993SM - Laboratory of Computational Physics Week XII - Friday Dec. 13, 2024

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Classical fluids

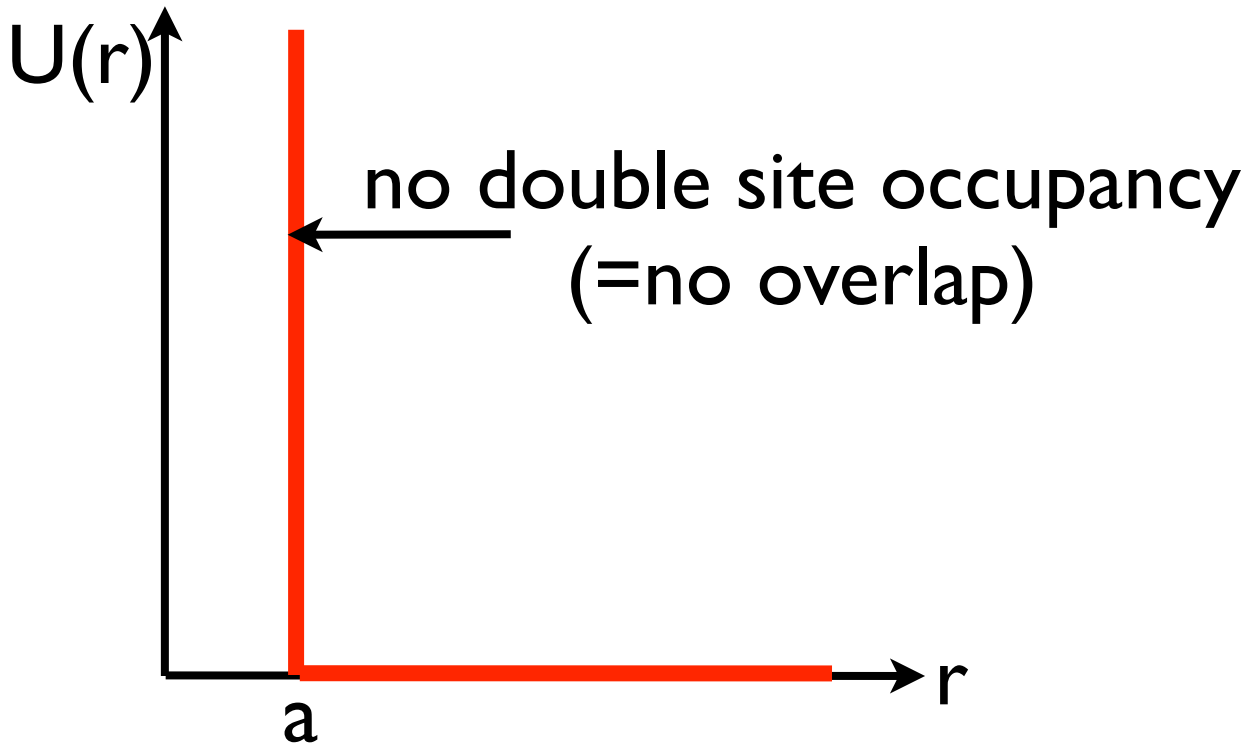
- Interactions
- Measurable and interesting physical quantities
- Metropolis Monte Carlo approach (mainly)
- Molecular dynamics

(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

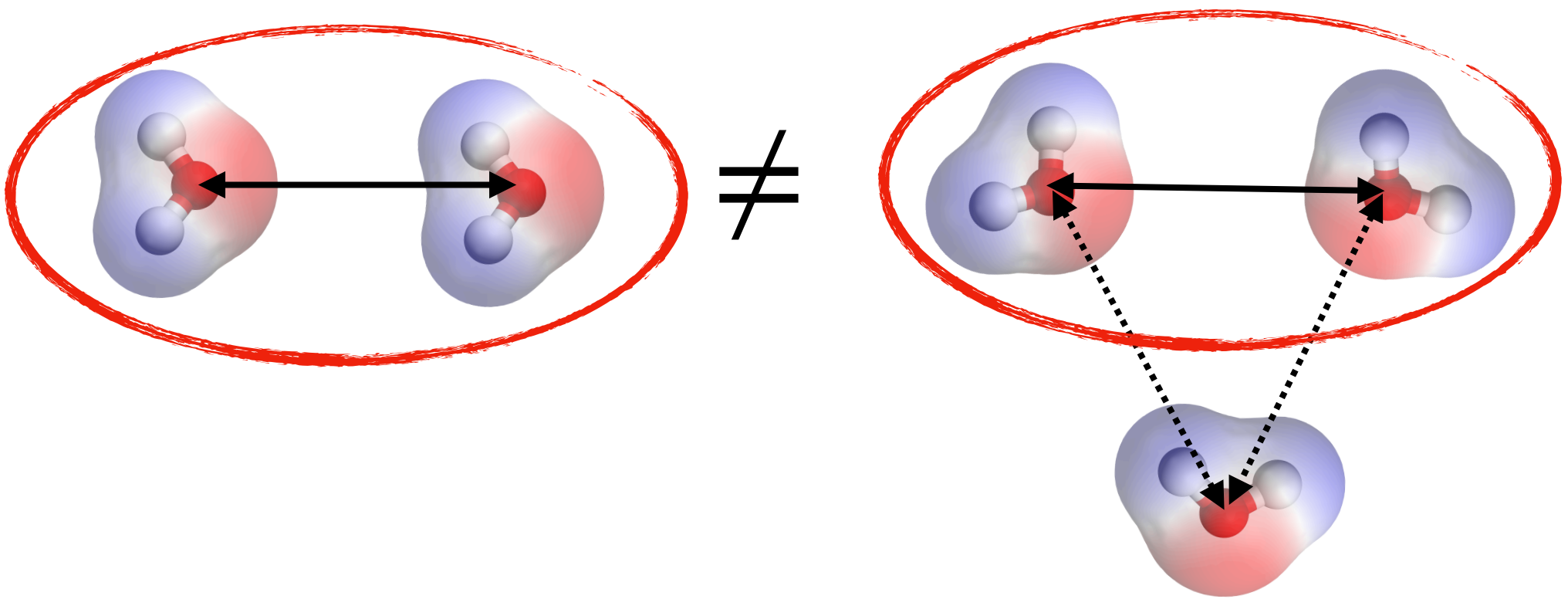
assume that the force between any pair of molecules (or atoms) depends only on the distance

