

Properties, static correlations, order parameters

What do we get out of a simulation?

- Static properties: pressure, specific heat, etc.
- Density
- Pair correlations in real space and Fourier space.
- Order parameters and broken symmetry: How to tell a liquid from a solid
- Dynamical properties –next lecture

Thermodynamic properties

- We can get averages over distributions
- **Total (internal) energy** = kinetic energy + potential energy
- **Kinetic energy** = $k_B T/2$ per momentum (degree of freedom)
- **Specific heat** = mean squared fluctuation in energy
- **Pressure** can be computed from the *virial theorem*.
- **Compressibility, bulk modulus, sound speed**

- We have problems with **entropy** and **free energy** because they are **not averages** with respect to the Boltzmann distribution. We will discuss this later.

Thermodynamic Estimators

Name	Symbol	Formula
Kinetic Energy	$K = mdF/dm$	$\frac{1}{2} \sum_i m_i v_i^2 = \frac{1}{2} k_B T \times (\text{degrees of freedom})$
Potential Energy	U	$\sum_{i<j} \phi(r_{ij}) = \frac{N}{2} \rho \int d^3r \phi(r) g(r)$
Pressure	$P = -\frac{\partial F}{\partial \Omega}$	$\frac{1}{3\Omega} [2K - \sum_{i<j} r_{ij} \frac{d\phi}{dr}] = \frac{k_B T}{\Omega} - \frac{\rho^2}{6} \int d^3r g(r) r \frac{d\phi}{dr}$
Specific Heat	$C_V = \frac{\partial E}{\partial T}$	$\frac{1}{(k_B T)^2} \langle (E - \langle E \rangle)^2 \rangle = (3/2)N + \frac{1}{(k_B T)^2} [\langle V^2 \rangle - \langle V \rangle^2]$

Microscopic Density

- In real space: $\rho(r) = \left\langle \sum_i \delta(r - r_i) \right\rangle$ its Fourier transform: $\rho(k) = \left\langle \sum_i e^{ik \cdot r_i} \right\rangle$

- The Fourier transform is a good way to smooth the density.
- A solid has **broken symmetry** (order parameter): density is *not constant*.
- At a liquid-gas transition, the density is also inhomogeneous.
- In periodic boundary conditions. the k-vectors are on a grid:

$$(k_x, k_y, k_z) = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right)$$

- Long wavelength modes are absent.
- In a solid, **Lindemann's ratio** gives a rough idea of melting:

$$\langle u^2 \rangle = \frac{1}{d^2} \langle (r_i - r_i^0)^2 \rangle$$

- When deviations about lattice are greater than $\sim 15\%$, the solid has melted (Lindemann's criterion)

Order parameters

- Systems have symmetries: e.g. **translation invariance**.
 - At high T , one expects the system to have those same symmetries at the microscopic scale (e.g., a gas).
 - BUT, as the system cools, those symmetries can be **broken**
 - (e.g., a gas *condenses* or *freezes*).
 - The best way to monitor the transition is to look how the order parameter changes *during the simulation*.
- **Examples:**
 - At a liquid gas-transition, density no longer fills the volume: droplets form. The **density** is the order parameter.
 - At a liquid-solid transition, both **rotational** and **translational** symmetry are broken.

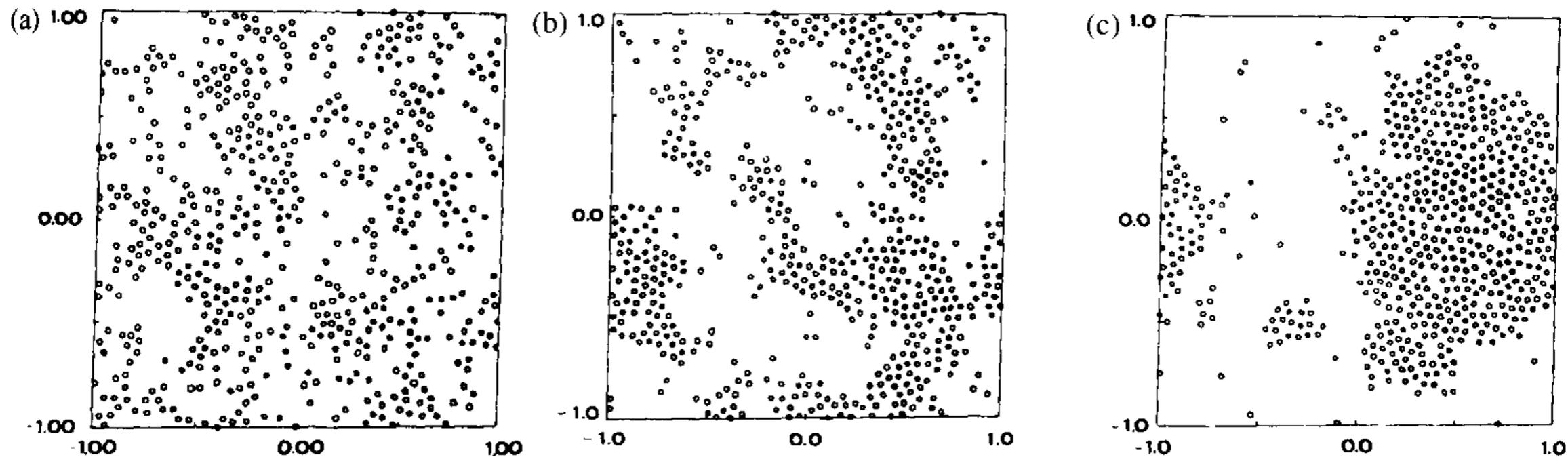


Fig. 6.1 Snapshots of 576 particles at a density $\rho^* = 0.3$ for $T^* =$ (a) 0.7, (b) 0.5, and (c) 0.45. Here ρ^* , T^* are density and temperature in reduced units, i.e. the Lennard-Jones parameters σ and ε/k_B are used as units of length and temperature, respectively. From Rovere *et al.* (1990).

