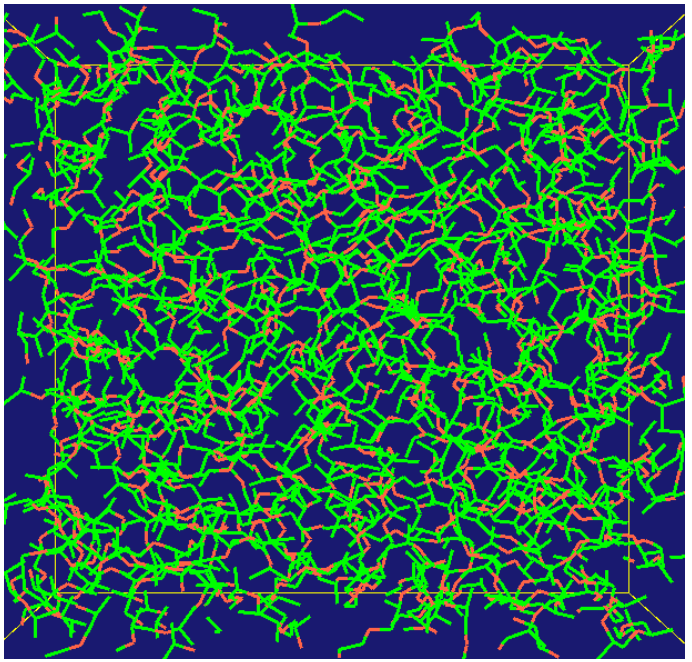
Molecular dynamics simulation

A numerical technique to compute
the equilibrium and transport properties
of classical many-particle systems
by solving Newton's equation of motion.

$$H = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + V_{\mathrm{pot}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$$



van der Waals system

van der Waals bonding - fluctuating electric dipole moments

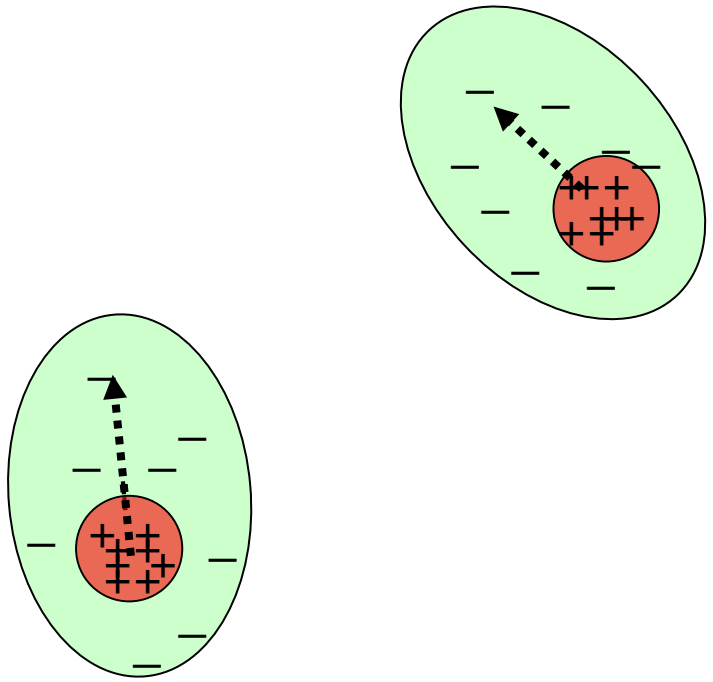
$$V_{\text{pot}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = \sum_i \sum_{j>i} v_2(\mid \boldsymbol{r}_i - \boldsymbol{r}_j \mid)$$

Model for rare gas solids

Ex. Lennard-Jones potential
(the generic model potential in MD)

$$v_2(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]$$

$$r_{ij} \equiv \mid \boldsymbol{r}_i - \boldsymbol{r}_j \mid$$



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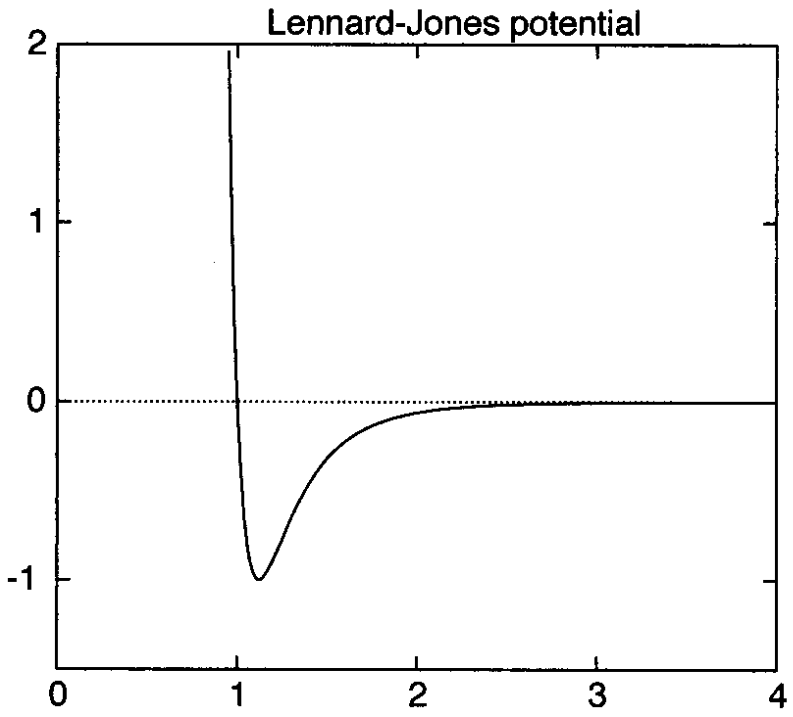


