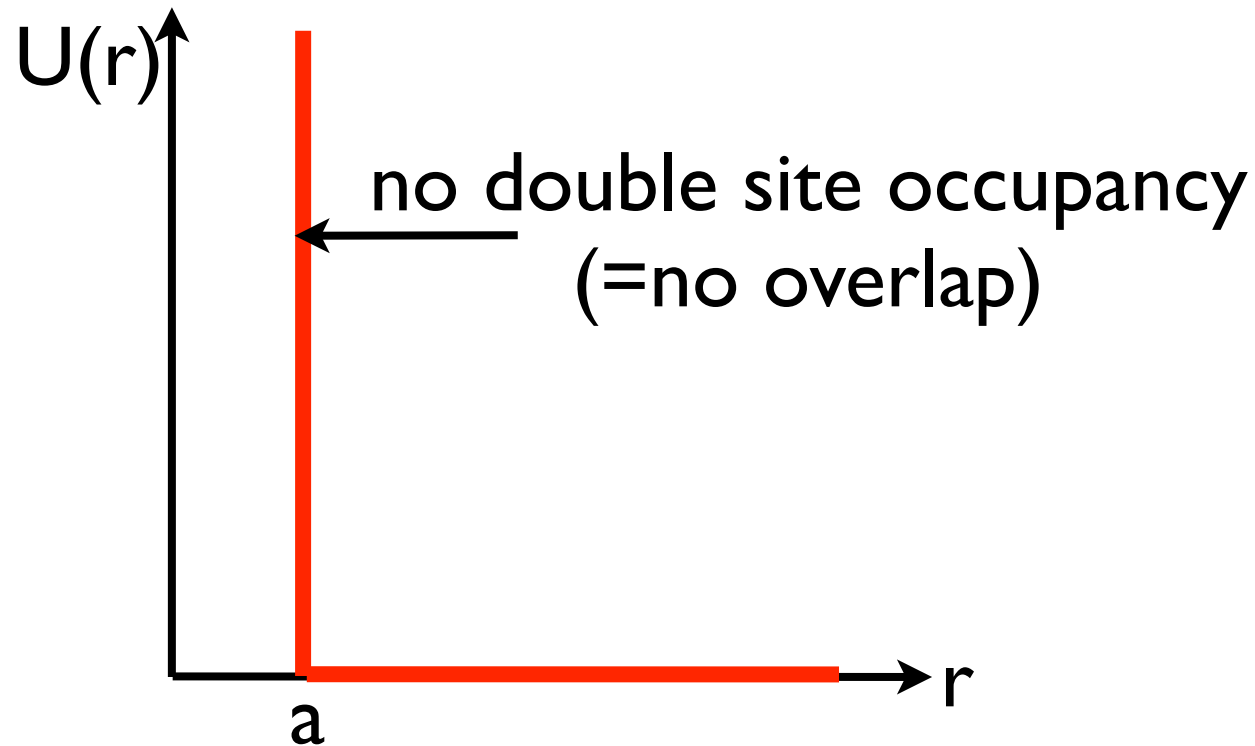
(here: several slides; but today only few basic concepts will be discussed)

M. Peressi - UniTS - Laurea Magistrale in Physics  
Laboratory of Computational Physics - Unit XI

# Interactions

# A very simple interaction

The lattice gas model :



but in general: ...

# Interactions

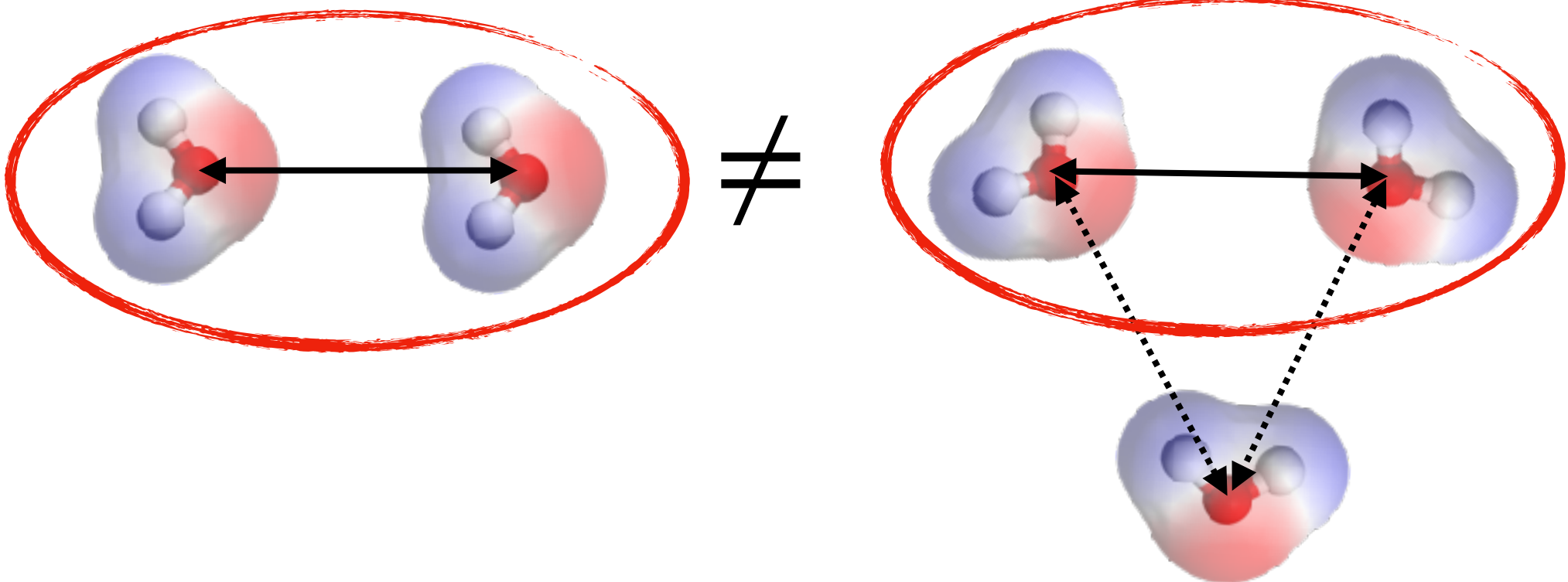
assume that the force between any pair of molecules depends only on the distance  
(or atoms)  
( $u(r_{ij})$  depends only on the magnitude of the distance  $r_{ij}$  between particles  $i$  and  $j$ )

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

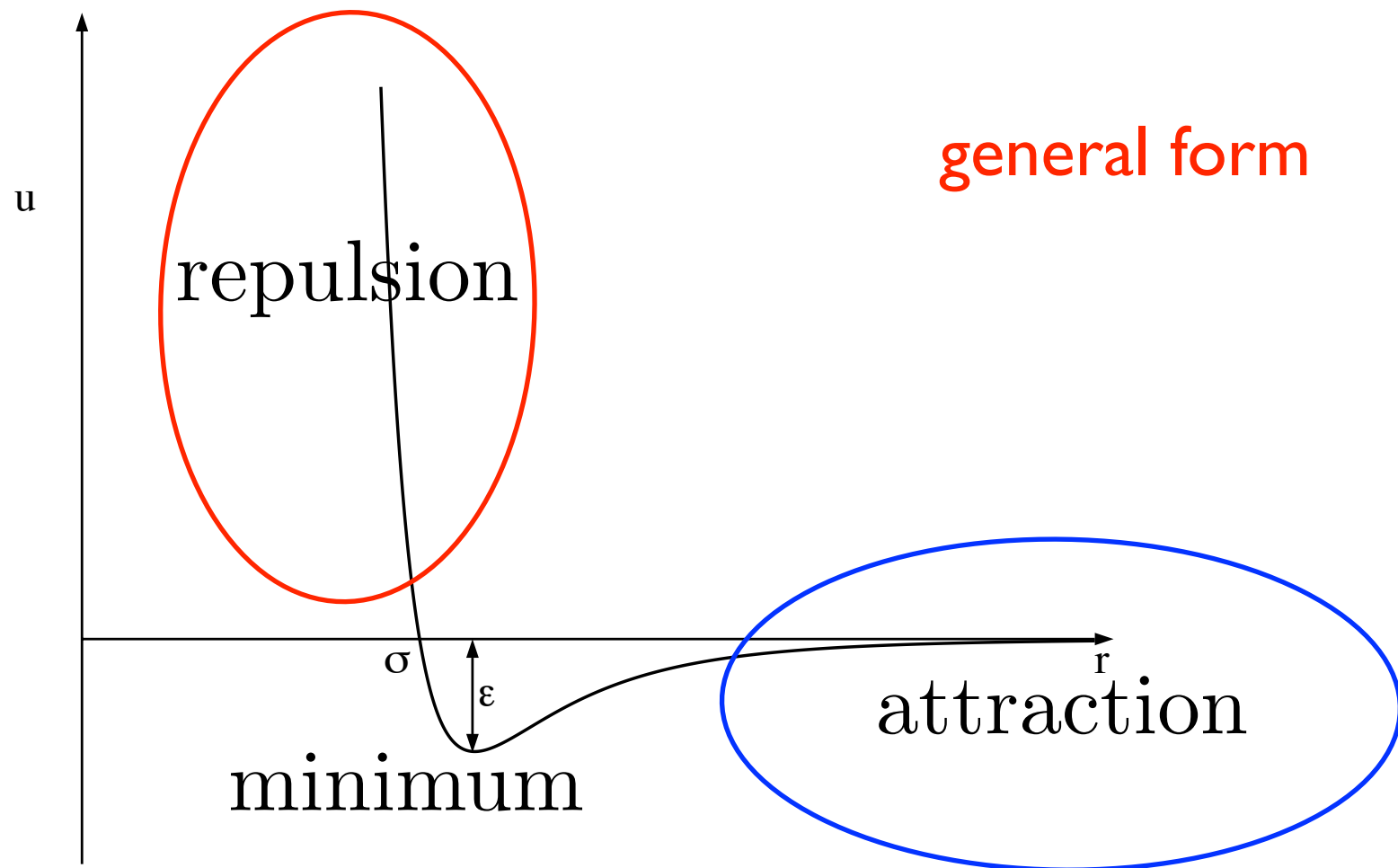
$$U = u(r_{12}) + u(r_{13}) + \cdots + u(r_{23}) + \cdots = \sum_{i=1}^{N-1} \sum_{j=i+1}^N u(r_{ij})$$

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

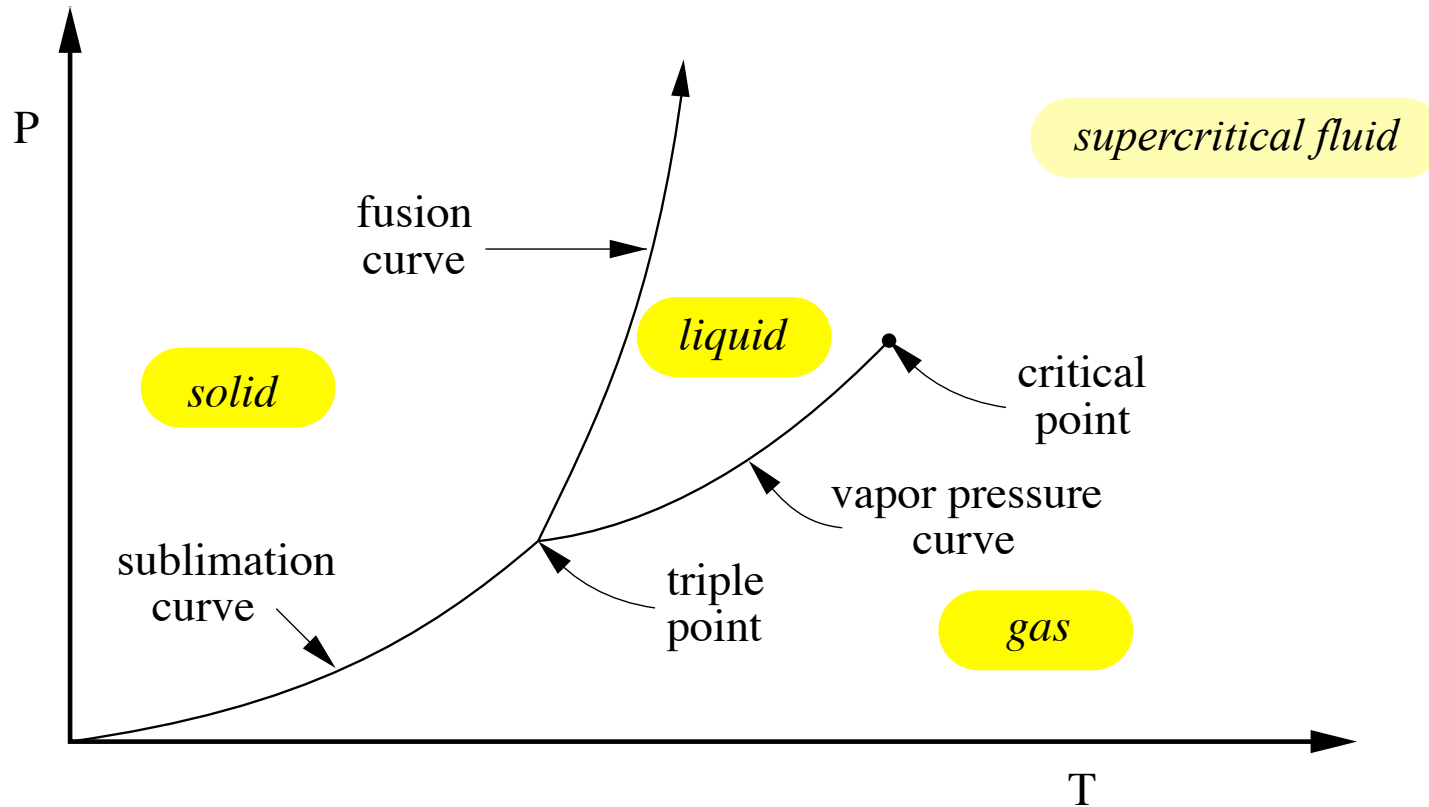


a strong repulsion for small  $r$  and a weak attraction at large  $r$ .