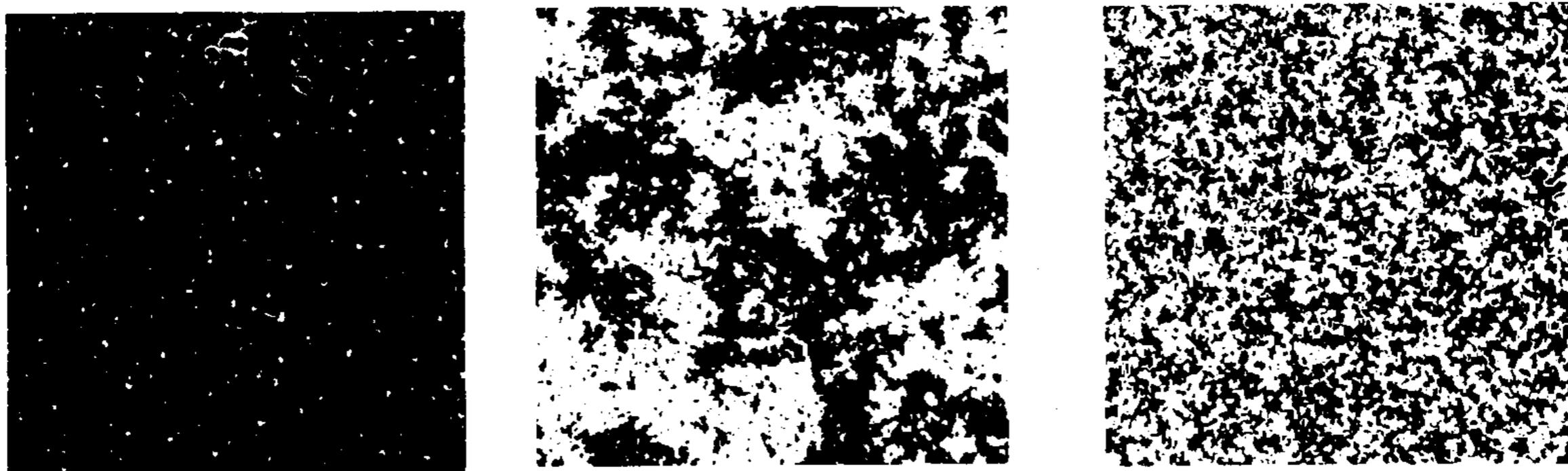
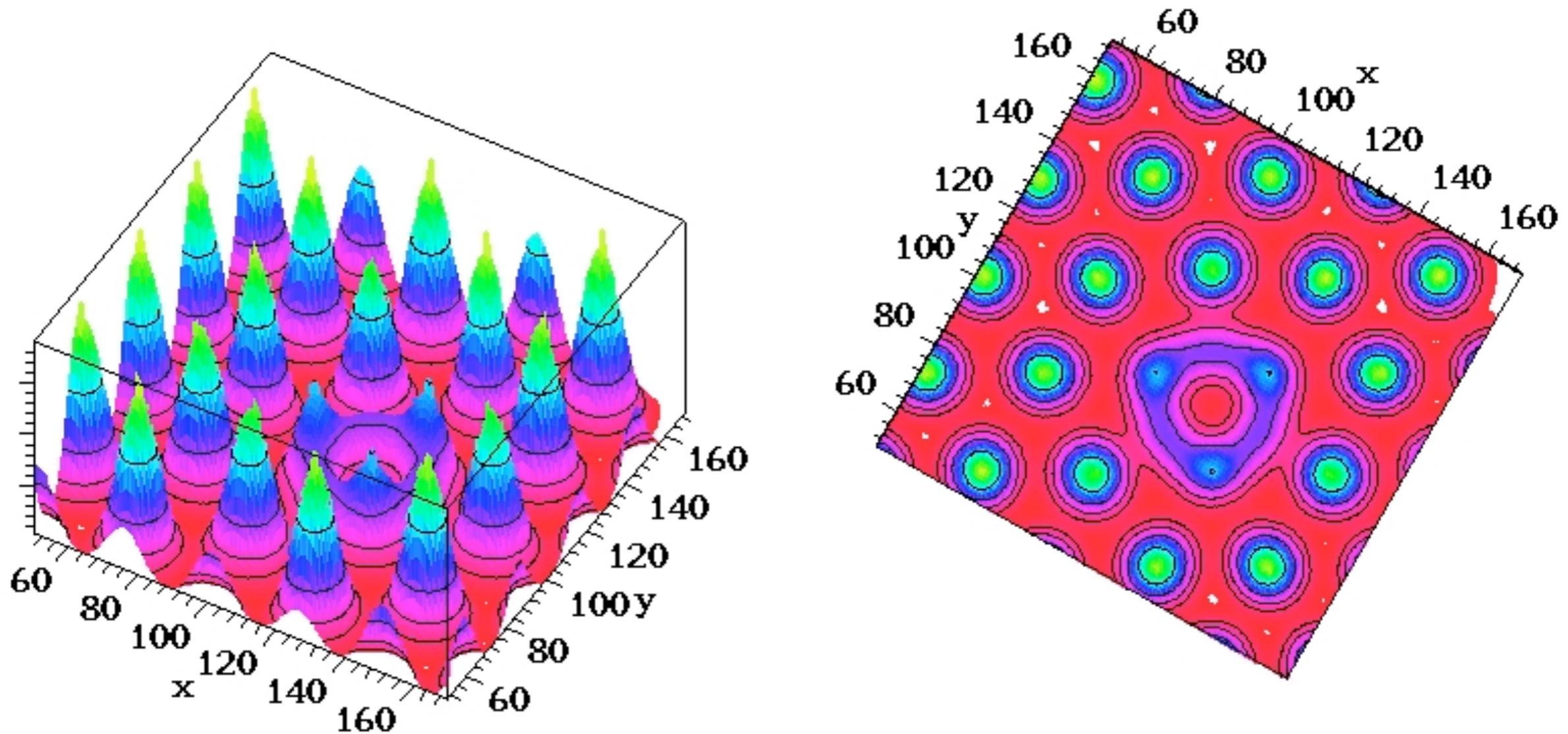


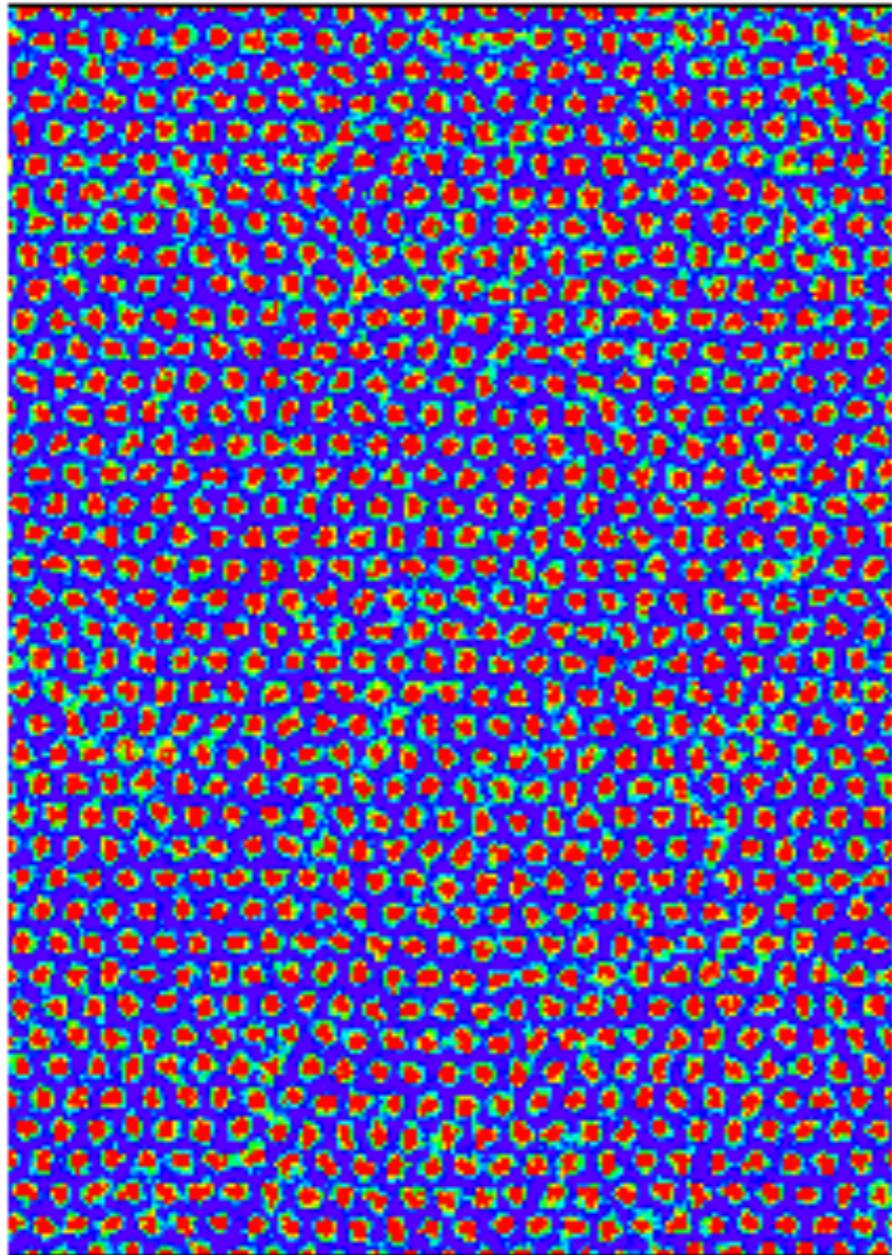
Fig. 4.1 Typical spin configurations for the two-dimensional Ising square lattice: (left) $T \ll T_c$; (center) $T \sim T_c$; (right) $T \gg T_c$.

