993SM - Laboratory of Computational Physics
week XIII - II part
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Classical fluids

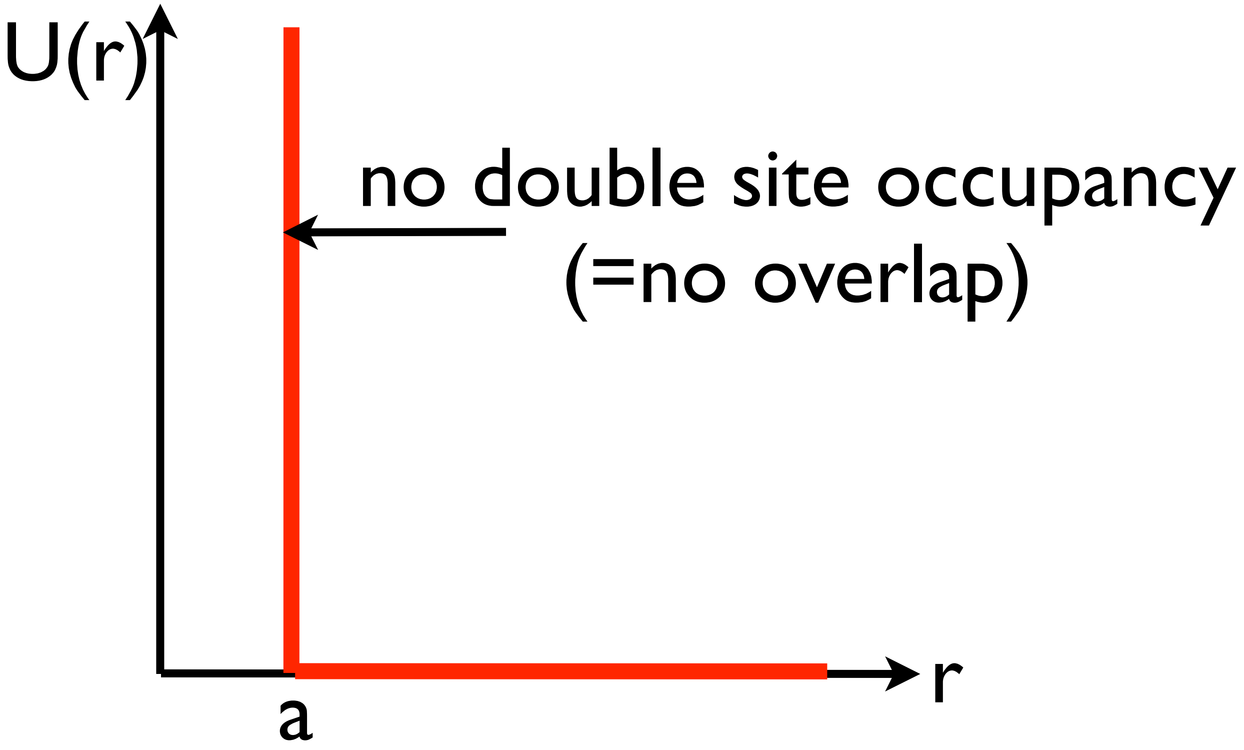
- Interactions
- Measurable and interesting physical quantities
- Metropolis Monte Carlo approach (mainly)
- Molecular dynamics

(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 depends only on the distance
(or atoms)

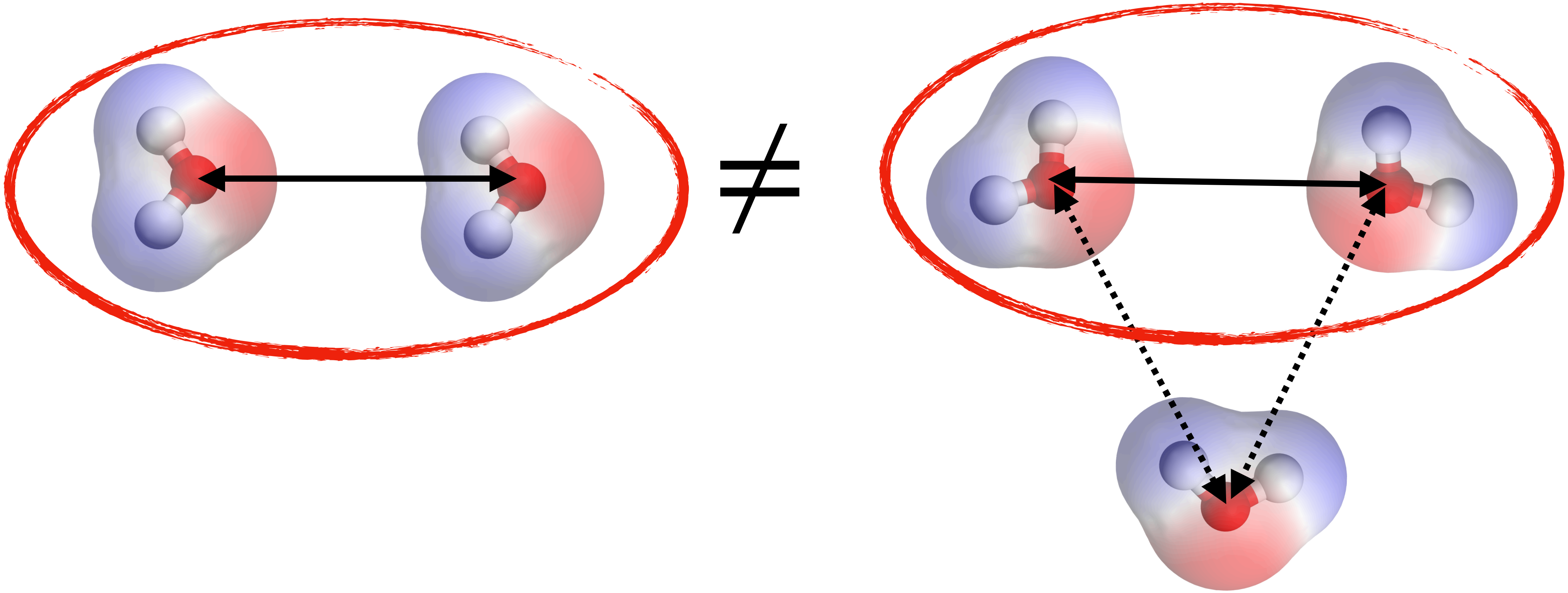
$\left(u(r_{ij})\right.$ depends only on the magnitude of the distance $\mathbf{r}_{ij}$ between particles i and $\left.j\right)$)

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

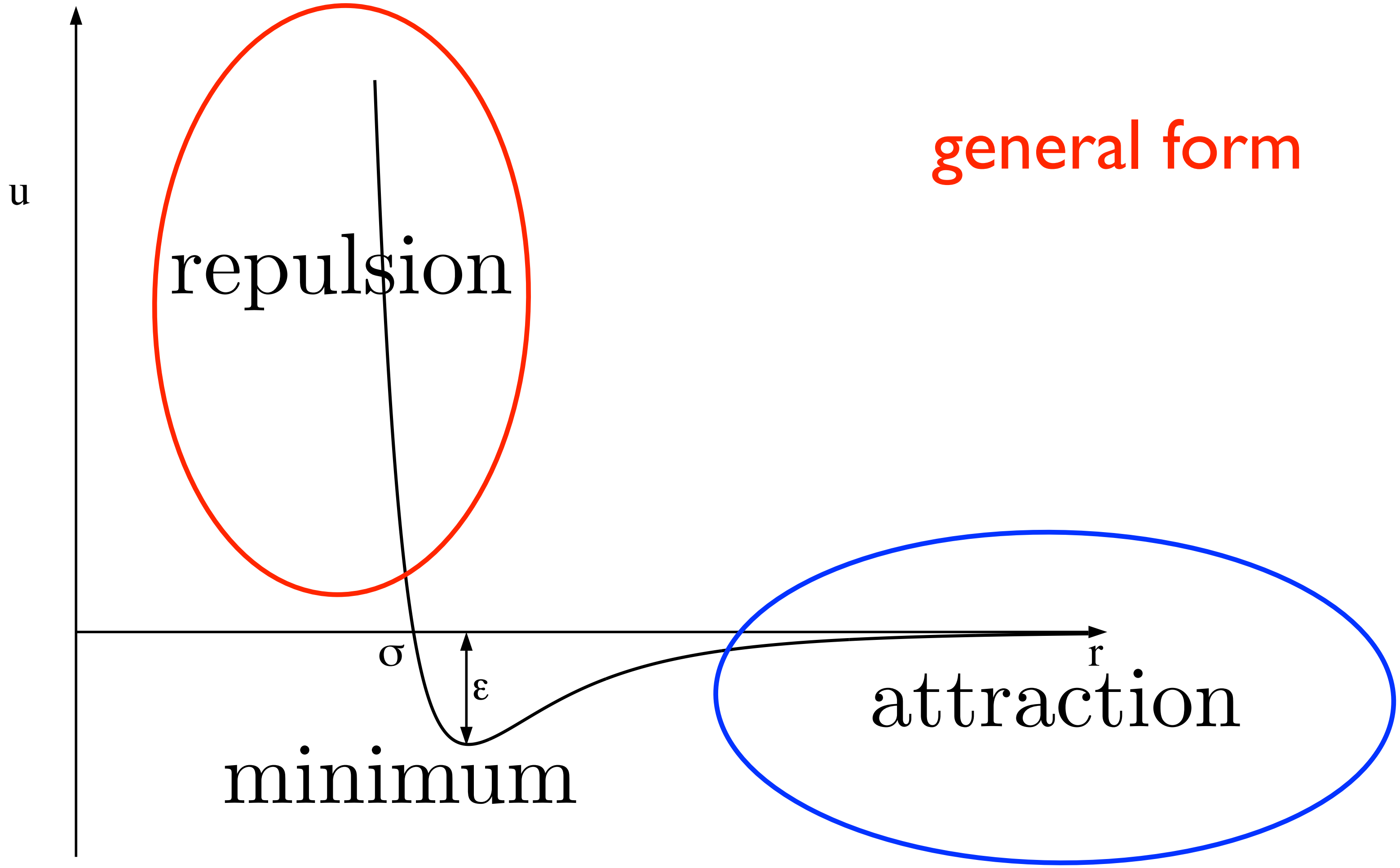
$$U = u(r_{12}) + u(r_{13}) + \cdots + u(r_{23}) + \cdots = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij})$$

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



general form

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

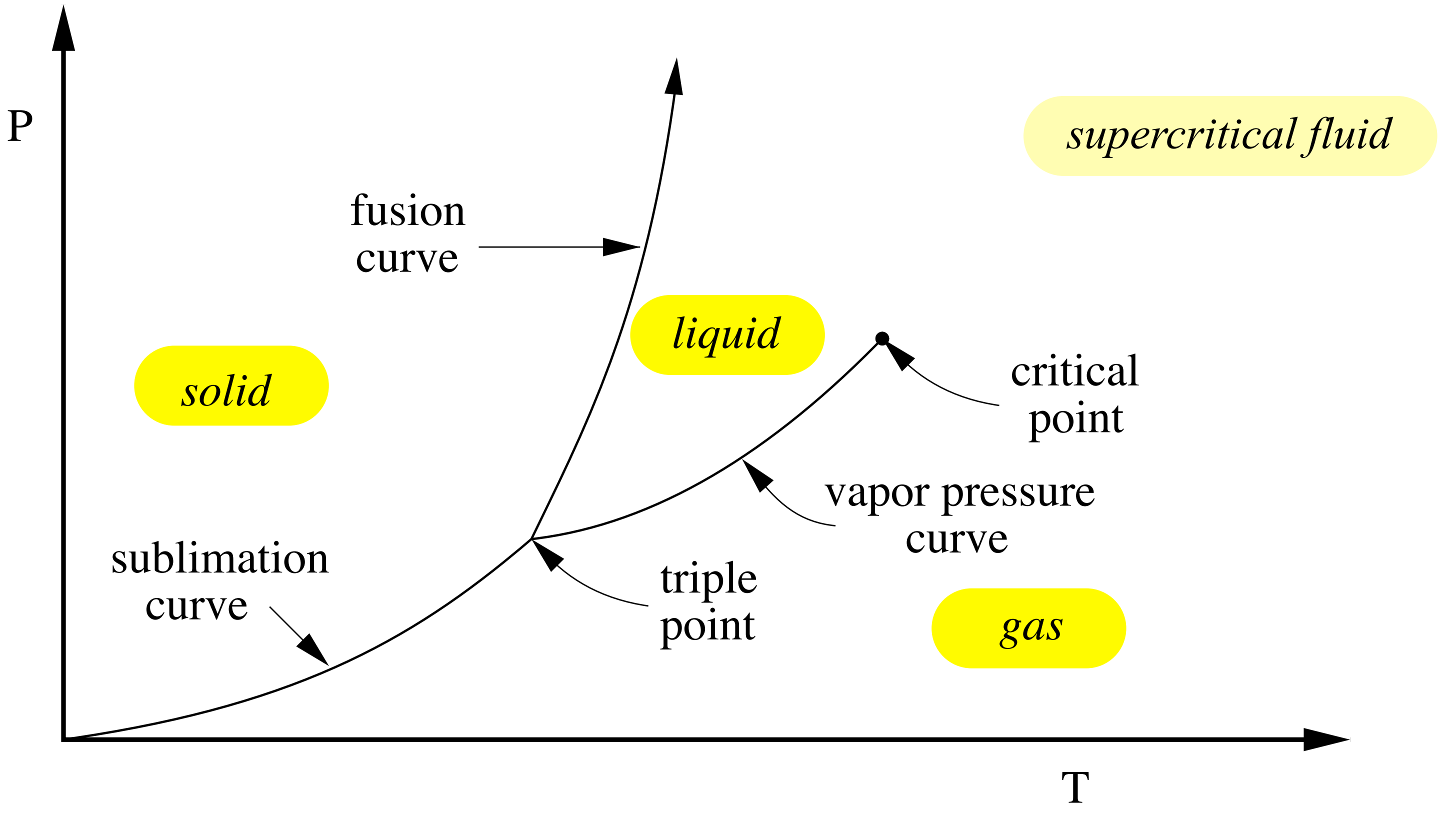
consequence of the Pauli exclusion principle