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

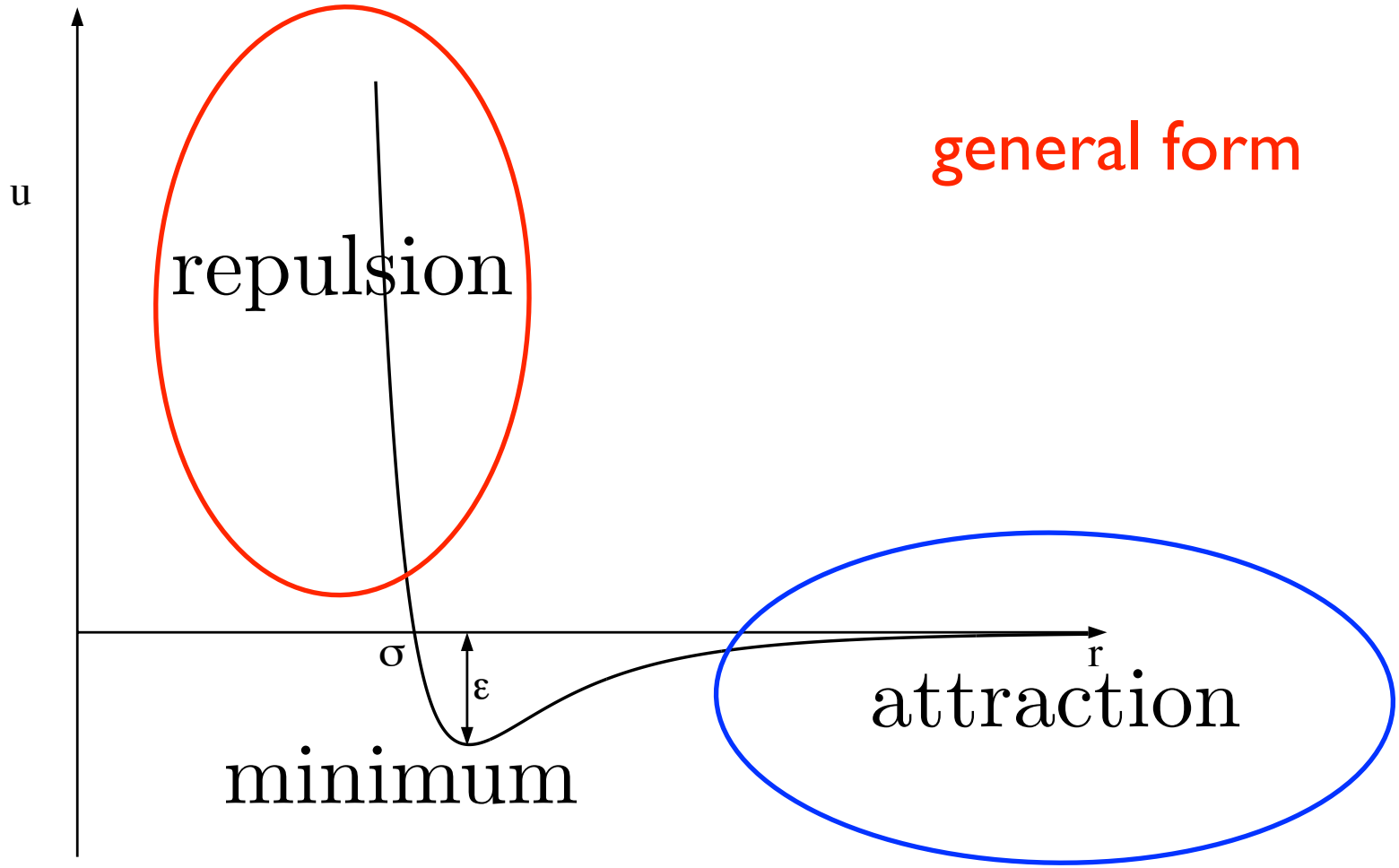
the total potential energy U is a sum of two-particle interactions:

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

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



A typical 2-body effective potential



general form

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

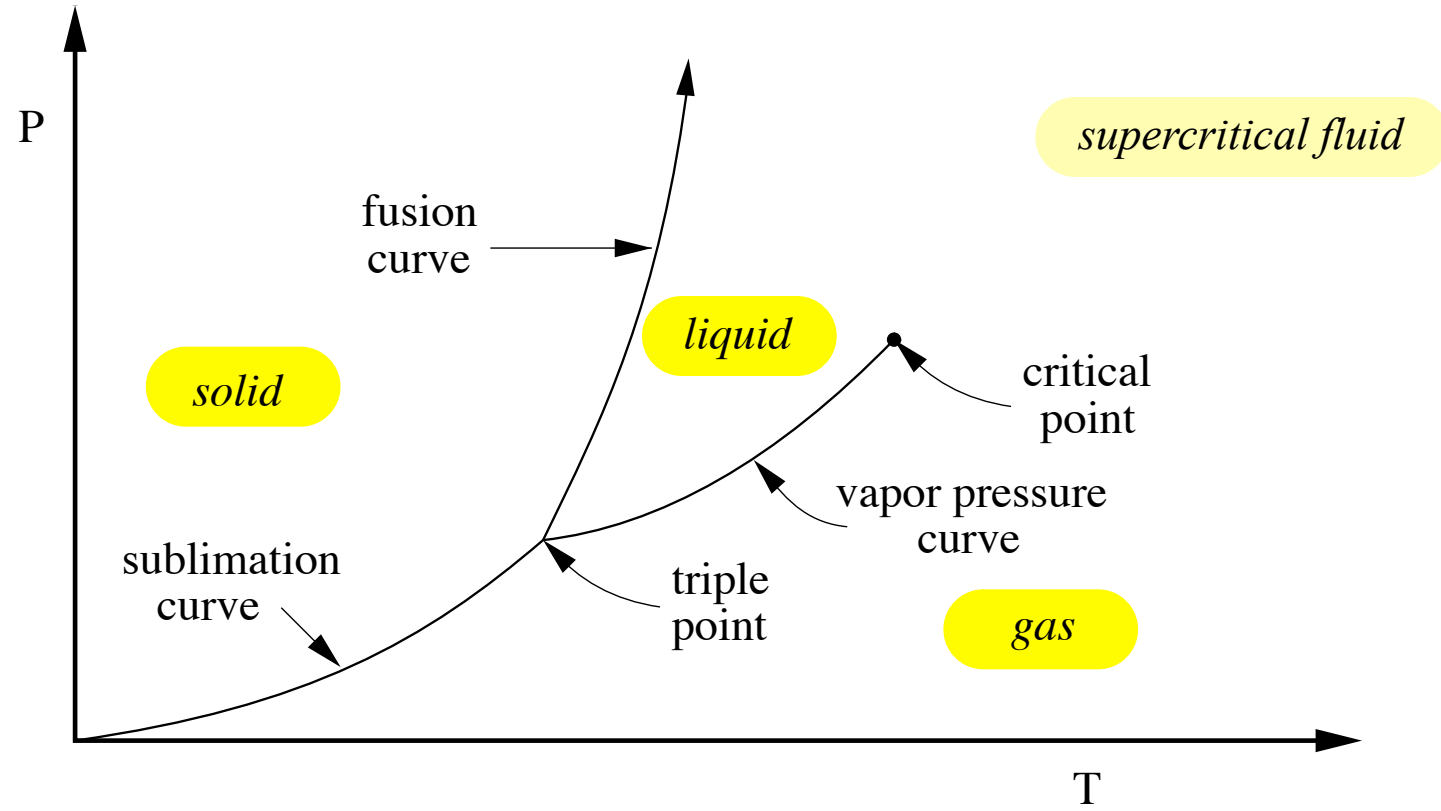
consequence of the Pauli exclusion principle