Electron Density during exchange 2d Wigner crystal (quantum)

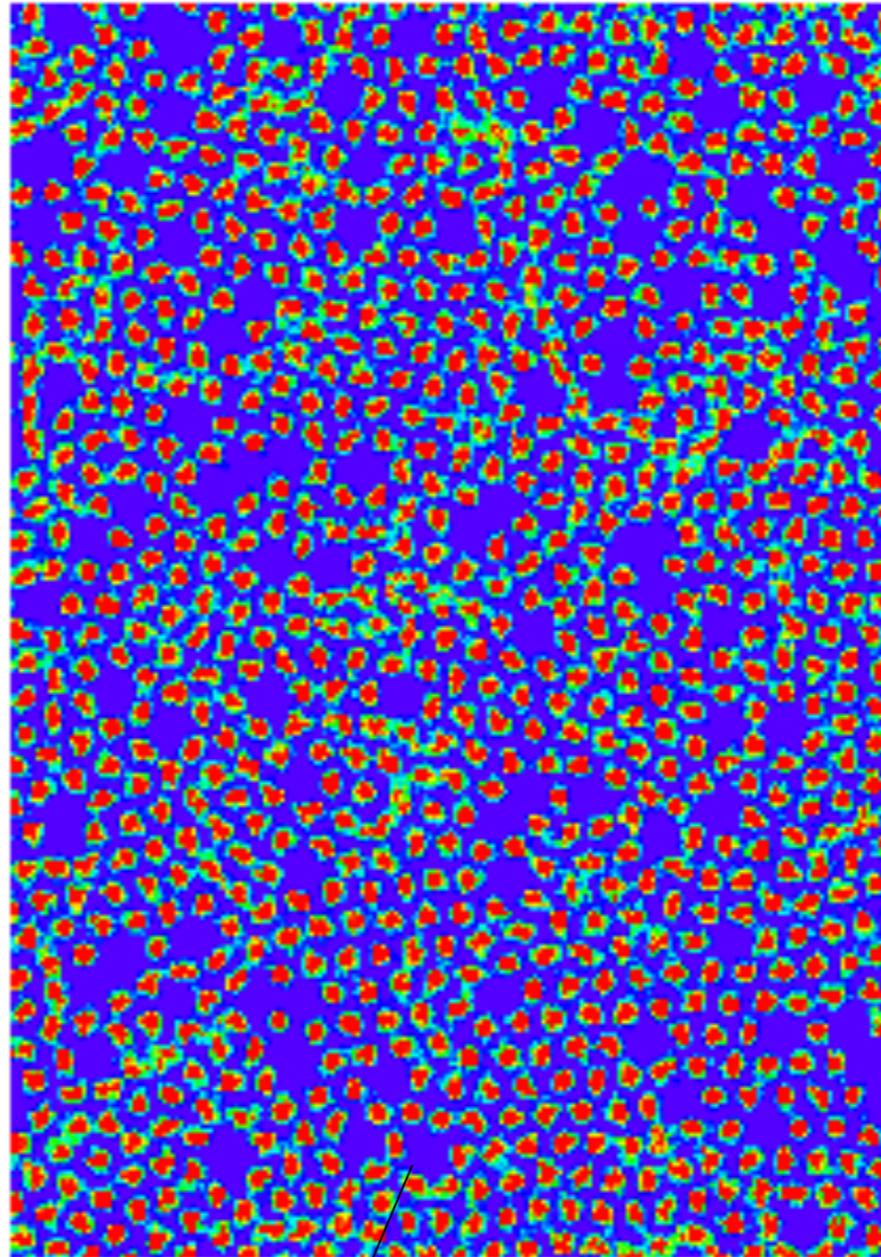


Contour levels are 0.0005, 0.001, 0.002, 0.004, 0.008

Snapshots of densities



Liquid or crystal or glass?



Blue spots are defects

Pair Correlation Function: $g(r)$

Radial distribution function: rdf

Density-Density correlation function

Primary quantity in a liquid is the probability distribution of pairs of particles. What is the density of atoms around a given atom?

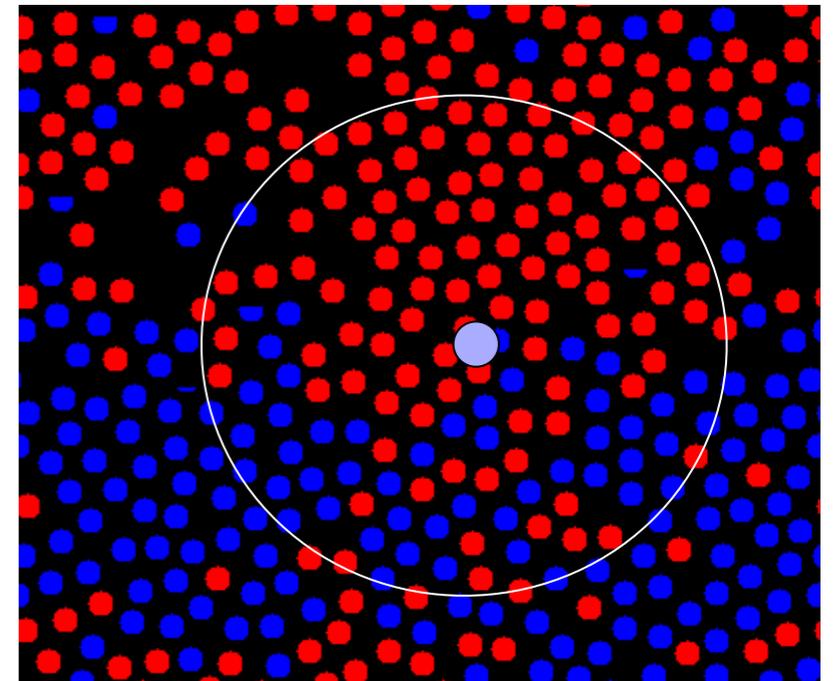
$$g(r) = \left\langle \sum_{i < j} \delta(r - |r_i - r_j|) \right\rangle \frac{2\Omega}{N^2}$$

- In practice, the delta-function is replaced by *binning* and making a *histogram*.

From $g(r)$ you can calculate all pair quantities (potential, pressure, ...):

$$V = \sum_{i < j} v(r_{ij}) = \frac{N\rho}{2} \int d^3r v(r)g(r)$$

A function gives more information than a number!



Calculating $g(r)$

```
for i in range(Natoms):
    for j in range(i+1,Natoms):
        dx=x[i]-x[j]          # this will be a vector if x&y are array
        for d in range(3):    # more clever ways to do this?
            if dx[d]>L[d]/2:  dx[d] -= L[d]
            if dx[d]<-L[d]/2: dx[d] += L[d]
        r2 = sum(dx*dx)       # dx[0]*dx[0]+dx[1]*dx[1]+dx[2]*dx[2]
        if r2>rcutoff2: continue # outside of cutoff distance^2
        r2i = sigma/r2
        index = sqrt(r2i)*dr_inverse
        g[index] += 1
# normalize g...
```

Note: **same loop** as force calculations = do simultaneously

Need to normalize so that $g(r) = 1$ for *uniform density* in shell of radius r
Need to be careful about **periodic boundary conditions**

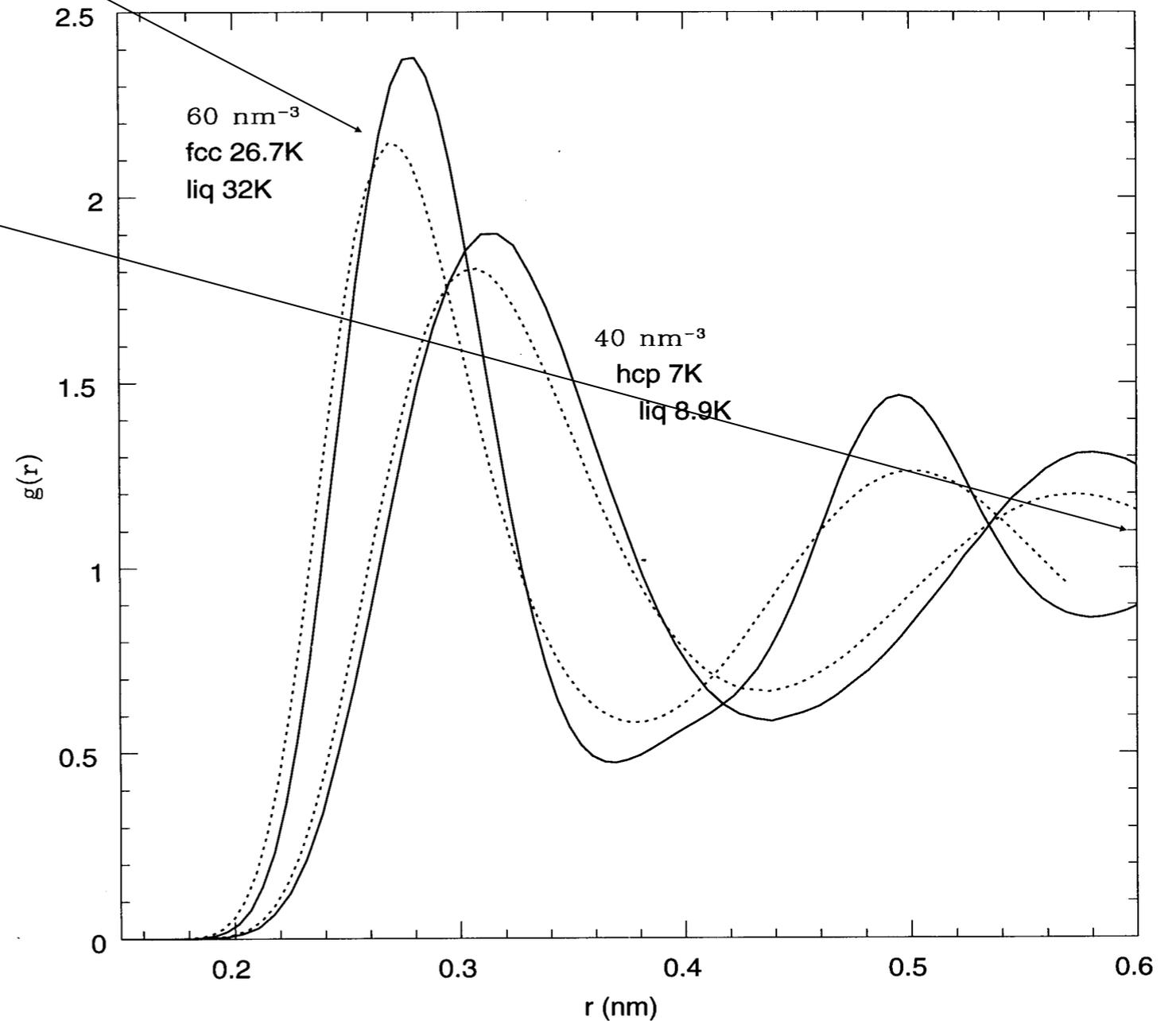
Example: $g(r)$ in liquid and solid helium