Metallic systems

Metallic bonding - delocalization of valence electrons

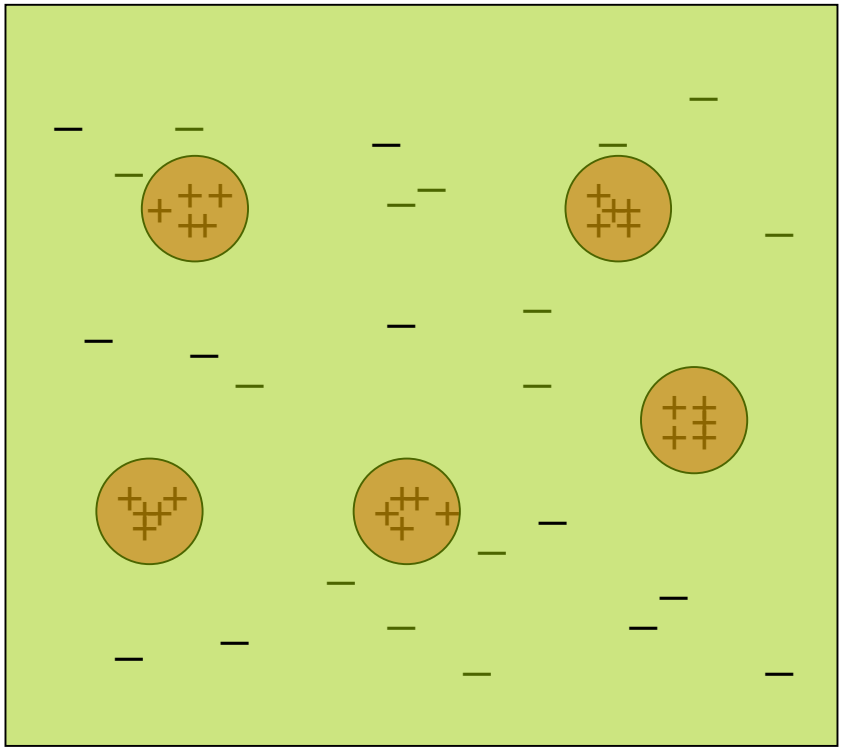
Physical fact: Pairwise interaction fails. The bonds become weaker when the local environment becomes more crowded.

Pair-functional model

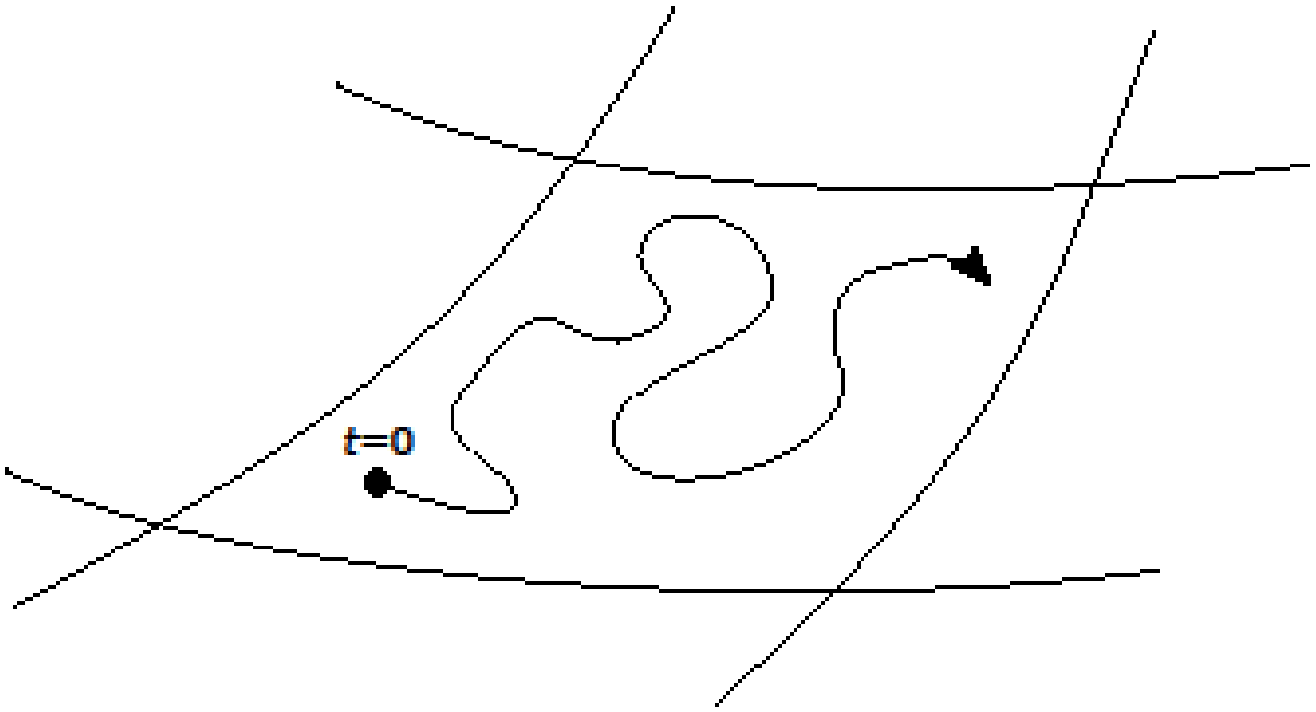
$$V_{\mathrm{pot}}(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) = \sum_i g_i(\rho_i) + \sum_i \sum_{j>i} v_2(|\,\boldsymbol{r}_i - \boldsymbol{r}_j\,|)$$

with

$$\rho_i = \sum_{j\neq i} h_i(|\,\boldsymbol{r}_i - \boldsymbol{r}_j\,|)$$



6N-dim. phase-space trajectory



Instability of trajectories

Lyaponov instability

$\boldsymbol{r}_i(t)$ - parent trajectory

$\boldsymbol{r}'_i(t)$ - perturbed trajectory

The initial velocity for ***two*** particle is changed slightly to obtain the perturbed trajectory

