Classical fluids

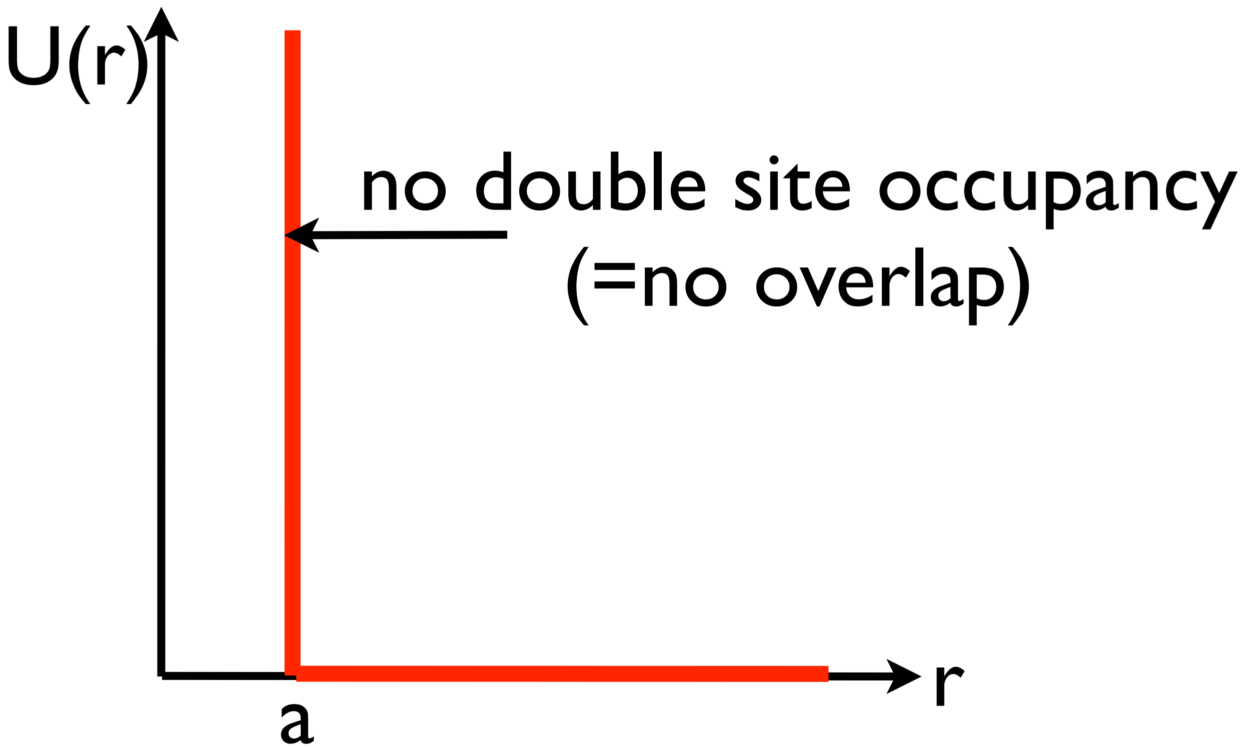
- Interactions
- Measurable and interesting physical quantities
- Metropolis Monte Carlo approach (mainly)
- Molecular dynamics (here: several slides; but today only few basic concepts will be discussed)

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 (or atoms) depends only on the distance

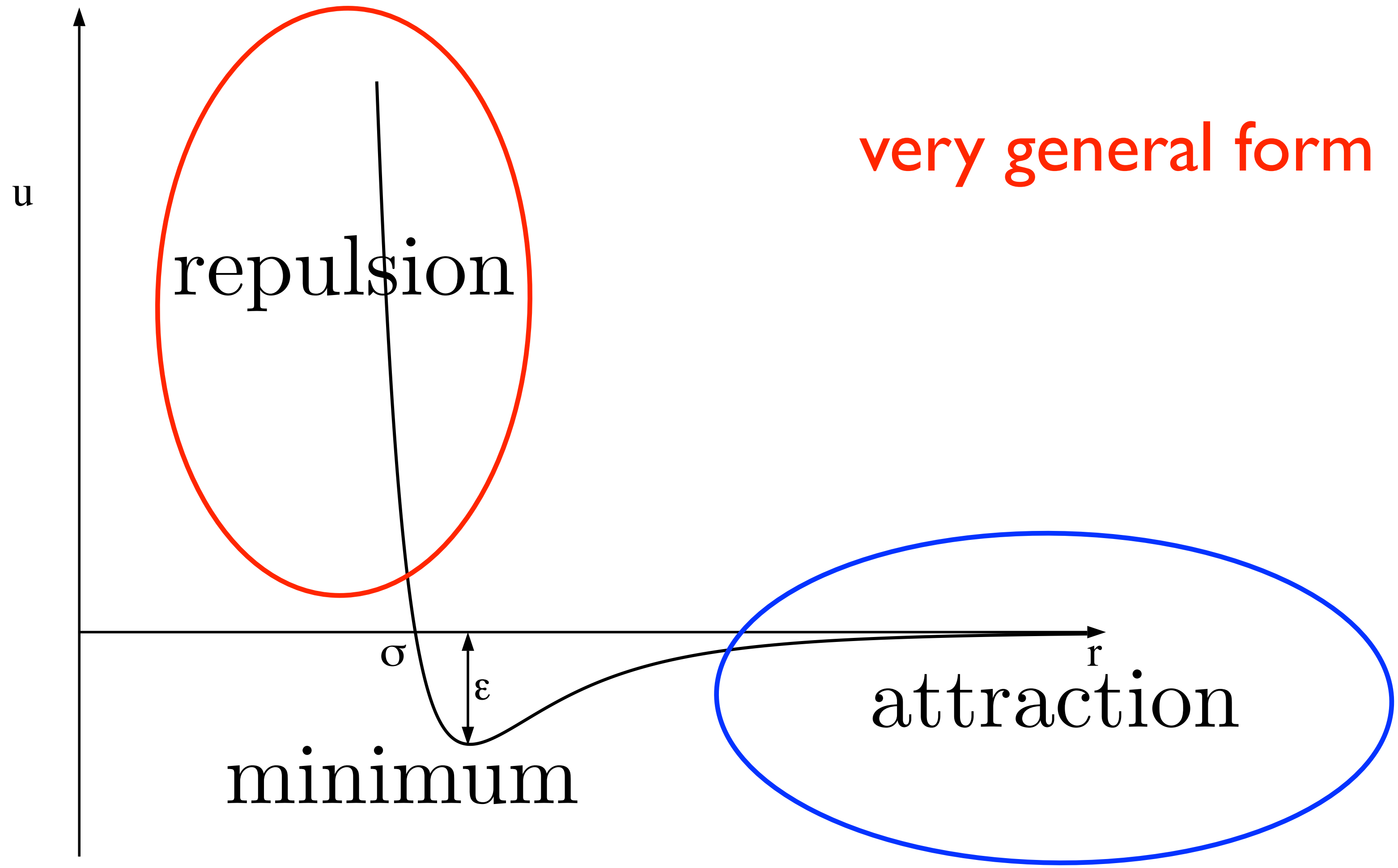
$\left(u(r_{ij})\text{ depends only on the magnitude of the distance } \mathbf{r}_{ij} \text{ between particles } i \text{ and } j\right)$

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)

2-body effective potential



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

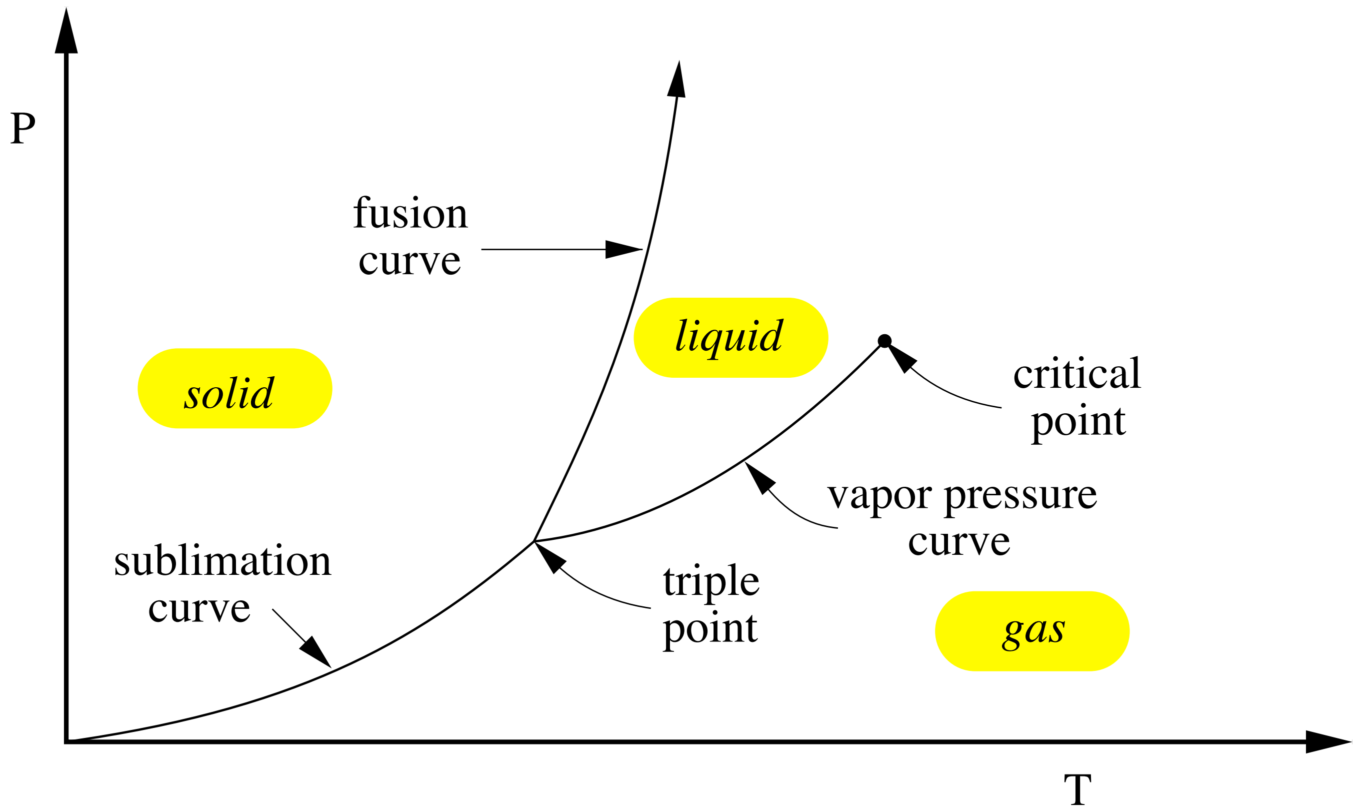
consequence of the Pauli exclusion principle.