`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

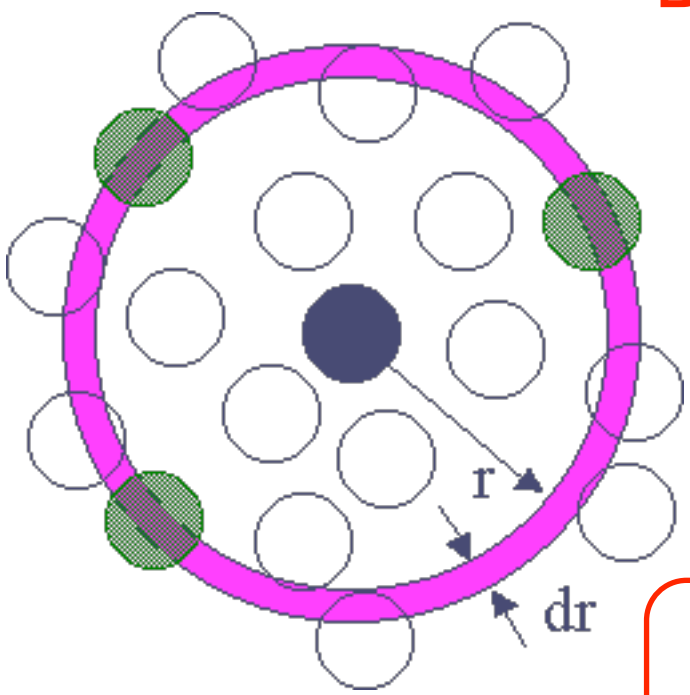
Measurable and interesting quantities

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

Measurable and interesting quantities

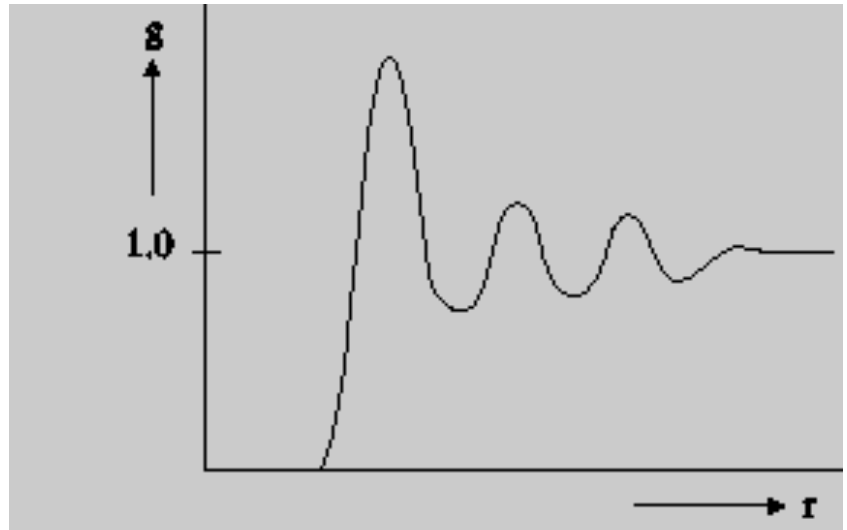
- pair correlation function $\mathbf{g(r)}$ { concepts and qualitative features; mathematical formulation and expressions useful for computation }
- energy $\mathbf{E}$
- pressure $\mathbf{p}$
- ...

Radial distribution function



Definition

$g(r)$



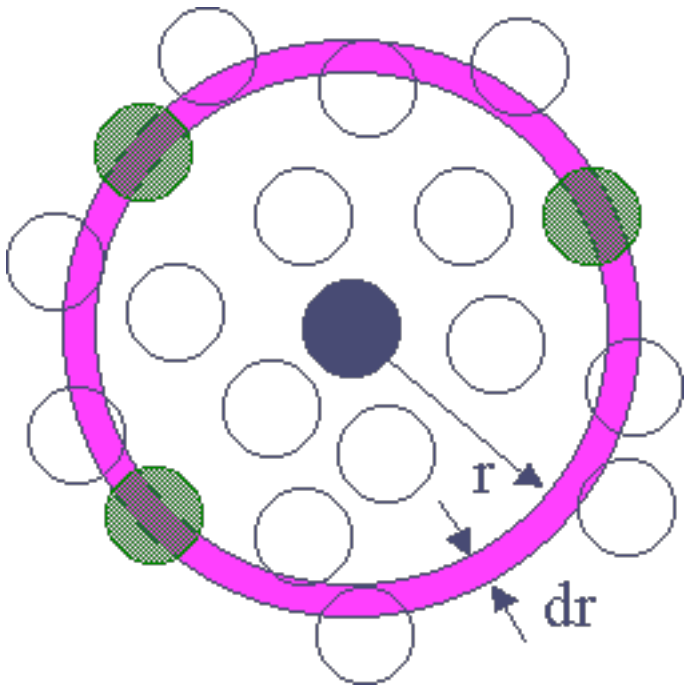
$g(r)d\mathbf{r}$ ($d\mathbf{r}$ = infinitesimal volume of the shell)

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**|)

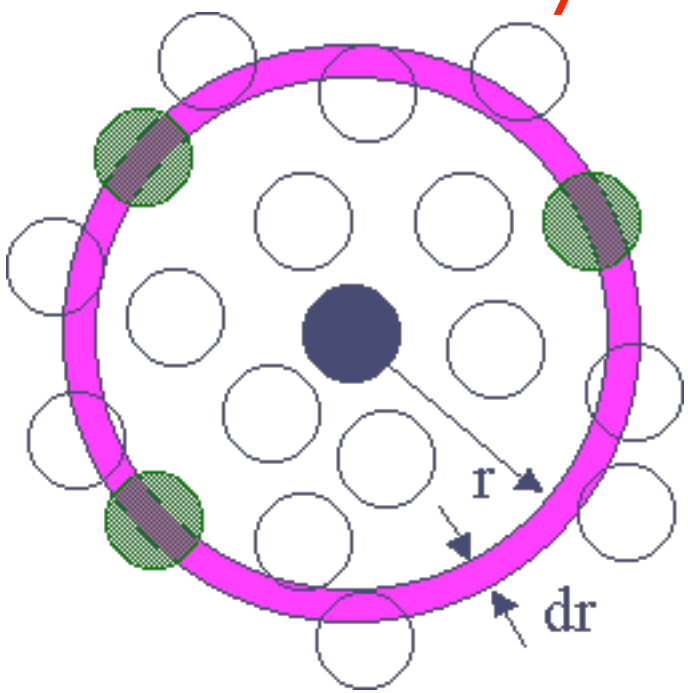
volume element $d\mathbf{r} = 4\pi r^2 dr\,(d=3),\ 2\pi r dr\,(d=2),$ or $2\,dr\,(d=1)$

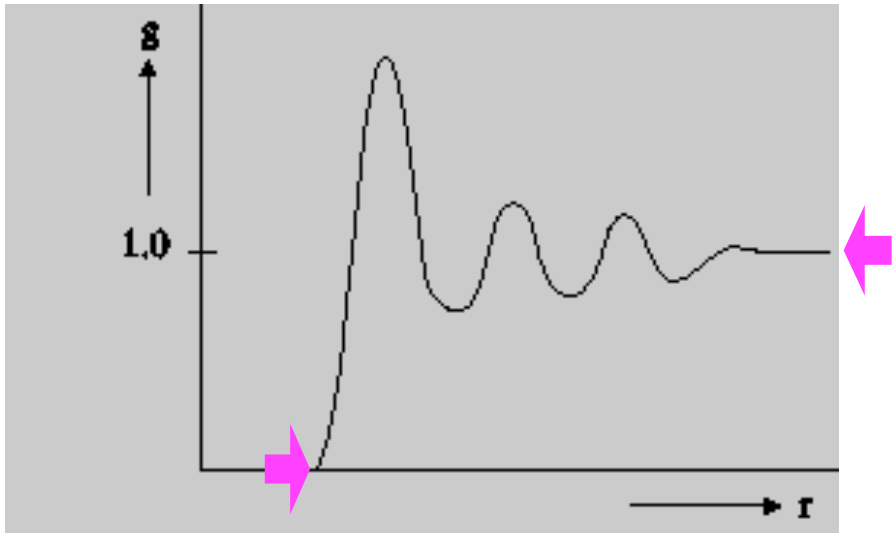
normalization condition $$\rho \int_0^\infty g(r)\, d\mathbf{r} = N - 1 \approx N$$