`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

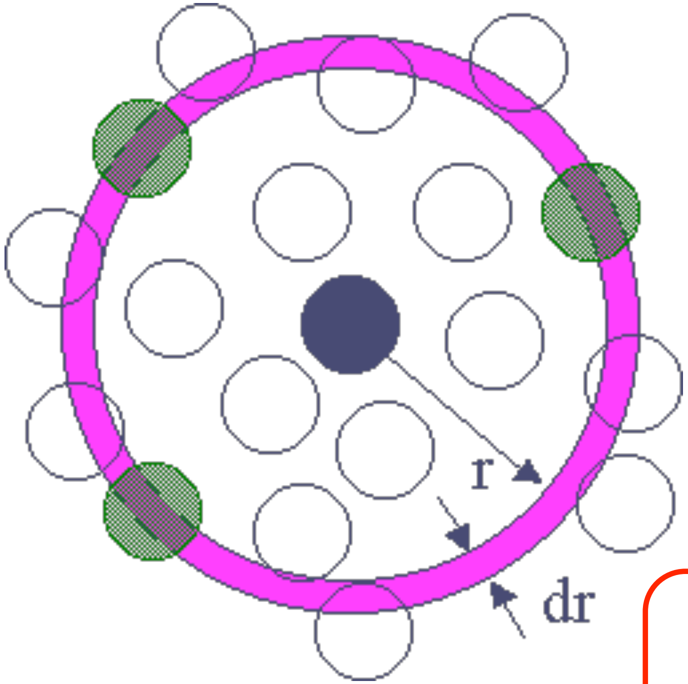
Measurable and interesting quantities

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

Measurable and interesting quantities

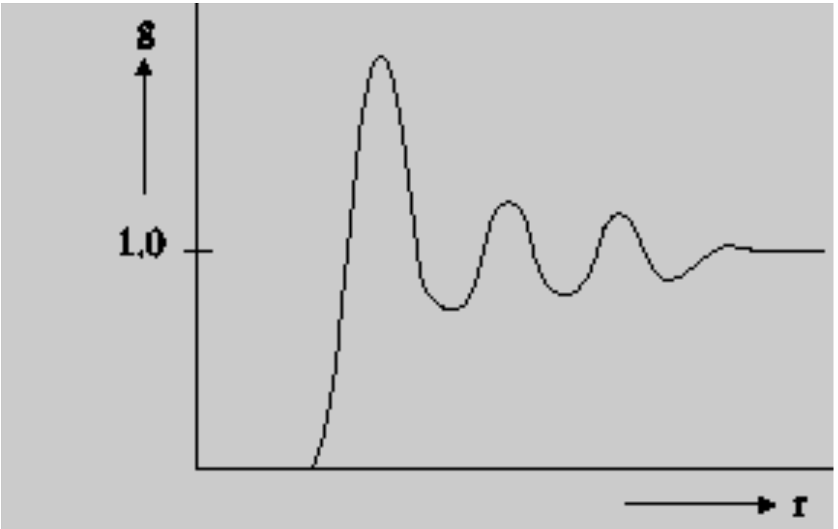
- pair correlation function $g(r) \left\{ \begin{array}{l} \text{concepts and qualitative features} \\ \text{mathematical formulation and expressions useful for computation} \end{array} \right.$
- energy E
- pressure p
- ...

Radial distribution function



Definition

$$g(r)$$



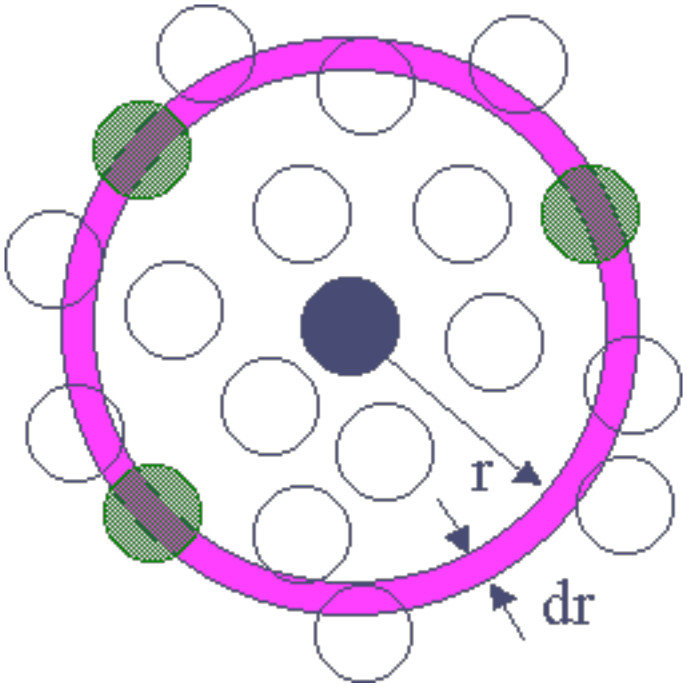
$g(r)d\mathbf{r}$ ($d\mathbf{r}$ = infinitesimal volume of the shell)

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:

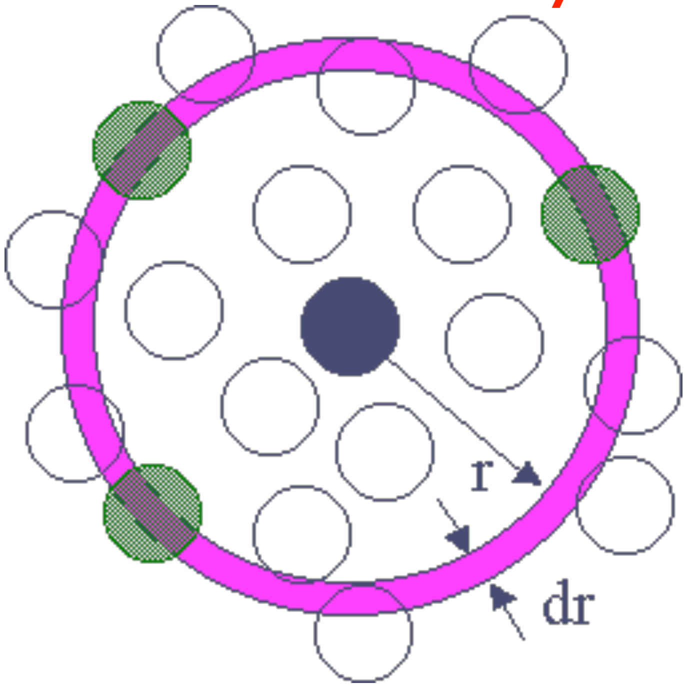
$$\rho g(r) d\mathbf{r}$$

(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 $2\,dr\,(d=1)$

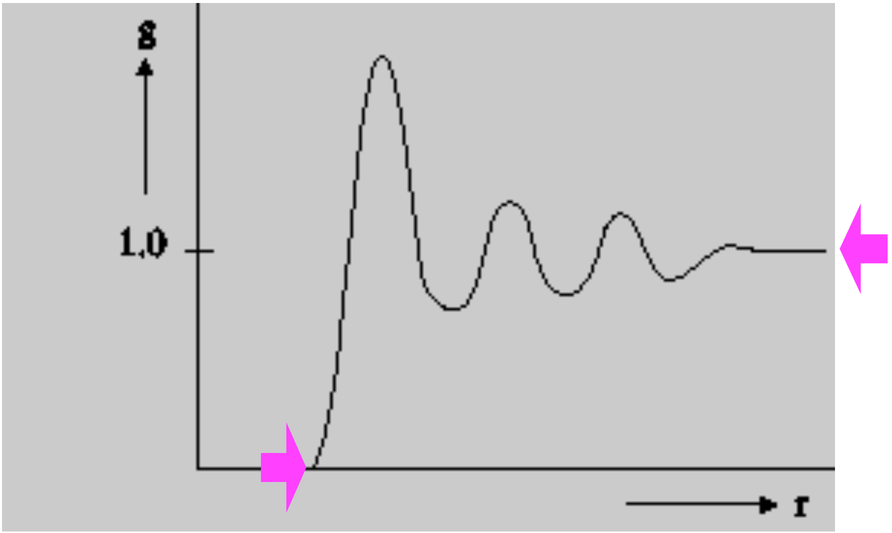
normalization condition $$\rho \int_0^\infty g(r)\, d\mathbf{r} = N - 1 \approx N$$

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

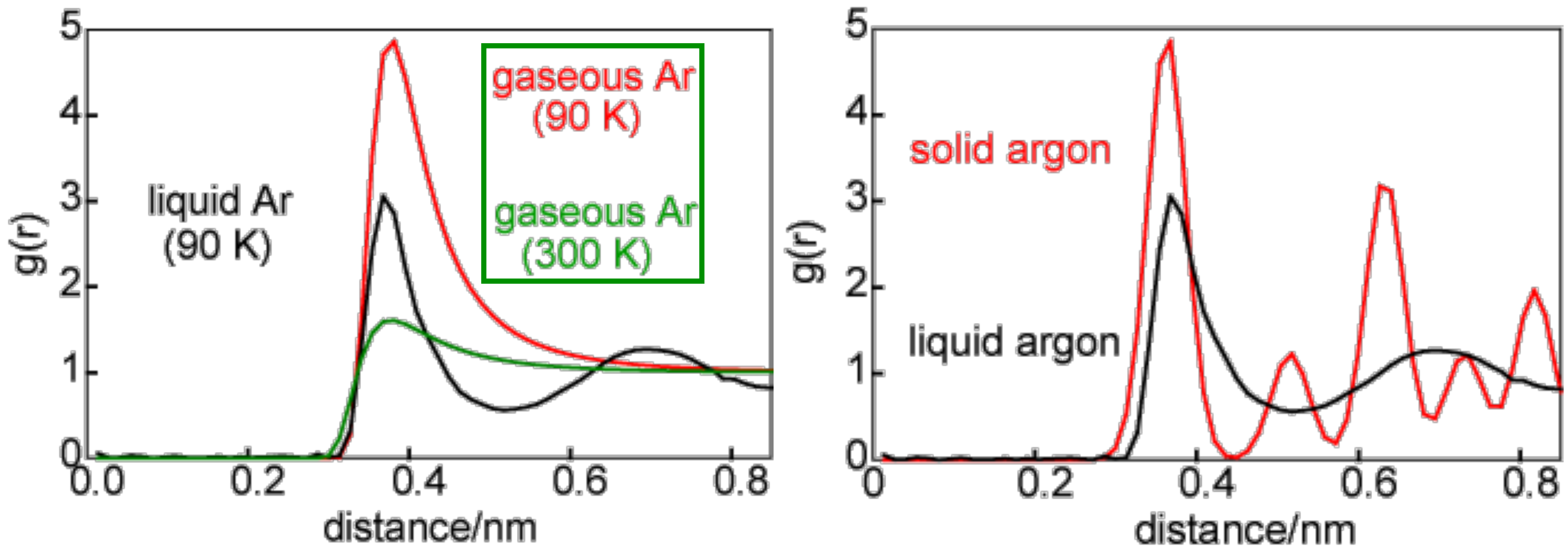
Typical features:

gas: almost structureless

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

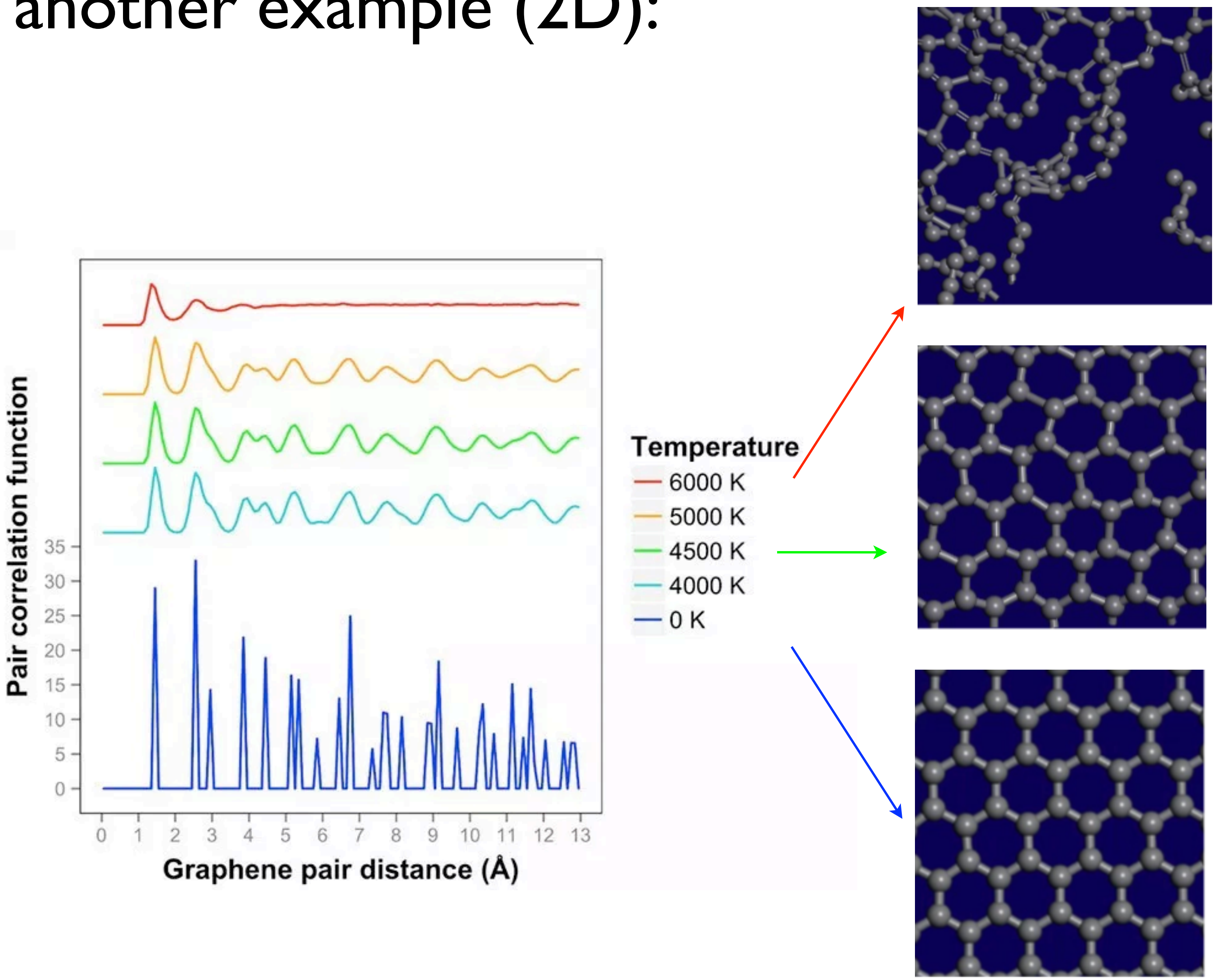
liquid: some structure with broad peaks

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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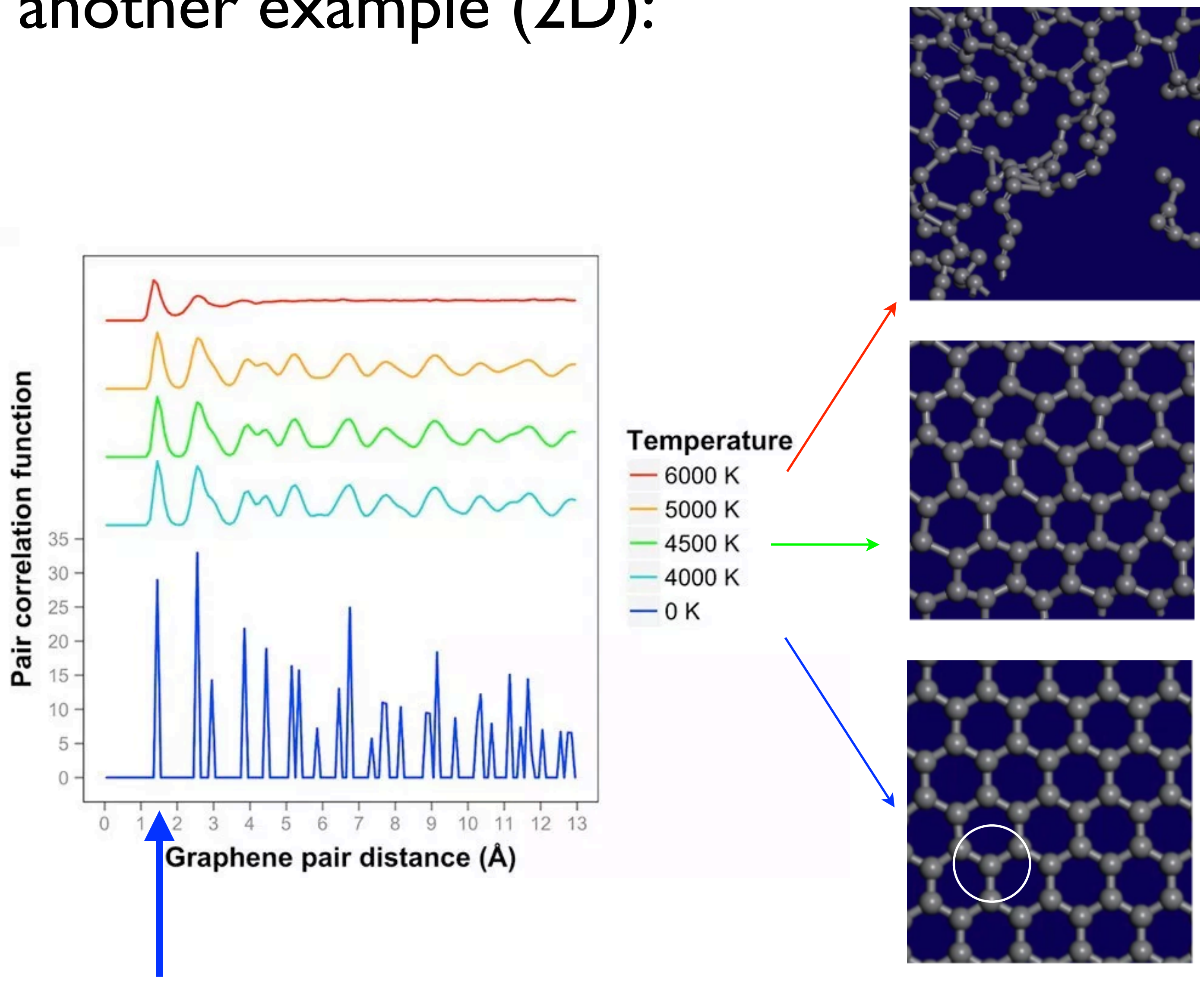

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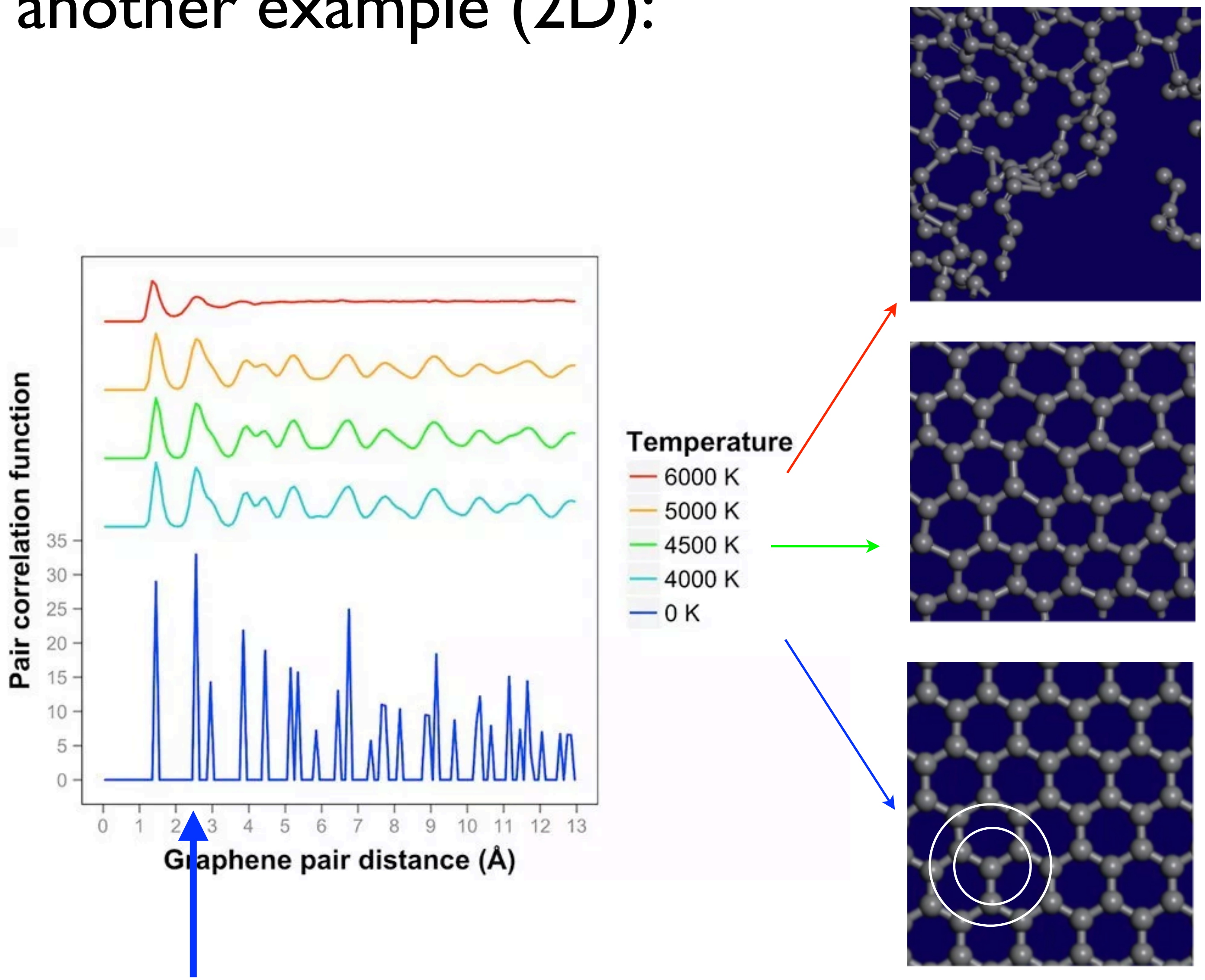

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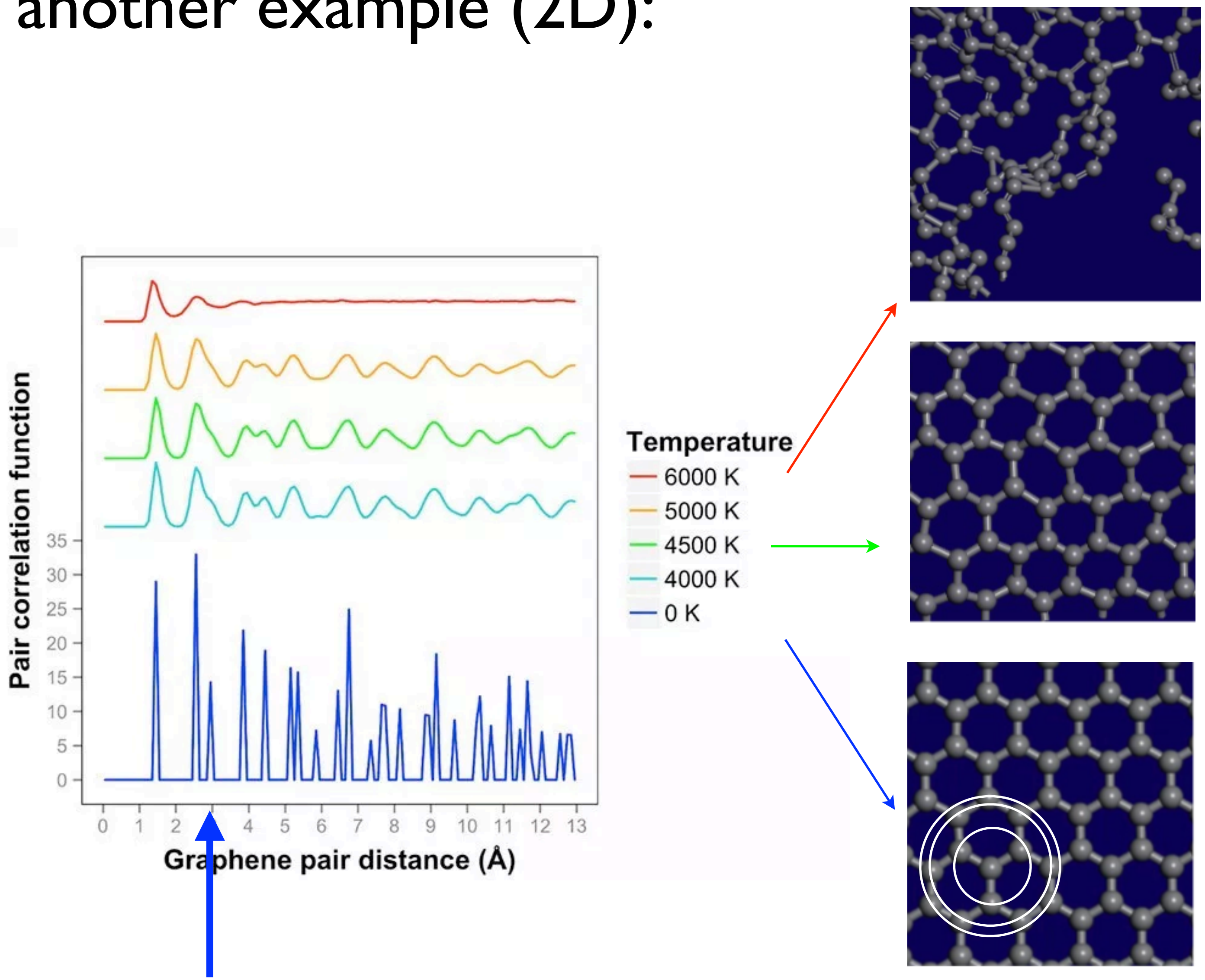