`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 the qualitative differences between different phases

Measurable and interesting physical quantities

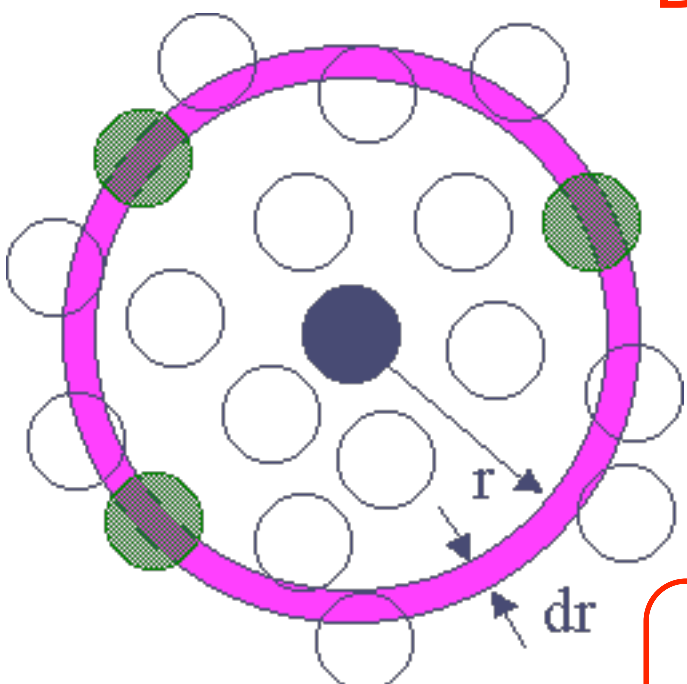
Measurable and interesting quantities

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

Measurable and interesting quantities

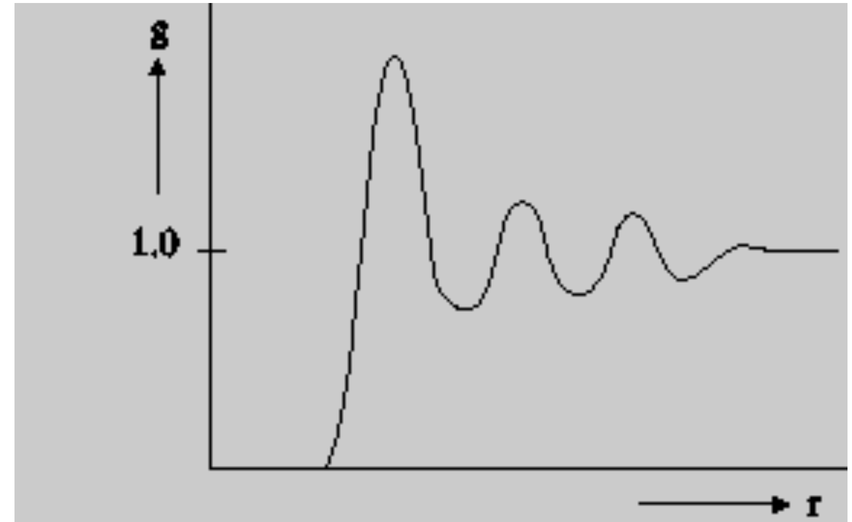
- pair correlation function $g(r)$ $\begin{cases} \text{concepts and qualitative features} \\ \text{mathematical formulation and forms useful for computation} \end{cases}$
- energy E
- pressure p
- ...

Radial distribution function



Definition

$g(r)$



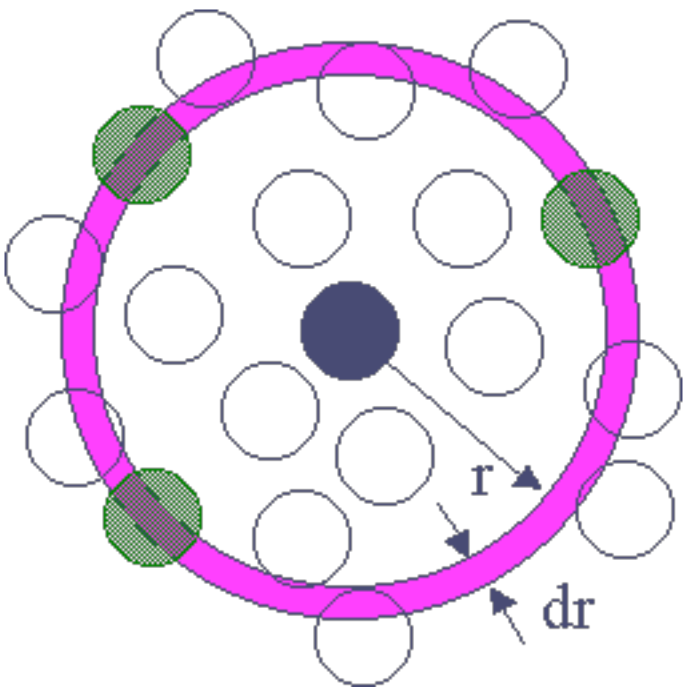
$g(r)d\mathbf{r}$ ($d\mathbf{r}$ = infinitesimal volume of the shell)

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**|)

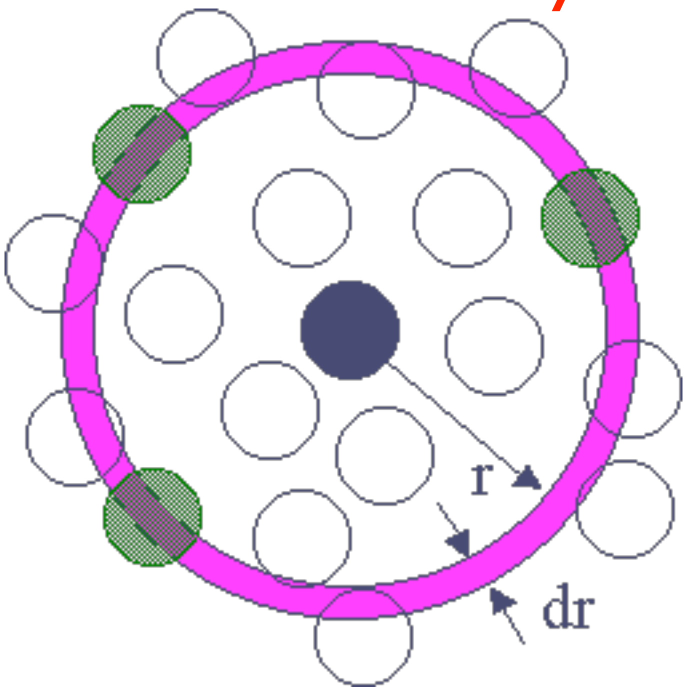
volume element $d\mathbf{r} = 4\pi r^2 dr\,(d=3),\ 2\pi r dr\,(d=2),$ or $2\,dr\,(d=1)$

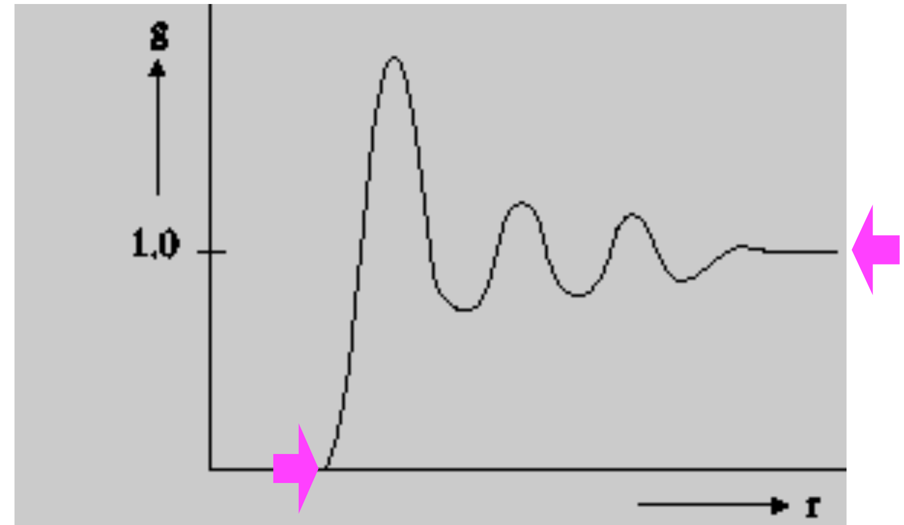
normalization condition $$\rho \int_0^\infty g(r)\, d\mathbf{r} = N - 1 \approx N$$