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

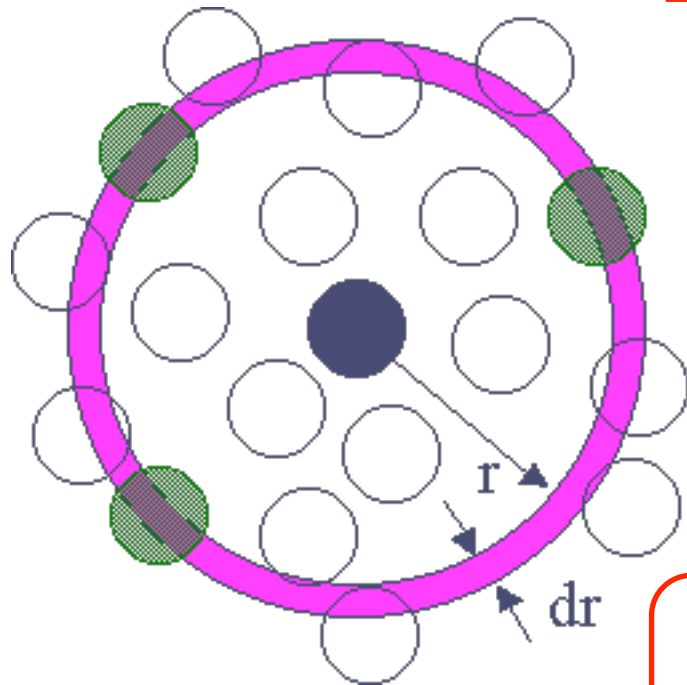
- pair correlation function  $g(\mathbf{r})$
- energy  $E$
- pressure  $p$
- ...

# Measurable and interesting quantities

- pair correlation function  $g(\mathbf{r})$ 

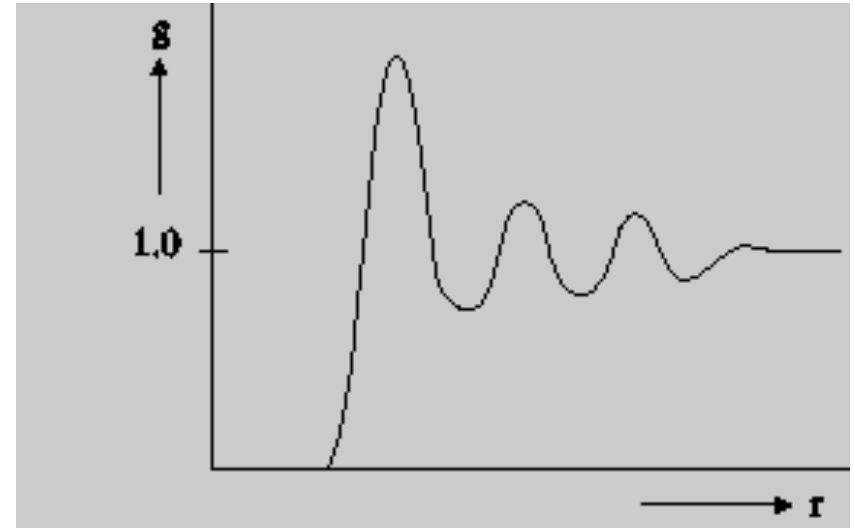
{	concepts and qualitative features
	mathematical formulation and expressions useful for computation
- energy  $E$
- pressure  $p$
- ...

# Radial distribution function



Definition

$$g(r)$$



$$g(r)dr \quad (dr = \text{infinitesimal volume of the shell})$$

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

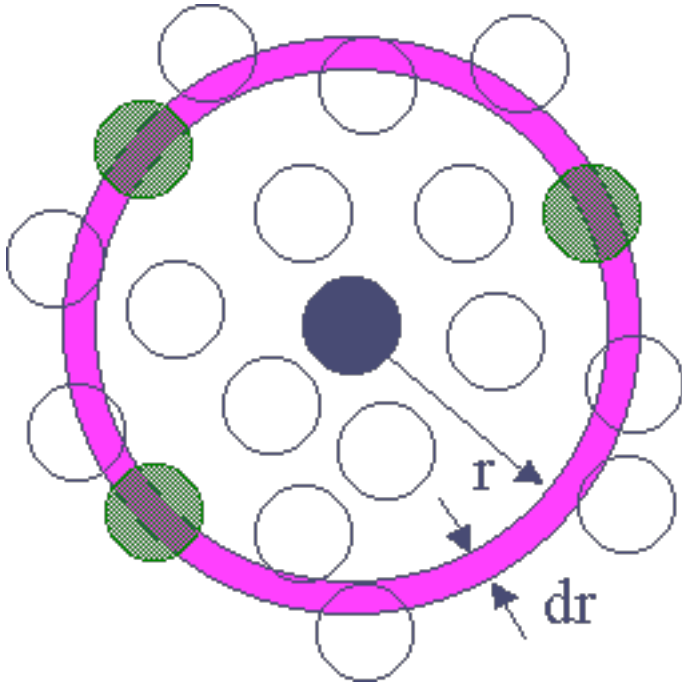
Consider one reference particle at the origin and count the others; then, average over the reference particles

(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:

$$\rho g(r) dr$$

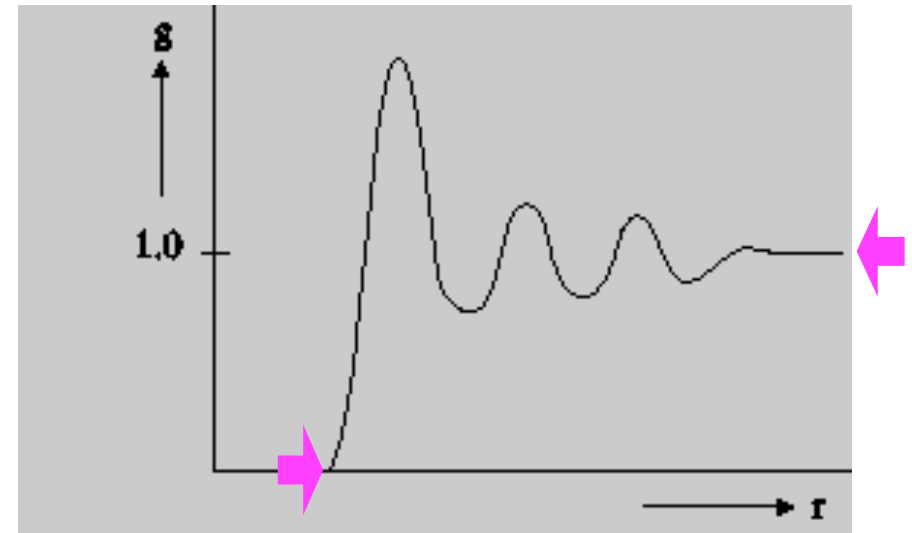
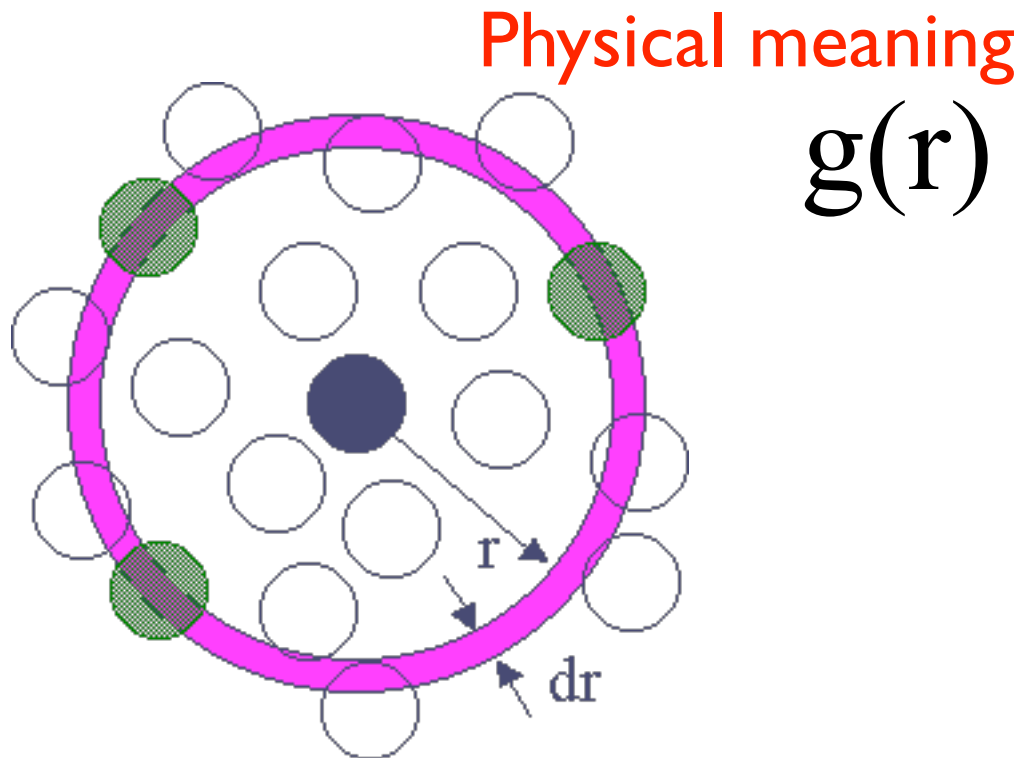
(Reminder: spherically symmetric interactions assumed;  $g$  depends only on  $r=|\mathbf{r}|$ )

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



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

General behavior at short and long distances:

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

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

# Radial distribution function

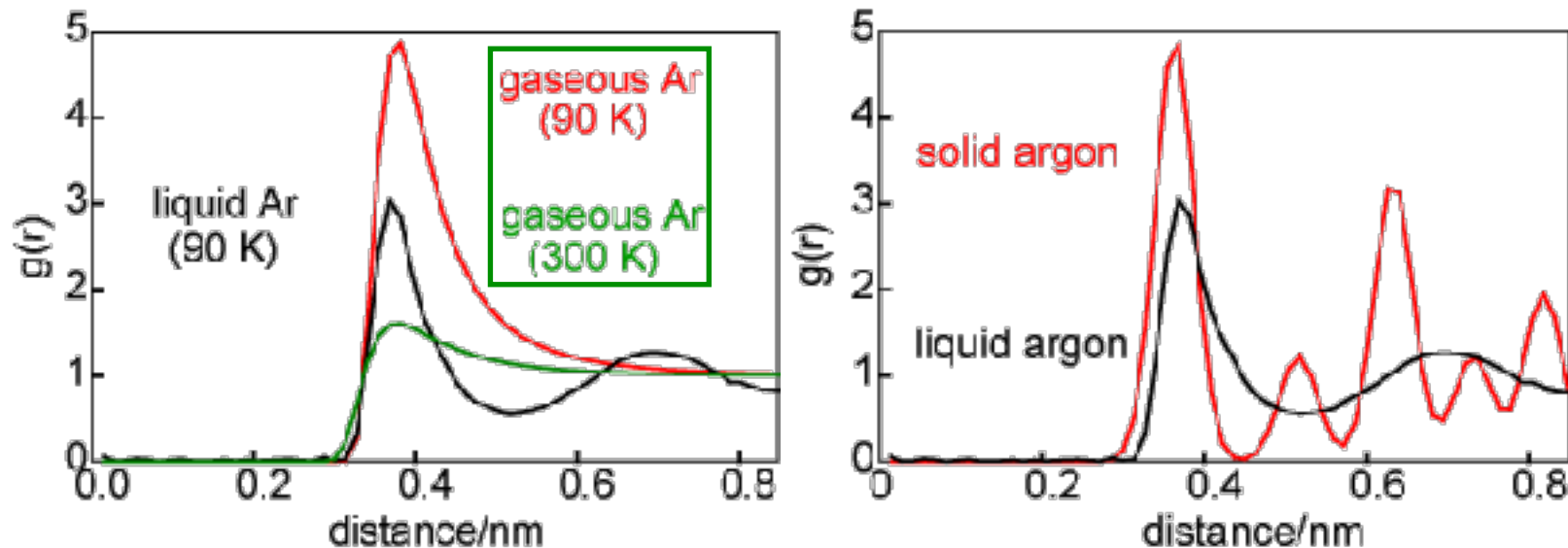
Typical features:

**gas:** almost structureless

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

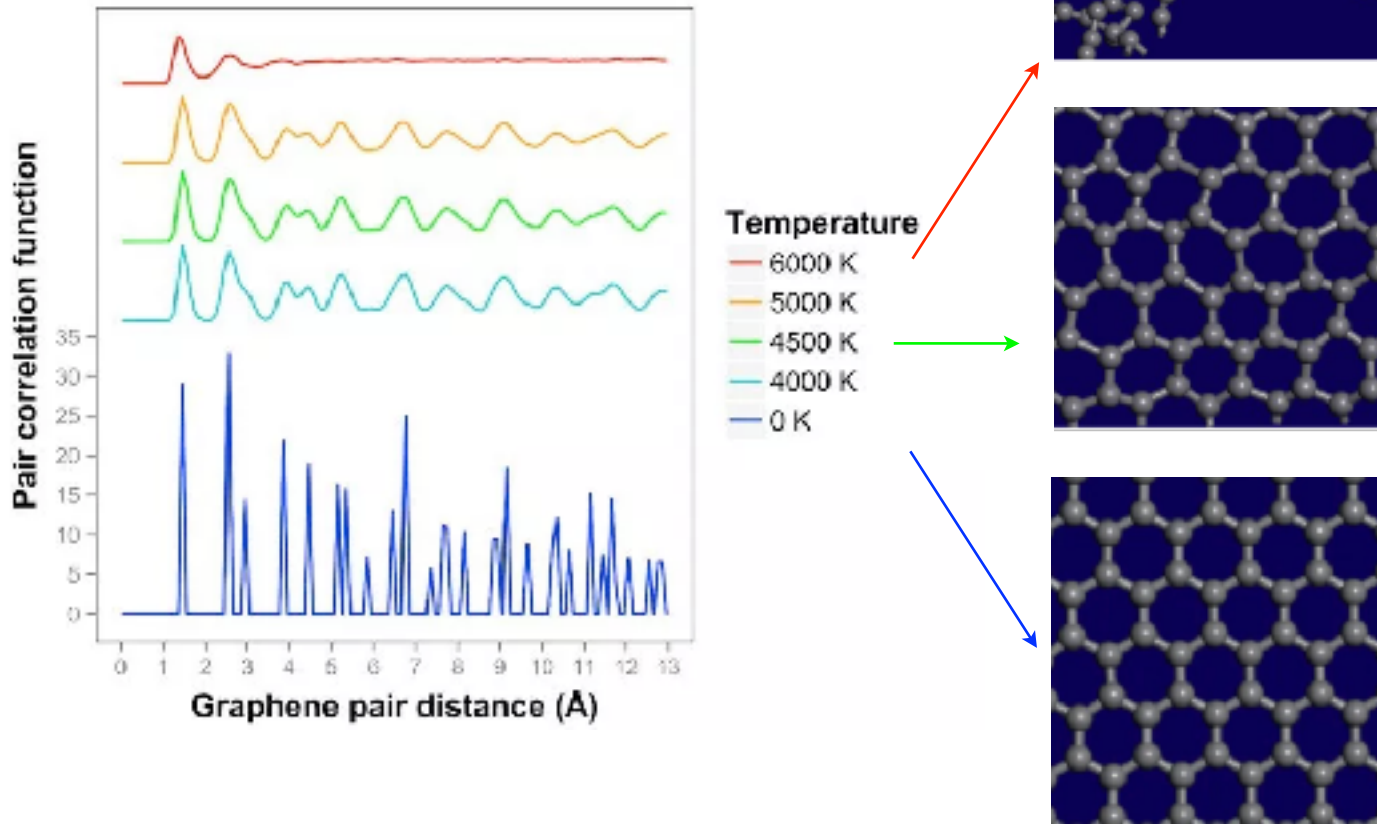
**liquid:** some structure with broad peaks

**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/> )

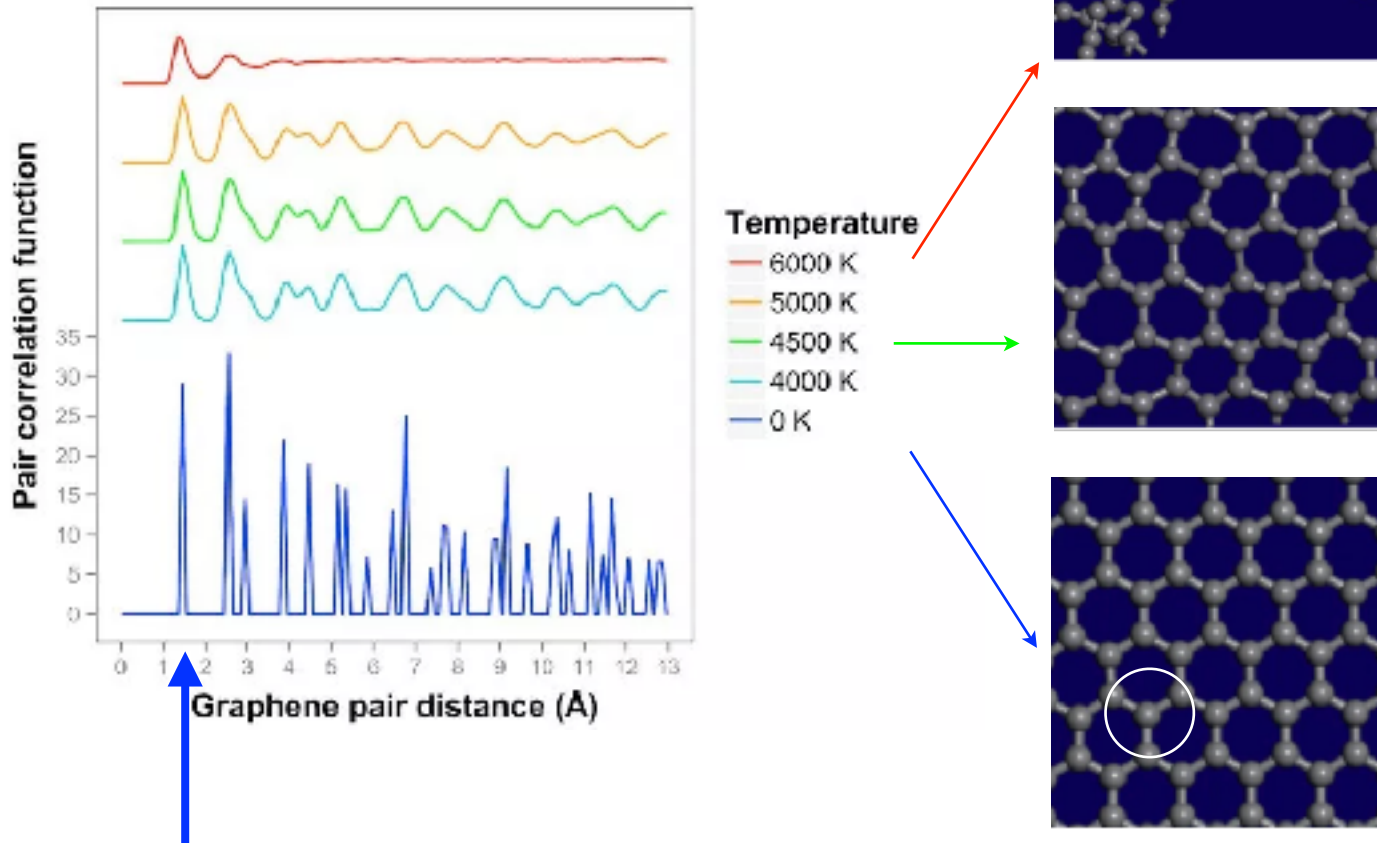
another example (2D):



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

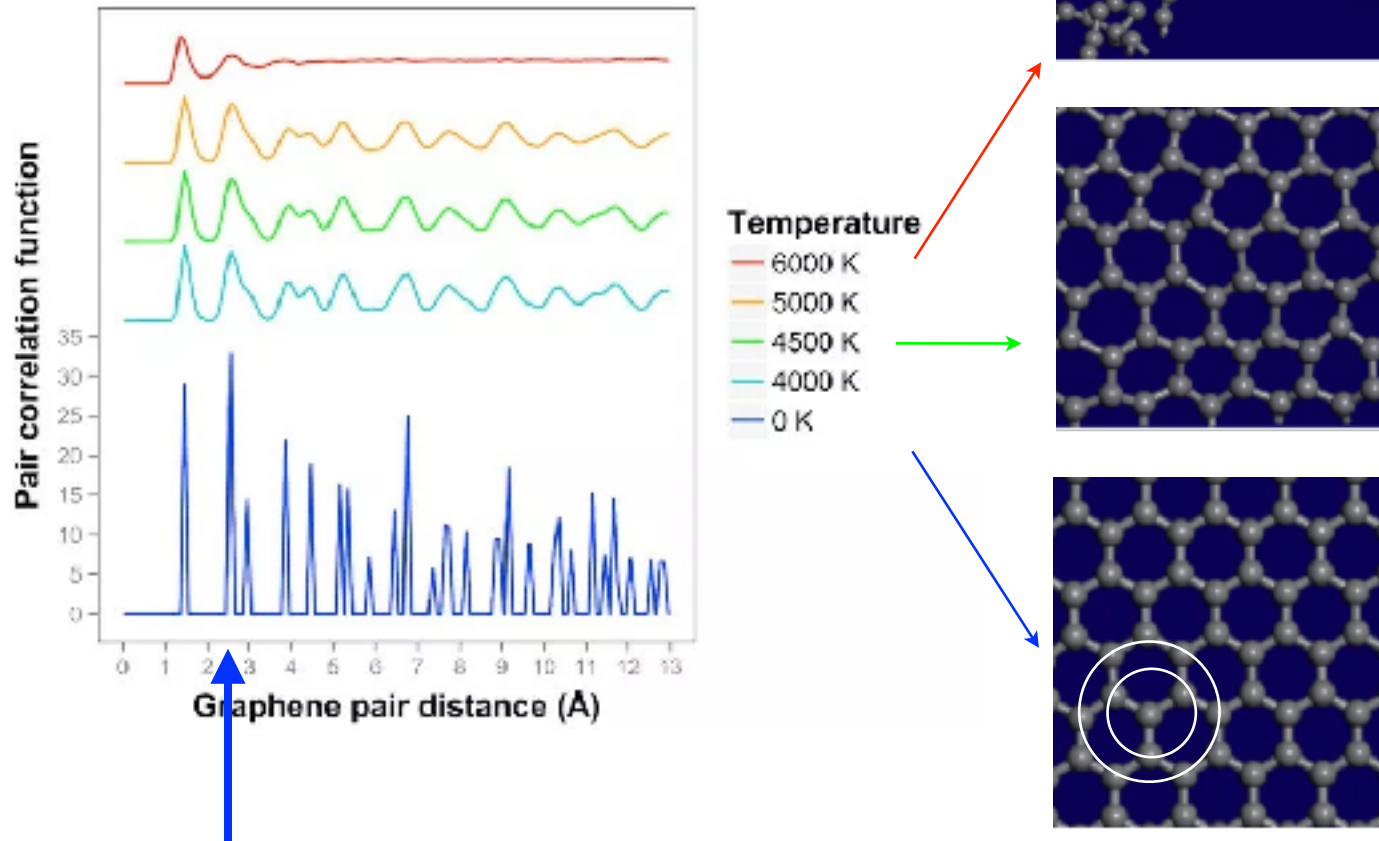


another example (2D):



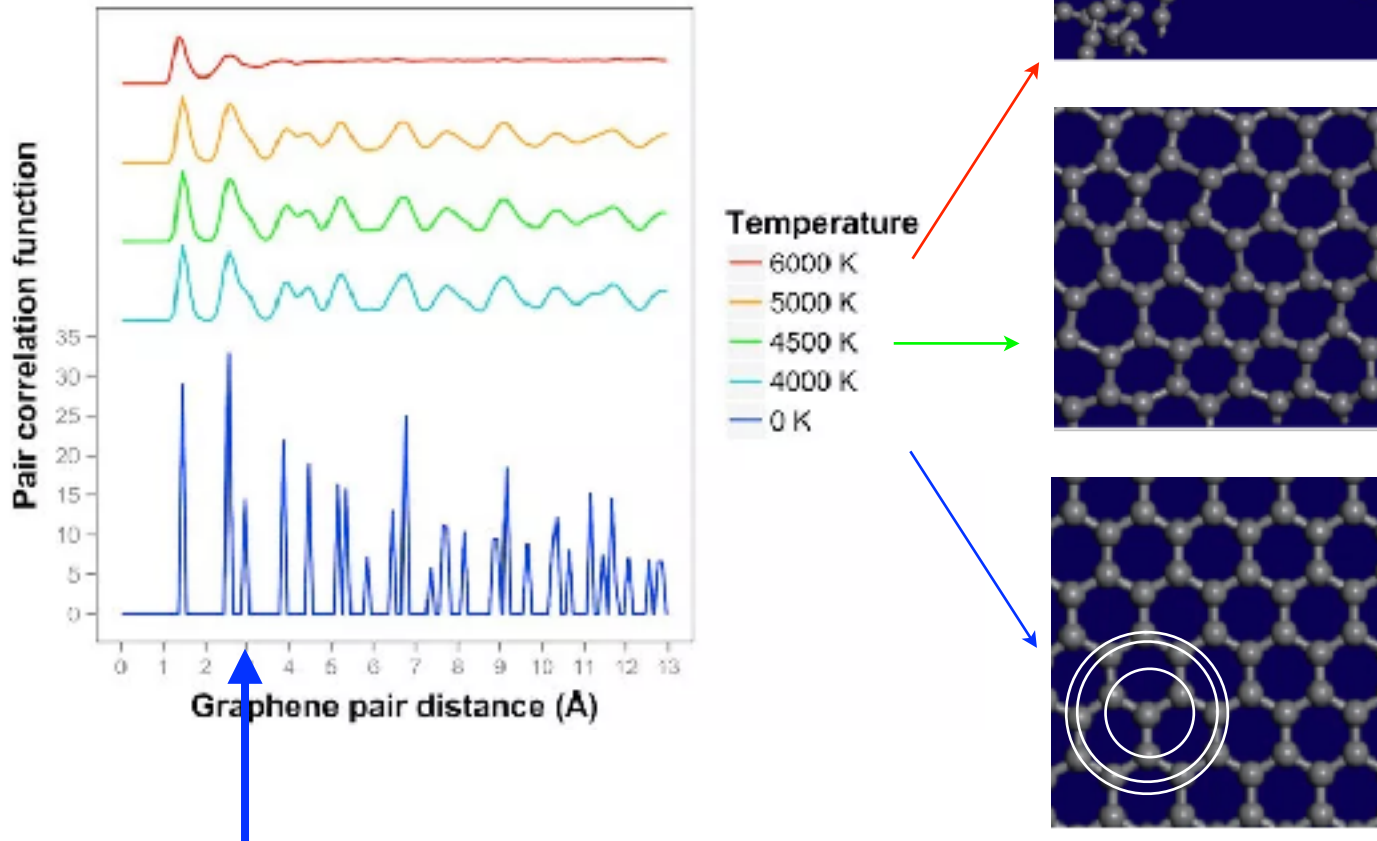
*The initial stages of melting of graphene between 4000 K and 6000 K, E. Ganz et al., Phys. Chem. Chem. Phys., 2017, 19, 3756*