- Exclusion hole around the origin
- First peak is at inter-particle spacing.

(shell around the particle)

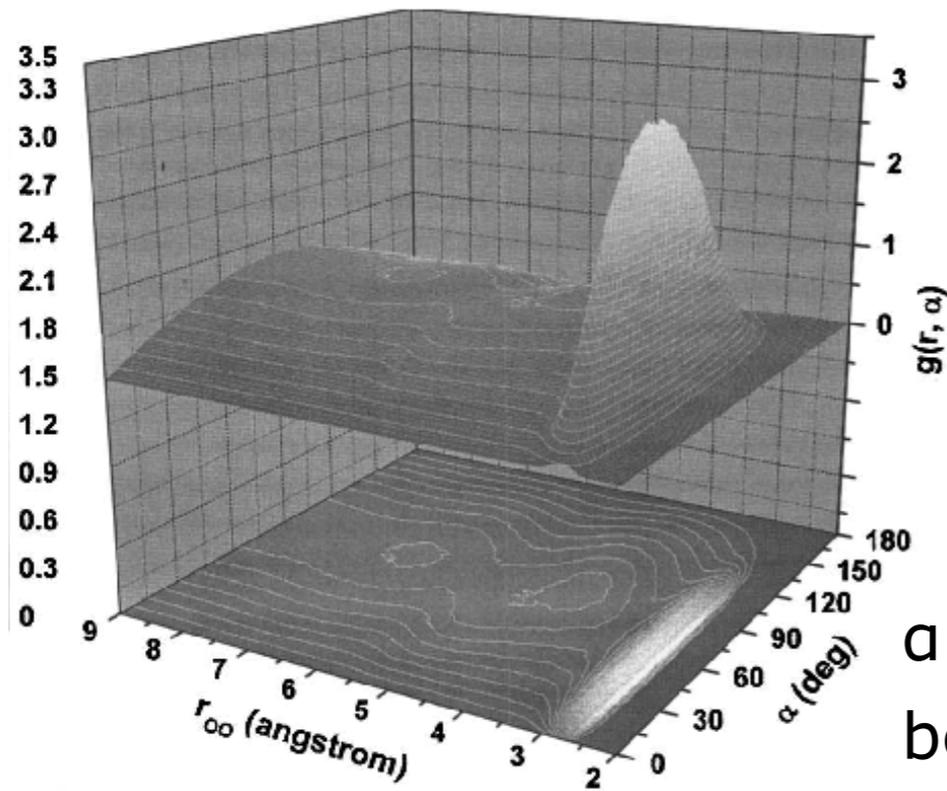
- Only can go out to $r < L/2$ in periodic boundary conditions without bringing in images.