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

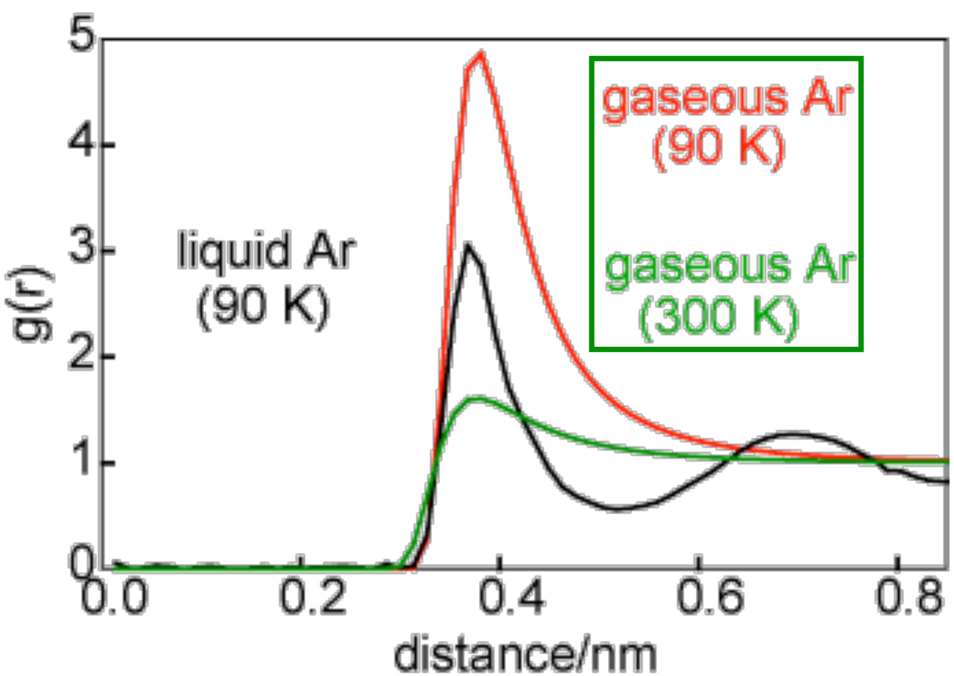
Typical features:

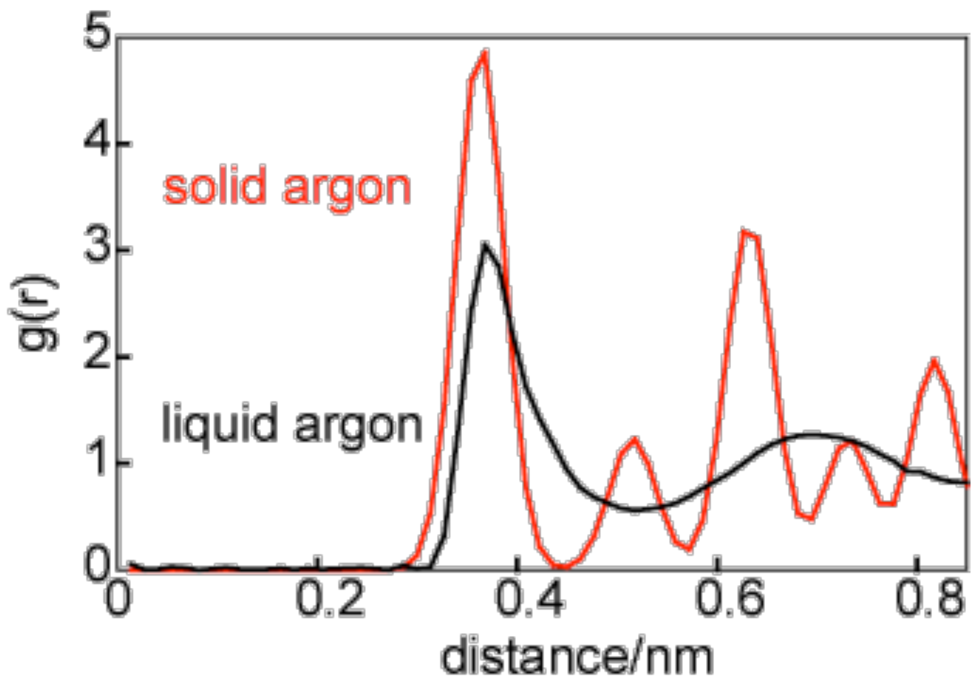
gas: almost structureless

(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





Radial distribution function

formulation in case of spherically symmetric interactions:

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

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 greater that i

a total of $\frac{1}{2}N(N-1)$ separations considered

in 2D: 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:

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

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

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

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)

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

Radial distribution function

Relevance of g(r) for other physical quantities

Not only for structural informations, but also to calculate ensemble averages of quantities depending on pair interactions, e.g., energy:

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

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

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:

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

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:

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

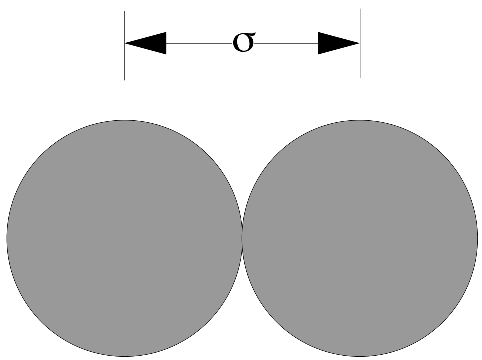
(average also over time)

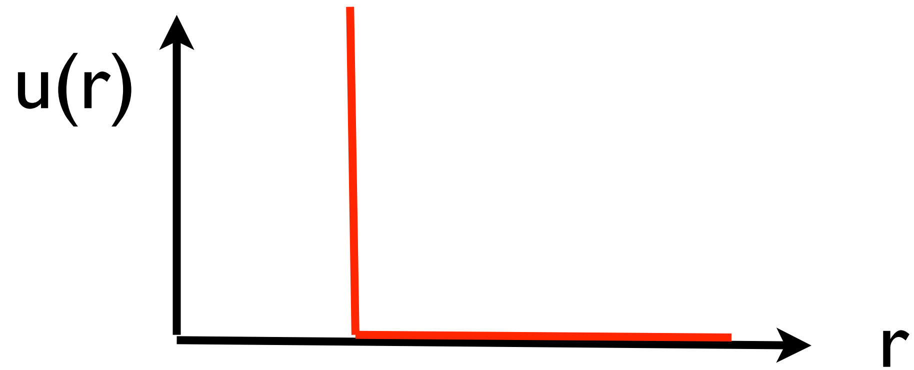
Simple interaction potentials

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

Hard disks

A particular form of interacting potential
(similar to our lattice gas model of past week, but in a continuum)

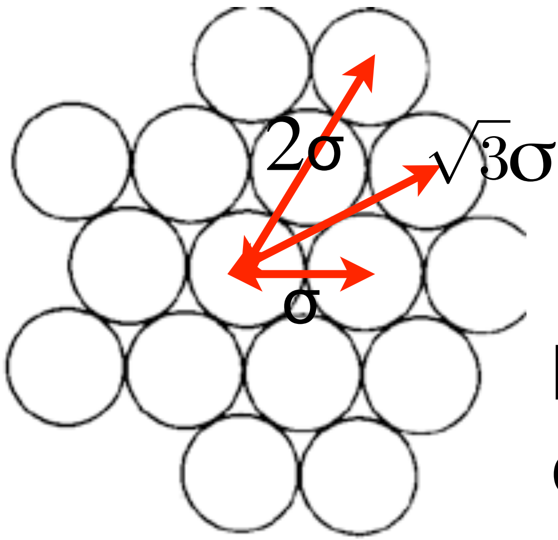




$$u(r) = \begin{cases} +\infty, & r < \sigma \\ 0, & r \geq \sigma \end{cases}$$

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 (triangular lattice); position of the peaks:

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

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

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

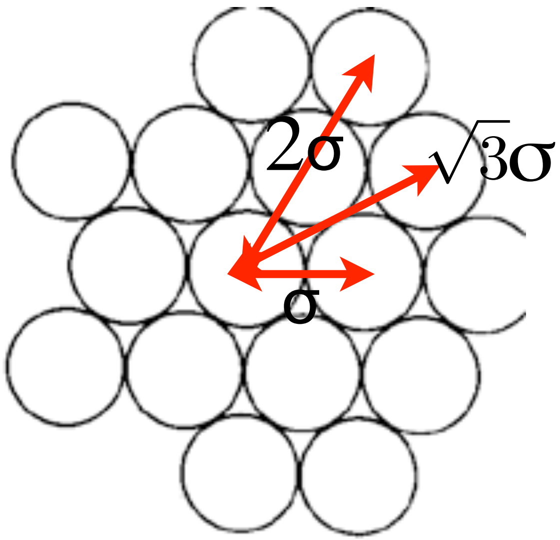
reduced density : $\rho^* = \rho\sigma^2$ (non-dimensional quantity)