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Radial distribution function

formulation in case of spherically symmetric interactions:

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

(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 Δr 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, ***n****(r,Δr)* 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:

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

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

<= (δ: to be considered within the accuracy of Δr ; up to here: double counting of pairs)

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

<= (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 $\rho = N/V$

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

ensemble average over pairs

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

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(k);
fluctuations in g(r) are related to S(k):

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

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

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

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

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: $\dfrac{U}{N} = \dfrac{\rho}{2}\displaystyle\int g(r)u(r)\,d\mathbf{r}$

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:

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

Virial theorem

If $\langle E_{kin} \rangle$ is the time average of the total kinetic energy and **F**$_k$ is the force acting on the particle *k* at the position **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 $V(r) = ar^{n}$ where r is the inter-particle distance, the virial theorem is simply:

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

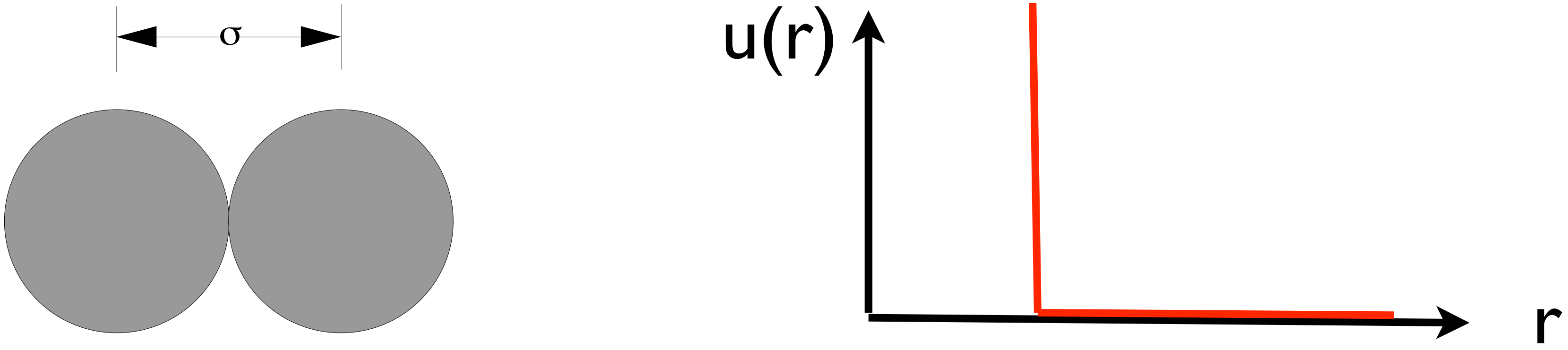
(average
also over time)

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)

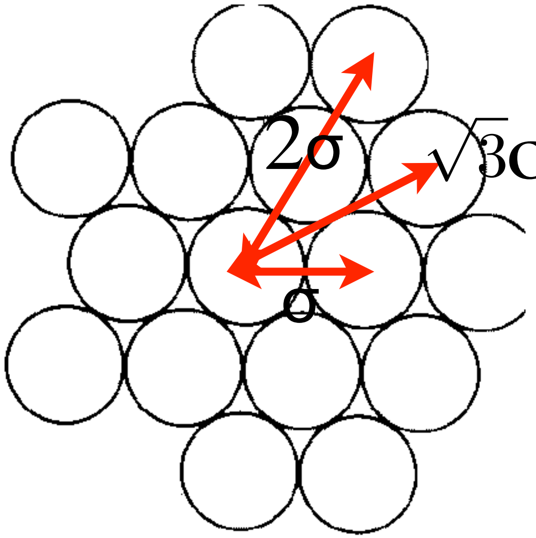


$$u(r) = \begin{cases} +\infty, & r < \sigma \\ 0, & r \geq \sigma \end{cases}$$

No minimum; check overlap!
No attractive part => 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)

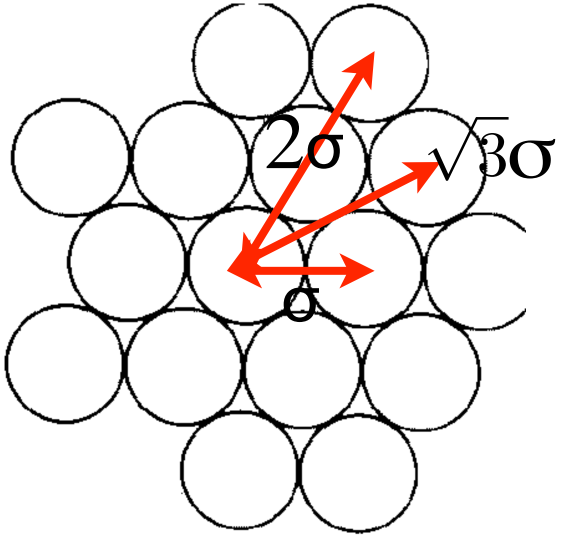
max reduced density : $\rho^*_{max} = \dfrac{2}{\sqrt{3}} = 1.1547$

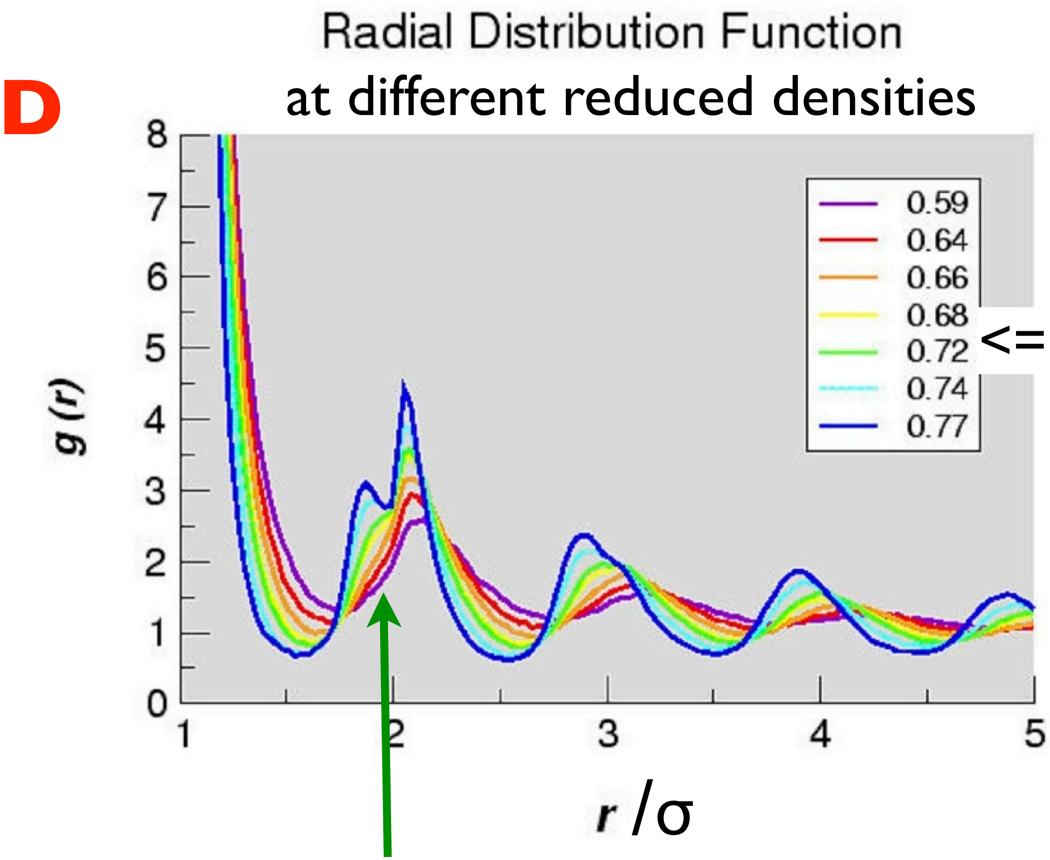
max packing fraction: $f = \dfrac{area_{occupied}}{area_{available}} = \dfrac{\pi}{2\sqrt{3}} = 0.907$

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

Radial distribution function

of **hard disks in 2D**





at different reduced densities

<= liquid

<= transition ?

<= solid

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

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

PHYSICAL REVIEW E VOLUME 58, NUMBER 3 SEPTEMBER 1998

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]

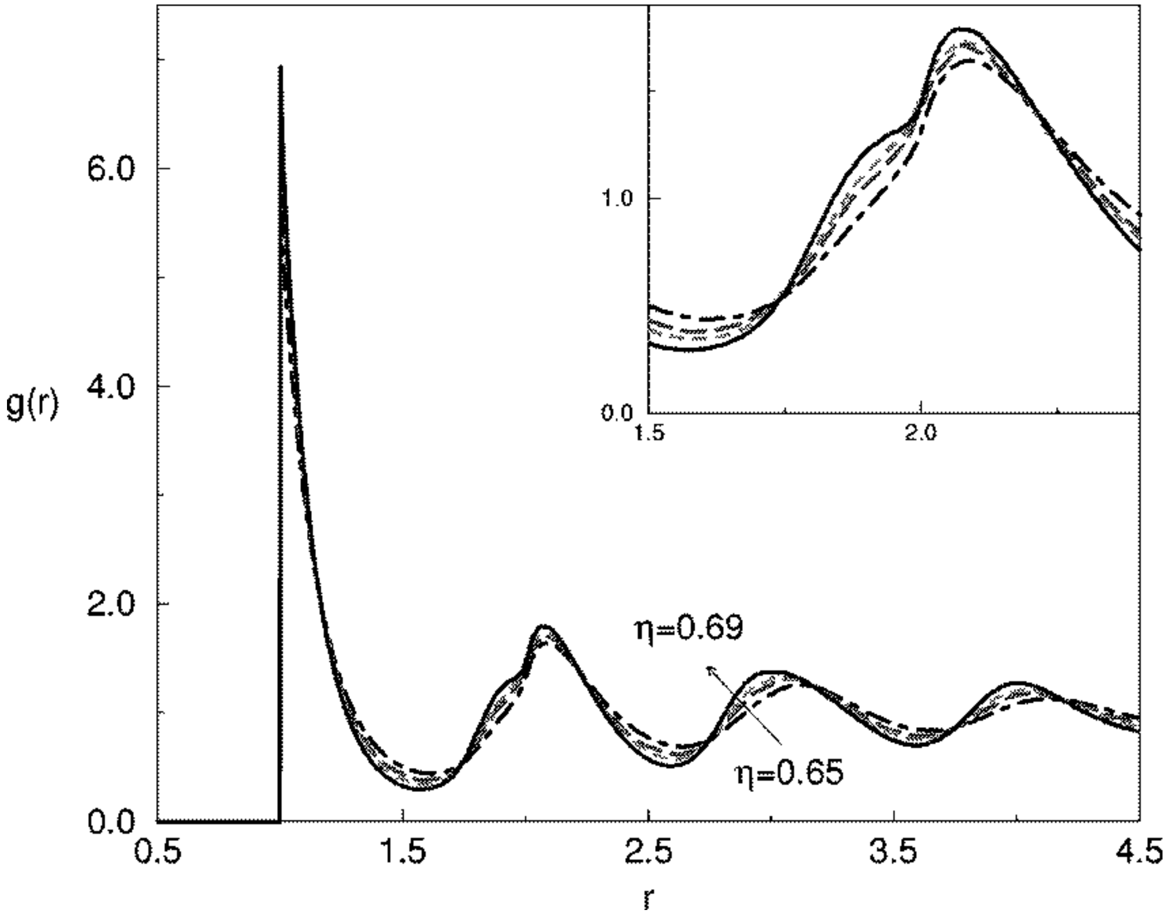


FIG. 1. Radial distribution function $g(r)$ for hard disks plotted versus distance r (in units of diameters). Curves represent the fluid phase with $\eta=0.65$, 0.67, 0.68, and 0.69 (freezing point).