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*

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*

# Radial distribution function

formulation in case of spherically symmetric interactions:

$$\rho g(r) = \frac{\overline{n(r, \Delta r)}}{\frac{1}{2} N 2\pi r \Delta r}.$$

(two dimensions)

- first compute  $n(r, \Delta r)$ , the number of particles in a spherical (circular) shell of radius  $r$  and small, but nonzero width  $\Delta r$  with the center of the shell centered about each particle
- For a given particle  $i$ , consider only those with  $j > i$
- Integrated all over the space,  $\overline{n(r, \Delta r)}$  gives the number of pairs considered, which is  $N(N-1)/2$ , times the area of the circular shell  $2\pi r \Delta r$

Remember:  $\rho \int g(r) d\mathbf{r} = N - 1 \approx N$

# Radial distribution function

Again in the case of spherically symmetric interactions  
Mathematical formulation - details for the 2D case:

$$g(r) = \frac{\text{number of pairs with distance between } r \text{ and } r + \Delta r}{2\pi r \Delta r \cdot \rho N}$$

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

$\Leftarrow$  ( $\delta$ : to be considered within the accuracy of  $\Delta r$  ; up to here: double counting of pairs)

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

$\Leftarrow$  (here: no double counting of pairs)

*OK for a numerical implementation*

# Pair correlation function

(similar to the radial distribution function,  
but more general definition,  
i.e., interactions not spherically symmetric)

## Mathematical formulation:

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

$$g(\mathbf{r}) = \frac{1}{\rho^2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r}_i) \delta(\mathbf{r}_j - \mathbf{r}_i) \right\rangle$$

ensemble average over  
pairs

$$= \frac{N}{V^2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle$$

OK for numerical  
implementation

(Here:  $V$  instead of  $A$ , for a 3D case in general)

# Radial distribution function

## Related quantities

For comparison with experiments:  
geometrical structure factor  $S(\mathbf{k})$ ;  
fluctuations in  $g(r)$  are related to  $S(\mathbf{k})$ :

$$\rho(\mathbf{k}) = \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_i)$$

$$S(\mathbf{k}) = \frac{1}{N} \langle \rho(\mathbf{k}) \rho(-\mathbf{k}) \rangle = \frac{1}{N} \left\langle \sum_{i,j=1}^N \exp(i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)) \right\rangle =$$

$$= 1 + 4\pi\rho \int_0^\infty r^2 \frac{\sin(kr)}{kr} g(r) dr$$

*(average also over time  
if the configuration of  
the fluid evolves)*

# 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<sup>(see next slide)</sup> 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:

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

↑  
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:

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

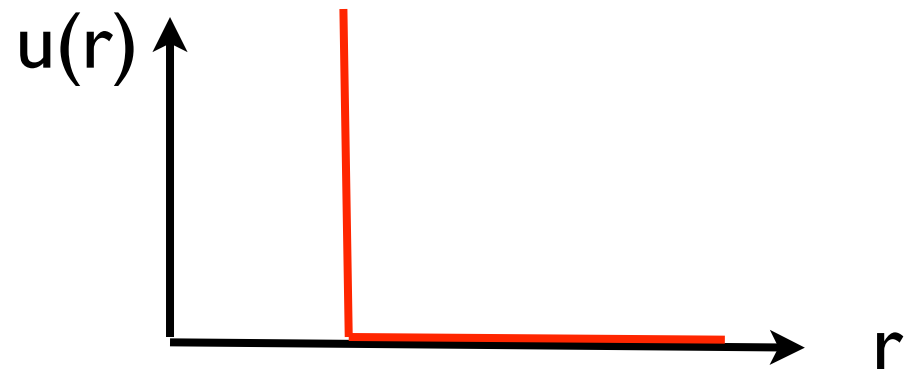
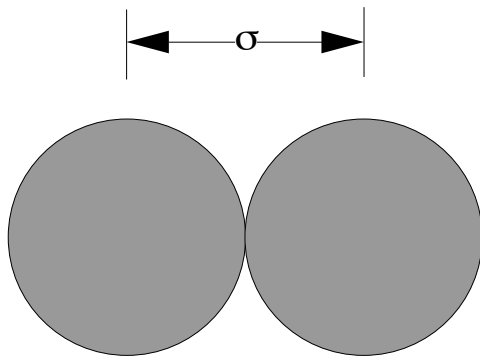
*(average  
also over time)*

# Simple interaction potentials

- Hard disks (spheres)
- Lennard-Jones
- ...

# 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)



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

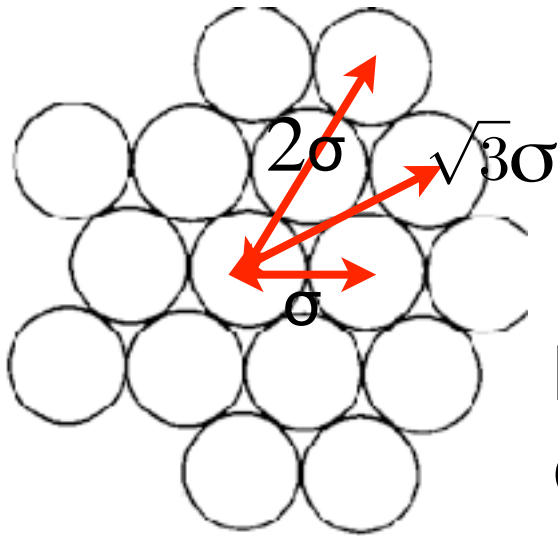
No minimum; check overlap!

No attractive part  $\Rightarrow$  no transition from gas to liquid

# Hard disks

$\sigma$ : diameter of the disks

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



NN shell:  
 $\sigma$

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

3NN shell:  
 $2\sigma$

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

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

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

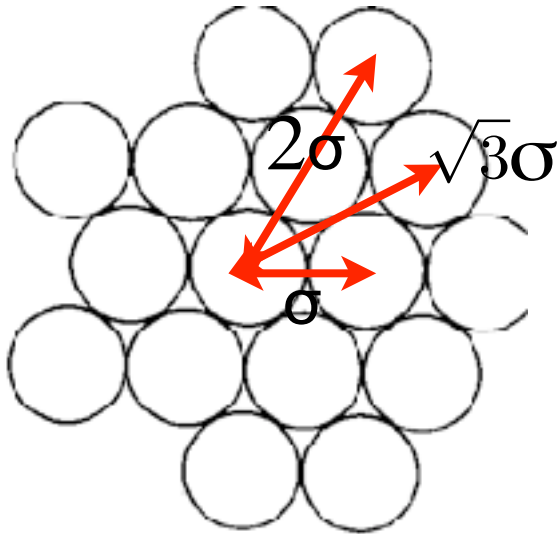
max reduced density :  $\rho_{max}^* = \frac{2}{\sqrt{3}} = 1.1547$

max packing fraction:  $f = \frac{\text{area}_{occupied}}{\text{area}_{available}} = \frac{\pi}{2\sqrt{3}} = 0.907$

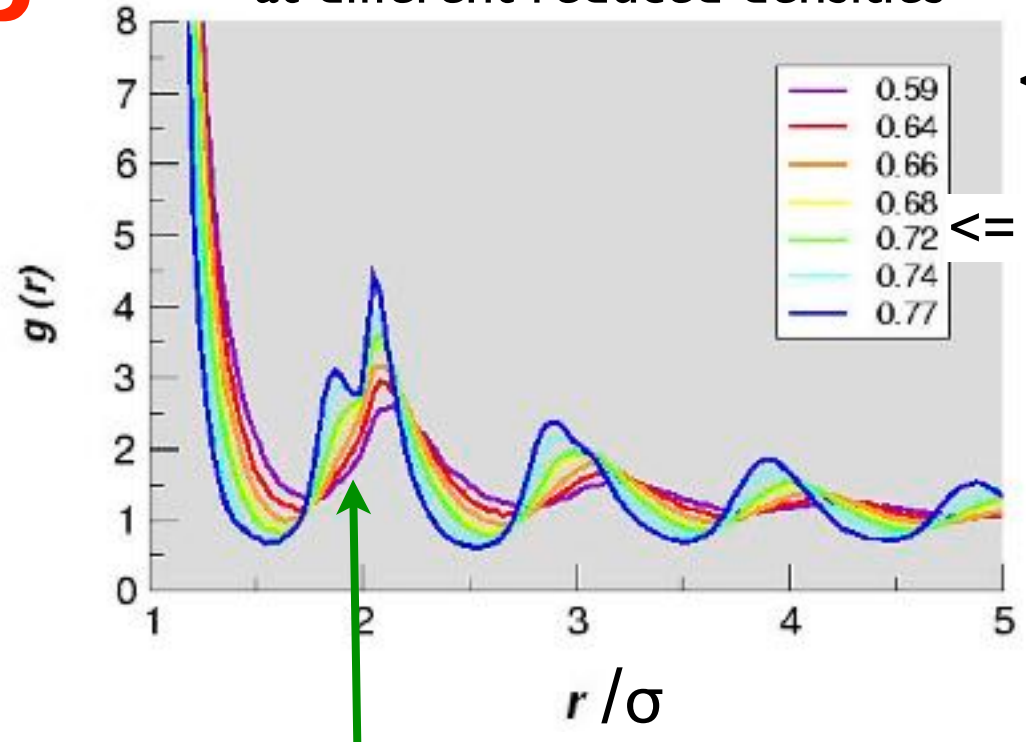
$$f = \frac{\pi}{4}\rho^*$$

# Radial distribution function

of **hard disks in 2D**



Radial Distribution Function  
at different reduced densities



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

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

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,<sup>1</sup> Salvatore Torquato,<sup>2,3,\*</sup> Srikanth Sastry,<sup>1</sup> Pablo G. Debenedetti,<sup>1</sup> and Frank H. Stillinger<sup>4,2</sup>

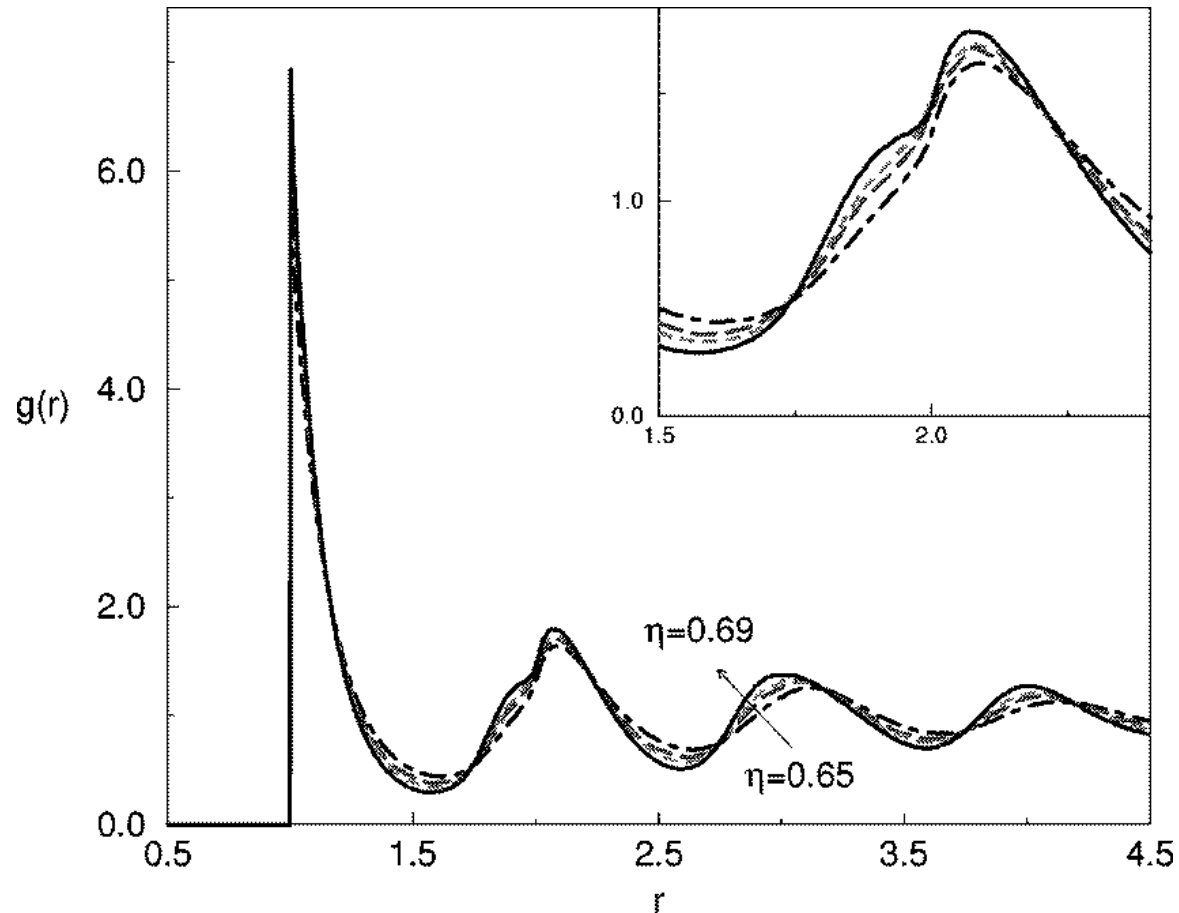


FIG. 1. Radial distribution function  $g(r)$  for hard disks plotted versus distance  $r$  (in units of diameters). Curves represent the fluid phase with  $\eta=0.65, 0.67, 0.68,$  and  $0.69$  (freezing point).