- Crystal shows up as shoulder

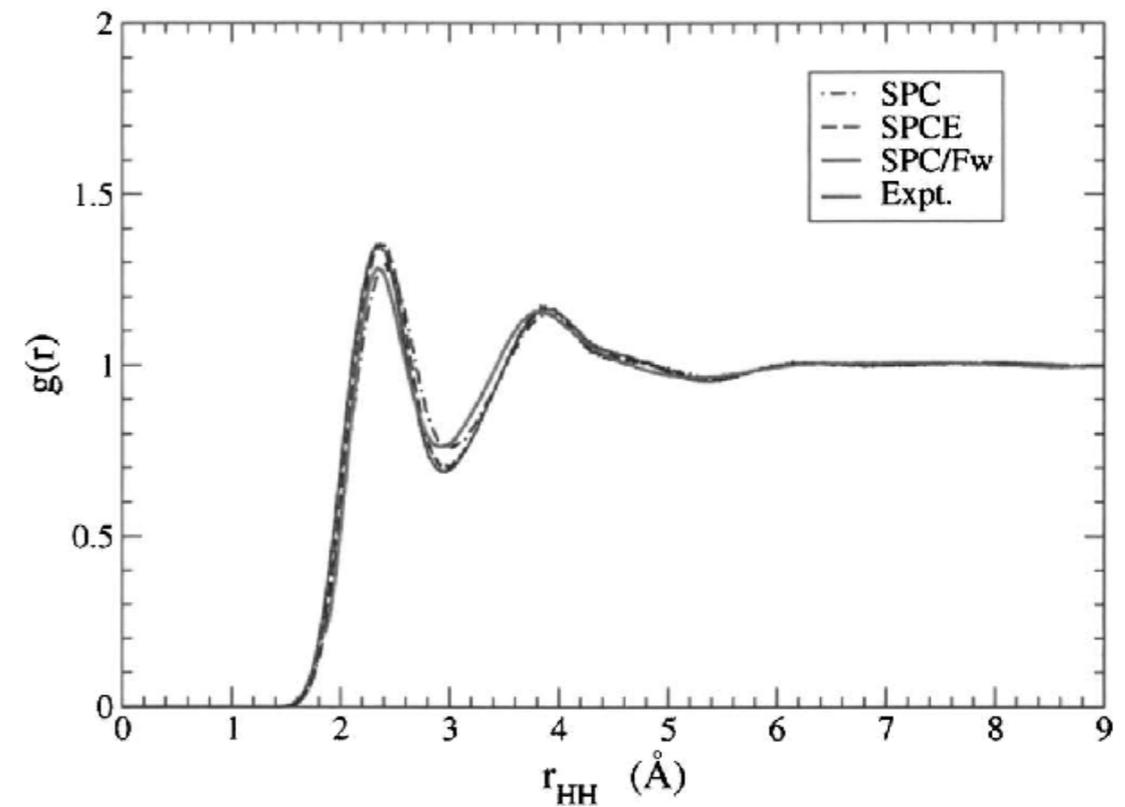
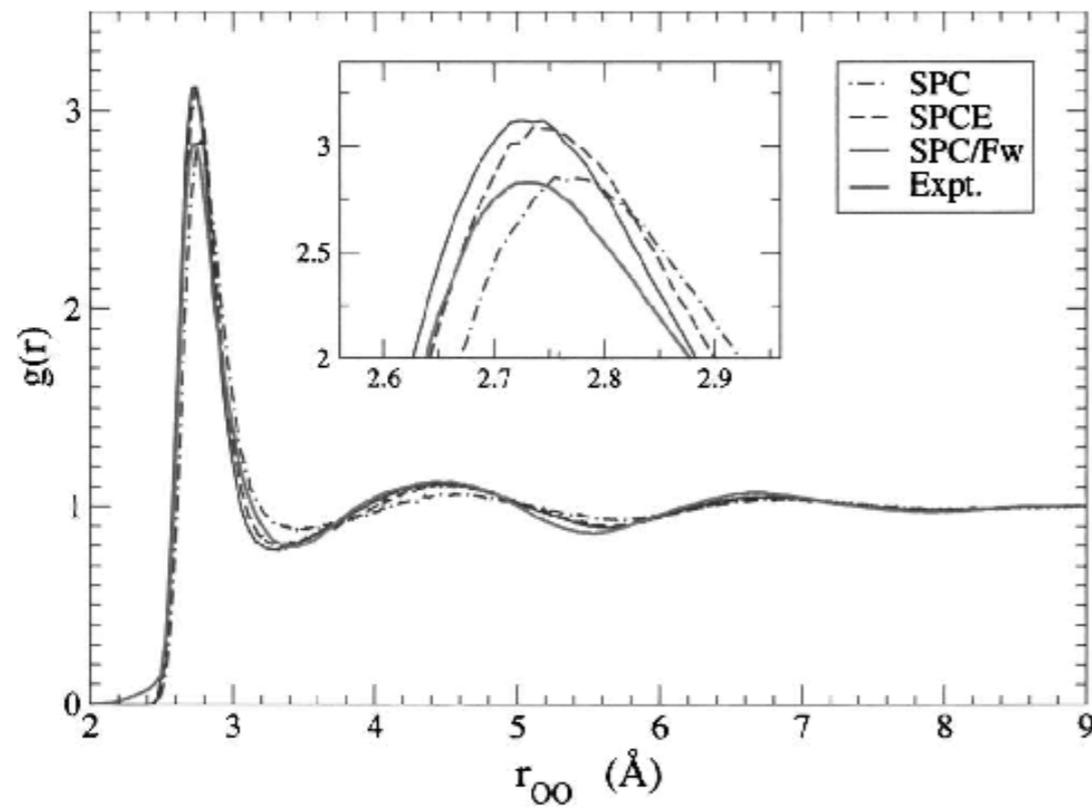
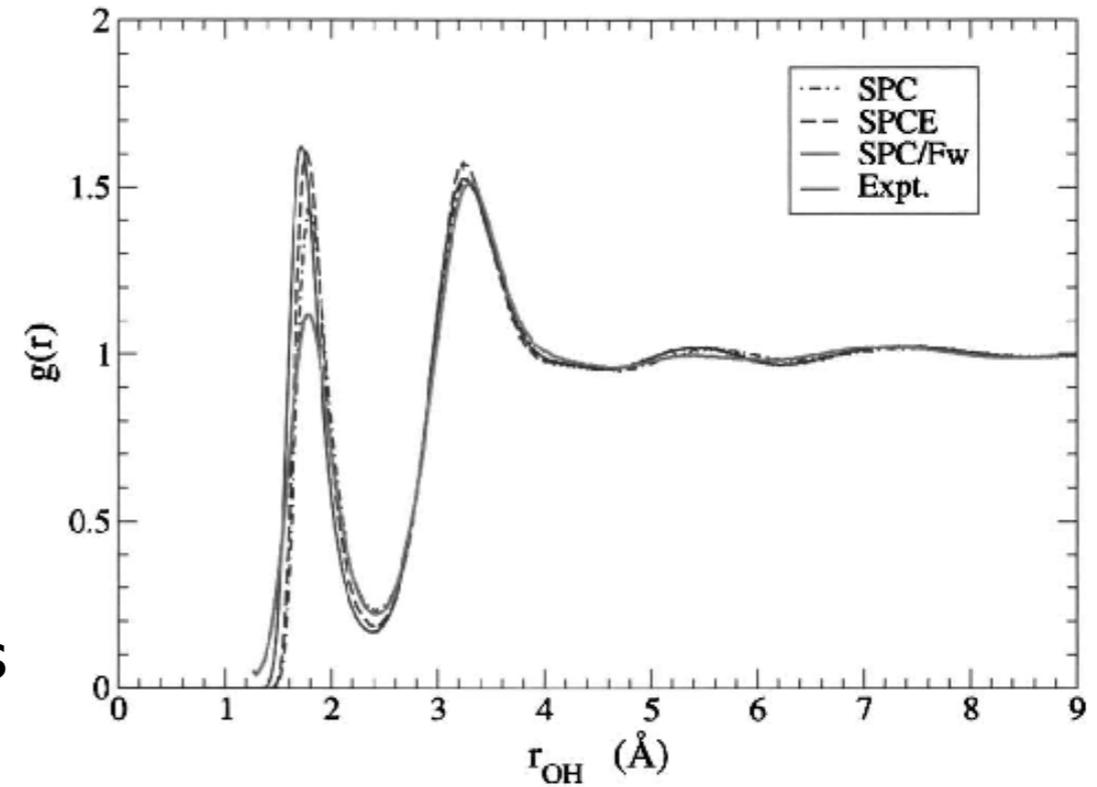


Pair correlation in water

SPC J. Chem. Phys. 124, 024503 (2006)



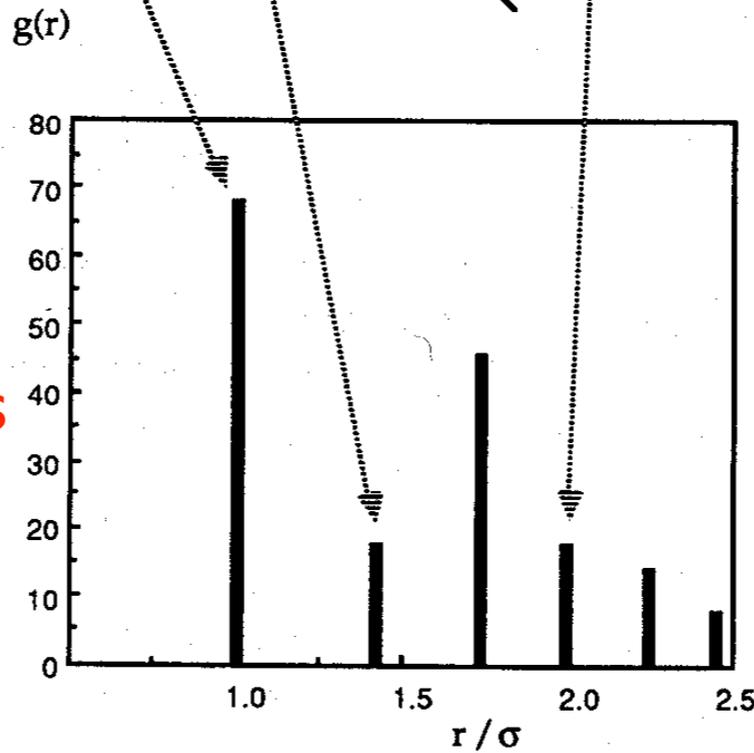
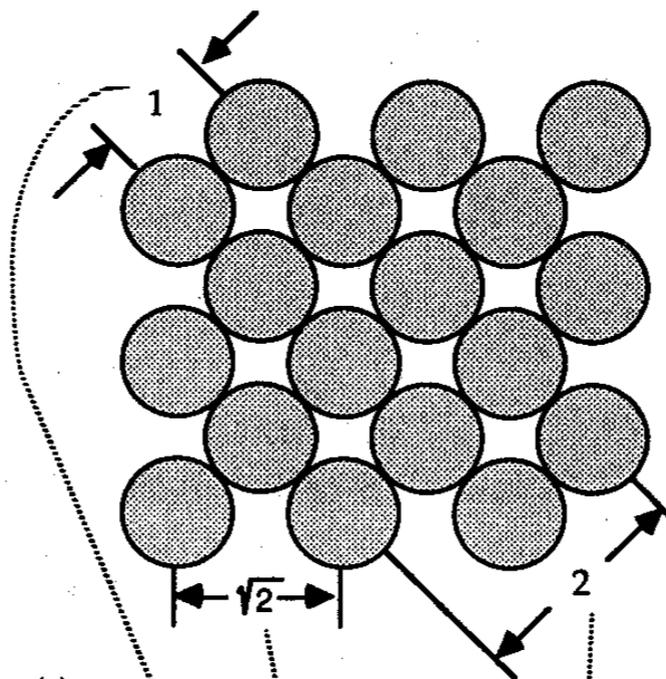
α is angle
between dipoles