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

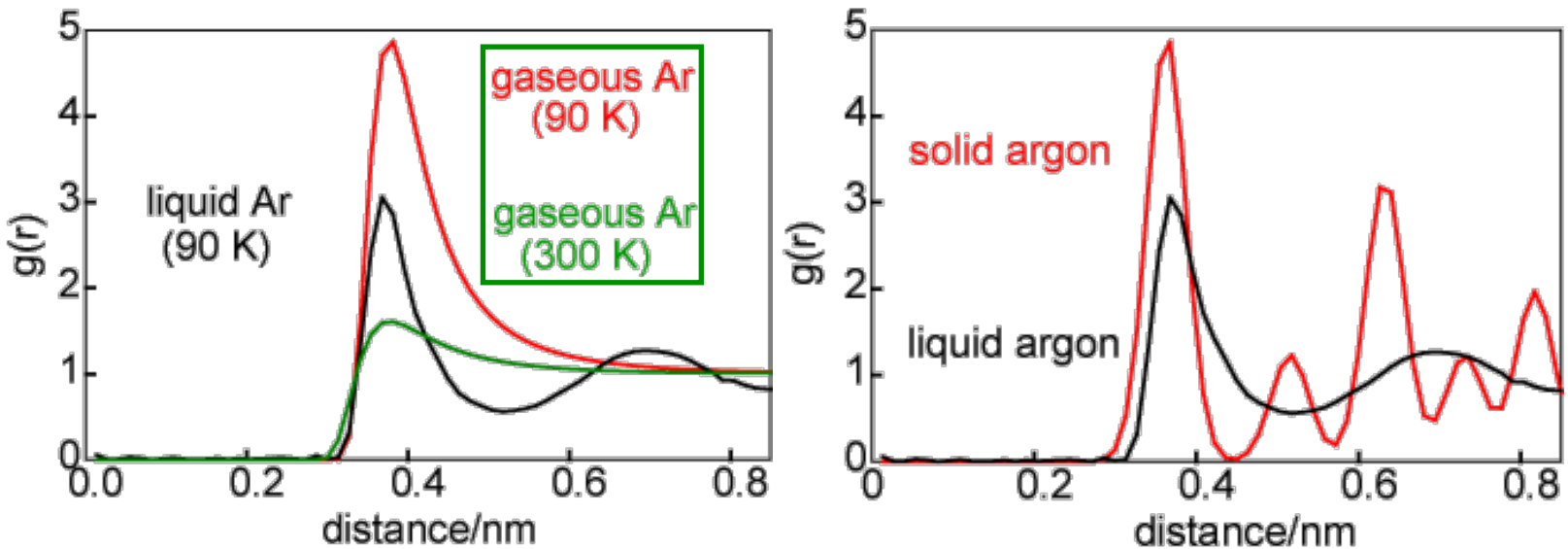
Typical features:

gas: almost structureless

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

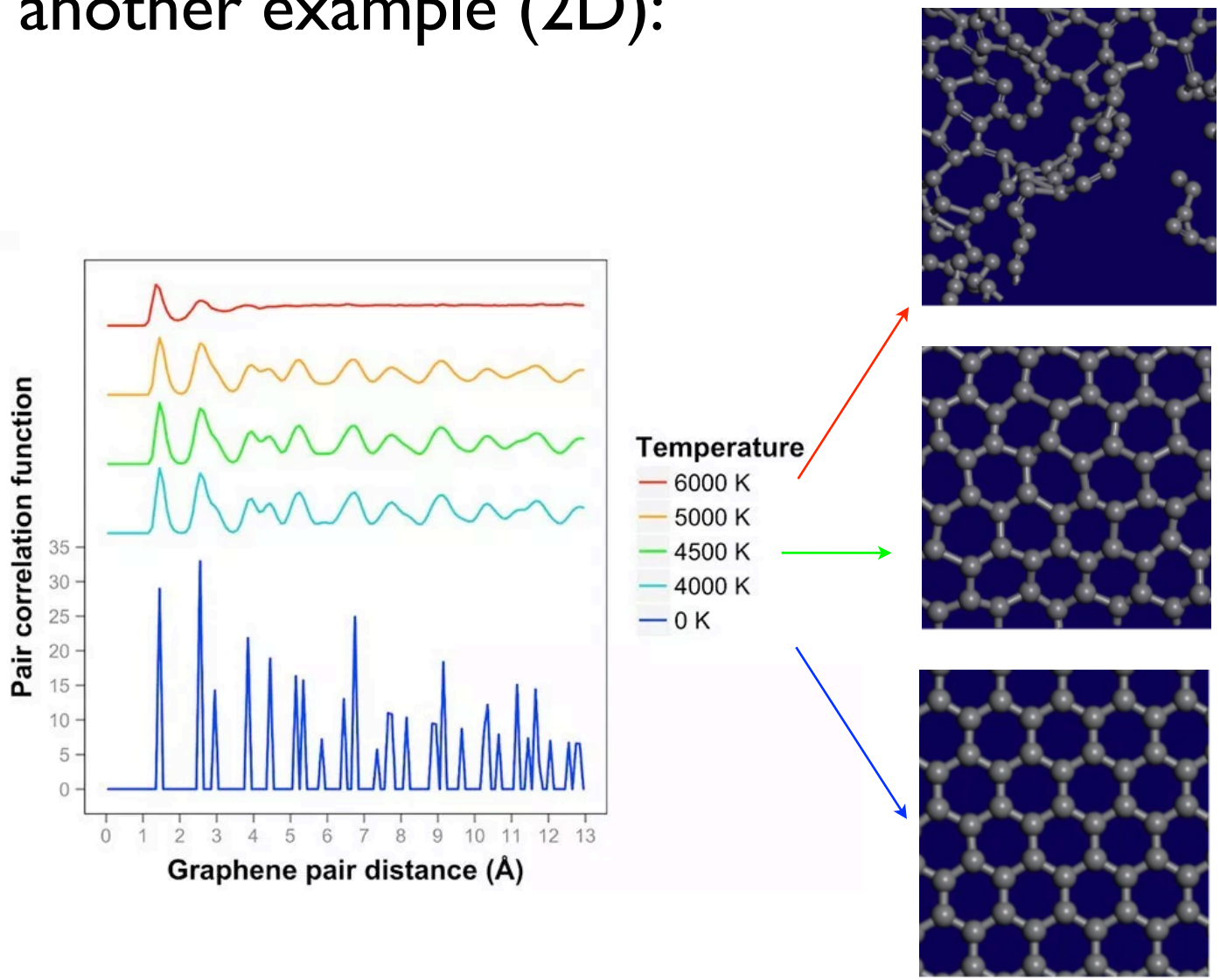
liquid: some structure with broad peaks

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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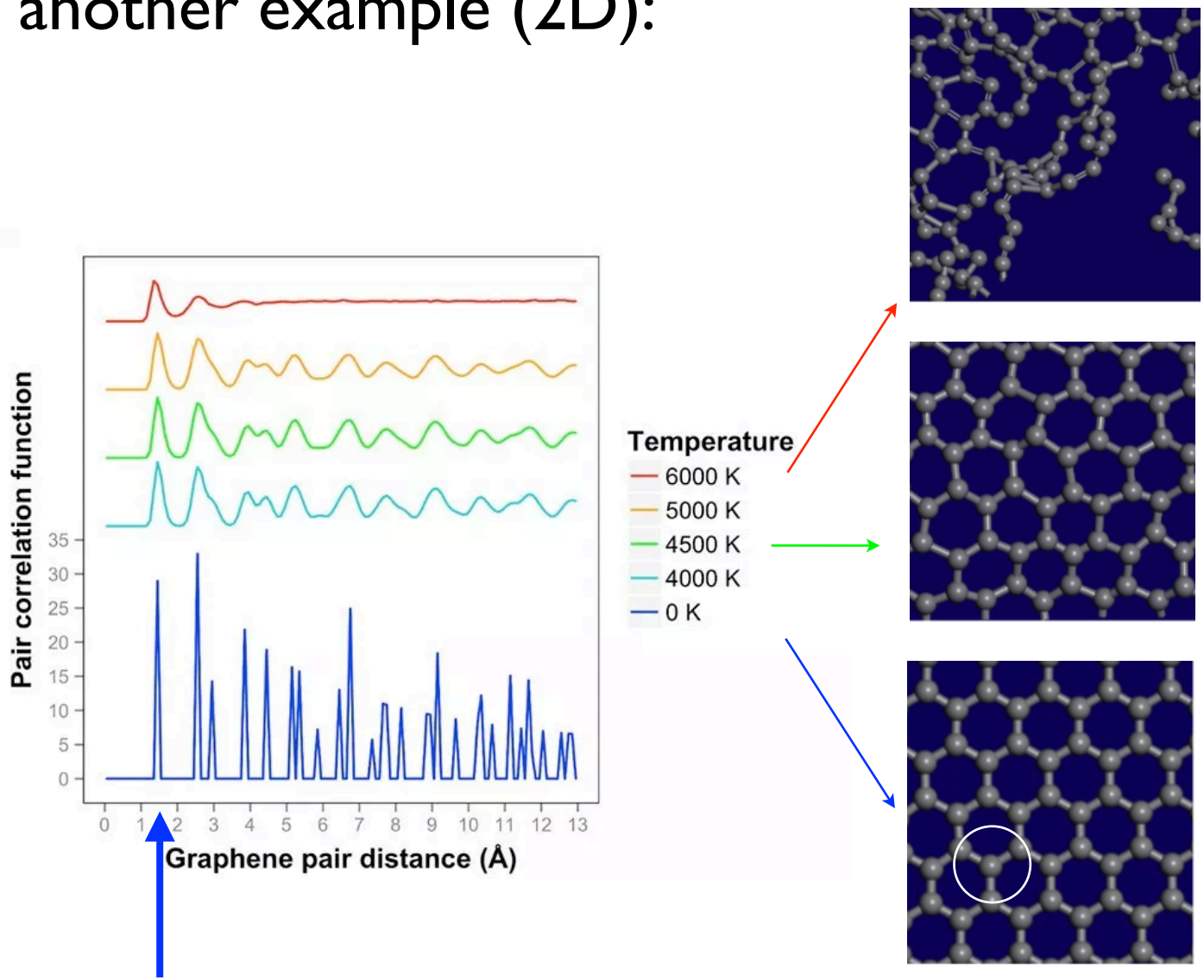