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

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:

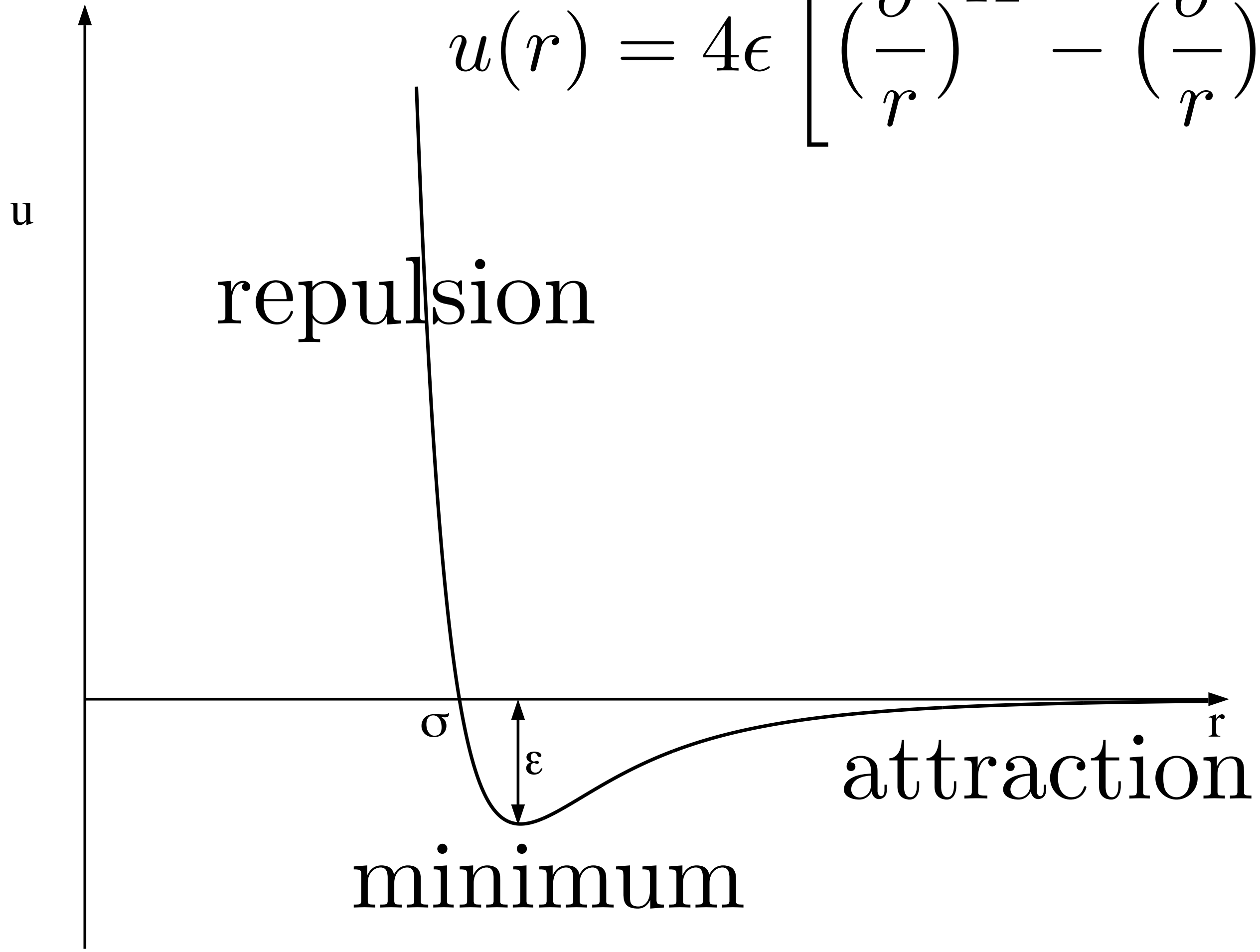
$$d\mathbf{r} = 4\pi r^2 dr \qquad \frac{\beta P}{\rho} = 1 + \frac{2}{3}\pi\rho\sigma^3 g(\sigma) \qquad (d = 3)$$

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

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

Lennard-Jones potential

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



Lennard-Jones potential

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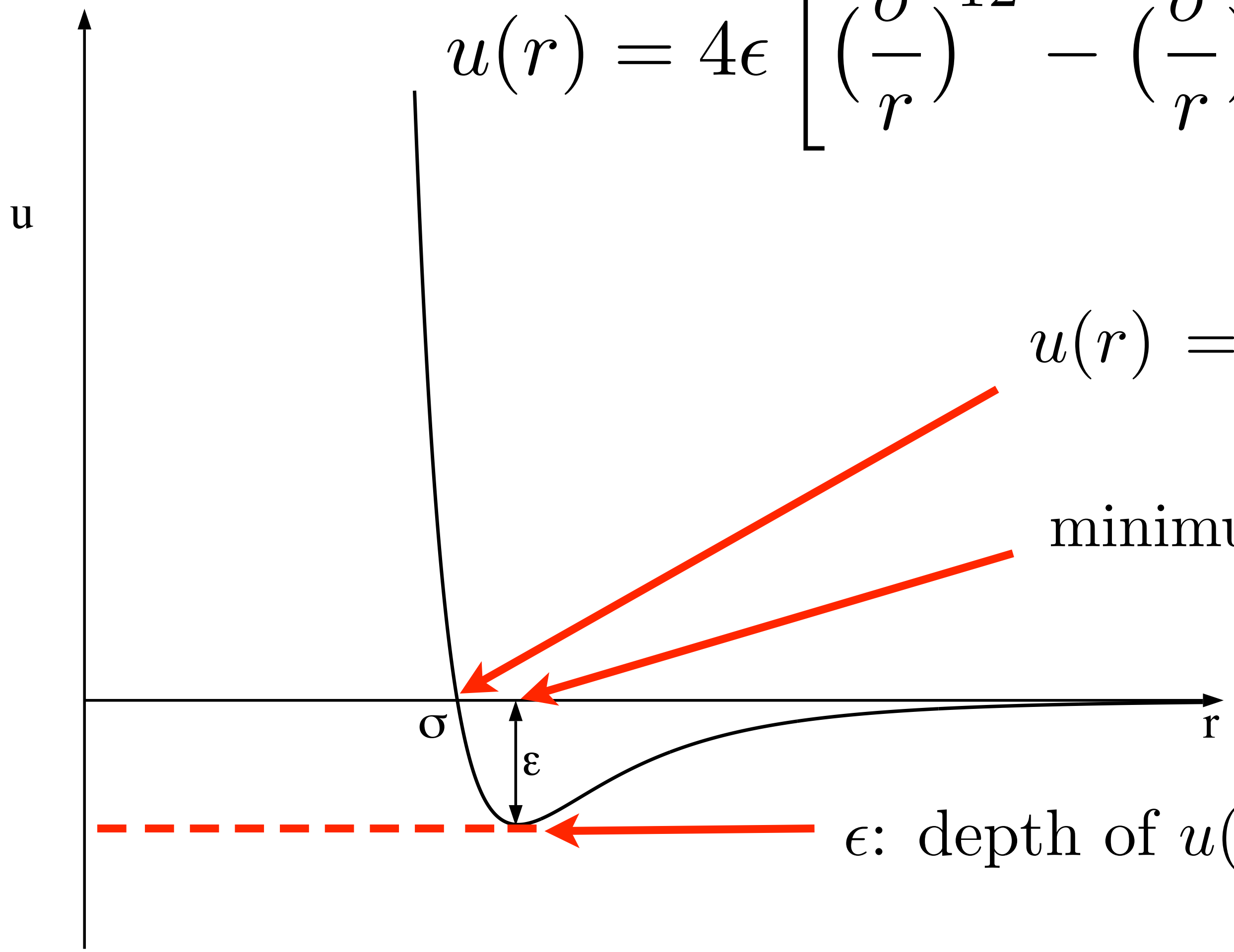


$u(r) = 0$ at $r = \sigma$

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
```

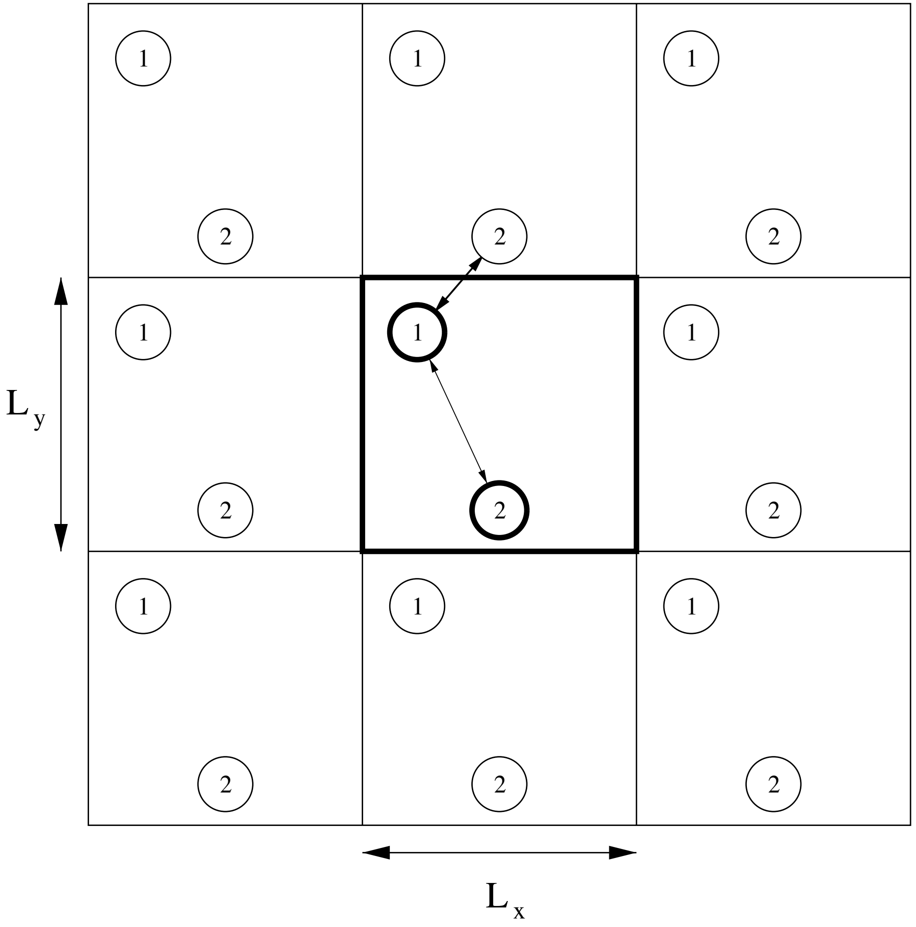
(OK
in the hypothesis that
-L < pos <2L)

new!

Minimum Image convention

for the interactions

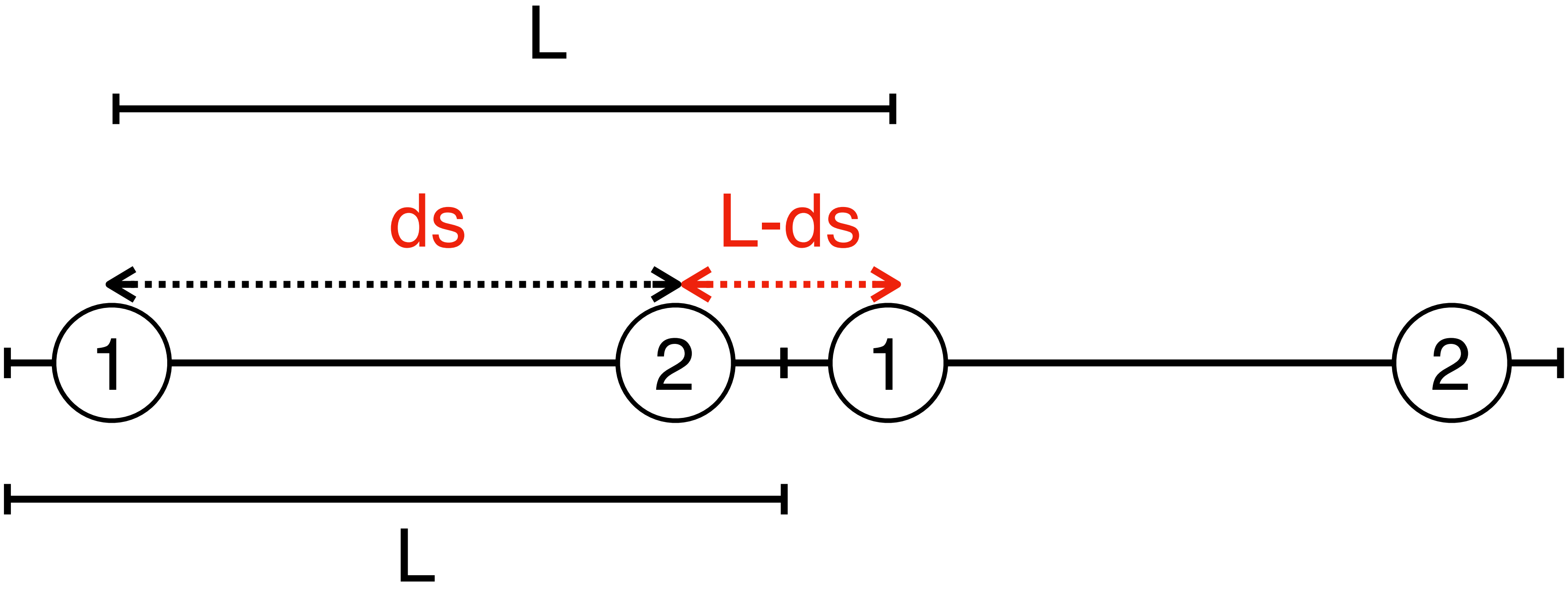
To compute the minimum distance `dx` between particles 1 and 2 at `x(1)` and `x(2)`



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

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