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

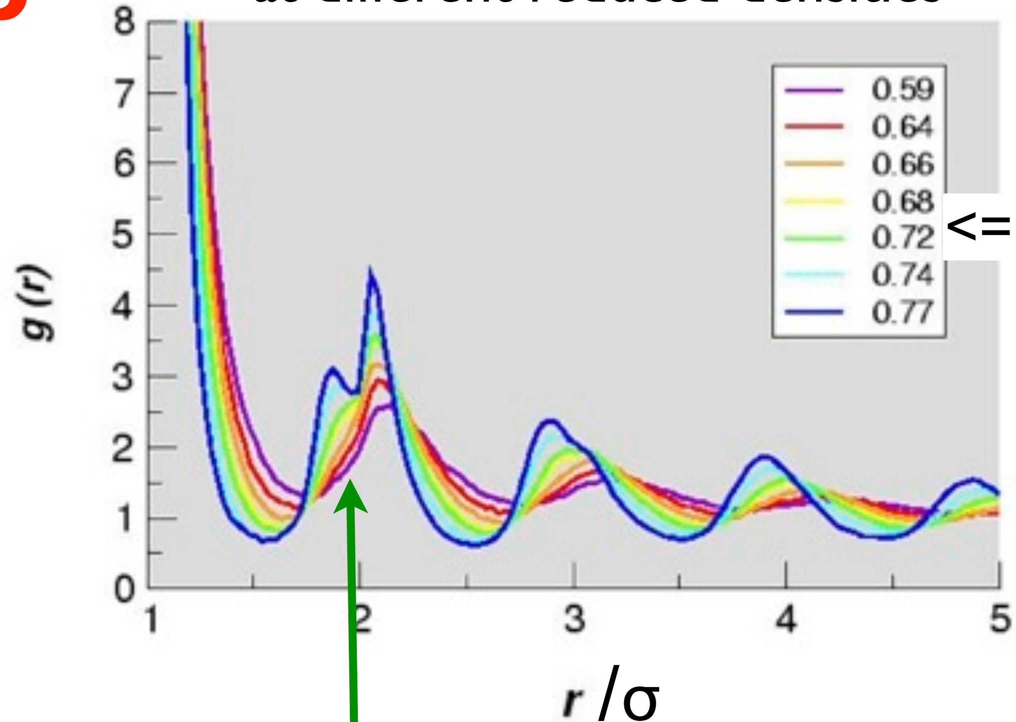
max packing fraction: $f = \frac{area_{occupied}}{area_{available}} = \frac{\pi}{2\sqrt{3}} = 0.907$ $\qquad f = \frac{\pi}{4}\rho^*$

Radial distribution function

of **hard disks in 2D**



Radial Distribution Function
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

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

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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]

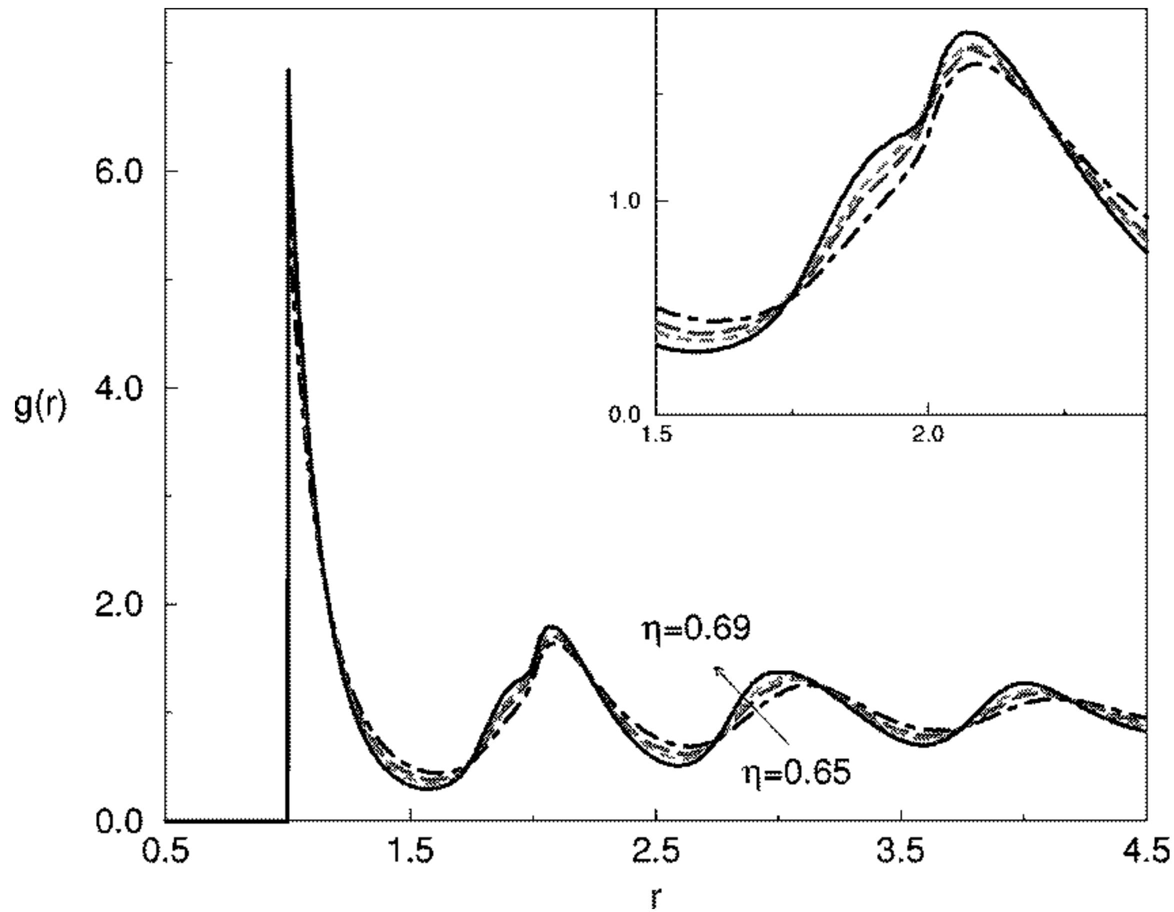


FIG. 1. Radial distribution function $g(r)$ for hard disks plotted versus distance r (in units of diameters). Curves represent the fluid phase with $\eta=0.65$, 0.67, 0.68, and 0.69 (freezing point).

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

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:

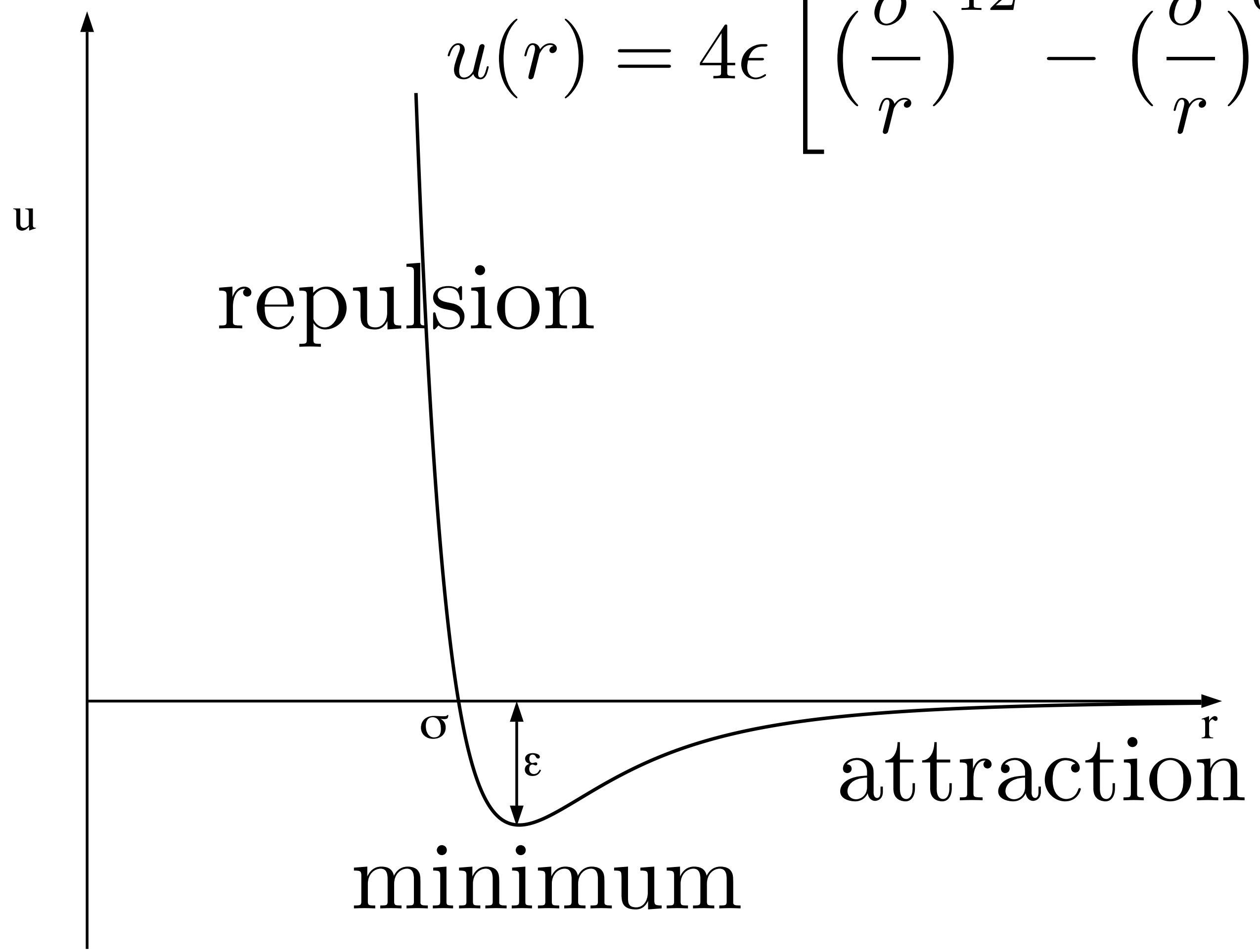
$d\mathbf{r} = 4\pi r^2 dr$ $$\frac{\beta P}{\rho} = 1 + \frac{2}{3}\pi \rho \sigma^3 g(\sigma) \qquad (d=3)$$