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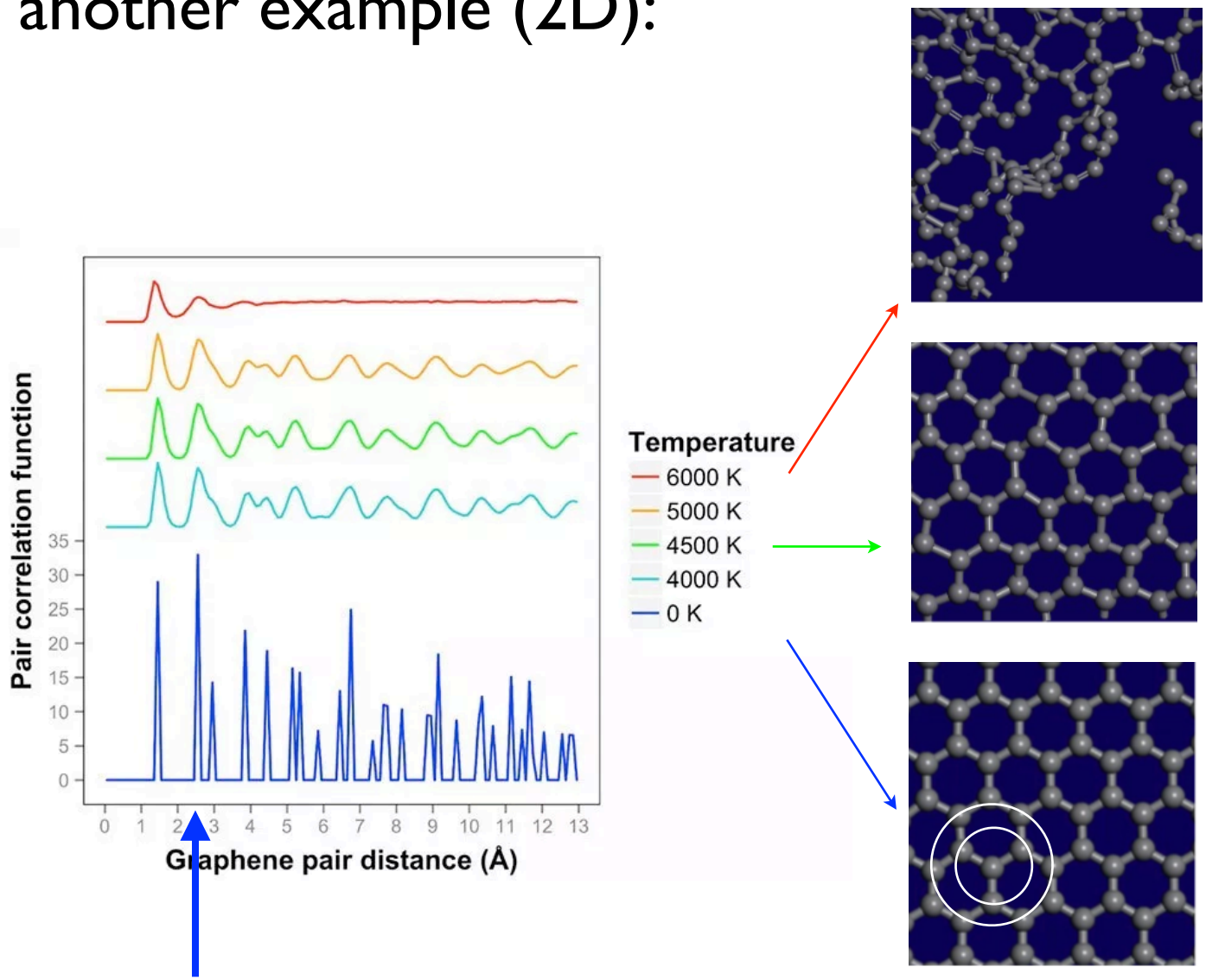

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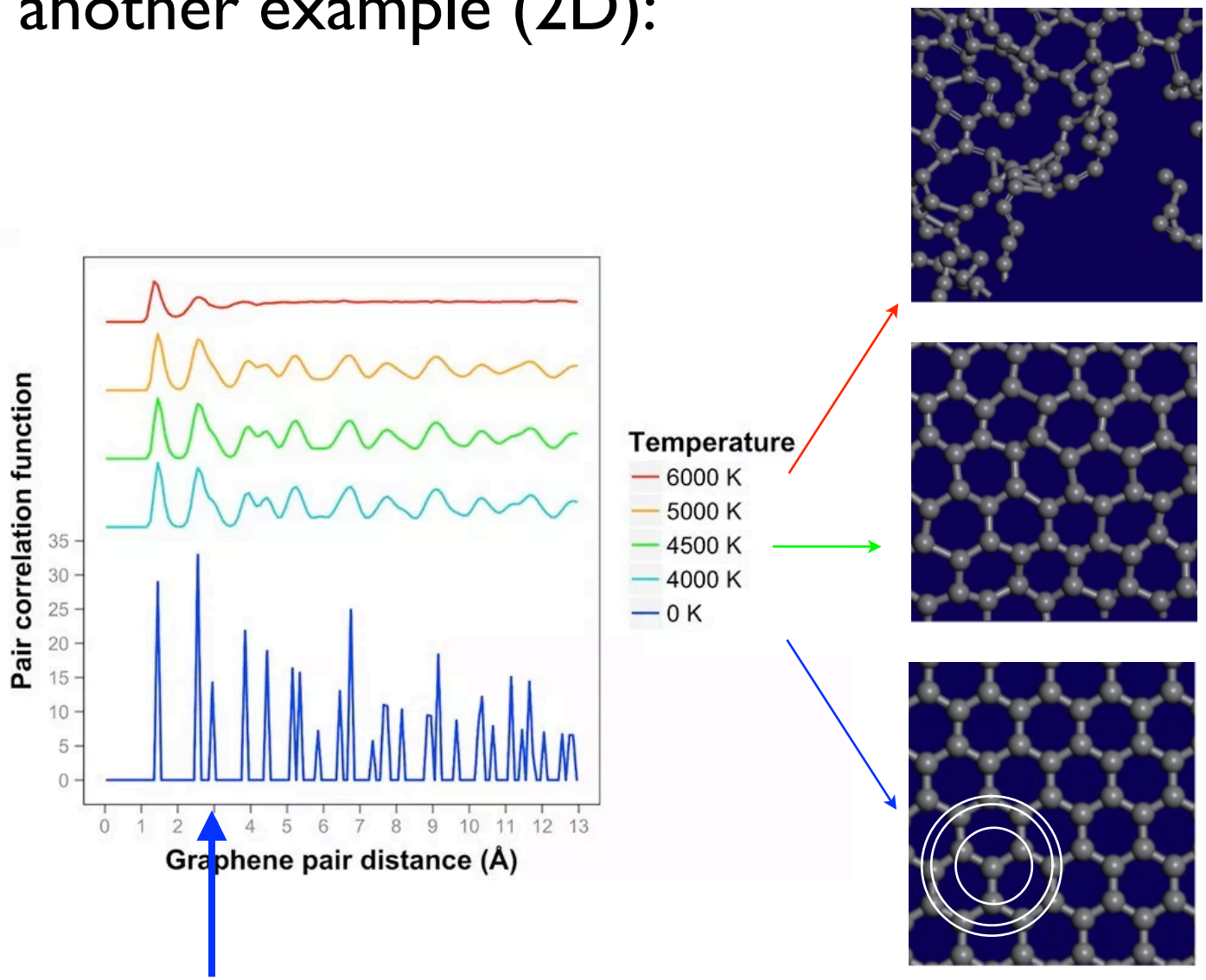