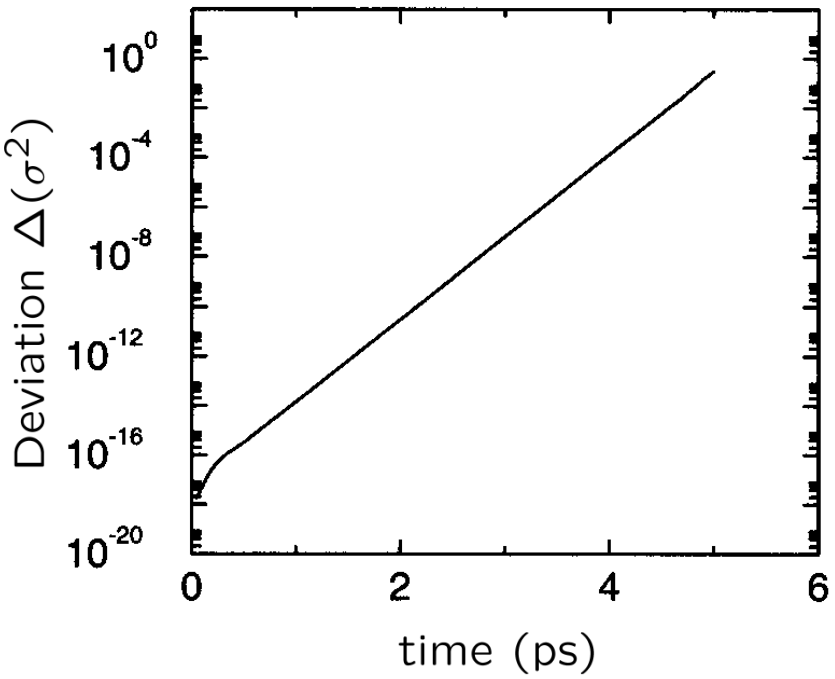
$$v'_{x1}(0) = v_{x1}(0)[1 + 10^{-10}]$$