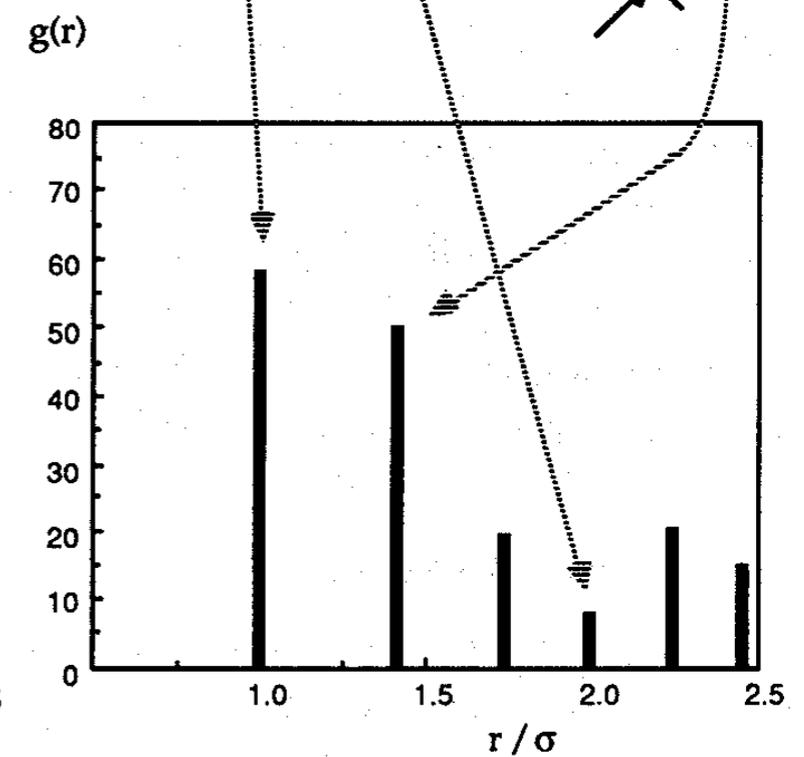
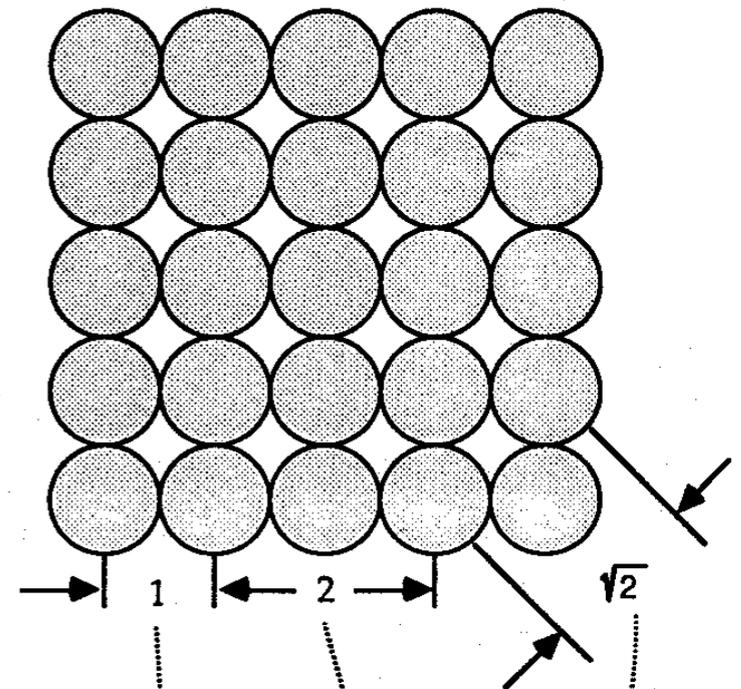
$g(r)$ for FCC and BCC lattices

1st neighbor
 2nd neighbor
 3rd neighbor
 distances are arranged
 in increasing distances.

(a) face-centered cubic lattice



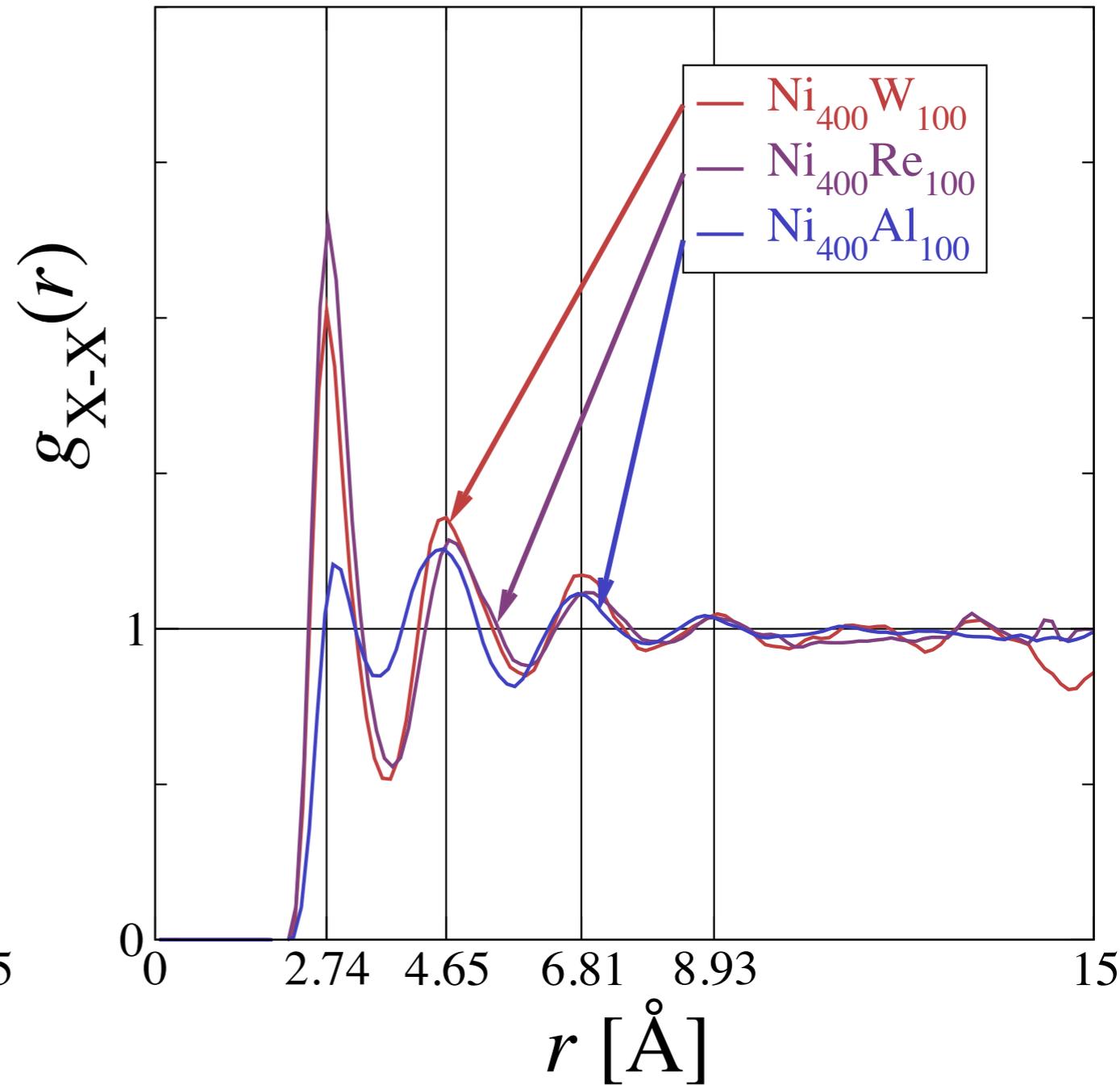
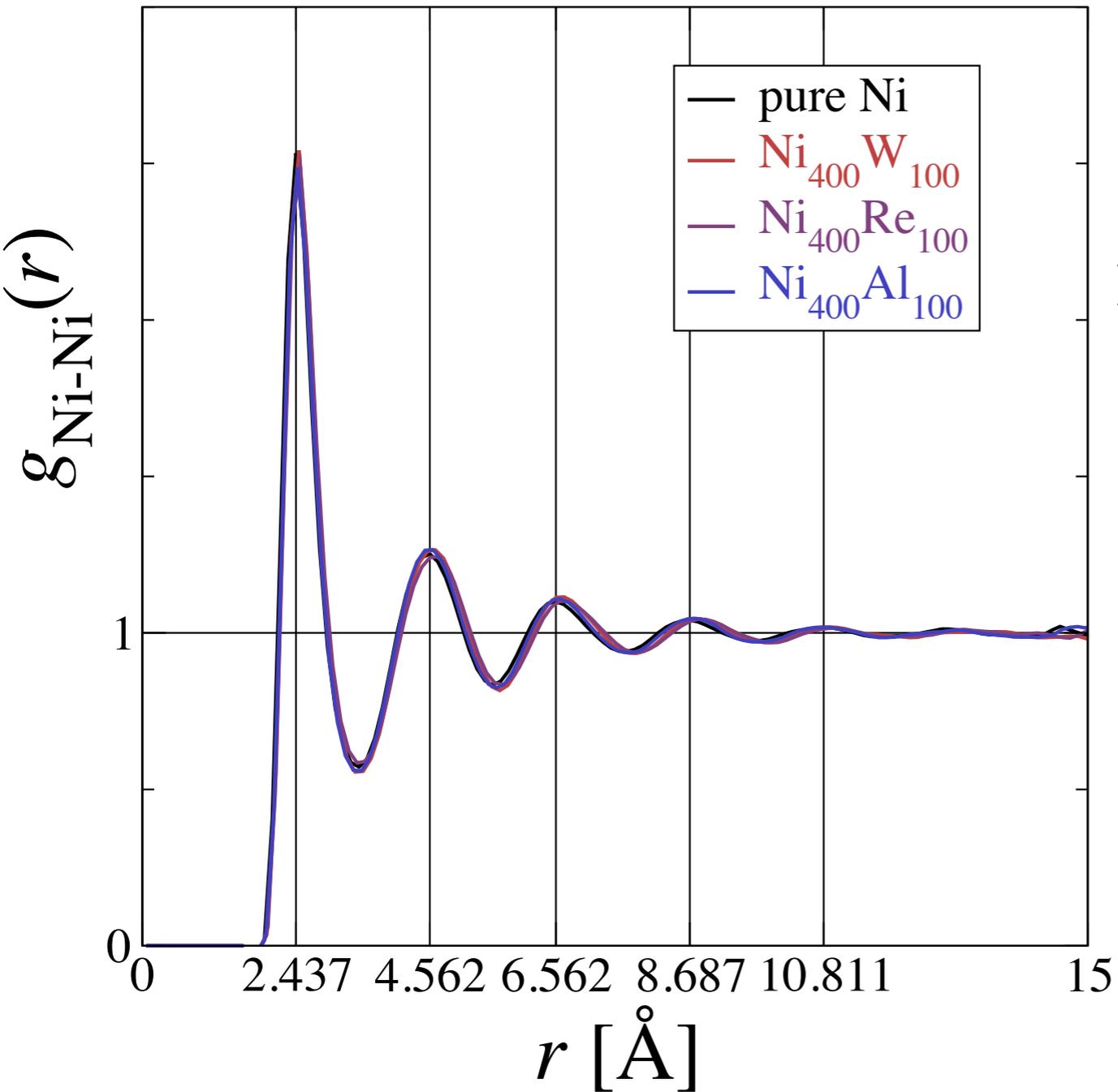
(b) simple cubic lattice