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Radial distribution function

formulation in case of spherically symmetric interactions:

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

(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)

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

<= (here: no double counting of pairs)

OK for a numerical implementation

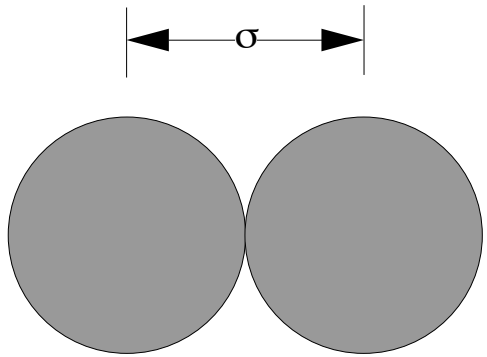
Simple interaction potentials

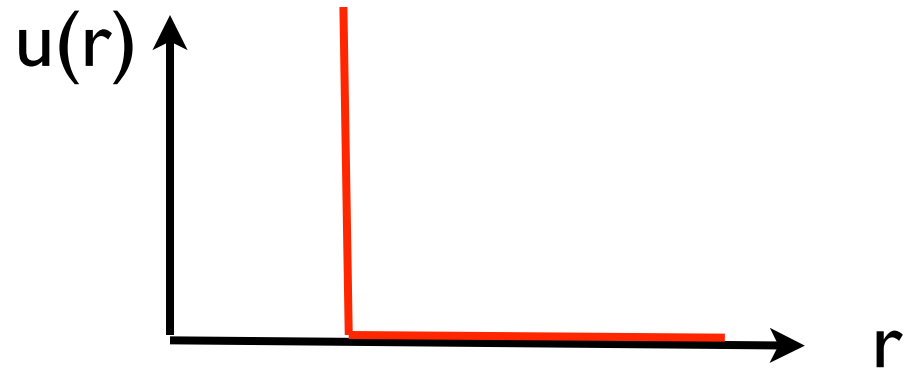
- Hard disks (spheres)
- Lennard-Jones
- ...

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)





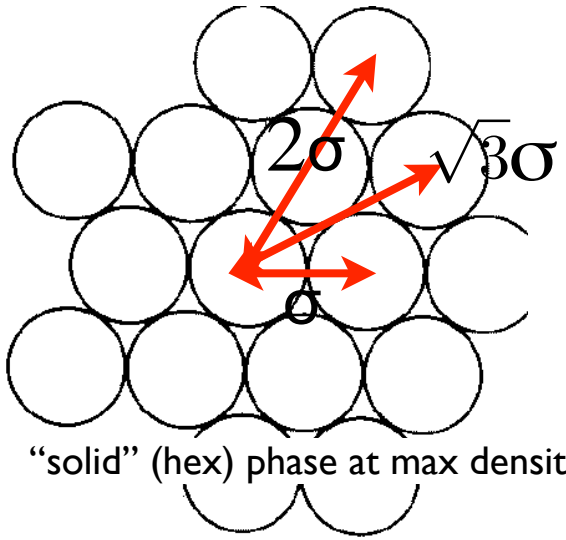
$$u(r) = \begin{cases} +\infty, & r < \sigma \\ 0, & r \geq \sigma \end{cases}$$

No minimum; check overlap!

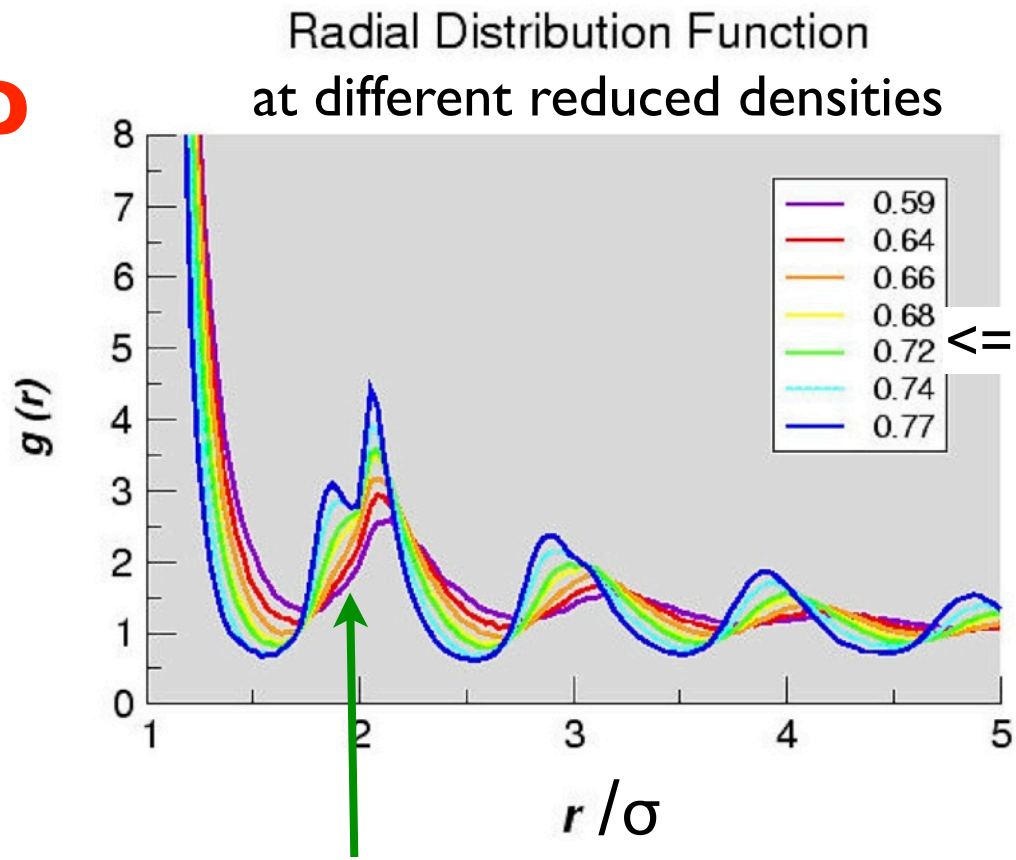
No attractive part => no transition from gas to liquid

Radial distribution function

of **hard disks in 2D**



"solid" (hex) phase at max density



<= 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)

