Scalar Properties, Static Correlations and 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 ratios with respect to the Boltzmann distribution*. We will discuss this in a few weeks.

Thermodynamic Estimators

Name	Symbol	Formula	
Kinetic Energy	$K = mdF/dm$	$\frac{1}{2}\sum_i m_i v_i^2$	$= \frac{1}{2}k_B T \times$ (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	$C_V = \frac{\partial E}{\partial T}$	$\frac{1}{(k_B T)^2}\langle (E - \langle E \rangle)^2 \rangle$	$= (3/2)N + \frac{1}{(k_B T)^2}[\langle V^2 \rangle - \langle V \rangle^2]$

Pressure: remember the virial theorem

Microscopic Density

In Real-Space:

$\rho(\mathbf{r}) = < \Sigma_i \, \delta(\mathbf{r}-\mathbf{r}_i) >$

Its Fourier transform:

$\rho_k = < \Sigma_i \exp(ikr_i) >$

This 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:

  $\mathbf{k=(2\pi/L)\ (n_x,n_y,n_z)}$ Long wavelength modes are absent.

- ***In a solid, Lindemann's ratio gives a rough idea of melting:***

  $u^2= <(r_i-z_i)^2>/d^2$ z_i=perfect lattice sites

When deviations about lattice are greater than ~15%, the solid has melted.

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 at 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***.

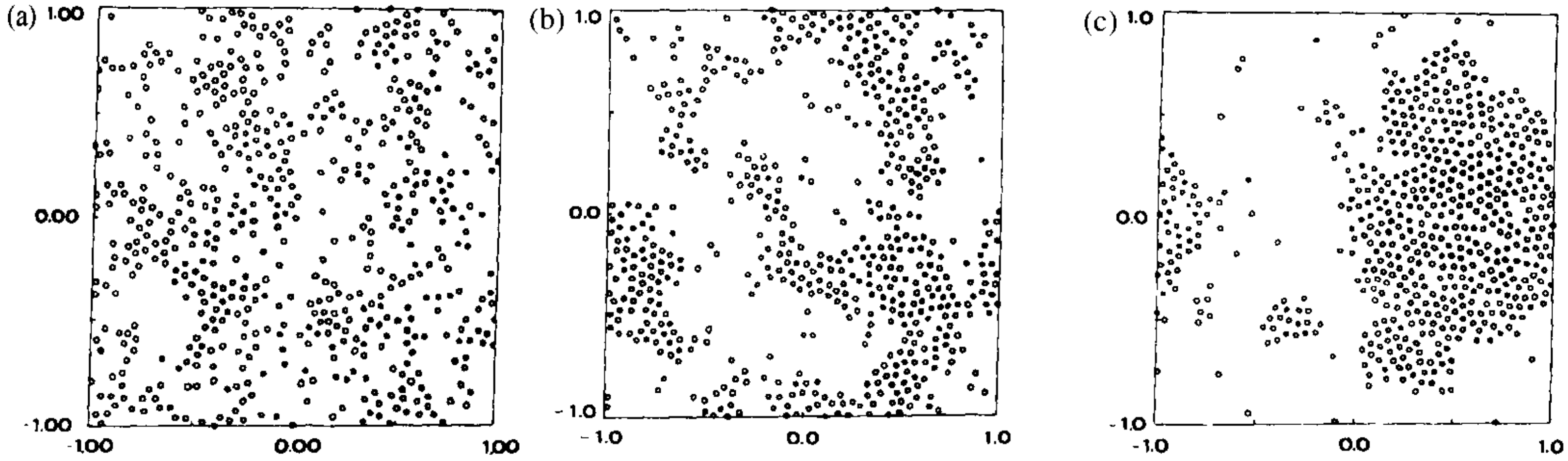


Fig. 6.1 Snapshots of 576 particles at a density $\rho^* = 0.3$ for $T^* =$ (a) 0.7, (b) 0.5, and (c) 0.45. Here ρ^*, T^* are density and temperature in reduced units, i.e. the Lennard-Jones parameters σ and ε/k_B are used as units of length and temperature, respectively. From Rovere *et al.* (1990).