$$v'_{x2}(0) = v'_{x2}(0)[1 - 10^{-10}]$$

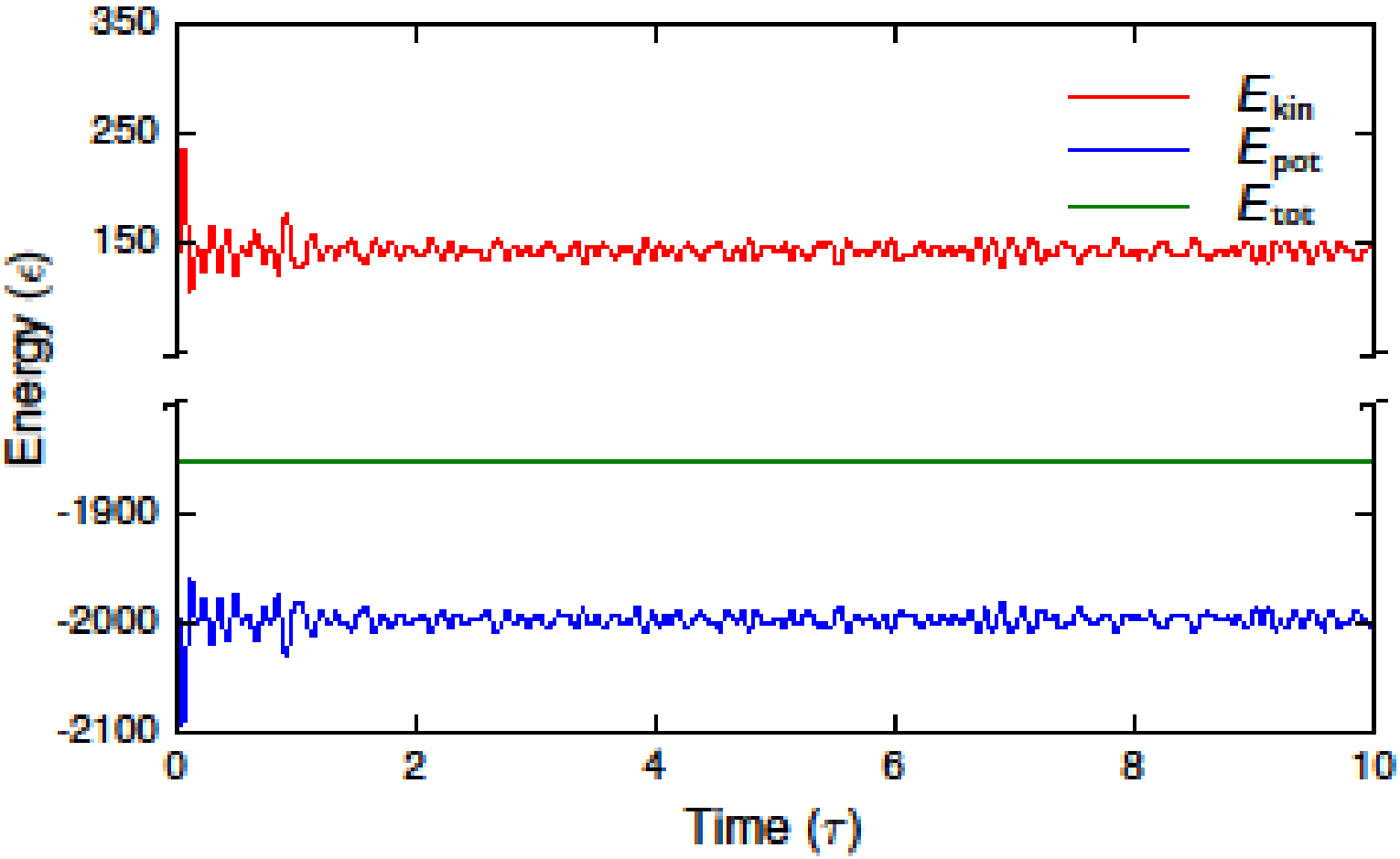
The following deviation is determined

$$\Delta(t) = \sum_{i=1}^{N} [\boldsymbol{r}_i(t) - \boldsymbol{r}'_i(t)]^2$$

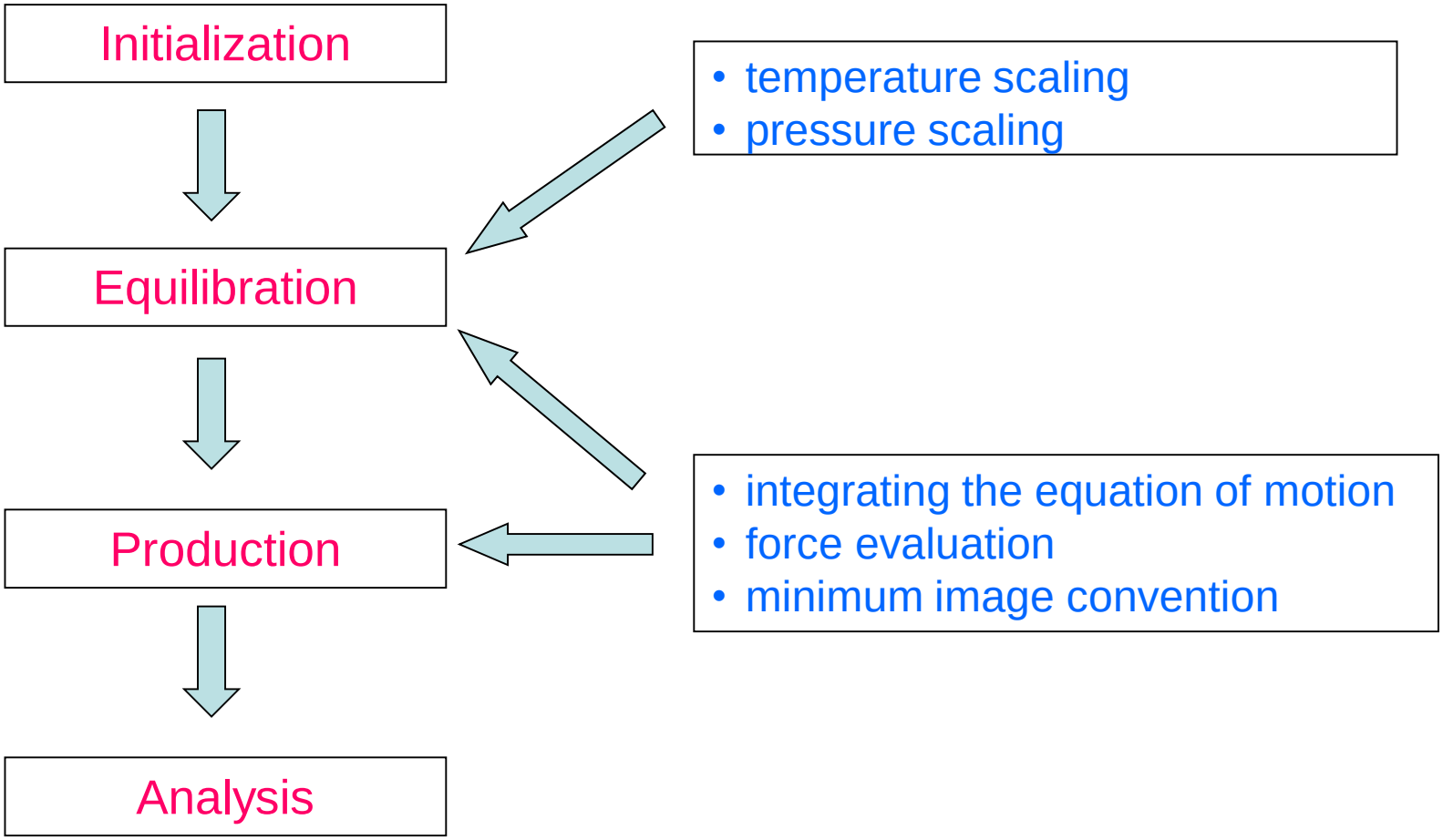
Liquid Argon, N=1000



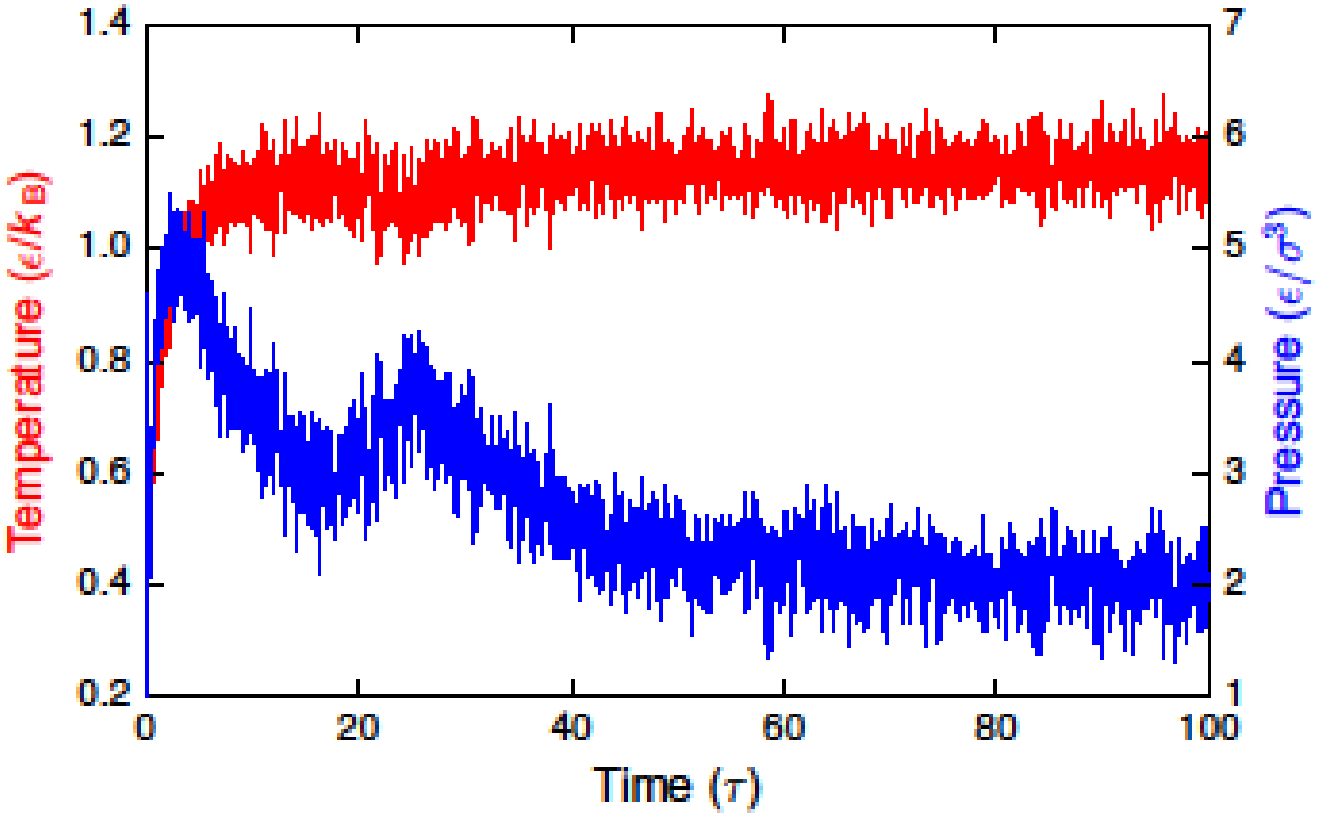