```
 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)

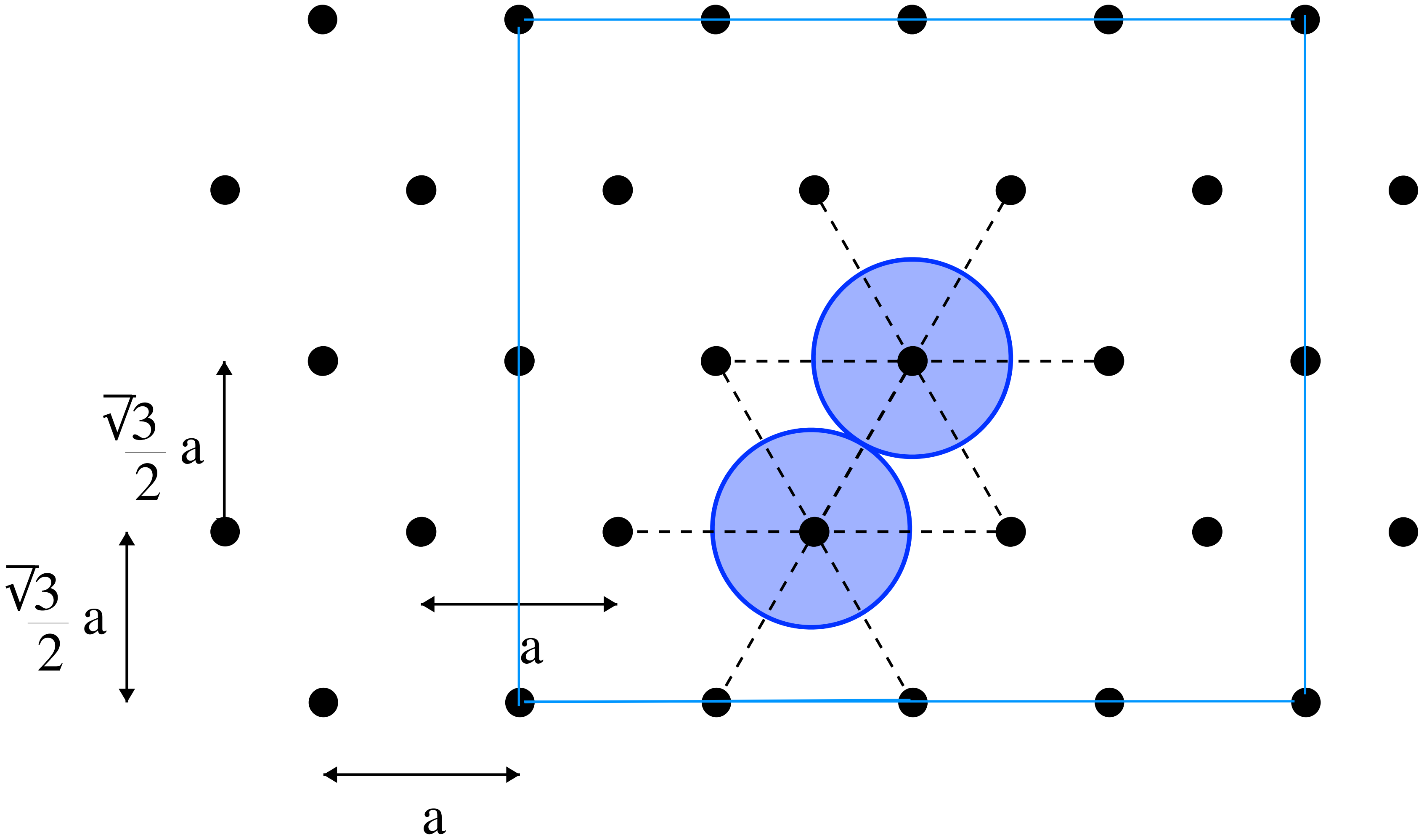
Metropolis Monte Carlo method for Hard Disks (Spheres)

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

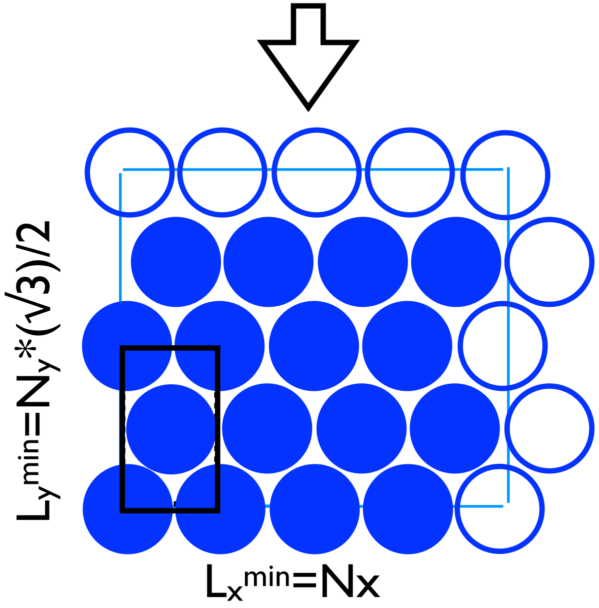
take the linear dimensions of the cell to be L_x and $L_y = \sqrt{3}L_x/2$ (here: N=16)

Initializing the positions

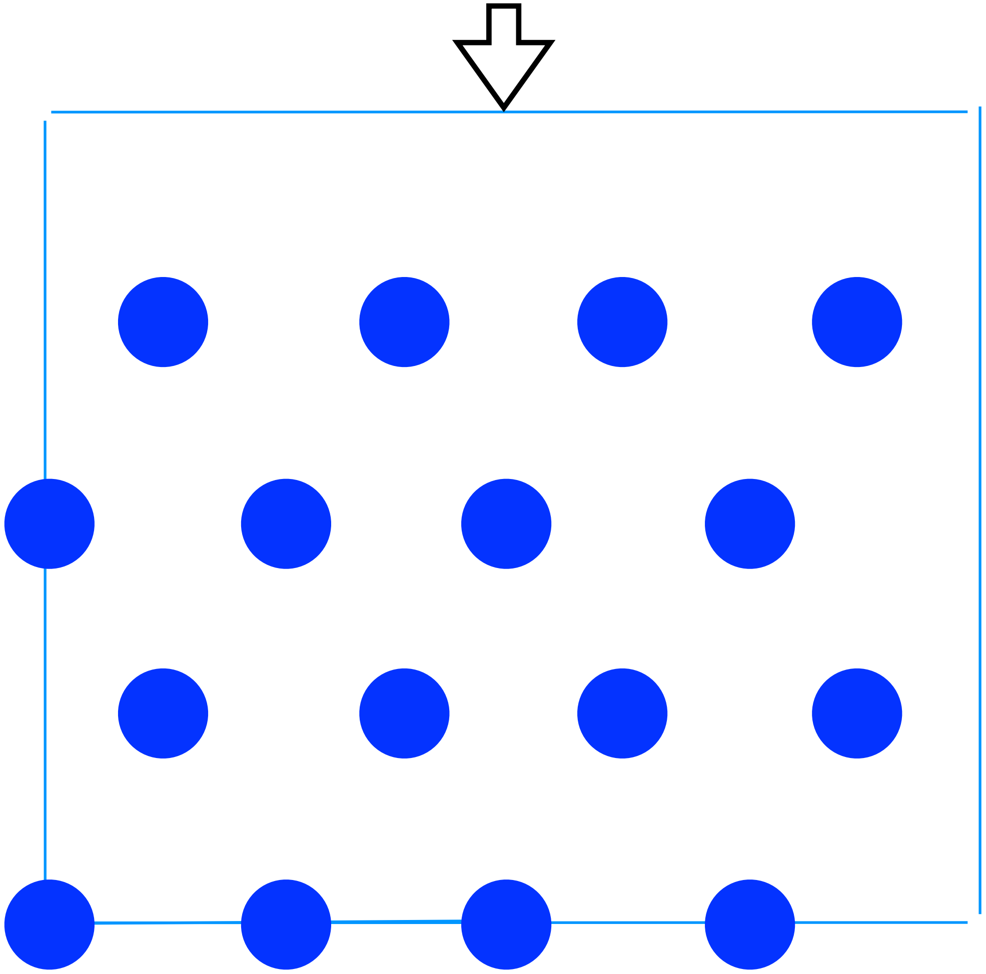
Convenient to start from maximum packing and then reduce the density:

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 <u>initial and boundary conditions</u>
- proper <u>interatomic potentials</u>
- while satisfying <u>thermodynamical (macroscopic) constraints</u>

<u>- and with a 'smart' algorithm for numerical integration</u>

Molecular dynamics

and Newton's equations of motion

$$F = ma$$

But not always easy to solve… In general:

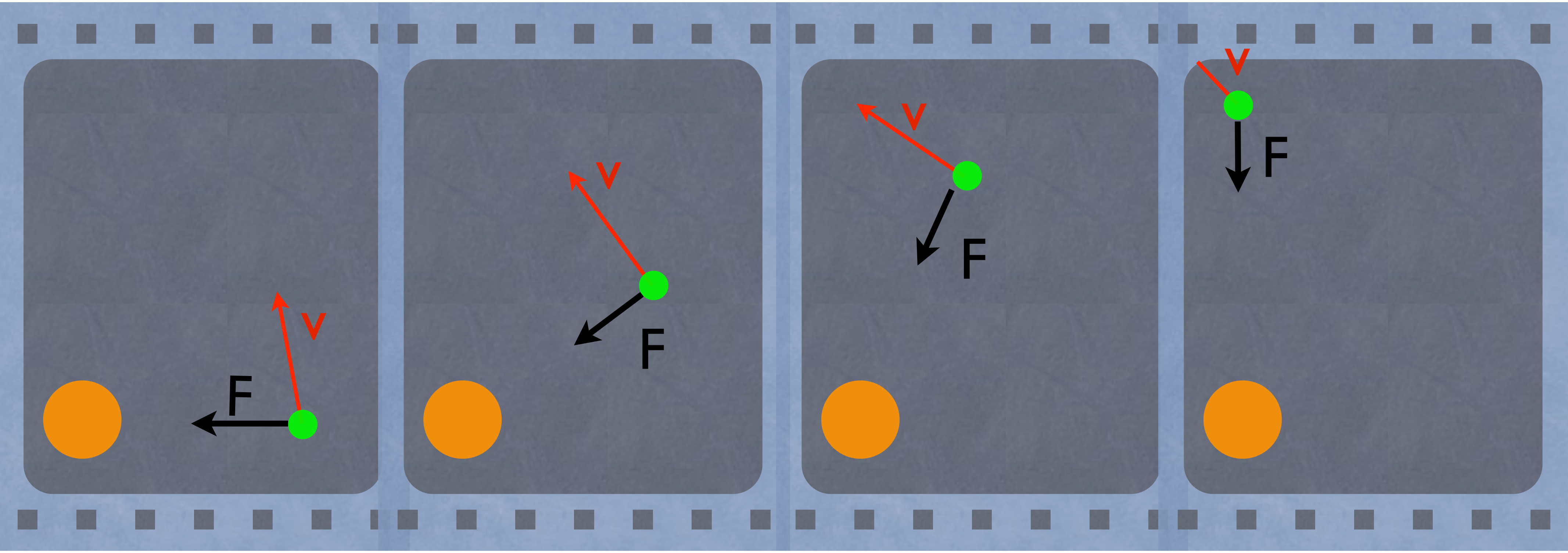
$$\frac{d^2x}{dt^2} = a(x, t, \ldots) = \frac{F(x, t, \ldots)}{m}$$