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

# Pressure

case of Hard Disks (Spheres):

Virial eq. of state

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

becomes:

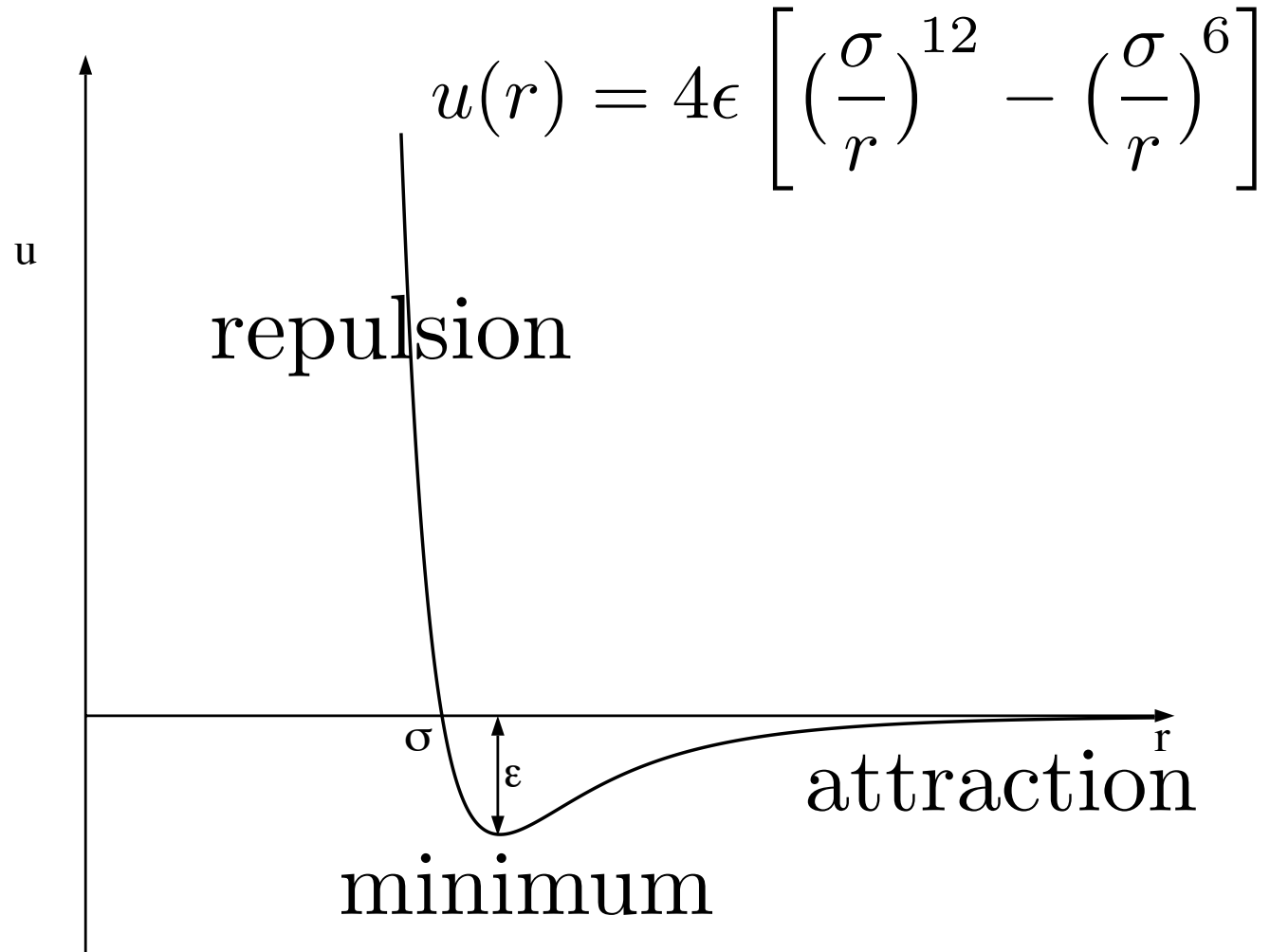
$$d\mathbf{r} = 4\pi r^2 dr \quad \frac{\beta P}{\rho} = 1 + \frac{2}{3} \pi \rho \sigma^3 g(\sigma) \quad (d = 3)$$

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

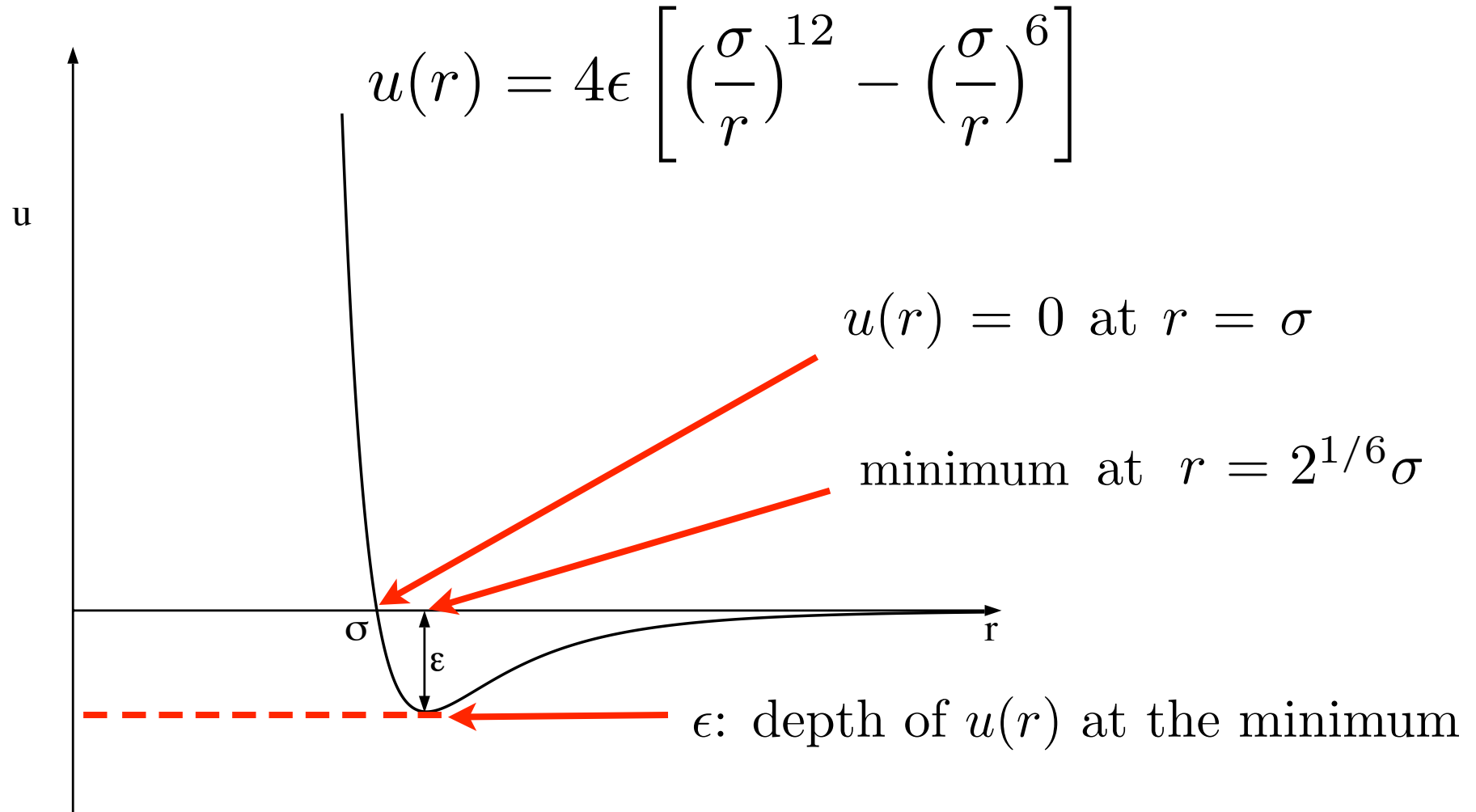
$$d\mathbf{r} = 2 dr \quad \frac{\beta P}{\rho} = 1 + \rho \sigma g(\sigma) \quad (d = 1)$$



# Lennard-Jones potential



# Lennard-Jones potential

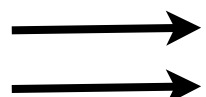


liquid argon:  $\epsilon = 1.65 \times 10^{-21}$  J       $\sigma = 3.4 \text{ \AA}$

# 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	$\sigma$	$3.4 \times 10^{-10}$ m
energy	$\epsilon$	$1.65 \times 10^{-21}$ J
mass	$m$	$6.69 \times 10^{-26}$ kg
time	$\sigma(m/\epsilon)^{1/2}$	$2.17 \times 10^{-12}$ s
velocity	$(\epsilon/m)^{1/2}$	$1.57 \times 10^2$ m/s
force	$\epsilon/\sigma$	$4.85 \times 10^{-12}$ N
pressure	$\epsilon/\sigma^2$	$1.43 \times 10^{-2}$ N · m <sup>-1</sup>
temperature	$\epsilon/k$	120 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  $\sigma$ ,  $\epsilon$ , and  $m$  are for argon. The quantity  $k$  is Boltzmann's constant and has the value  $k = 1.38 \times 10^{-23}$  J/K. The unit of pressure is for a two-dimensional system.

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

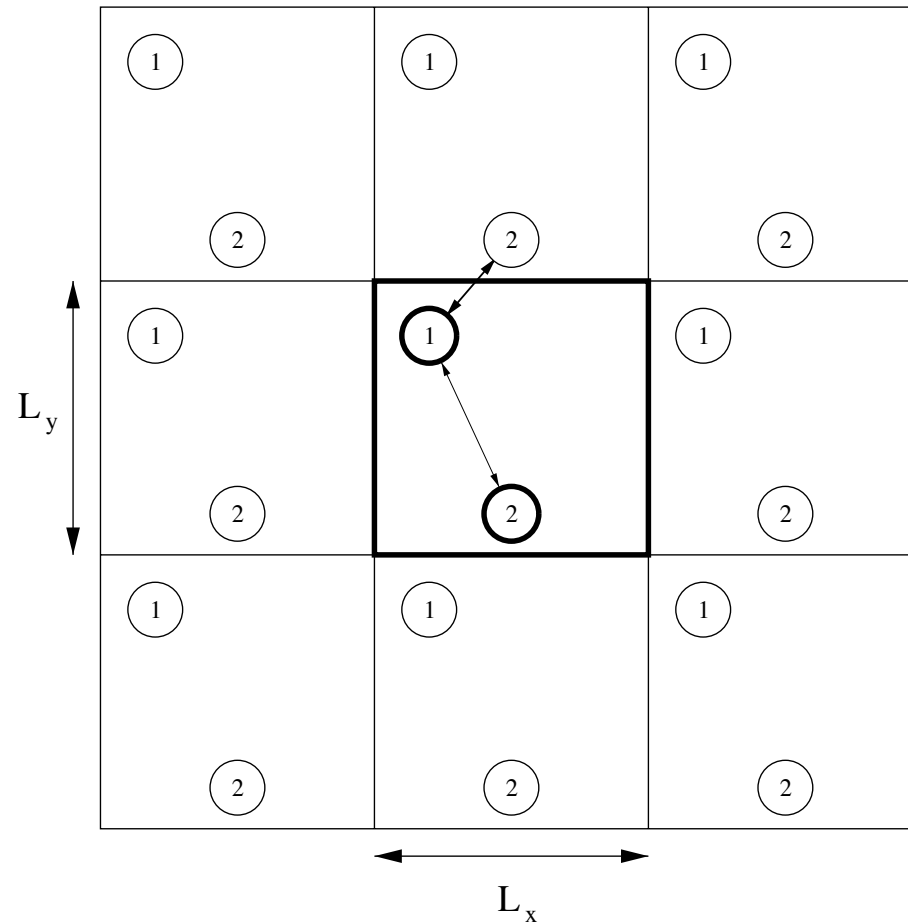
(OK  
in the hypothesis that  
 $-L < \text{pos} < 2L$ )

# Minimum Image convention

new!

for the interactions

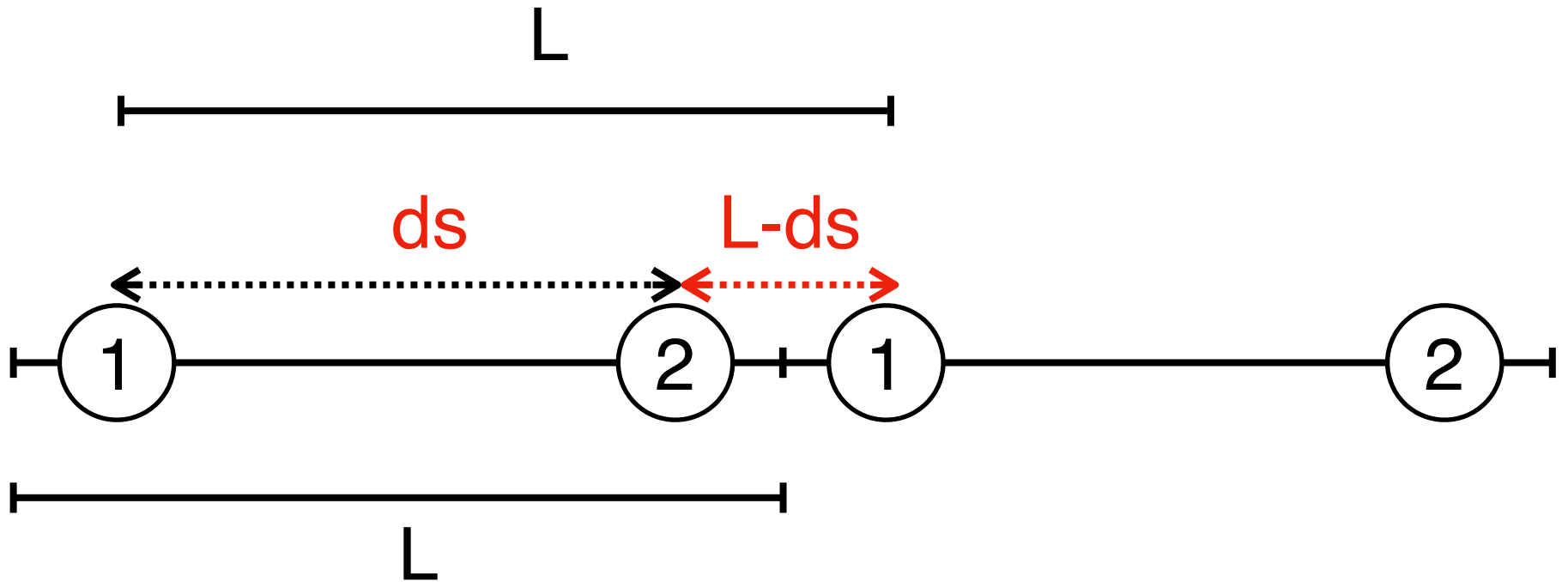
To compute the minimum distance  $dx$  between particles 1 and 2 at  $x(1)$  and  $x(2)$