Time evolution



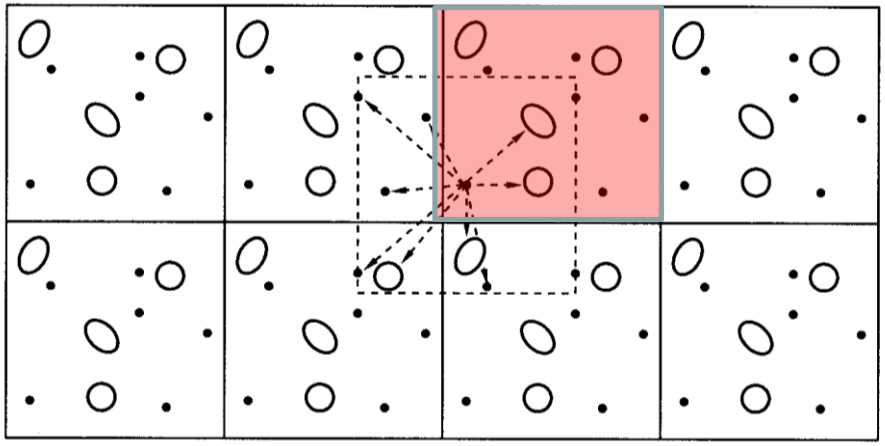
A typical program



Equilibration

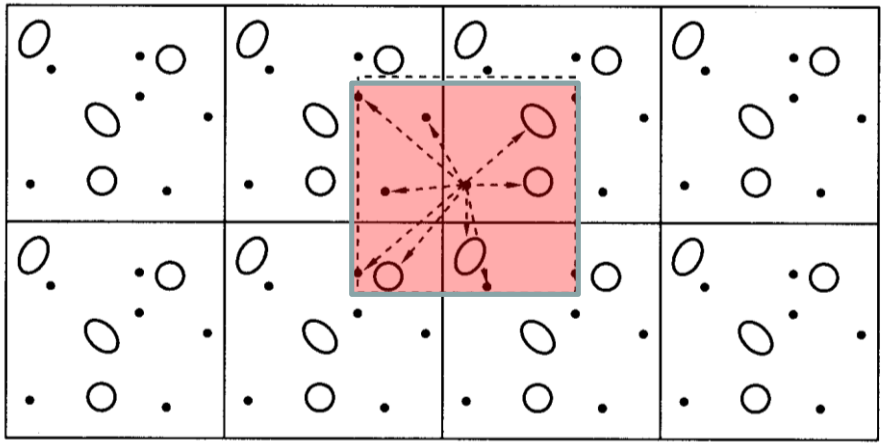


Periodic boundary conditions



- the simulation cell is replicated throughout space to form an infinite lattice
- only particles in the central box are stored