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

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



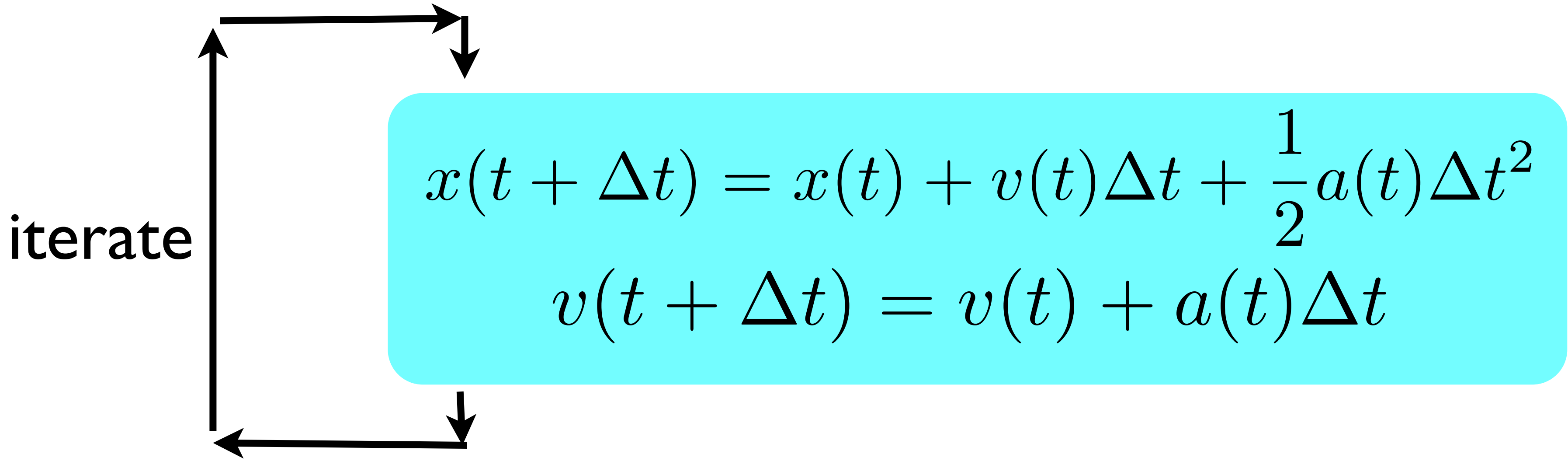
x(0) v(0) F(0)   x(1) v(1) F(1)   x(2) v(2) F(2)   ... ...

Uniformly accelerated motion in each time interval

$t \div t + \Delta t$

then iterate!

EULER algorithm



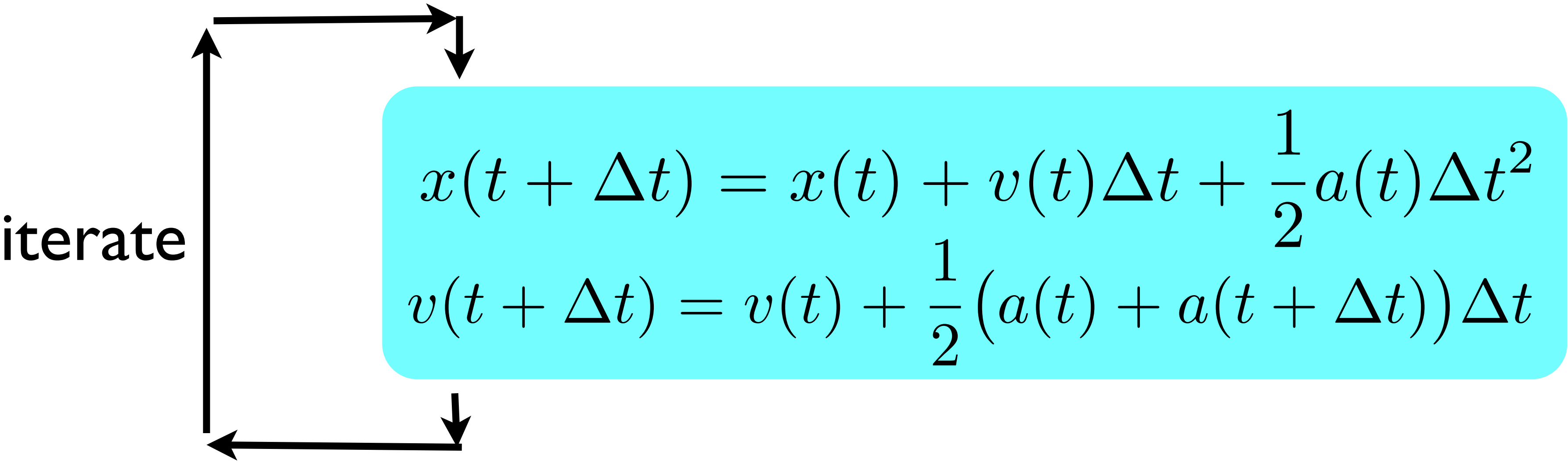
iterate

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

$$x(t) \Longrightarrow x(t+\Delta t) \Longrightarrow x(t+2\Delta t) \Longrightarrow x(t+3\Delta t) \Longrightarrow \dots$$
$$v(t) \Longrightarrow v(t+\Delta t) \Longrightarrow v(t+2\Delta t) \Longrightarrow v(t+3\Delta t) \Longrightarrow \dots$$

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



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

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)

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 ensambles with MD

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

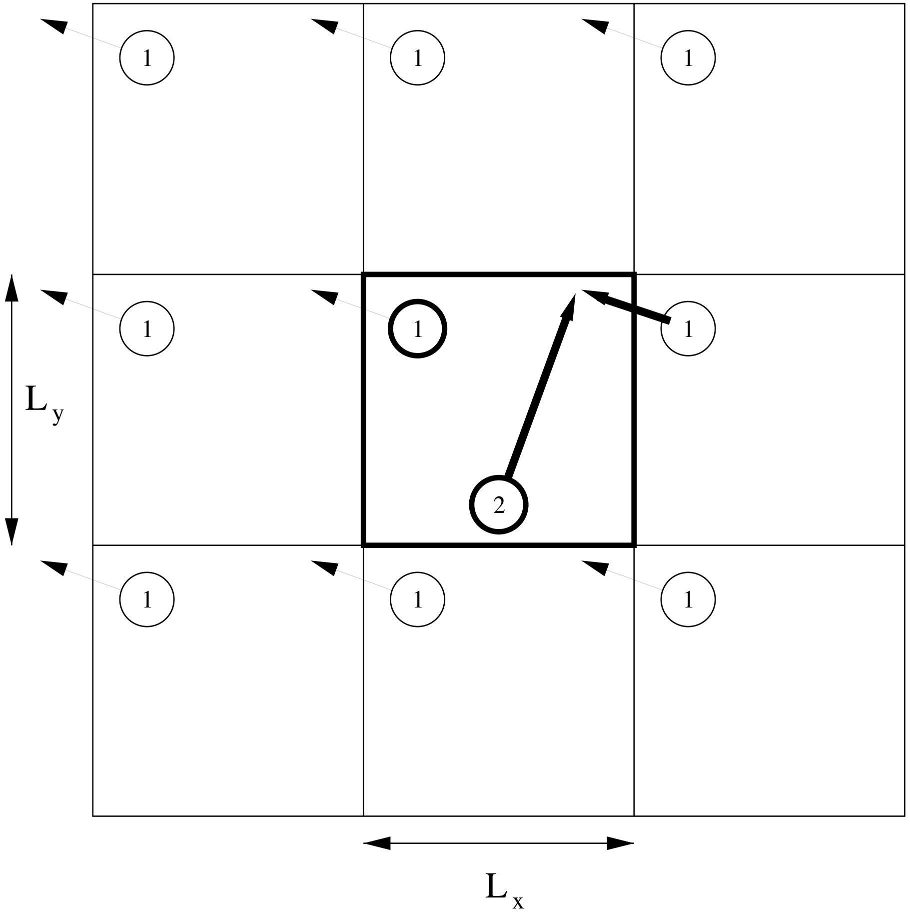
$$E_{kin} = \frac{1}{2} m \sum_{i}^{N} v_i^2$$

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

rescale velocities (use a “**thermostat**”) to keep T~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).

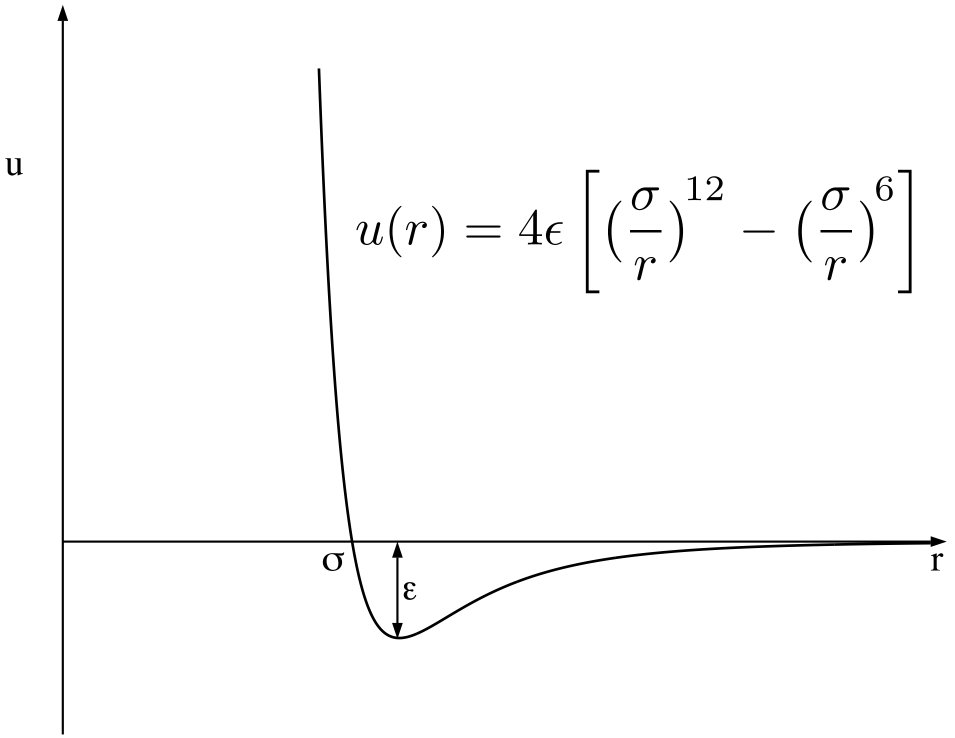
(AW) B. J. Alder and T. E. Wainwright
Phase Transition for a Hard Sphere System
J. Chem. Phys. 27, 1208 (1957); ibid. 31, 459 (1959)

- 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



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

$$\text{liquid argon:}$$

$$\epsilon = 1.65 \times 10^{-21}\ \mathrm{J}$$
$$\sigma = 3.4\ \mathring{A}$$

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

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MD simulation with
128 particles confined in a square box with length $L = \sigma\sqrt{128/\rho^*}$
$nmcs = 6000;\ \Delta t^* = 0.032$

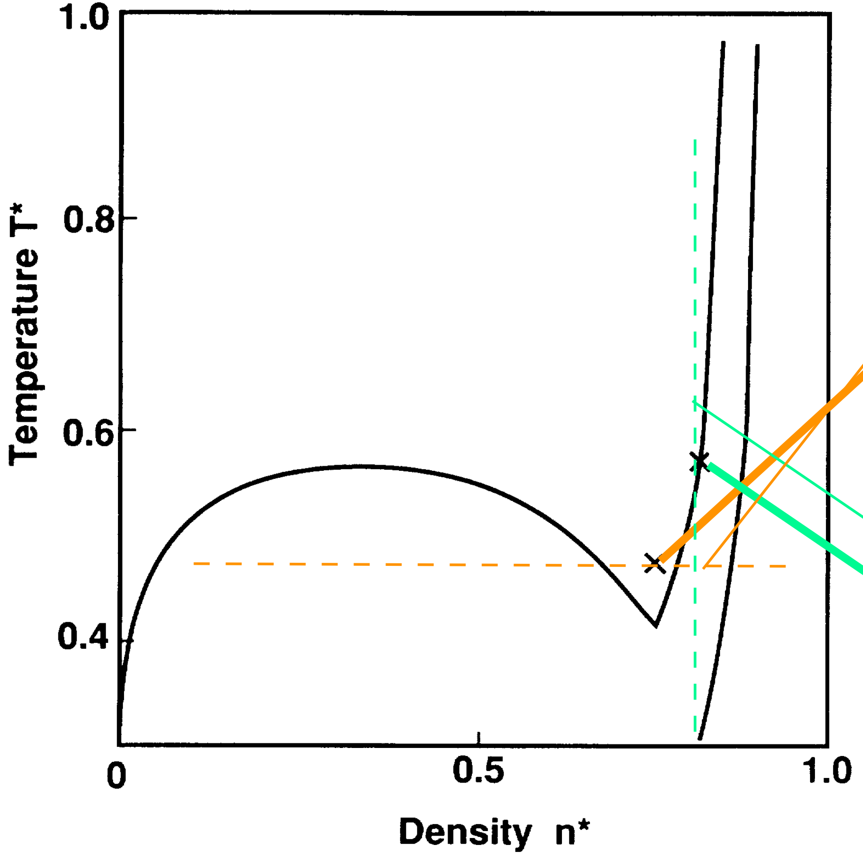


FIG. 1. Phase diagram for the two-dimensional Lennard-Jones system. The crosses indicate the (n^*, T^*) states (0.75, 0.48) and (0.81, 0.58).