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  $E_{\text{tot}}$

→ - displace an individual particle by a small amount: calculate  $\Delta E$   
(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:

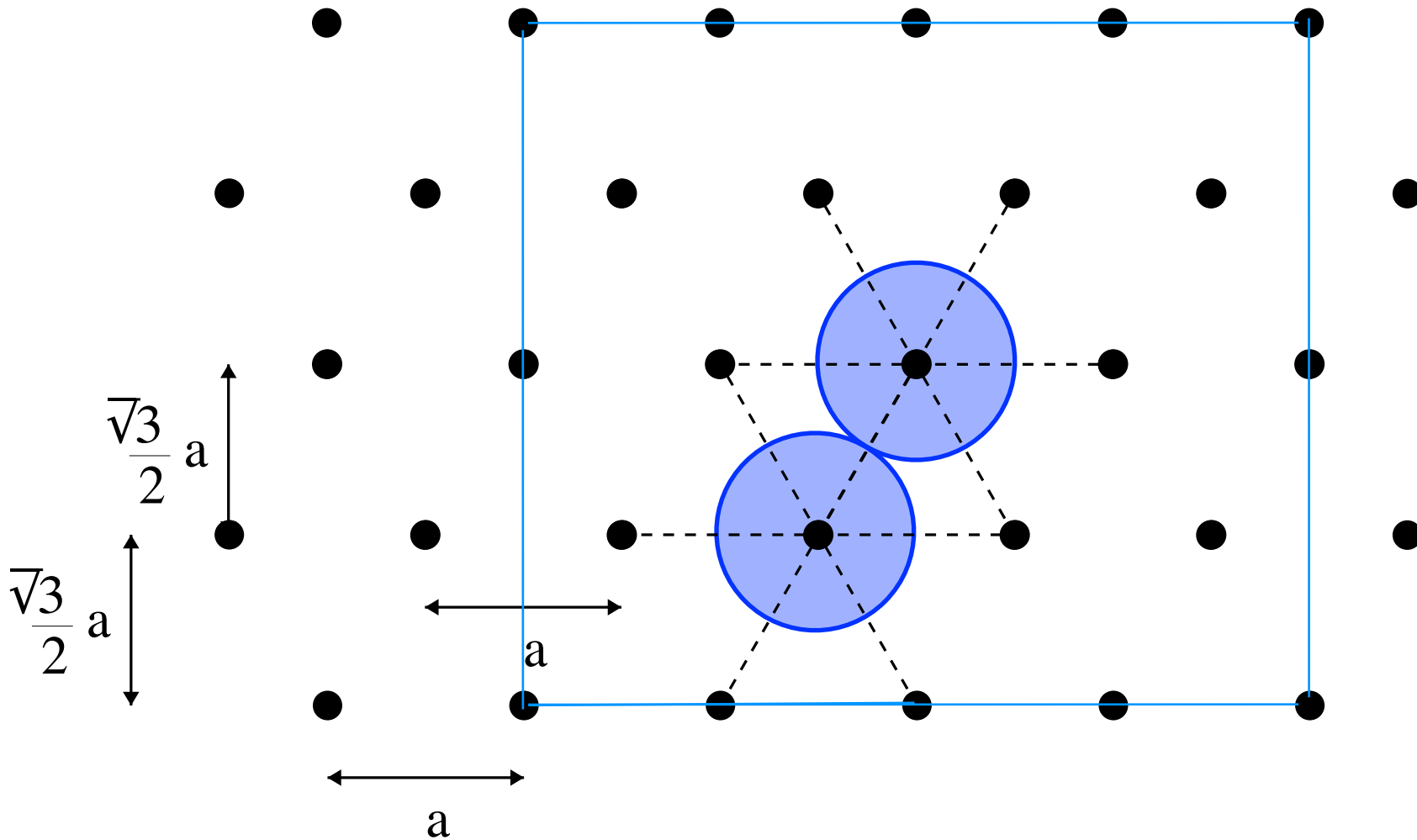
if overlap with another particle: REJECTED

if no overlap with any other particle: ACCEPTED

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

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

# Maximum package



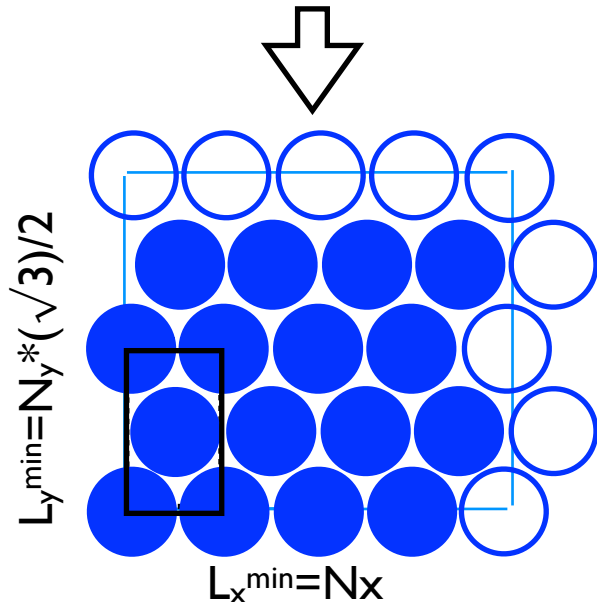
hexagonal lattice

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

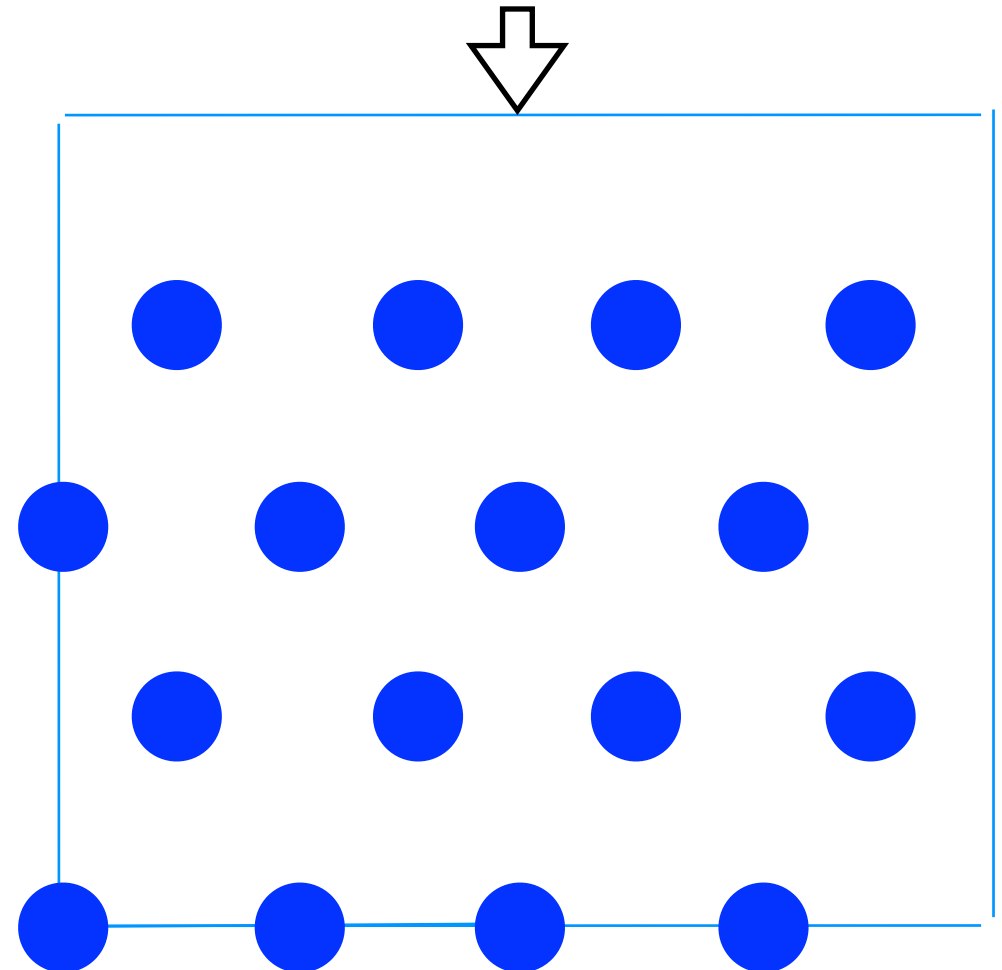
# Initializing the positions

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  $N_x$  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  $\rho^{\max}$
- 4) Calculate the individual positions:  
 $x(i) = \text{integer/semi-integer}$  for even/odd rows;  
 $y(i) = \text{multiple of } (\sqrt{3})/2$



- 1) choose  $\rho$
- 2) Determine the new  $L_x$  and  $L_y$  by scaling:  
 $L_x = kL_x^{\min}$  and  $L_y = kL_y^{\min}$ , 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:

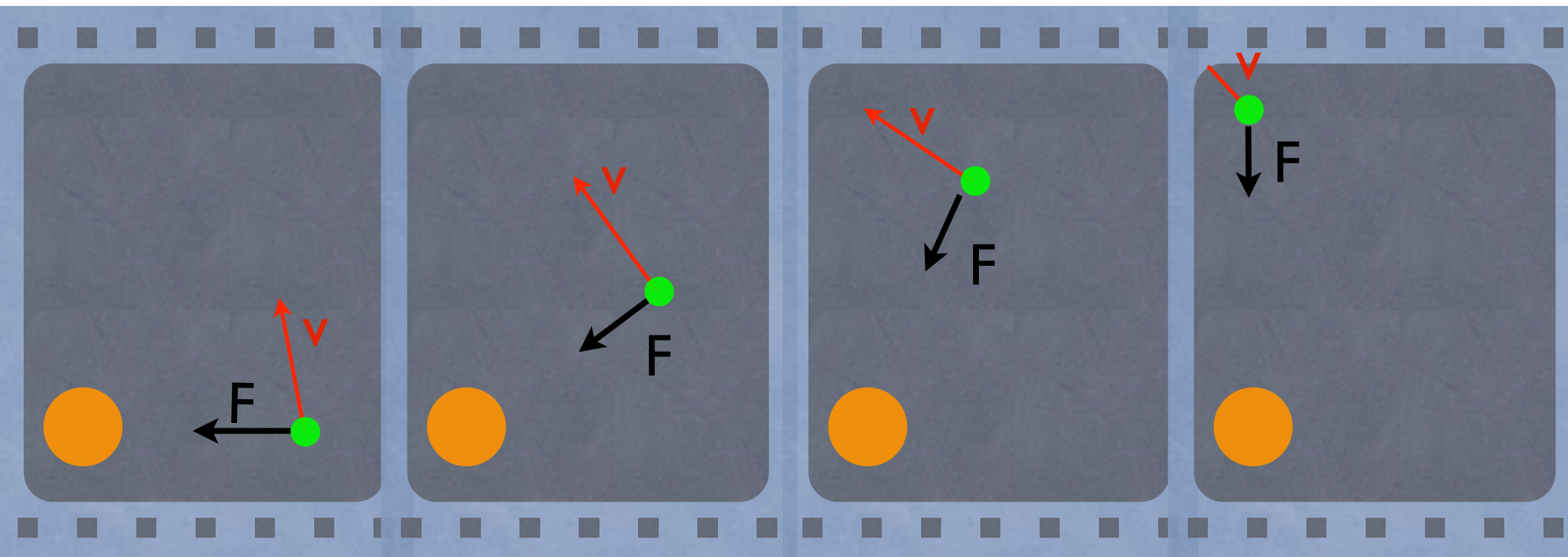
$$\frac{d^2x}{dt^2} = a(x, t, \dots) = \frac{F(x, t, \dots)}{m}$$

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

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



$x(0)$   $v(0)$   $F(0)$

$x(1)$   $v(1)$   $F(1)$

$x(2)$   $v(2)$   $F(2)$

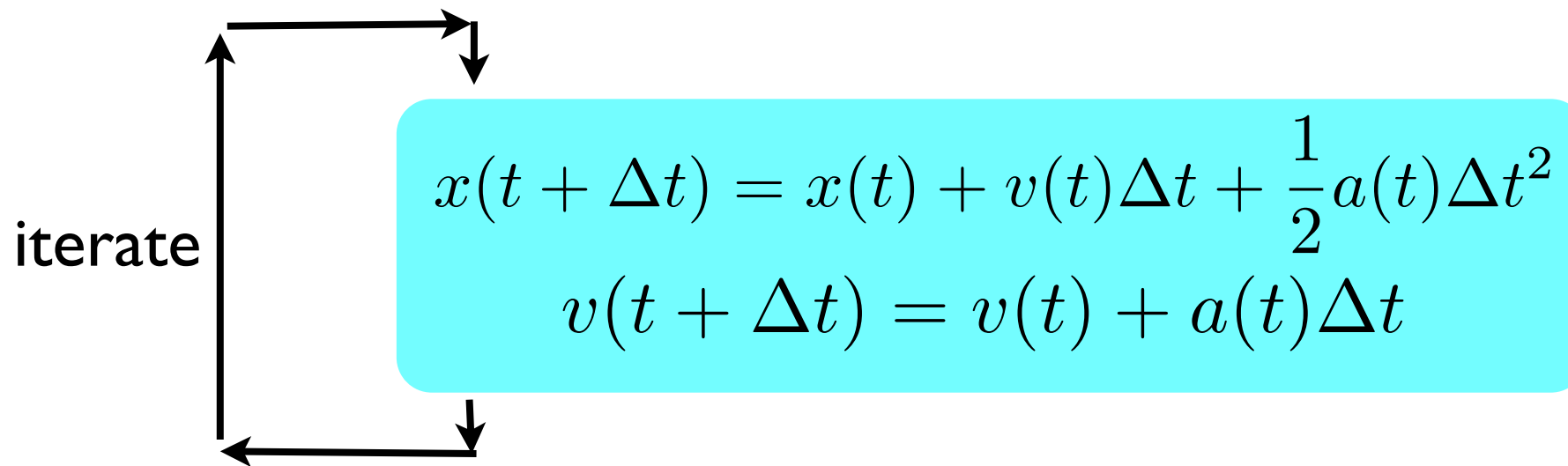
... ..