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

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

Lennard-Jones potential

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



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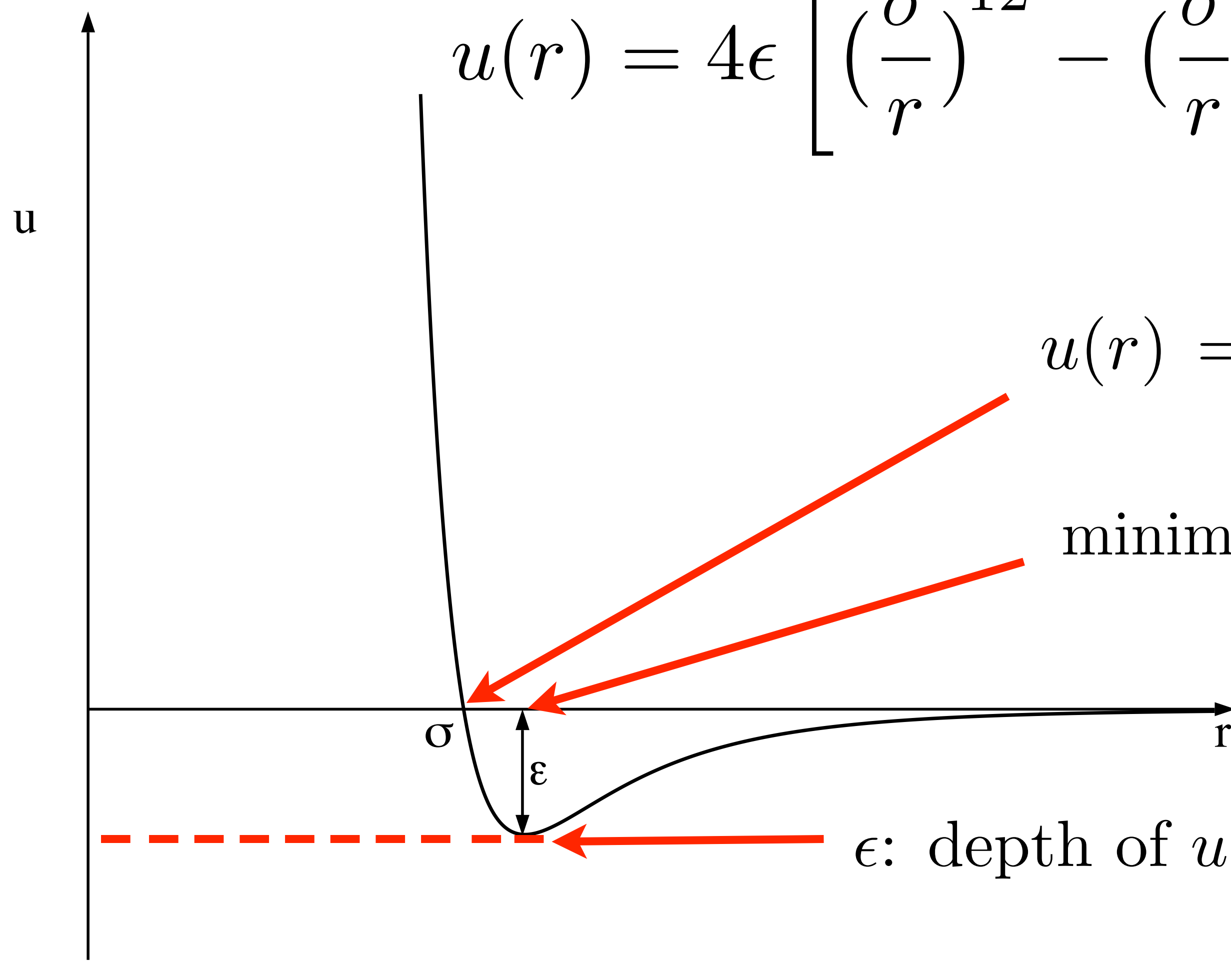


$u(r) = 0$ at $r = \sigma$

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

ϵ: depth of $u(r)$ at the minimum

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

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	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: $\Delta t = 0.01 \Longrightarrow 2.17 \times 10^{-14} s$