J. Haile, MD simulations

What happens at finite T?
 What happens when potentials
 are not hard spheres?

$g(r)$ for chemical short-range ordering



The (Static) Structure Factor $S(k)$

- The Fourier transform of $g(r)$ is the static structure factor:

$$S(k) = \left\langle |\rho_k|^2 \right\rangle / N$$
$$= 1 + \rho \int dr e^{ik \cdot r} [g(r) - 1]$$

- Problems with integral:
 - Need to extend $g(r)$ to infinity
 - Need to calculate at 3D $g(r)$.

Why is $S(k)$ important? $S(k)$ can:

- Be measured in neutron and X-ray scattering experiments.
- Provide a direct test of the assumed potential.
- Used to see the state of a system:
 - liquid, solid, glass, gas? (much better than $g(r)$)
- Order parameter in solid is ρ_G where G is a particular wavevector.

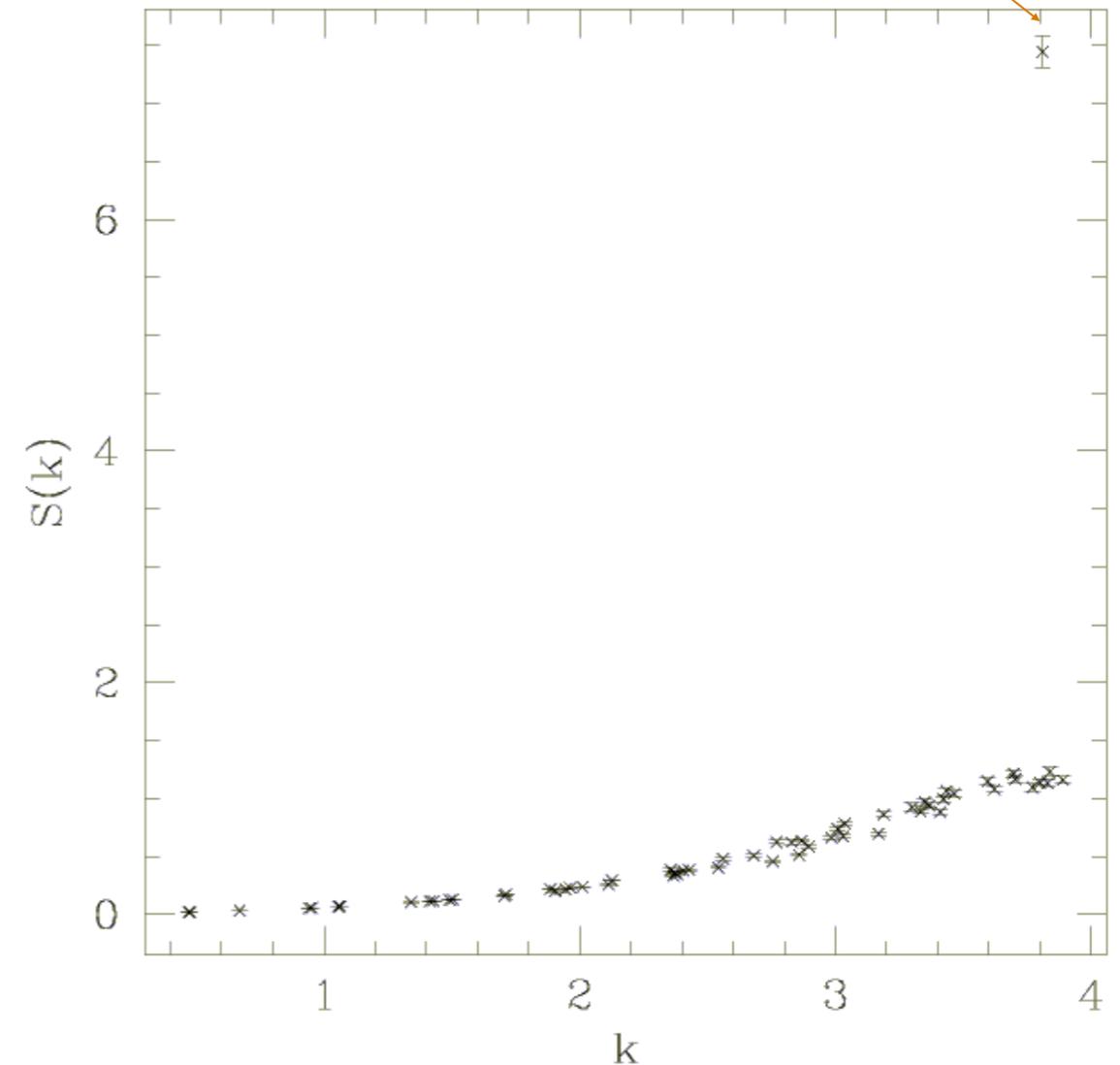
$S(k)$ is measured in x-ray and neutron scattering