Uniformly accelerated motion in each time interval

$$t \div t + \Delta t$$

then iterate!

## EULER algorithm

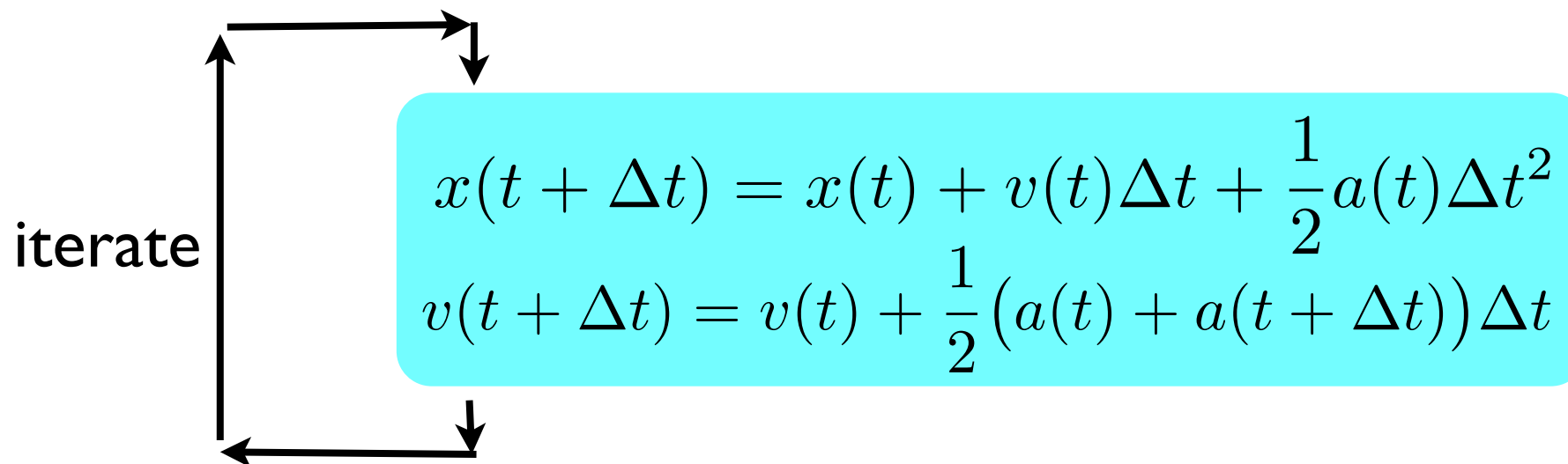


$$x(t) \implies x(t + \Delta t) \implies x(t + 2\Delta t) \implies x(t + 3\Delta t) \implies \dots$$

$$v(t) \implies v(t + \Delta t) \implies v(t + 2\Delta t) \implies v(t + 3\Delta t) \implies \dots$$

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



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 ( $E=\text{const.}$ )**

**Keep number of particles constant ( $N=\text{const.}$ )**

**Keep volume constant ( $V=\text{const.}$ )**

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  $\sim 1\%$



# 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)

# Further details

## Truncated and shifted potentials :

- Long range potentials (electrostatic) and also VdW interactions are often truncated at a finite cut-off distance.
- They are sometimes shifted so that the potential is zero at the cut-off, thus avoiding a discontinuity which can give rise to poor energy conservation.
- Truncations with periodic boundaries introduce the need for a long-range correction term (“tail corrections”)

# 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.

# Sampling other thermodynamical ensembles with MD

Other thermodynamical ensembles can be realized by changing the equations of motion (e.g. **NVT –coupling to heat bath...**, “**canonical ensemble**”). Since:

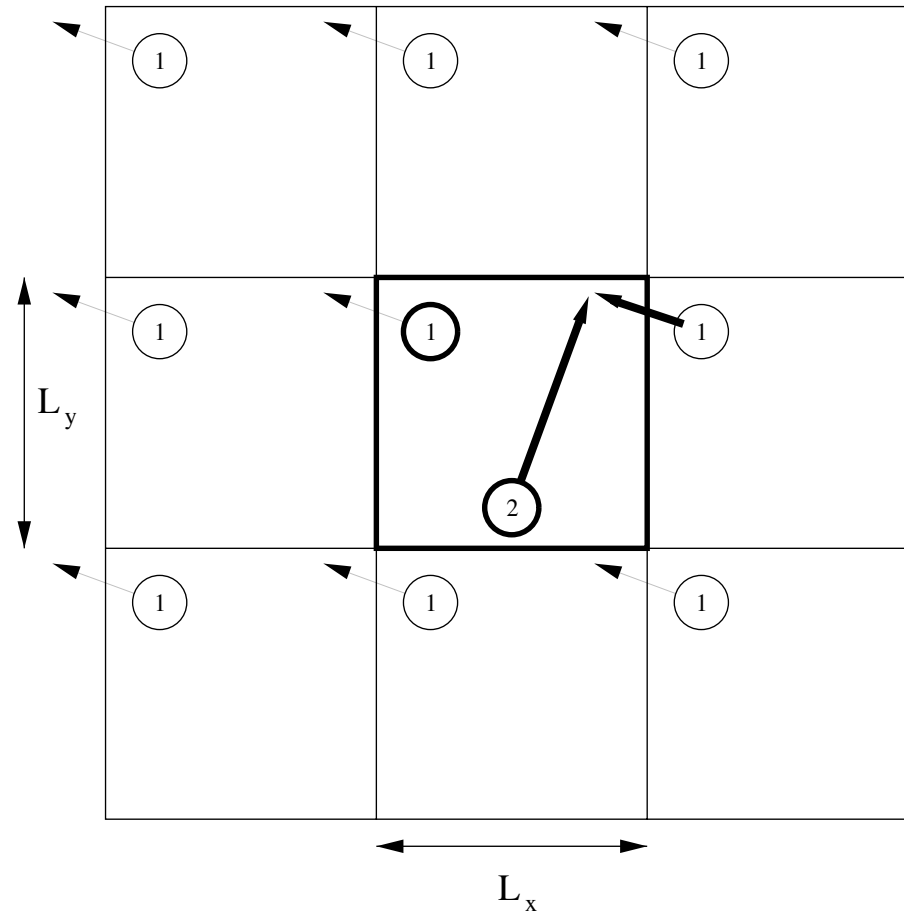
$$E_{kin} = \frac{1}{2} m \sum_i^N v_i^2$$

$$T = \frac{2}{3} \frac{E_{kin}}{N k_B}$$

rescale velocities (use a “**thermostat**”) to keep  $T \sim$  constant

# Collisions and PBC

check collisions!



The positions and velocities of disks 1 and 2 are such that disk 1 collides with an image of disk 2 that is not the image closest to disk 1.

two examples  
for the interaction potential:

HD and LJ

# A few basic references

The molecular dynamics method was first introduced by Alder and Wainwright in the late 1950's (AW) to study the interactions of **hard spheres**. Many important insights concerning the behavior of simple liquids emerged from their studies. The next major advance was in 1964, when Rahman carried out the first simulation using a realistic **potential for liquid argon** (R).

(AW) B. J. Alder and T. E. Wainwright  
Phase Transition for a Hard Sphere System  
J. Chem. Phys. 27, 1208 (1957); *ibid.* 31, 459 (1959)

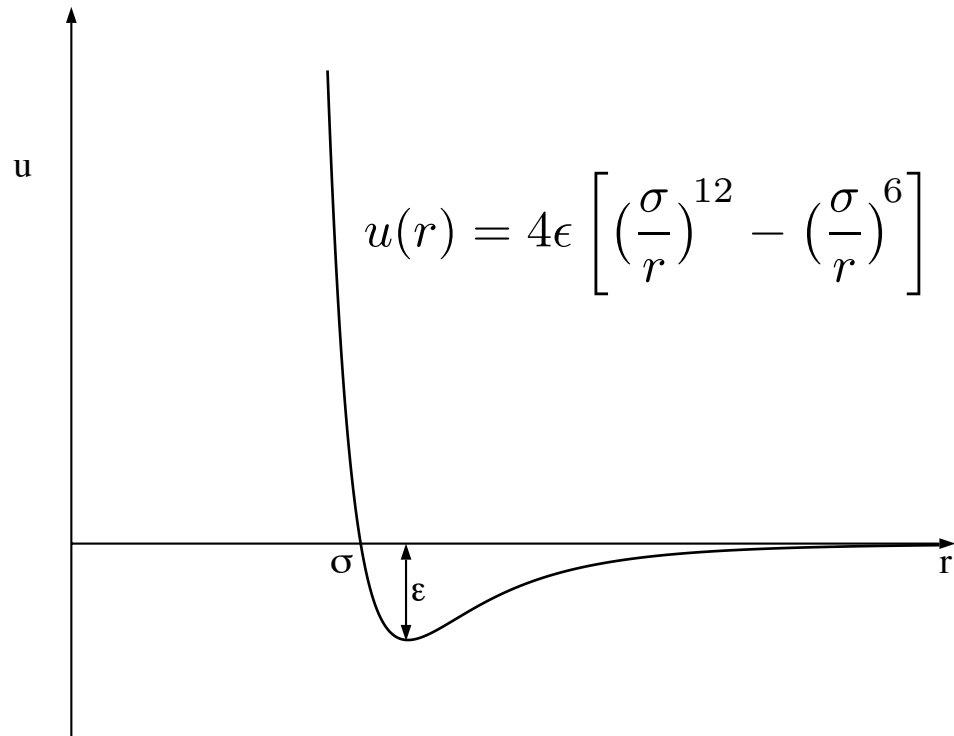
- more recently: Truskett et al., Phys. Rev. E 58, 3082 (1998) (see slide 25)

(R) A. Rahman  
Correlations in the Motion of Atoms in Liquid Argon  
A. Phys. Rev. A136, 405 (1964)

- more recently: S. Ranganathan et al., Phys. Rev. A 45, 5793 (1992) (next slides)



# A more recent case study (1992): 2D with Lennard-Jones potential



liquid argon :

$$\epsilon = 1.65 \times 10^{-21} \text{ J}$$

$$\sigma = 3.4 \text{ \AA}$$

# Liquid-to-glass transition in 2D LJ fluids

PHYSICAL REVIEW A

VOLUME 45, NUMBER 8

15 APRIL 1992

## Freezing transition of two-dimensional Lennard-Jones fluids

S. Ranganathan

Department of Mathematics and Computer Science, Royal Military College, Kingston, Ontario, Canada K7K 5L0

K. N. Pathak

Department of Physics, Panjab University, Chandigarh, India 160014

MD simulation with

128 particles confined in a square box with length

$nmcs = 6000$ ;  $\Delta t^* = 0.032$

$$L = \sigma \sqrt{128/\rho^*}$$

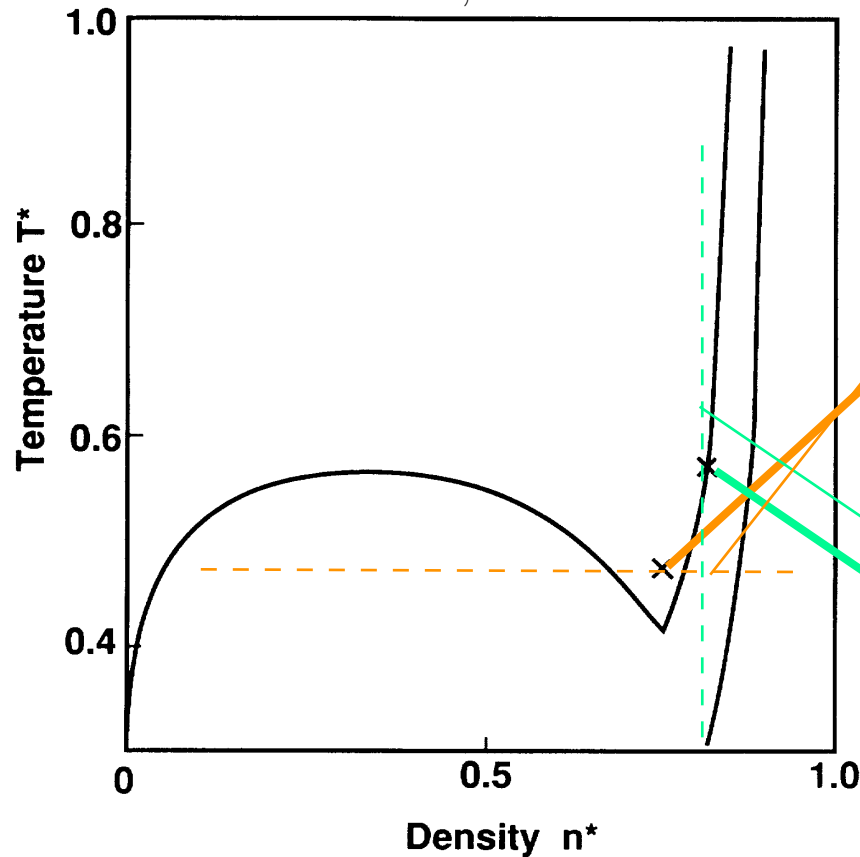


FIG. 1. Phase diagram for the two-dimensional Lennard-Jones system. The crosses indicate the  $(n^*, T^*)$  states  $(0.75, 0.48)$  and  $(0.81, 0.58)$ .