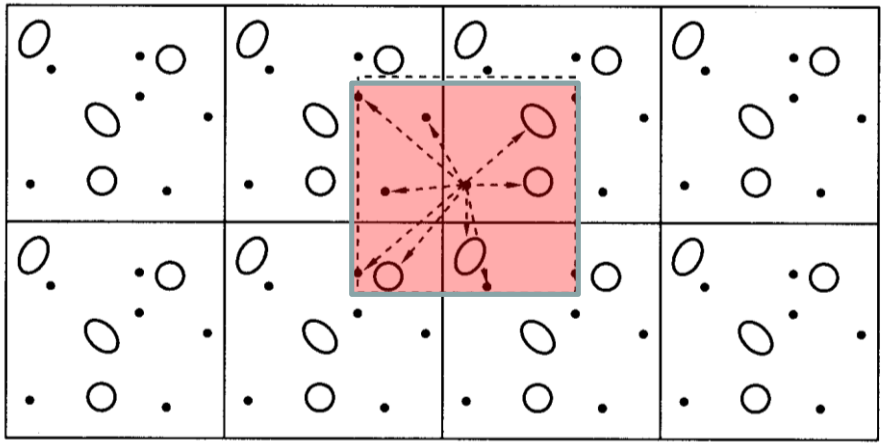
Periodic boundary conditions



Assume short range interaction: r_c < L/2

This implies interaction with only the nearest image

Periodic boundary conditions



Minimum image convention

$$\boldsymbol{r}_{ij} = \boldsymbol{r}_j - \boldsymbol{r}_i$$

$$\boldsymbol{r}_{ij} = \boldsymbol{r}_{ij} - L\left[\boldsymbol{r}_{ij}/L\right]$$