Typical runs: 10–10^4 in reduced units $\Longrightarrow 10^{-11}$–10^{-9} 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
```

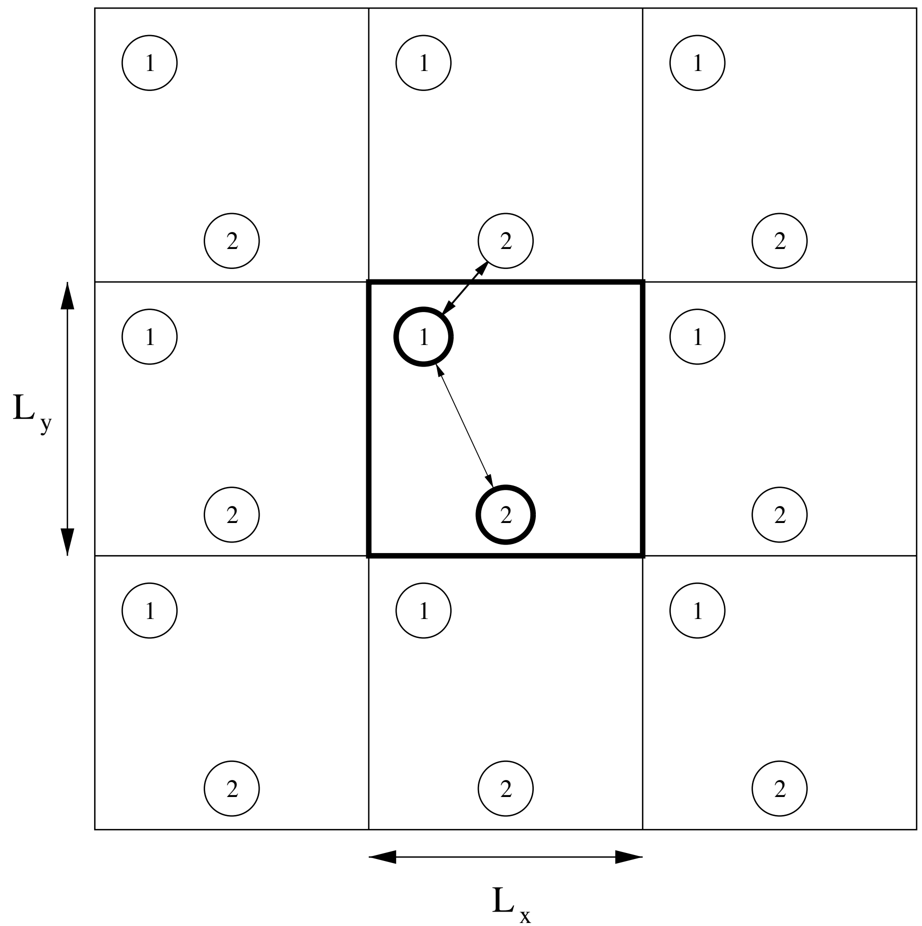
(OK
in the hypothesis that
$-L < pos < 2L$)

Minimum Image convention

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

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)

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

$/home/peressi/comp-phys/XI-fluids/

[do: $cp /home/peressi/.../XI-fluids/* .]

or moodle2

hd-MC.f90

hd-MD.f90

LJ-MD.f90

Classical fluids: Metropolis Monte Carlo method

- 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 $g(r)$

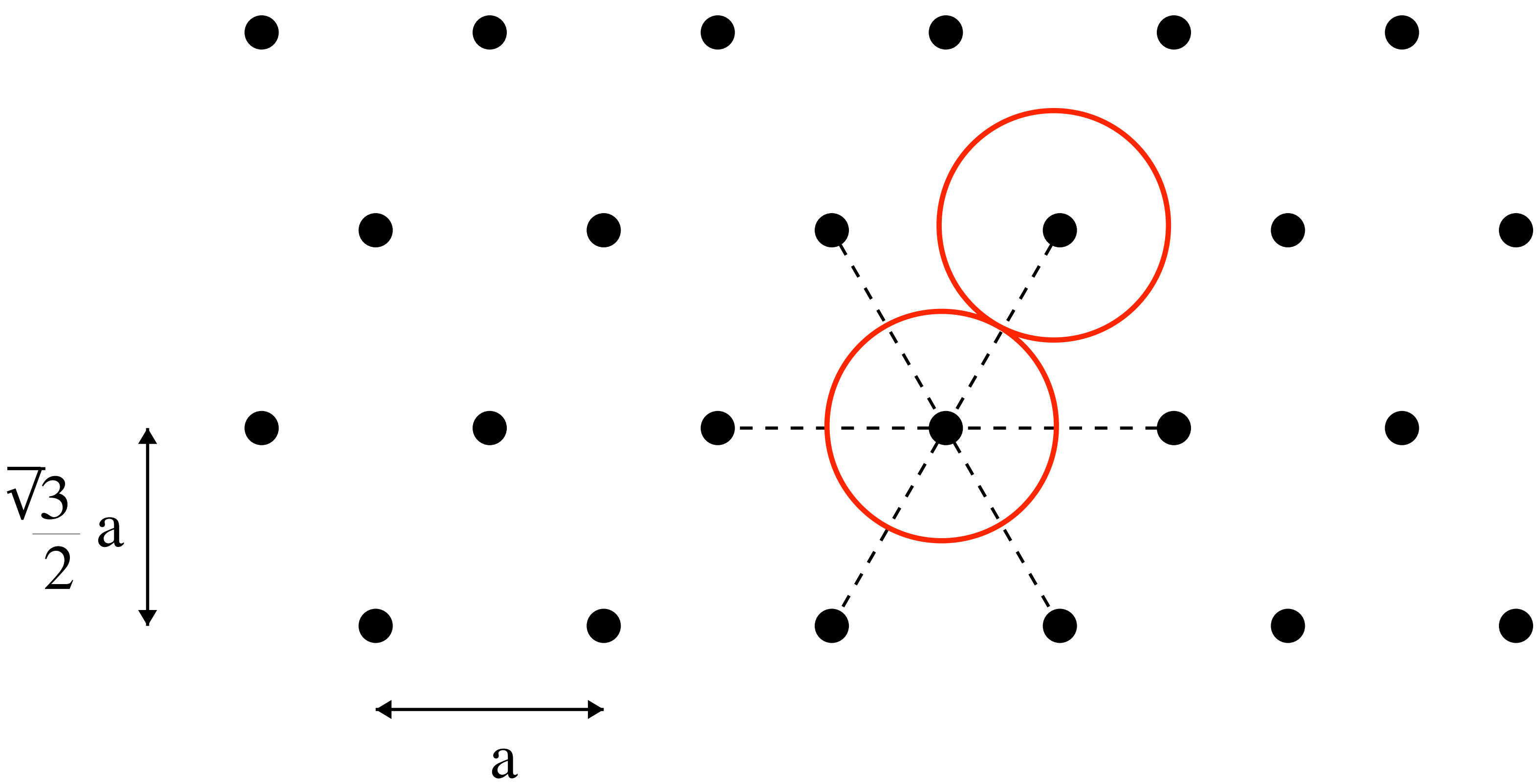
Metropolis Monte Carlo method
- canonical ensemble (NVT) -
for Hard Disks (Spheres)

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



triangular lattice.

take the linear dimensions of the cell to be L_x and $L_y = \sqrt{3}L_x/2$

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 i.e.

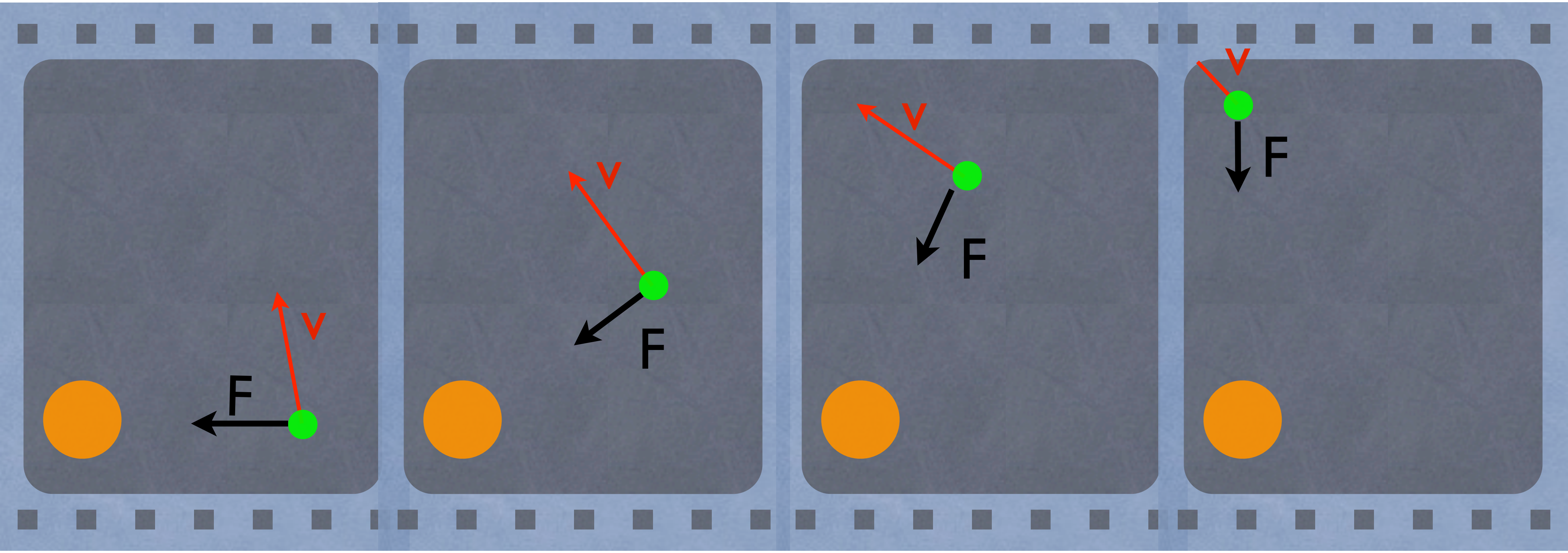
$$\mathbf{d^2x/dt^2=a(x,t,...)=F(x,t,...)/m}$$

Analytical solution for constant forces;
...?... for variable forces ...?...
(analytical integration 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

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

$$v(t+\Delta t) = v(t) + a(t)\Delta t$$

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

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

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

iterate

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

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?

$\downarrow$

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:

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

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 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

two examples
for the interaction potential:

HD and LJ

MD of hard disks - I

Set up the hard spheres/disks on a lattice; then assign random initial velocities to the N particles. Adjust these velocities such that

- the total kinetic energy is consistent with some desired temperature: $E_k = 3NkT/2$
- the total momentum (conserved in the simulation) equals zero.

Note that the adjustment of the temperature is only temporary; it will have to be repeated several times before thermal equilibrium is reached; even then, T will continue to fluctuate.

Now calculate, for each pair of particles (i, j) in the system, the time t_{ij} it would take that pair to meet:

$$t_{ij} = \frac{-b - \sqrt{b^2 - v^2(r^2 - d^2)}}{v^2}$$

where d is the sphere diameter, r is the distance between the centers of i and j, and

$$b = (r_j - r_i) \cdot (v_j - v_i)$$

$$v = |(v_j - v_i)|$$

Note that the above formula for t_{ij} derives from a straightforward solution of the quadratic equation $r_{ij}^2(t) - d^2 = 0$. As discussed in the appendix, this solution may give rise to numerical errors. A more secure alternative is, with the same meaning for b and v,

$$q = -\left[b + sgn(b)\sqrt{b^2 - v^2(r^2 - d^2)}\right], \quad t_{ij} = min\{q/v^2, (r^2 - d^2)/q\}$$

(Since b must be negative for a pair to meet in the future, we may restrict the calculation to the case $sgn(b) < 0$.)

MD of hard disks - II

Set up two arrays that contain, for each particle i, the smallest positive collision time $t(i) = min(t_{ij})$ and the next collision partner $j(i)$. If a particle has no collision partner at positive times we simply set $j(i) = 0$ and $t(i) = [\infty]$, i.e. the largest representable number.

This double loop over all $N(N-1)/2$ pairs need be performed only once, at the start of the simulation.

Now find the smallest element in the table of free flight times, calling it $t(i_0)$. This is the time until the very next encounter between two particles in the system. The indices of those two particles are named i_0 and j_0.

During the time $t(i_0)$ all particles perform a free flight, thus:

$$r_i \longrightarrow r_i + v_i \cdot t(i_0)$$

Now an elastic collision between $i = i_0$ and $j = j_0$ occurs, resulting in the new velocities

$$v_i' = v_i + \Delta v, \quad v_j' = v_j - \Delta v$$

where

$$\Delta v = b\frac{r_{ij}}{d^2}$$

Since i_0 and j_0 have new flight directions and speeds, all pairwise collision times t_{ij} involving these two must be recalculated. This means that $2N-3$ pairs have to be scanned.

This completes the basic hard sphere/disc MD step. Now all t_i are once more searched for the smallest element, etc.

MD of hard disks - summary

Hard Spheres MD:

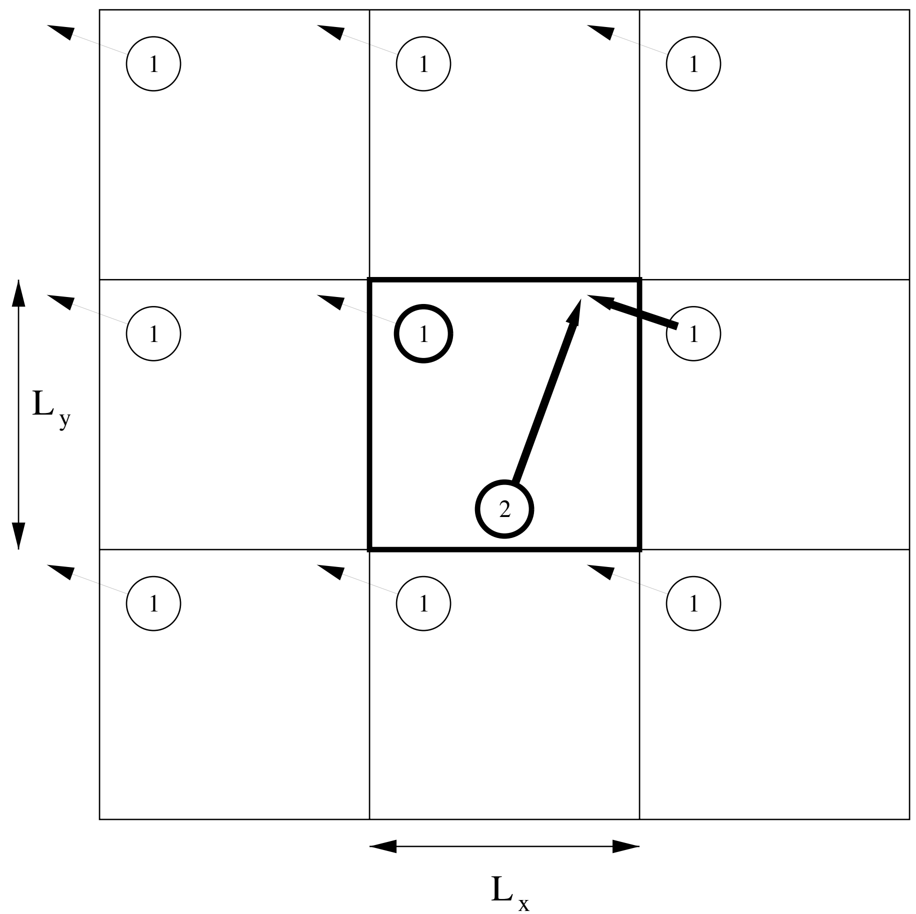
Immediately after a collision, for each particle i in the system the time $t(i)$ to its next collision and the partner $j(i)$ at that collision are assumed to be known.

- Determine the smallest positive element $t(i_0)$ among the $t(i)$, identify the corresponding particle i_0 and its collision partner $j_0 \equiv j(i_0)$.