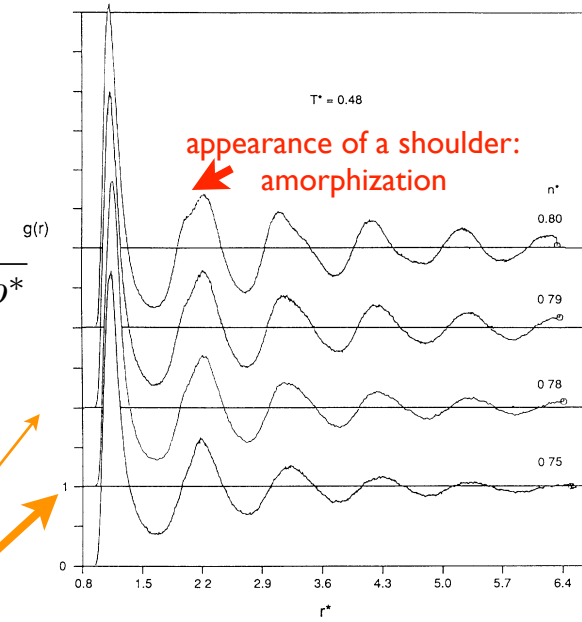


FIG. 2. Pair-distribution function along the isotherm  $T^* = 0.48$  at various densities. The curves are displaced for clarity.

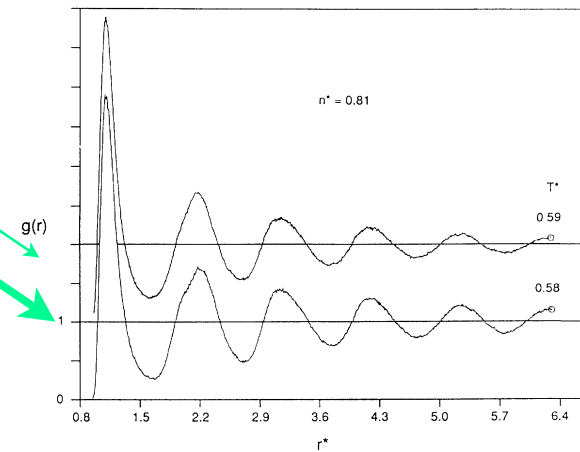


FIG. 3. Pair-distribution function along the isochore  $n^* = 0.81$  at two temperatures.

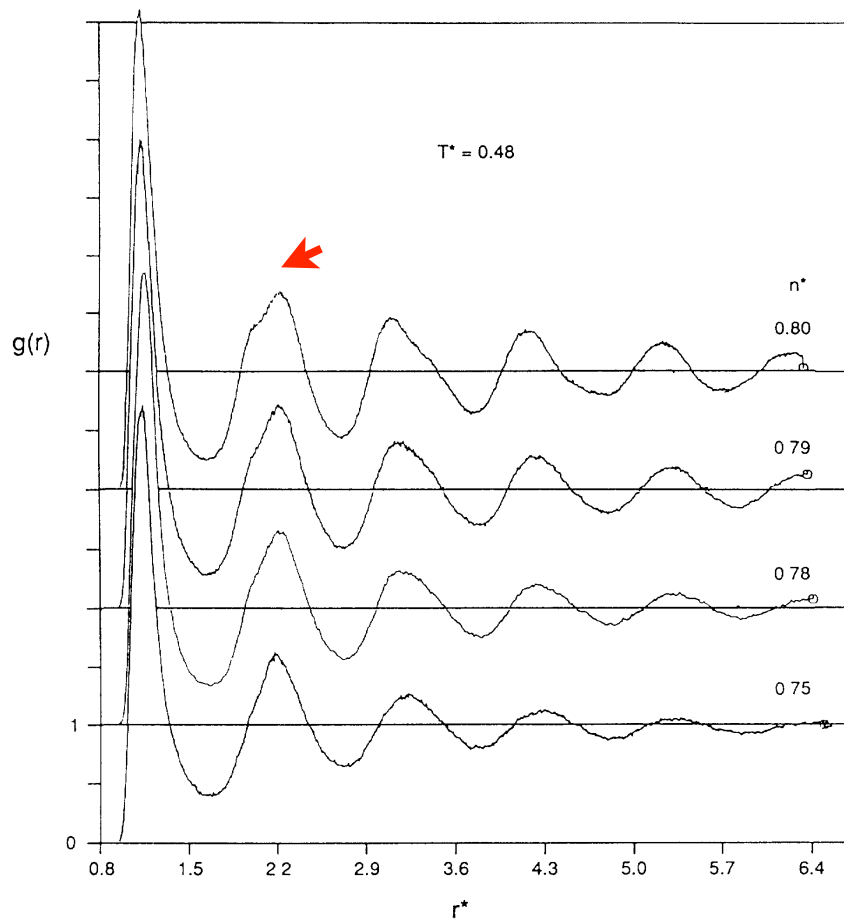


FIG. 2. Pair-distribution function along the isotherm  $T^* = 0.48$  at various densities. The curves are displaced for clarity.

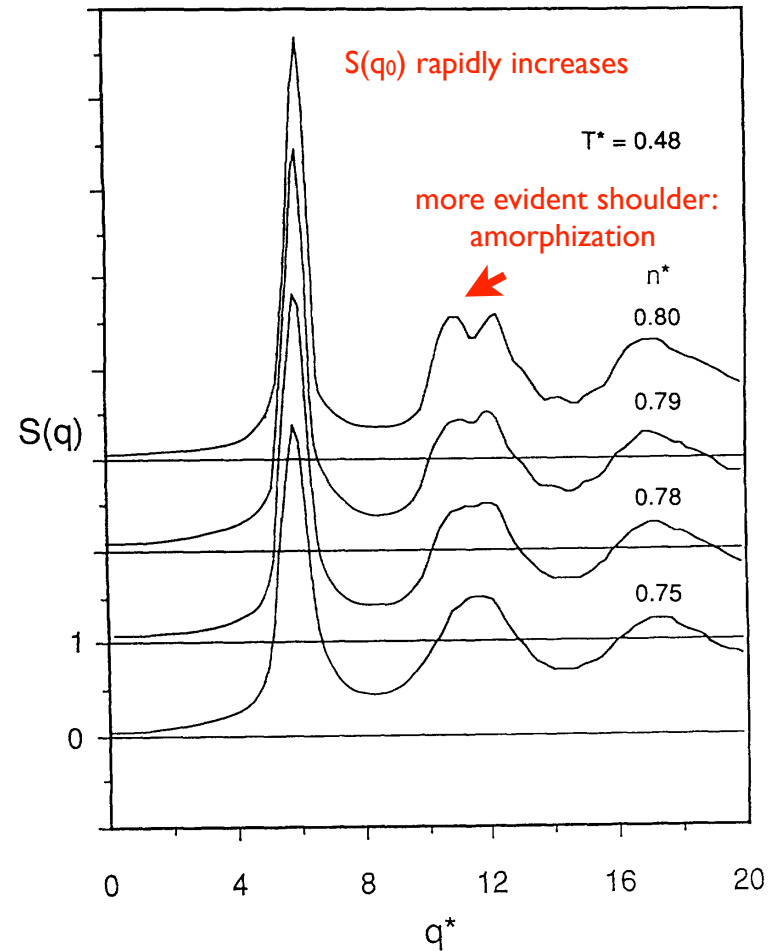


FIG. 4. Structure factor along the isotherm  $T^* = 0.48$  at various densities. The curves are displaced for clarity.

$$S(q) = 1 + 2\pi n \int_0^\infty r J_0(qr) [g(r) - 1] dr$$

The structure factor  $S(q_0)$  can amplify characteristic features of  $g(r)$

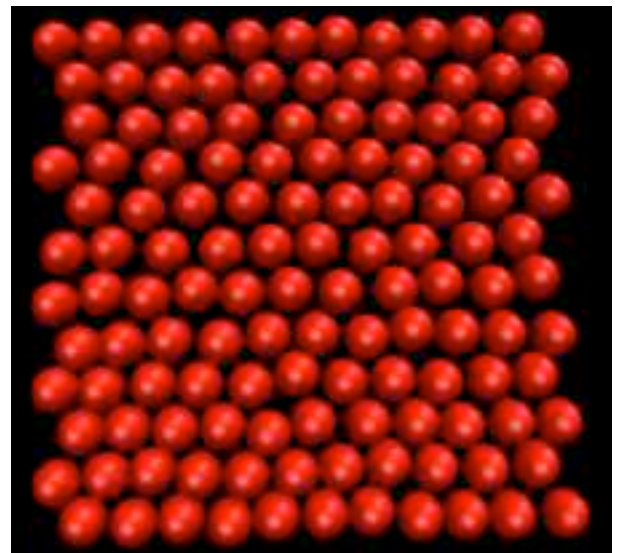
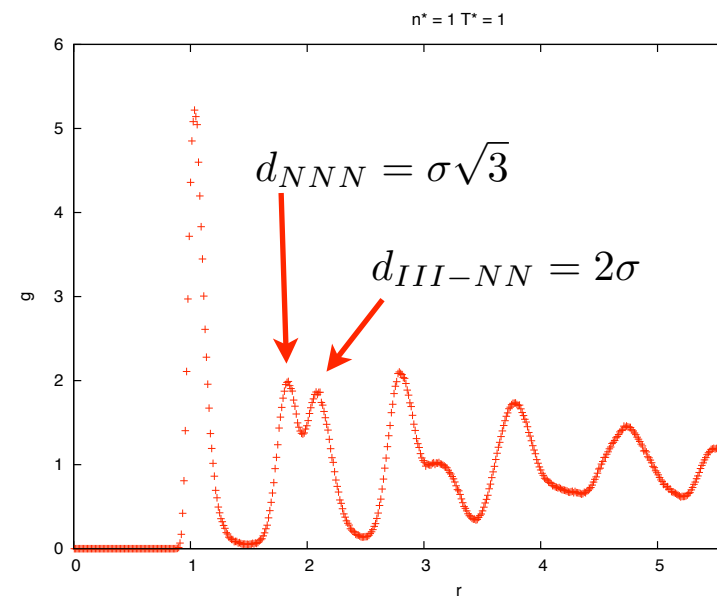
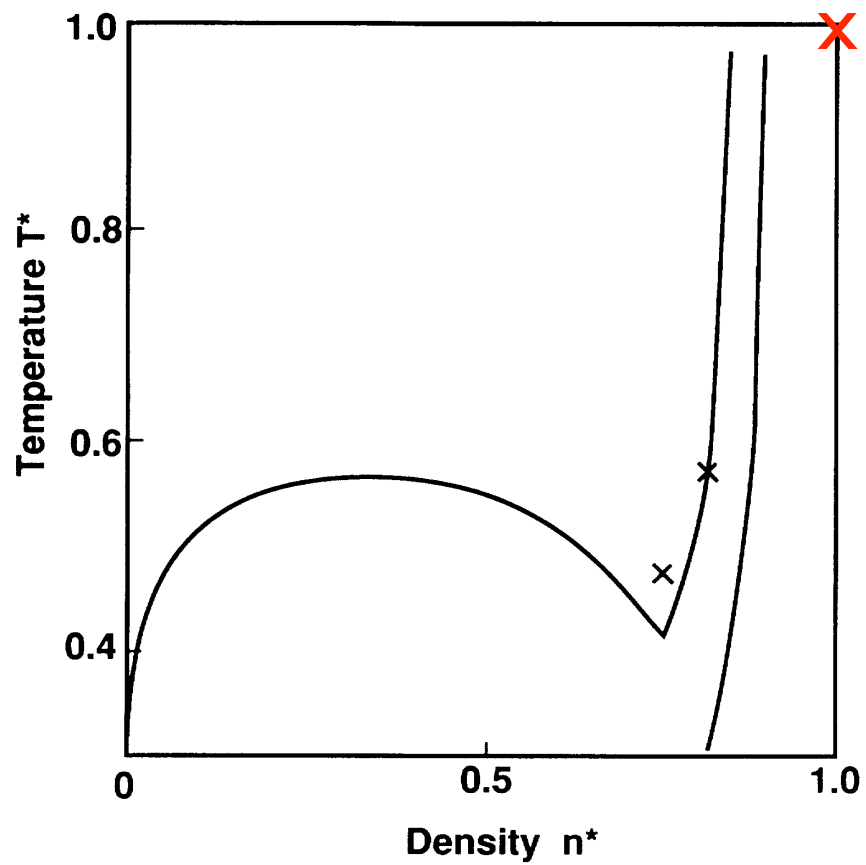


FIG. 1. Phase diagram for the two-dimensional Lennard-Jones system. The crosses indicate the  $(n^*, T^*)$  states  $(0.75, 0.48)$  and  $(0.81, 0.58)$ .

# References

- Simulation of liquids and solids, G. Ciccotti, D. Frenkel and I. R. McDonald (Eds.), North-Holland, 1987. A collection of key papers on MD simulation from the origins to 1986.
- Alder & Wainwright, J. Chem. Phys. 27, 1208 (1957) : phase diagram of hard spheres system (solid and liquid regions in particular)
- J.B. Gibson et al. , Phys. Rev. 120, 1229 (1960) : continuous potential; discretize time integration method
- A. Rahaman, Phys. Rev. 136, A405 (1964) : liquid Ar with LJ potential
- L.Verlet, Phys. Rev. 159, 98 (1967); Phys. Rev. 165, 201 (1967) : phase diagram of Ar using LJ; “Verlet neighbor list”; velocity-Verlet algorithm
- J.P. Hansen and L.Verlet, Phys. Rev. 184, 151 (1969) ; again phase diagram of Ar with LJ
- <http://rkt.chem.ox.ac.uk/lectures/liqsolns/liquids.html> (but also many others)

More details:  
in the course by E. Smargiassi,

“Classical simulations of many-body systems”  
(Simulazioni classiche di sistemi a molti corpi)  
1st semester