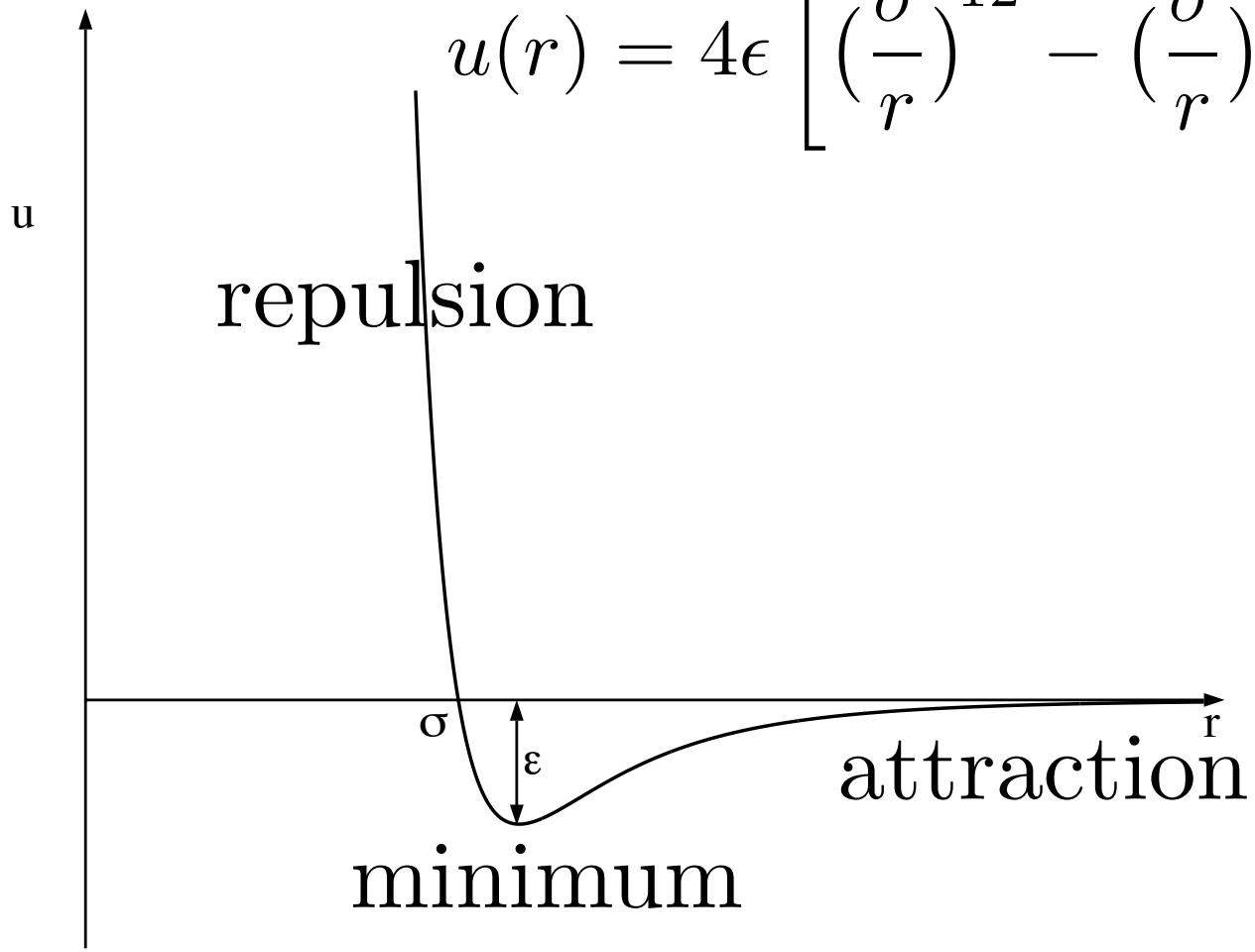
particle (or number) density : $\rho = \dfrac{\text{number of particles}}{\text{area}} = \dfrac{N}{A}$

reduced density : $\rho^* = \rho\sigma^2$

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

Lennard-Jones potential

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



Generalities in many-body simulations

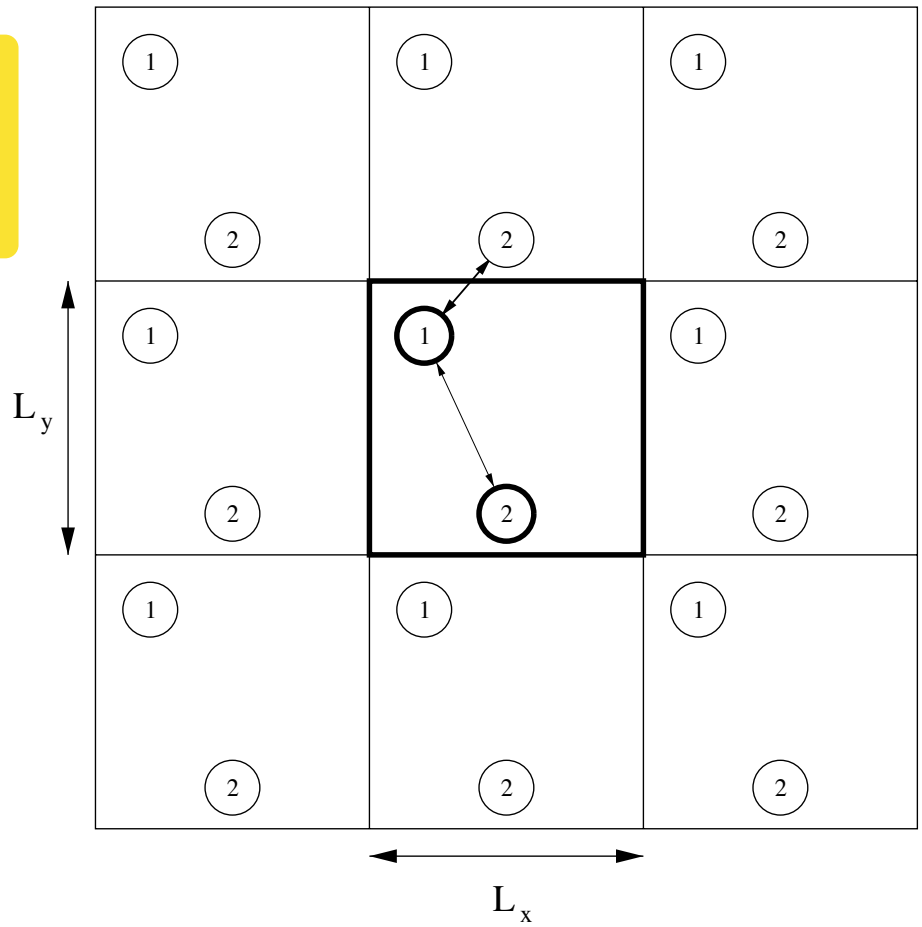
- periodic boundary conditions
- minimum image

Minimum Image convention

for the interactions

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

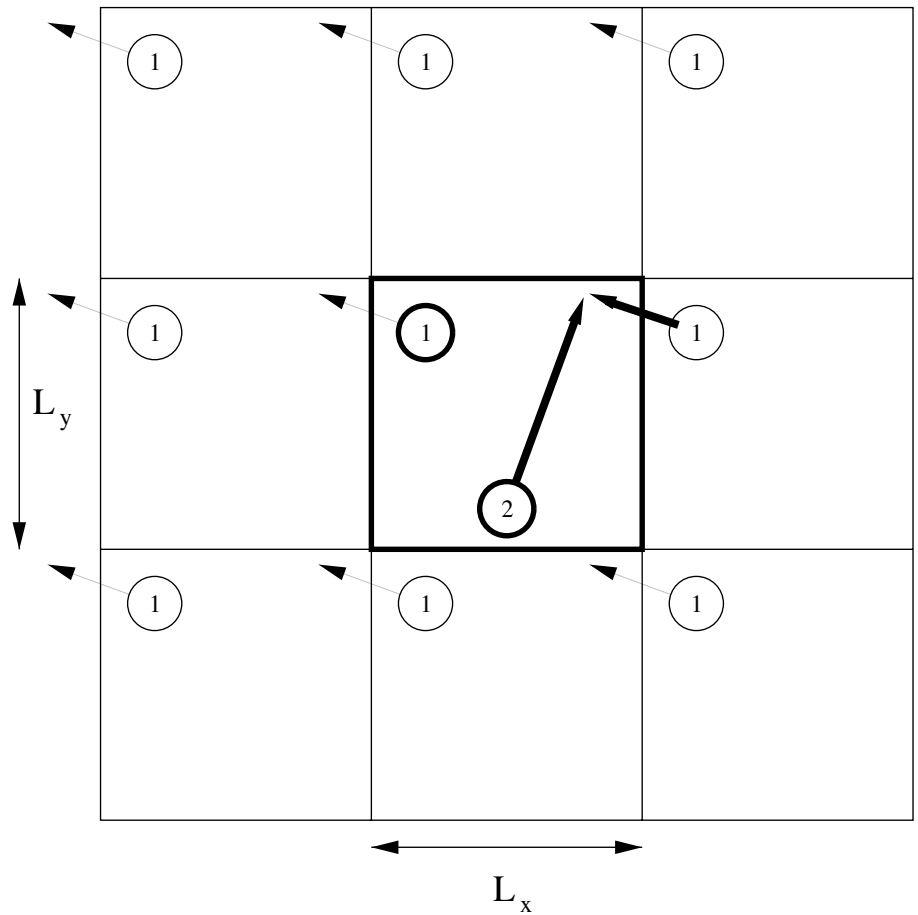
NEW! DIFFERENT
w.r.t. Ising, lattice gas, hard disks because here the interactions are not simply on-site or nearest neighbour but longer ranged