where

$[X]$ is the nearest integer to X

Example of average quantities

Simple averages $\langle A \rangle$

- temperature
- pressure

Fluctuations $\left\langle (\delta A)^2 \right\rangle$

- heat capacity

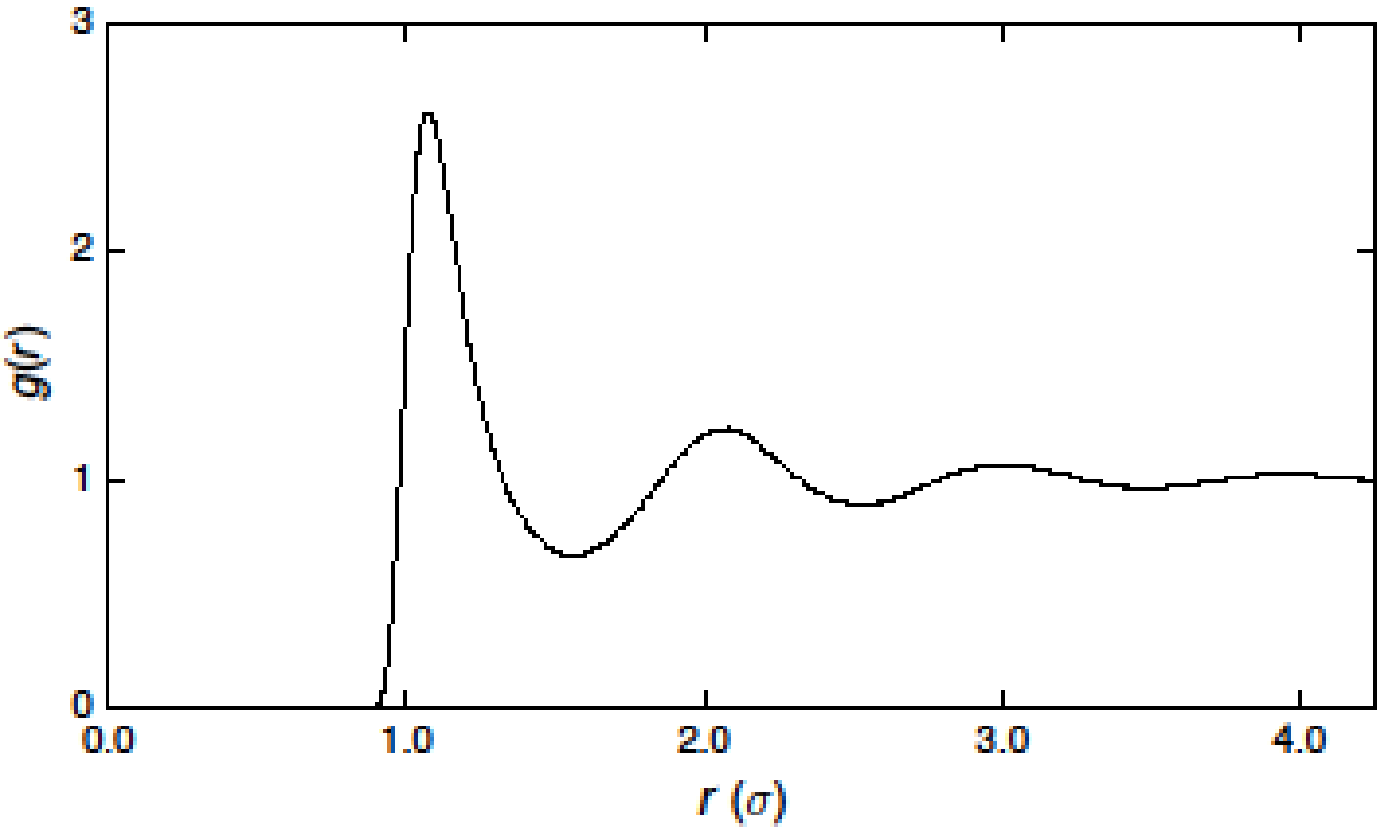
Static quantities $\langle AB \rangle$

- pair-distribution function
- static structure factor

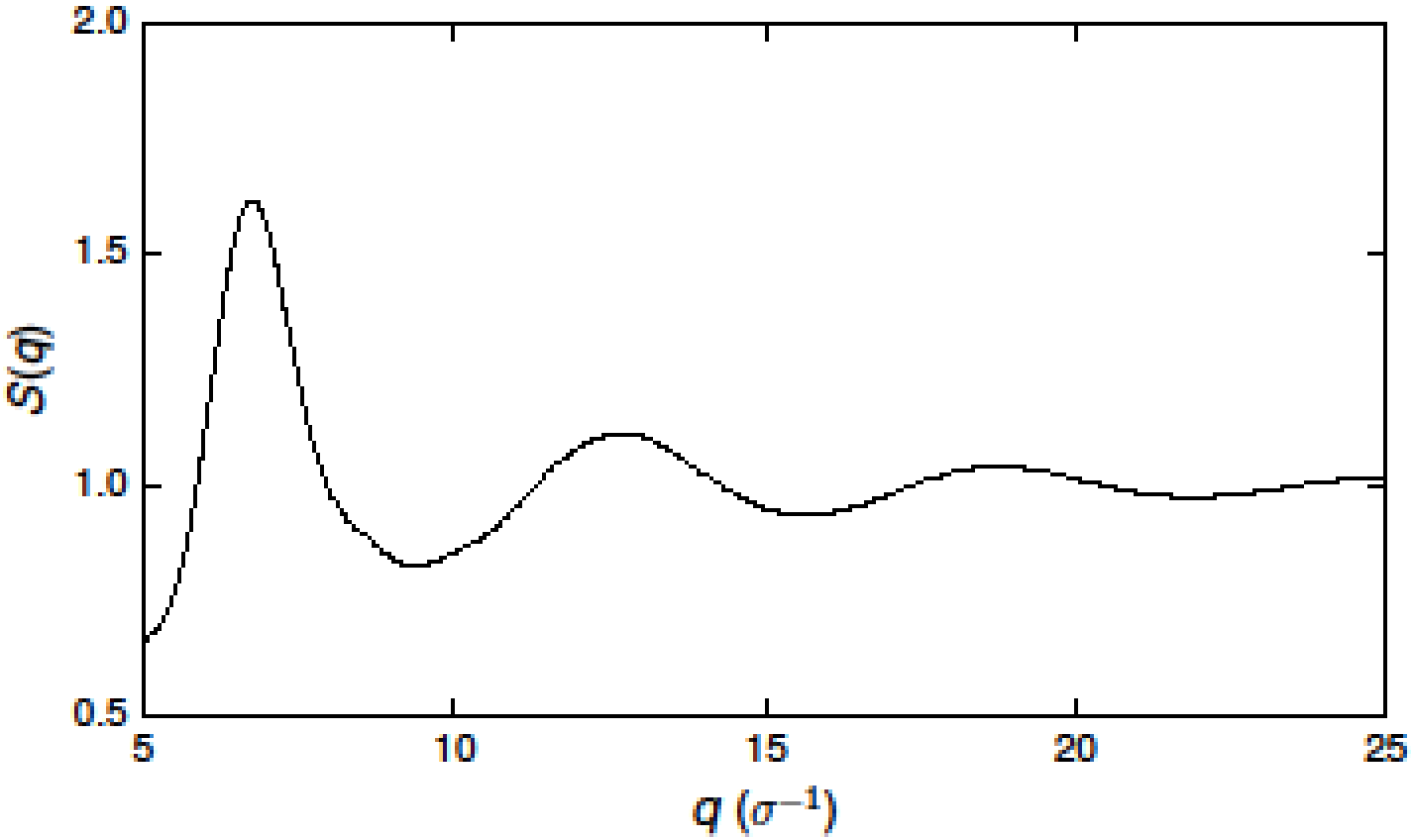
Dynamic quantities $\langle A(t)B(0) \rangle$

- mean squared displacement
- velocity correlation function
- diffusion coefficient
- dynamic structure factor