- Let all particles follow their free flight paths for a period $\Delta t \equiv t(i_0)$; subtract Δt from each $t(i)$.
- Perform the elastic collision between i_0 and j_0; after the collision these spheres have the new velocities $v' = v \pm \Delta v$, with $\Delta v = b\frac{r_{ij}}{d^2}$
- Recalculate all times $t(i)$ that involve either i_0 or j_0, i.e. for $i = i_0$, $i = j(i_0)$, $i = j_0$, and $i = j(j_0)$.
- Go to (1).

At low densities the large free path may create problems with the periodic boundary conditions, some particle suddenly appearing where it overlaps another. One therefore limits the time allowed for free flight such that for each particle and each coordinate α the free flight displacement fulfills
$\Delta x_\alpha \equiv v_\alpha \Delta t \leq L/2 - d$.

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.

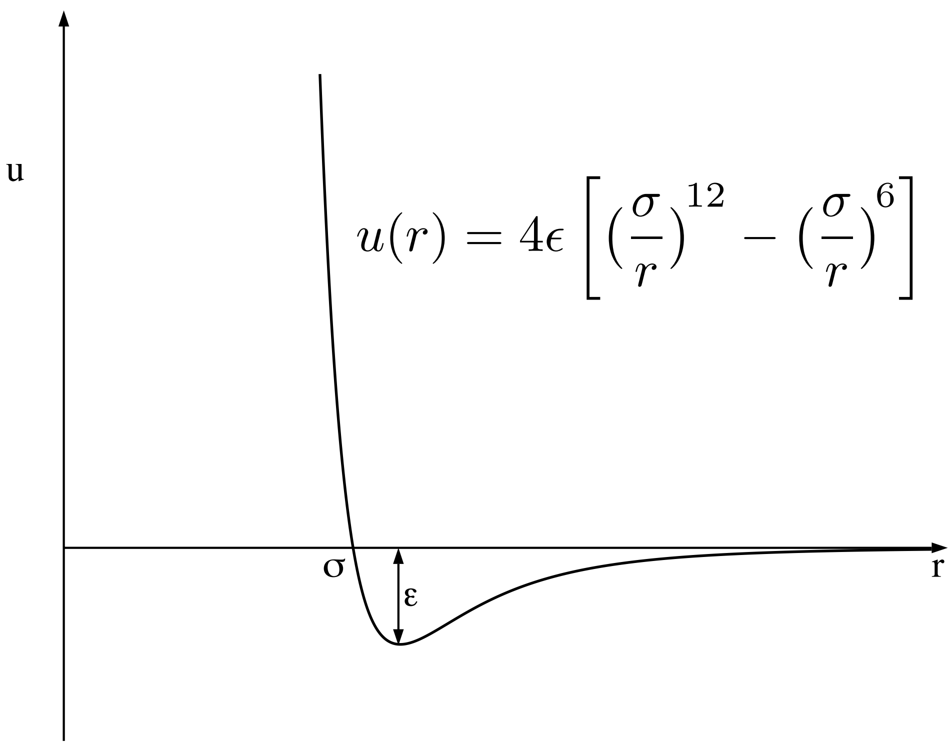
A few basic references

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)

(R) Rahman, A. Phys. Rev. A136, 405 (1964)

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



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

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

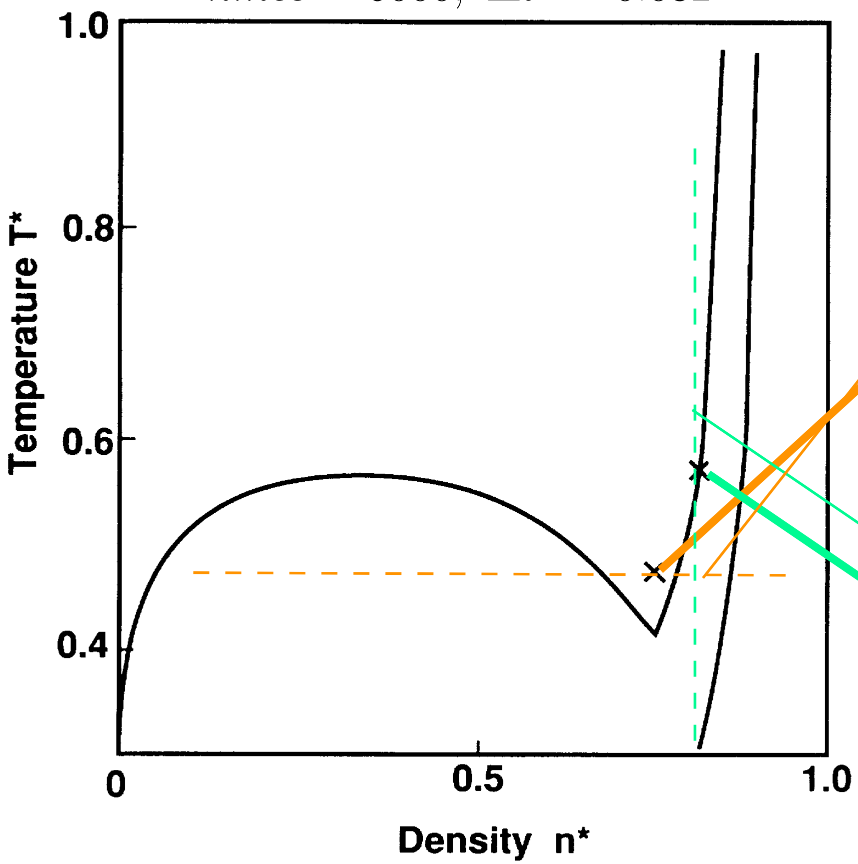


FIG. 1. Phase diagram for the two-dimensional Lennard-Jones system. The crosses indicate the (n^*, T^*) states (0.75, 0.48) and (0.81, 0.58).

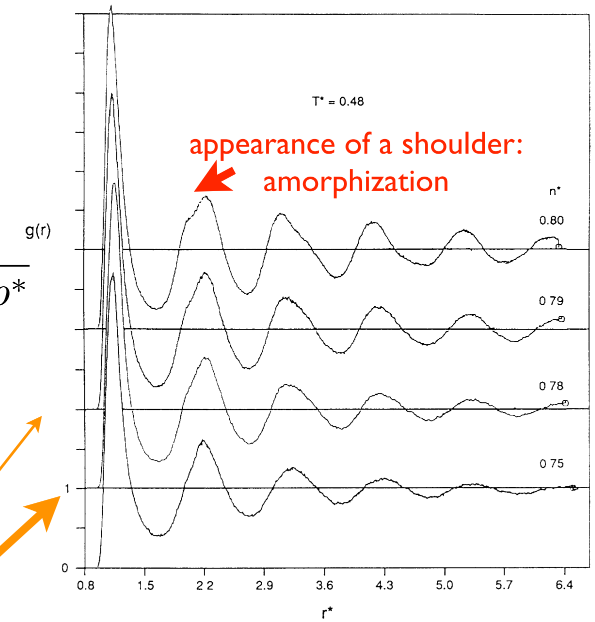


FIG. 2. Pair-distribution function along the isotherm $T^*=0.48$ at various densities. The curves are displaced for clarity.

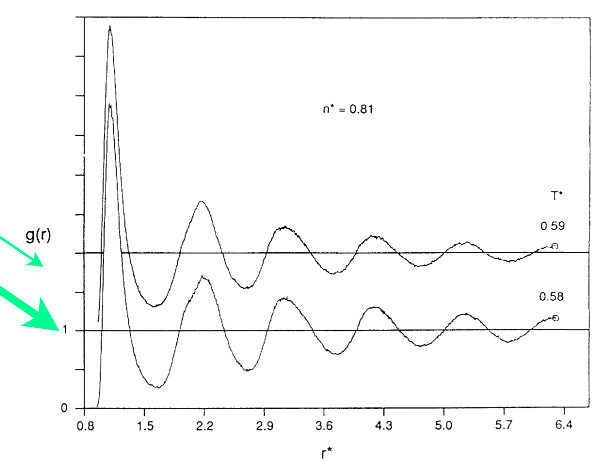


FIG. 3. Pair-distribution function along the isochore $n^*=0.81$ at two temperatures.

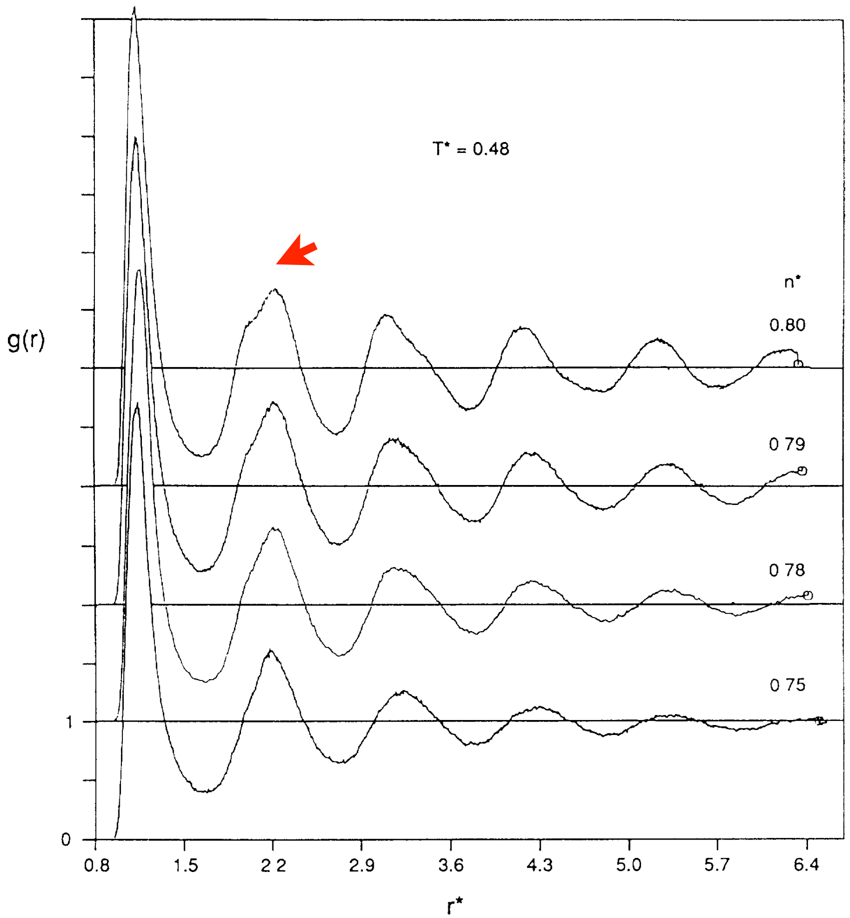


FIG. 2. Pair-distribution function along the isotherm $T^*=0.48$ at various densities. The curves are displaced for clarity.

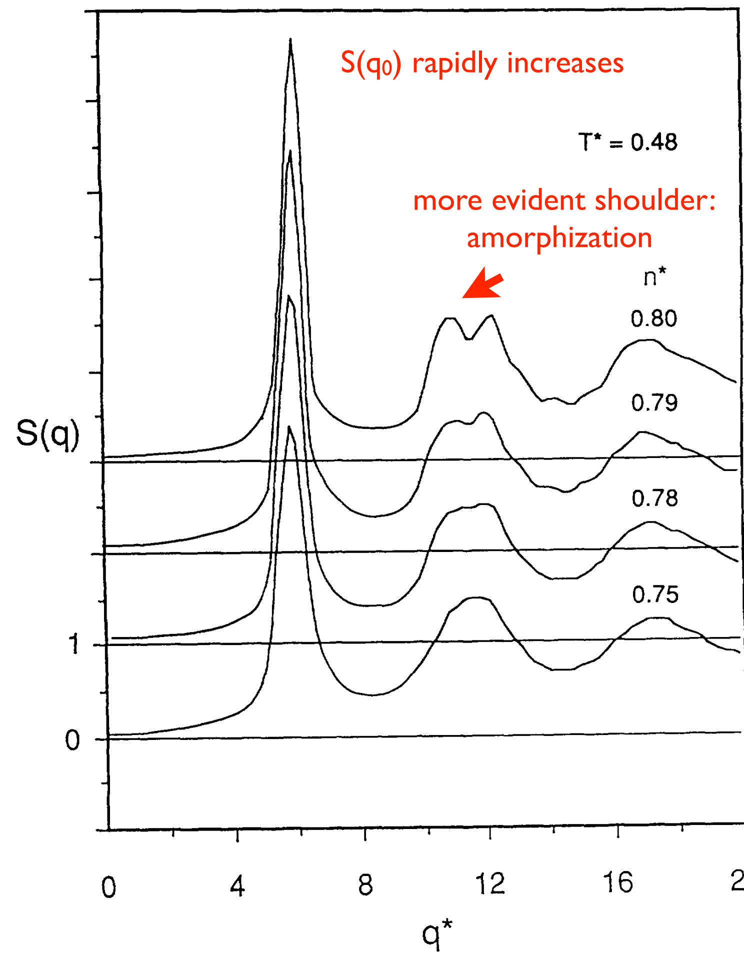


FIG. 4. Structure factor along the isotherm $T^*=0.48$ at various densities. The curves are displaced for clarity.

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

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

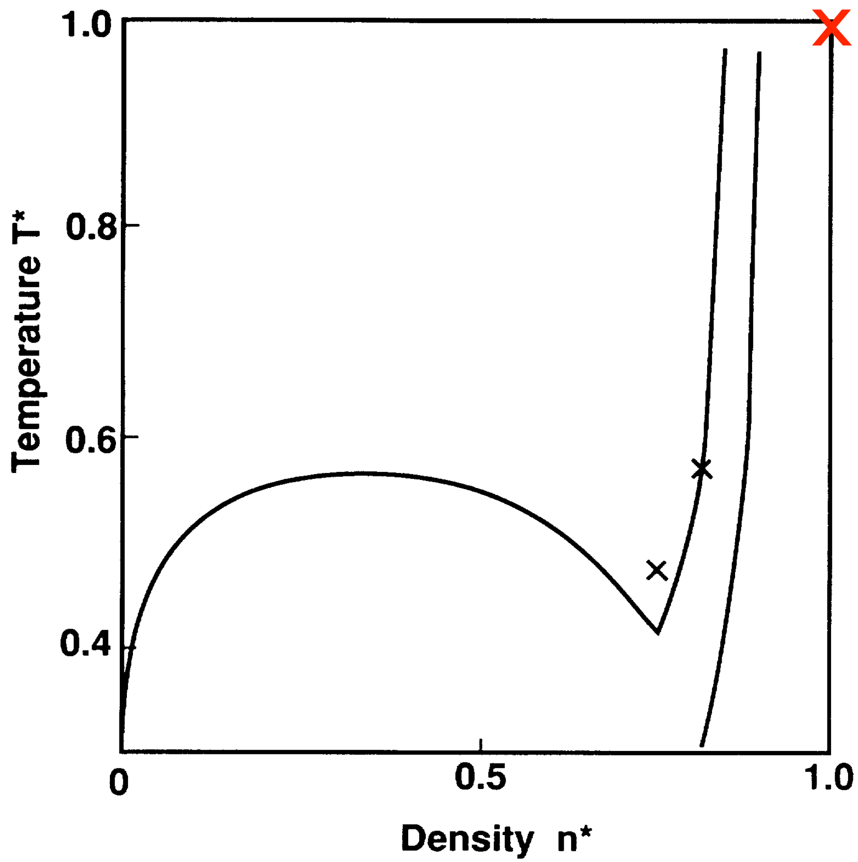
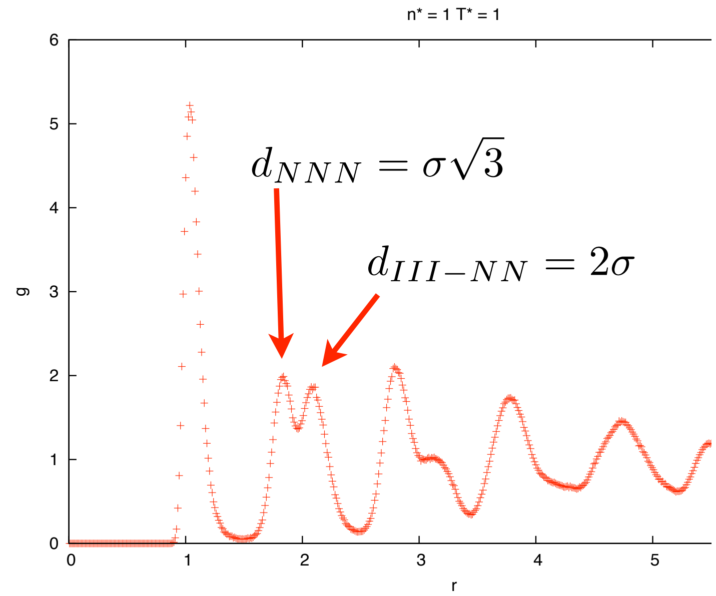
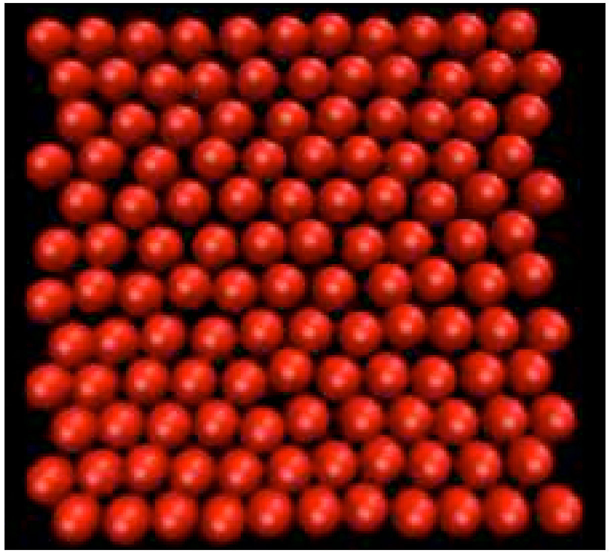


FIG. 1. Phase diagram for the two-dimensional Lennard-Jones system. The crosses indicate the (n^*, T^*) states (0.75, 0.48) and (0.81, 0.58).





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

More details:
in the course by E. Smargiassi,

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