Only the interactions with the nearest images are considered

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 approaches to simulate the evolution of the system

(to sample the configuration space)

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

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

Molecular dynamics

a deterministic approach to the dynamics of a system

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

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

- and with a 'smart' algorithm for numerical integration

Molecular dynamics

and Newton's equations of motion

$$F = ma$$

But not always easy to solve… In general:

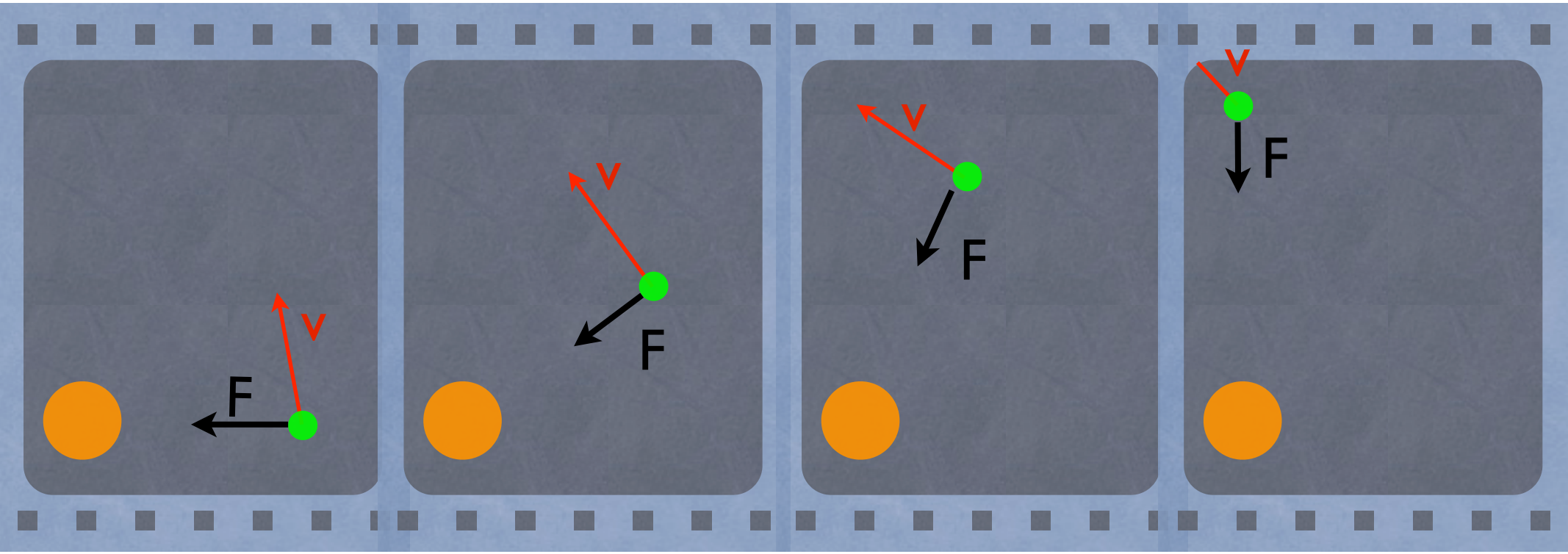
$$\frac{d^2x}{dt^2} = a(x, t, \dots) = \frac{F(x, t, \dots)}{m}$$

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

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

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

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



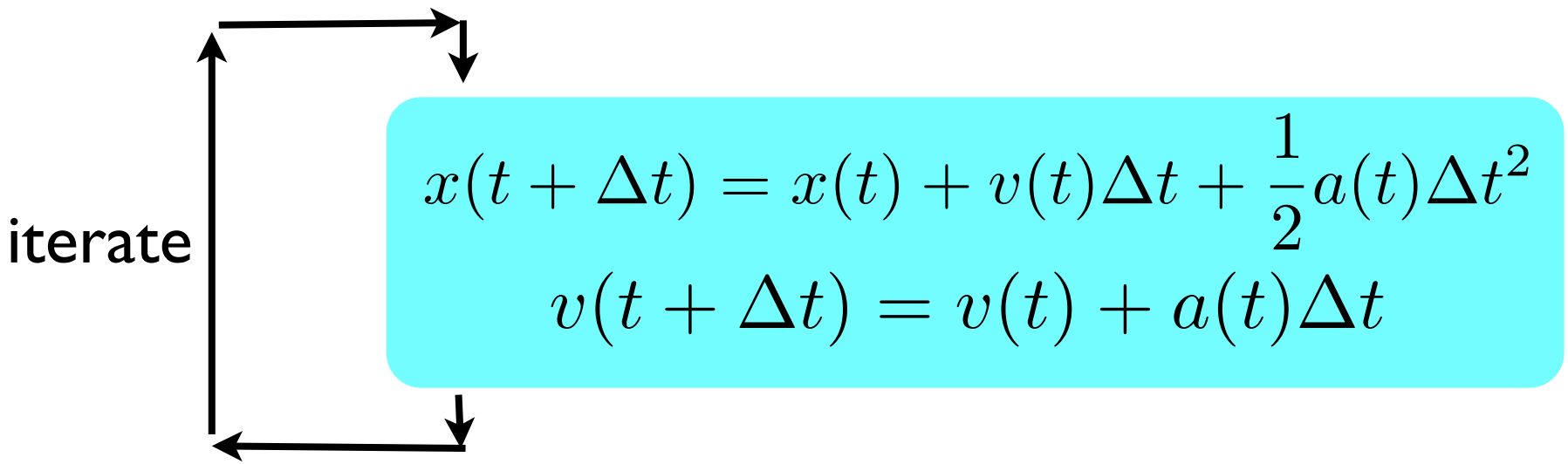
x(0) v(0) F(0) x(1) v(1) F(1) x(2) v(2) F(2) ... ...

Uniformly accelerated motion in each time interval

$t \div t + \Delta t$

then iterate!

EULER algorithm

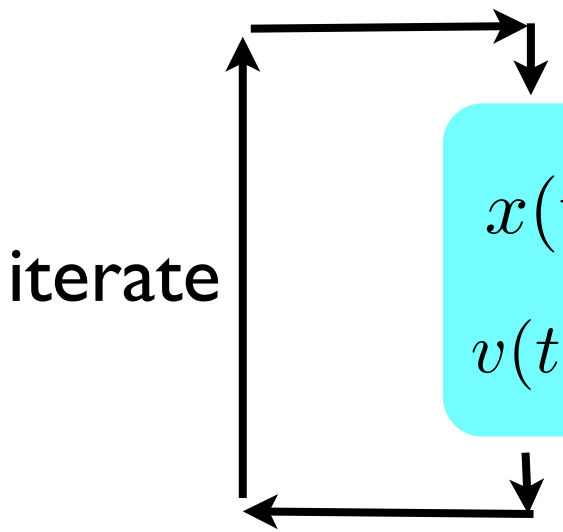


$$x(t) \Longrightarrow x(t + \Delta t) \Longrightarrow x(t + 2\Delta t) \Longrightarrow x(t + 3\Delta t) \Longrightarrow \ldots$$

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

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

Velocity-VERLET algorithm



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

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

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

Choice of an integration algorithm

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

Velocity- Verlet algorithm

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

Thermodynamical ensemble

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

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

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

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

Energy
in MD - NVE simulations

the TOTAL ENERGY of the system should be conserved!

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

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

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

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.