Bragg peak

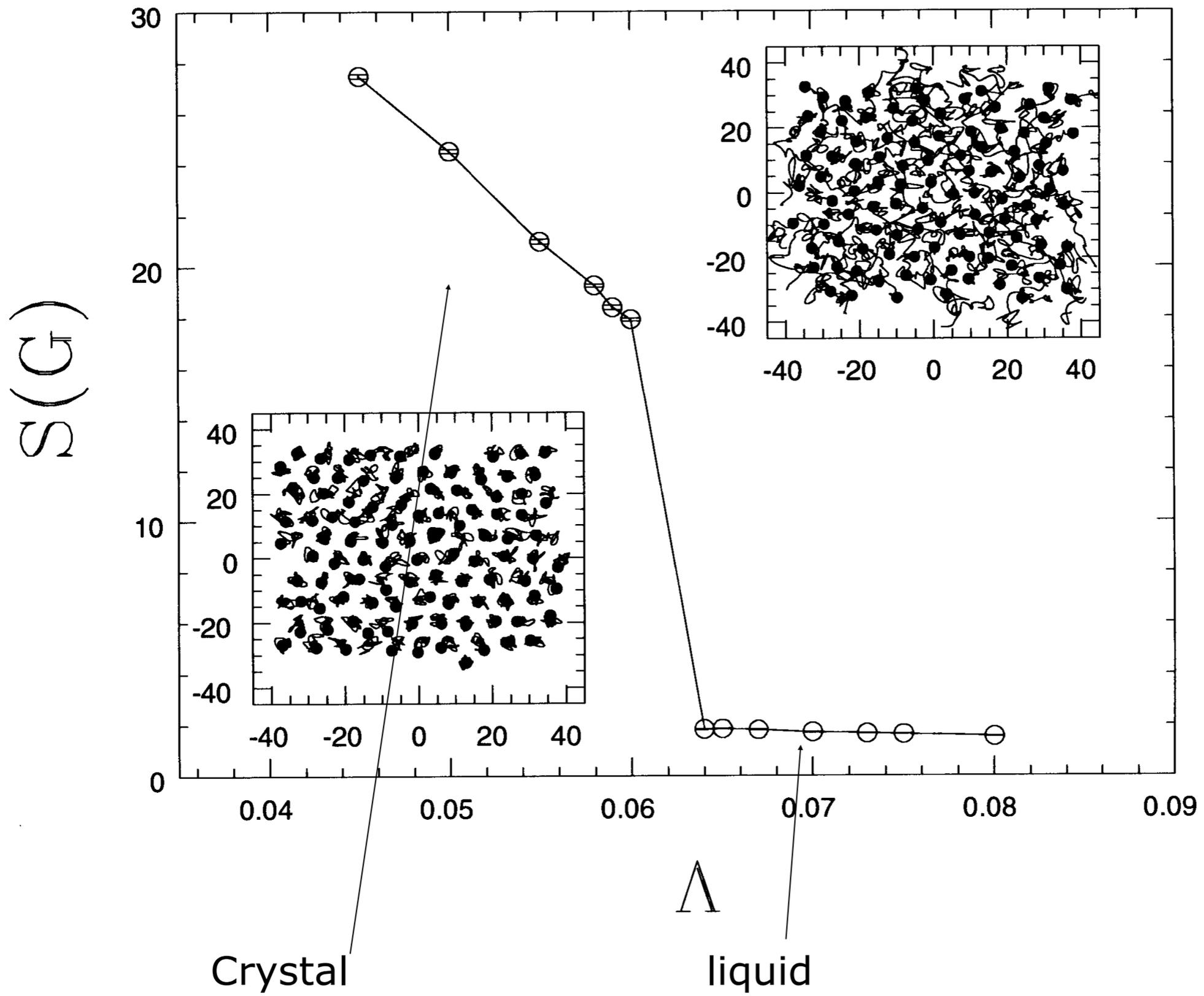
- In a perfect lattice, $S(k)$ is non-zero only at reciprocal lattice vectors G : $S(G) = N$
- At non-zero temperature (or for quantum systems) this structure factor is reduced by the Debye-Waller factor

$$S(G) = 1 + (N - 1) \exp(-G^2 u^2 / 3)$$

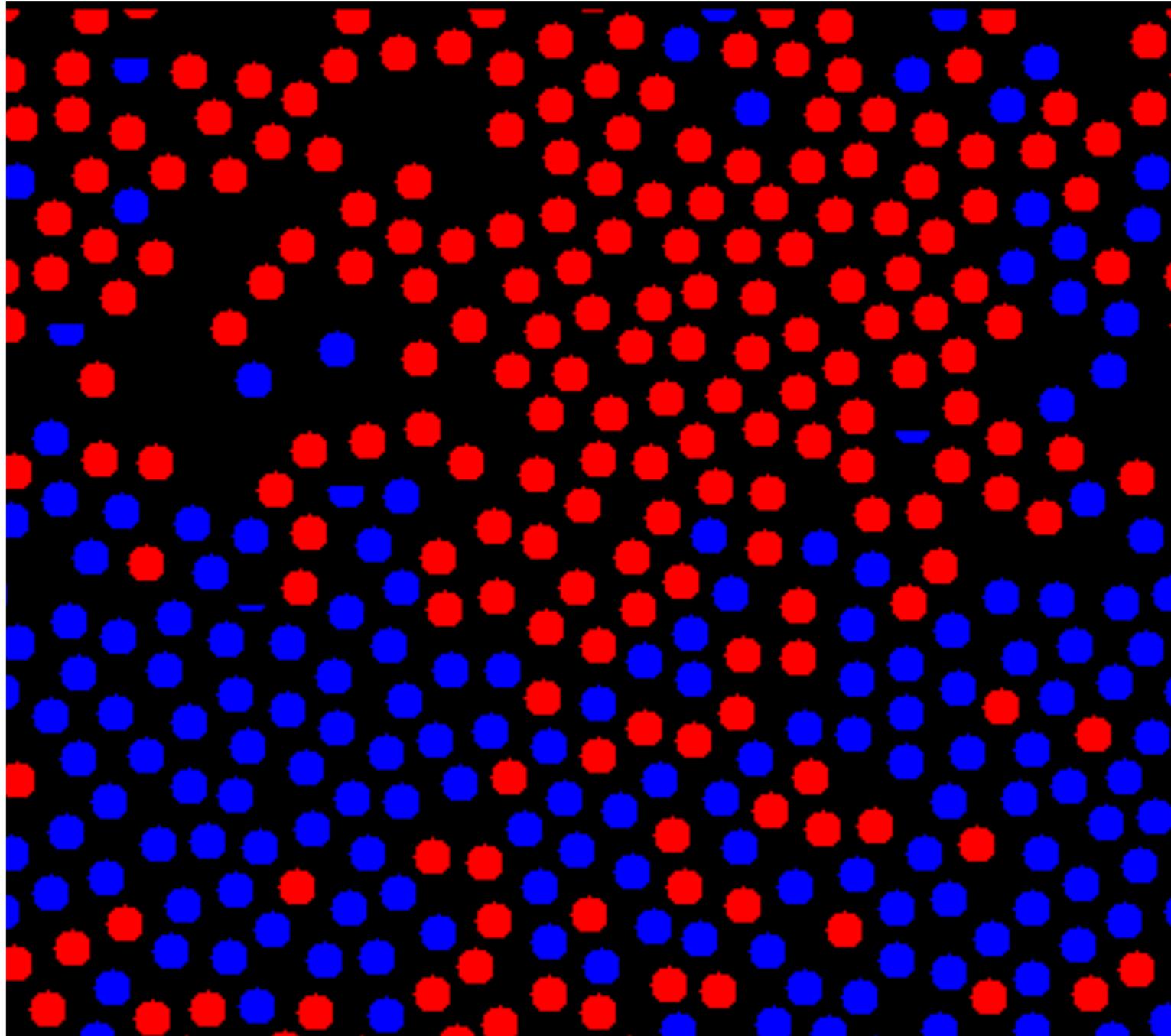
- To tell a liquid from a crystal, see how $S(G)$ scales as the system is enlarged. In a solid, $S(k)$ will have peaks that scale with the number of atoms.



- The compressibility is given by: $\chi_T = S(0)/(k_B T \rho)$
- We can use this to detect a liquid-gas transition as the compressibility should diverge as $k \rightarrow 0$. (order parameter is density)



Here is a snapshot of a binary mixture. What correlation function would be important to decide the order?



Questions to ask yourself:

What is the order parameter for a glass?

How to distinguish from a liquid?

Or from a crystal?