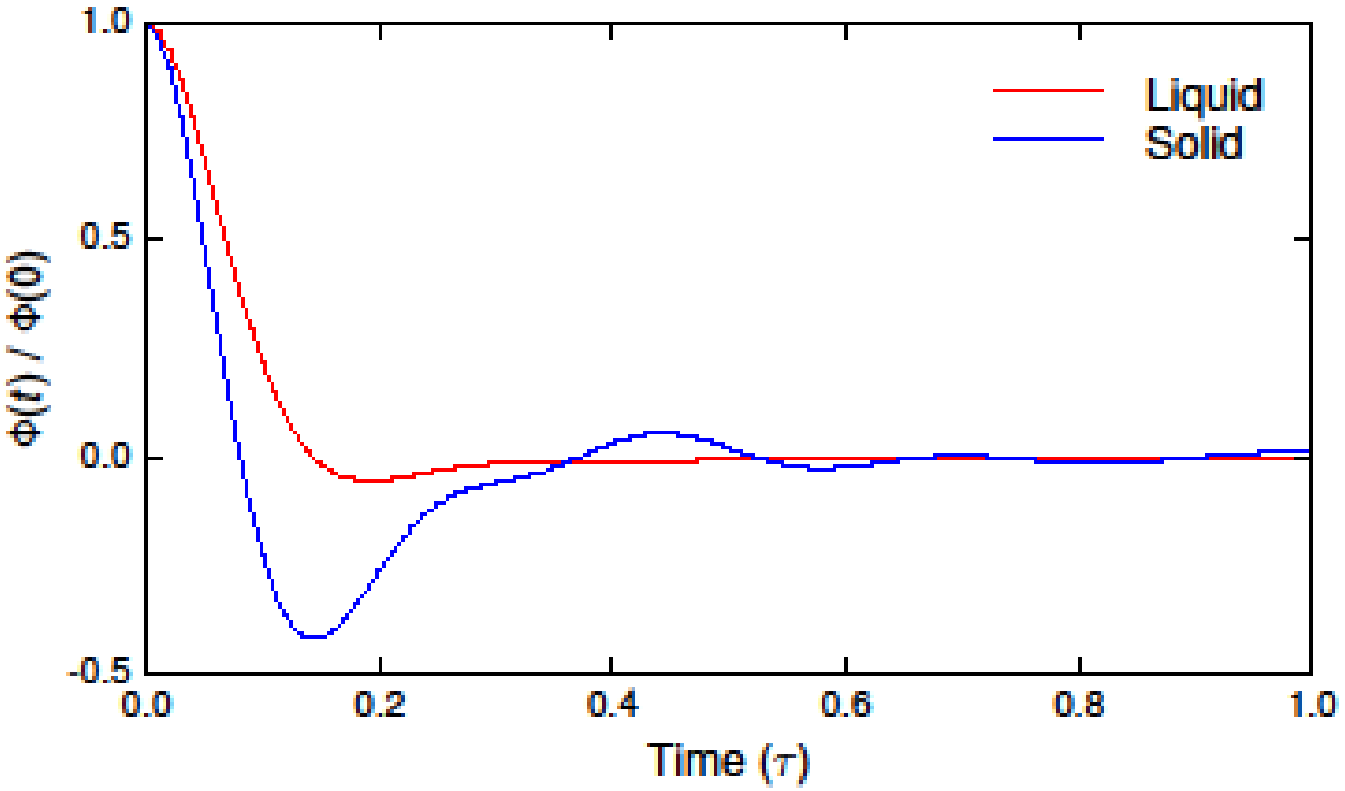
Pair distribution function



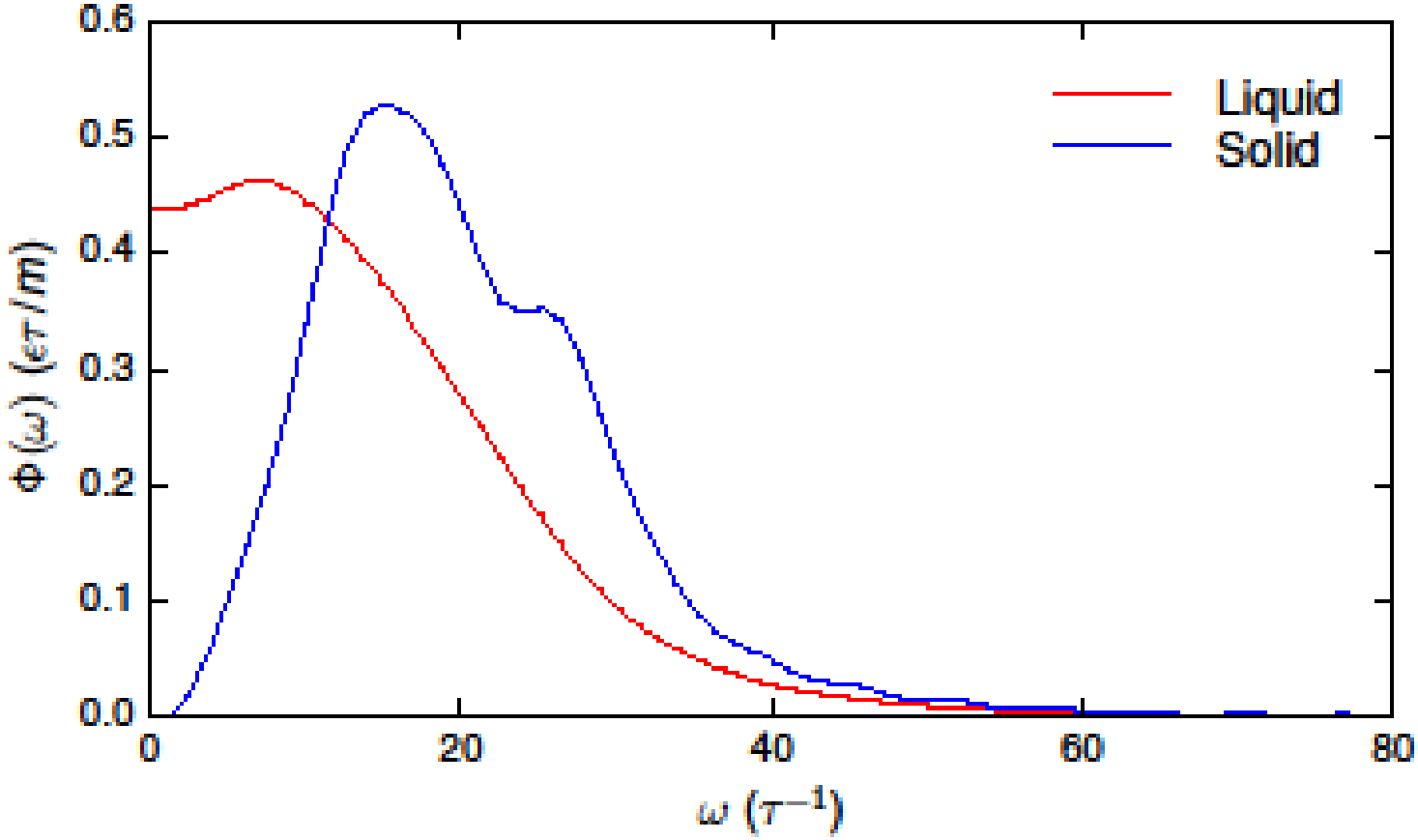
Static structure factor



Velocity correlation function



Velocity correlation function – spectral function



Mean squared displacement