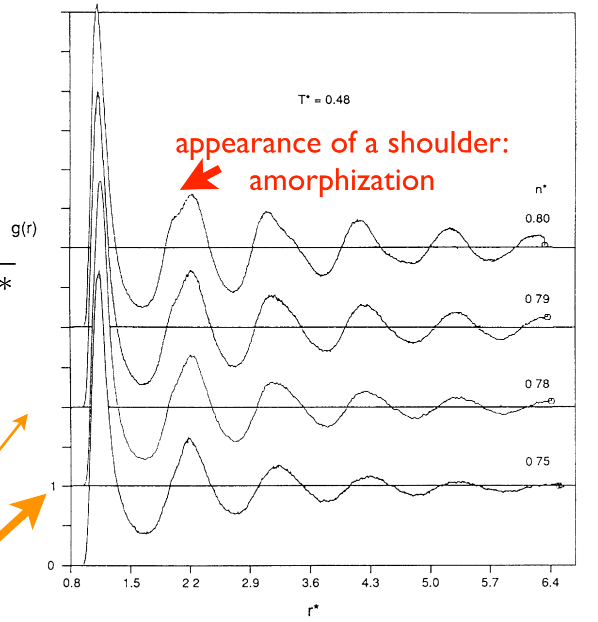


FIG. 2. Pair-distribution function along the isotherm $T^*=0.48$ at various densities. The curves are displaced for clarity.

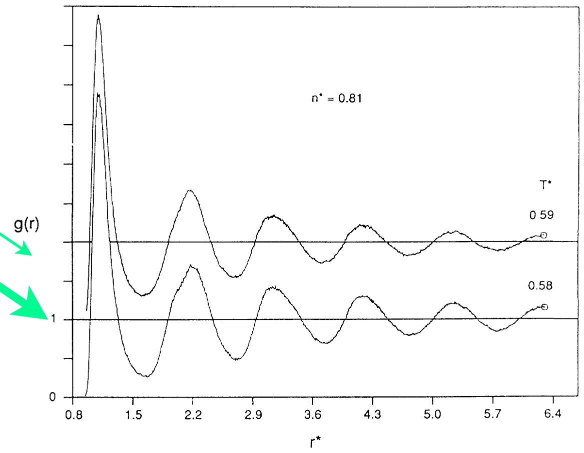


FIG. 3. Pair-distribution function along the isochore $n^*=0.81$ at two temperatures.

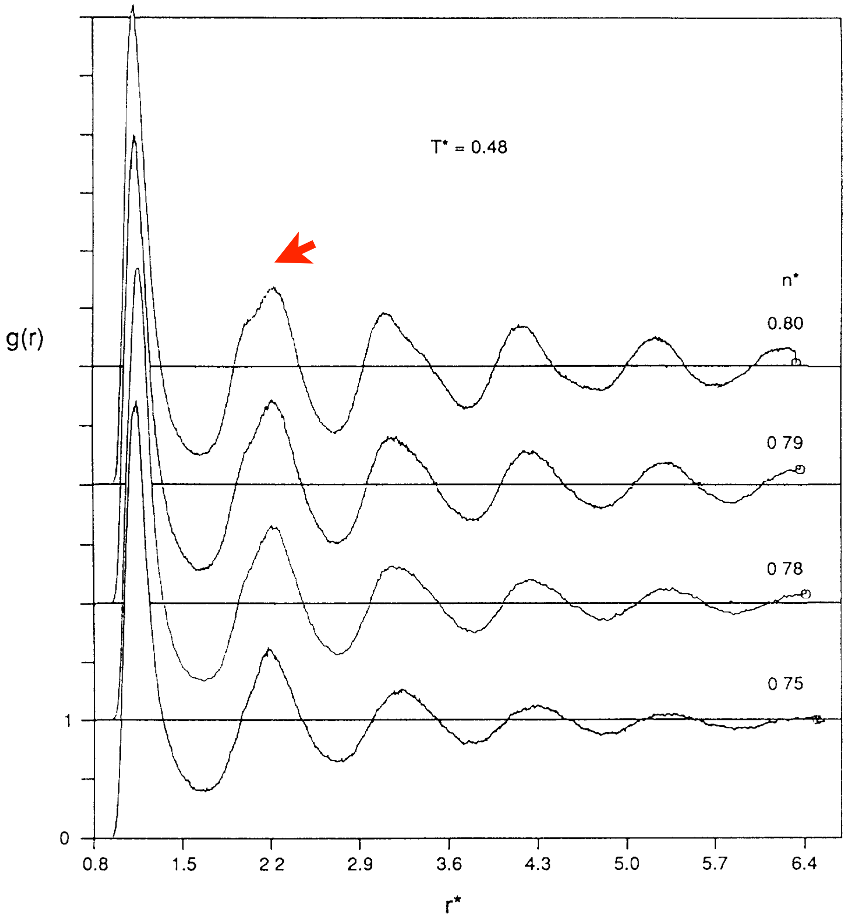
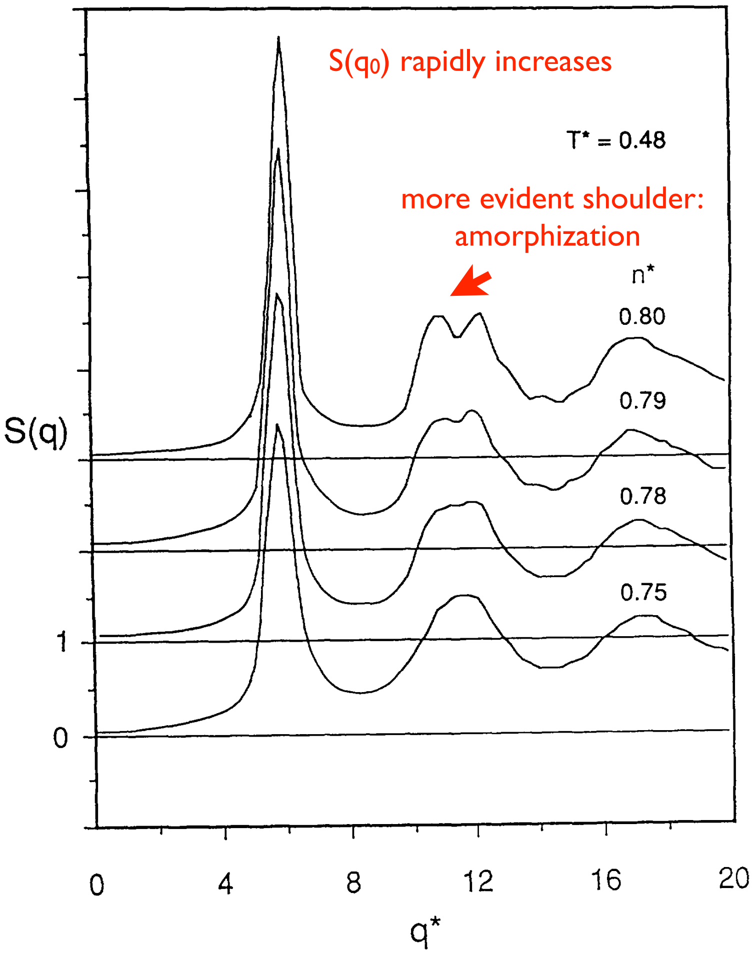


FIG. 2. Pair-distribution function along the isotherm $T^*=0.48$ at various densities. The curves are displaced for clarity.



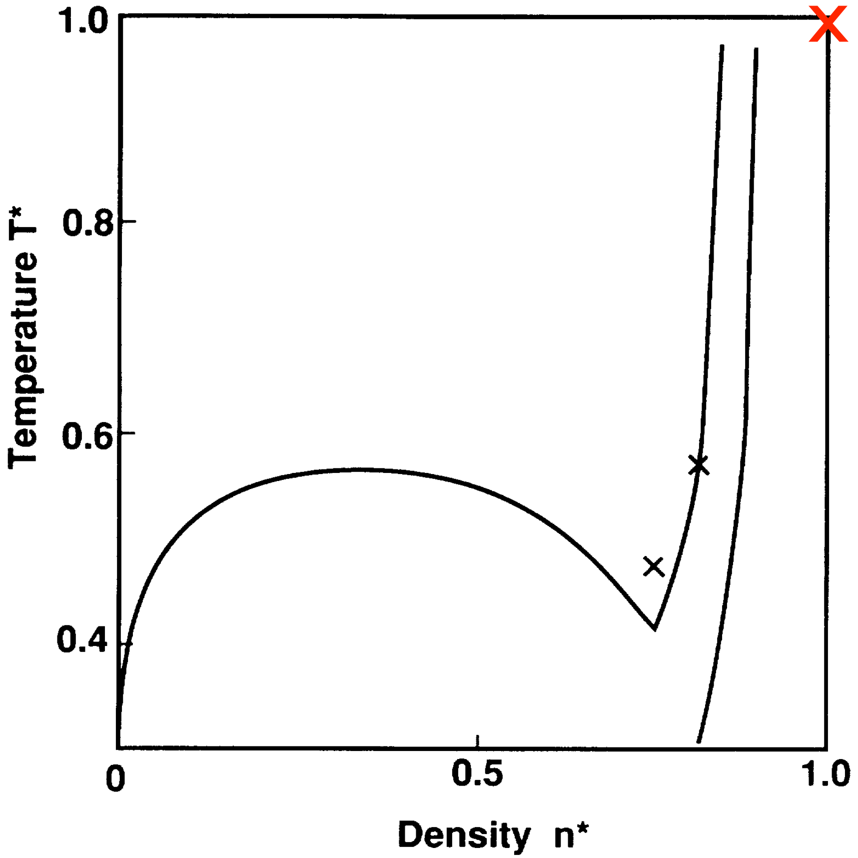
S(q_0) rapidly increases

more evident shoulder: amorphization

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

$$S(q)=1+2\pi n\int_0^\infty rJ_0(qr)[g(r)-1]dr$$

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



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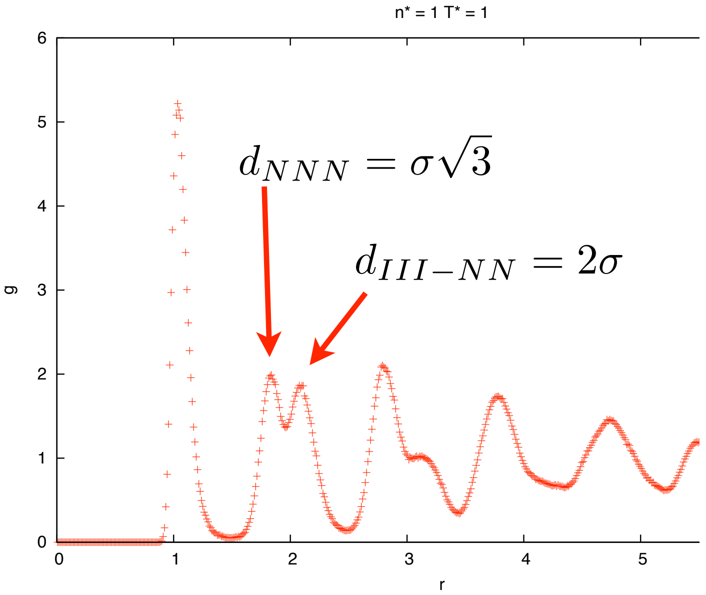

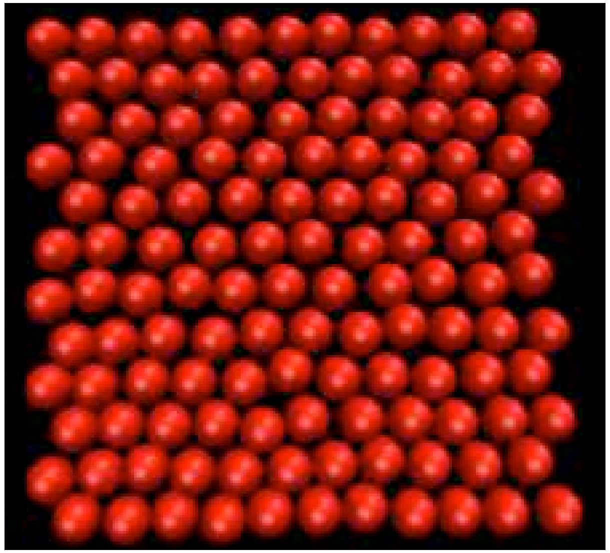

References

- 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)