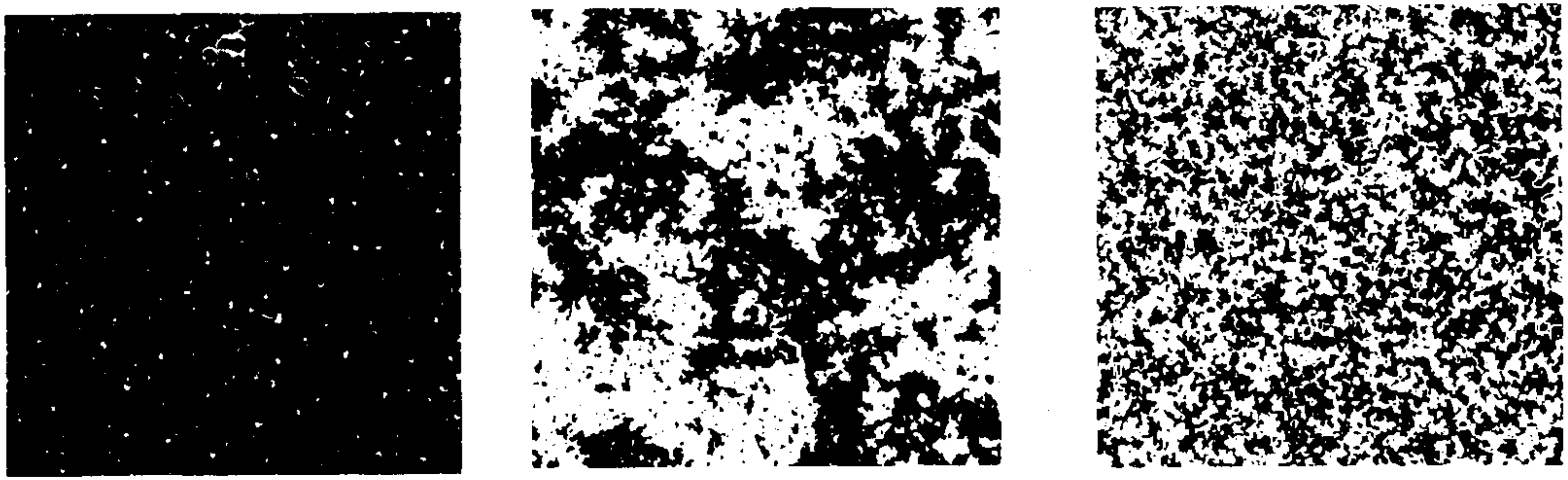
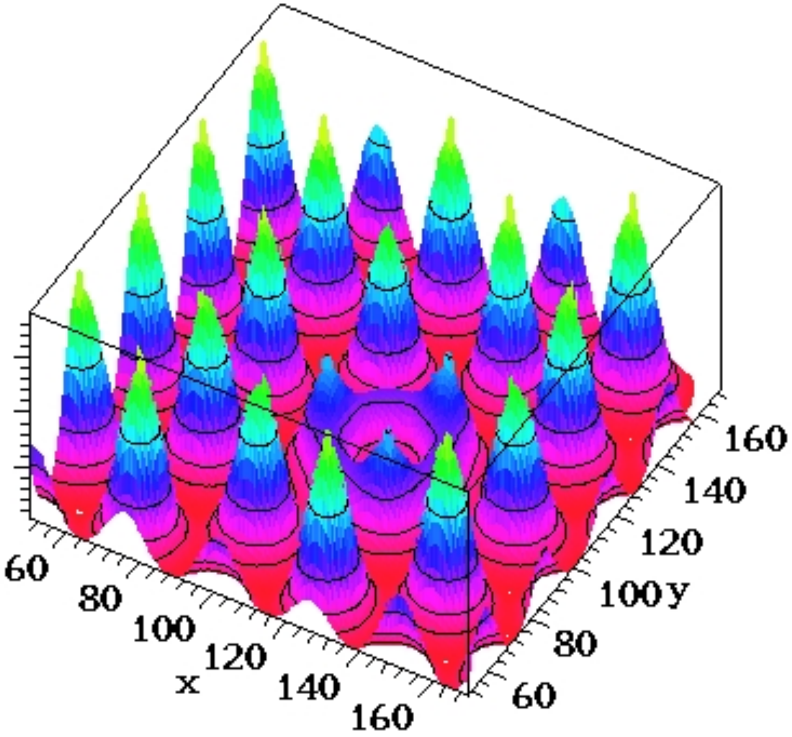
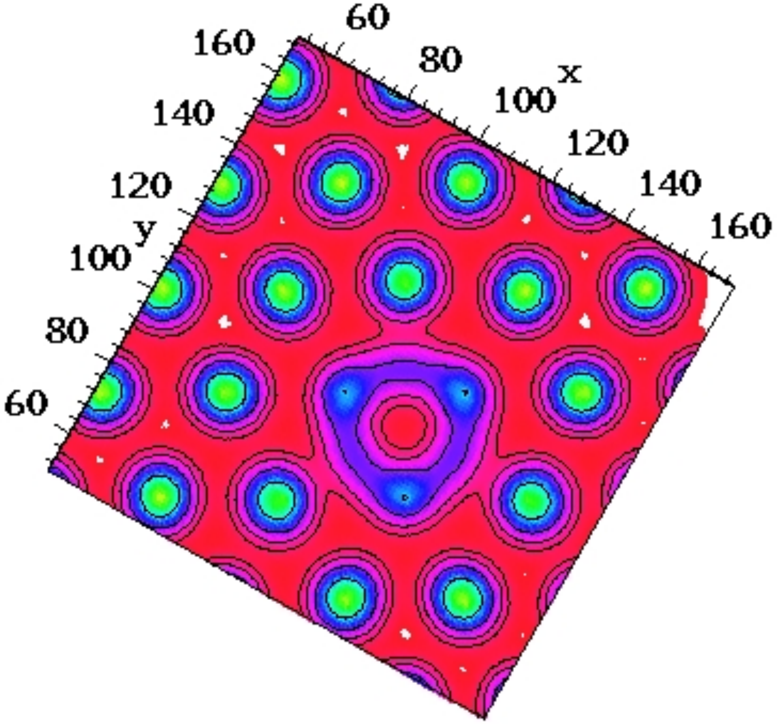


Fig. 4.1 Typical spin configurations for the two-dimensional Ising square lattice: (left) $T \ll T_c$; (center) $T \sim T_c$; (right) $T \gg T_c$.

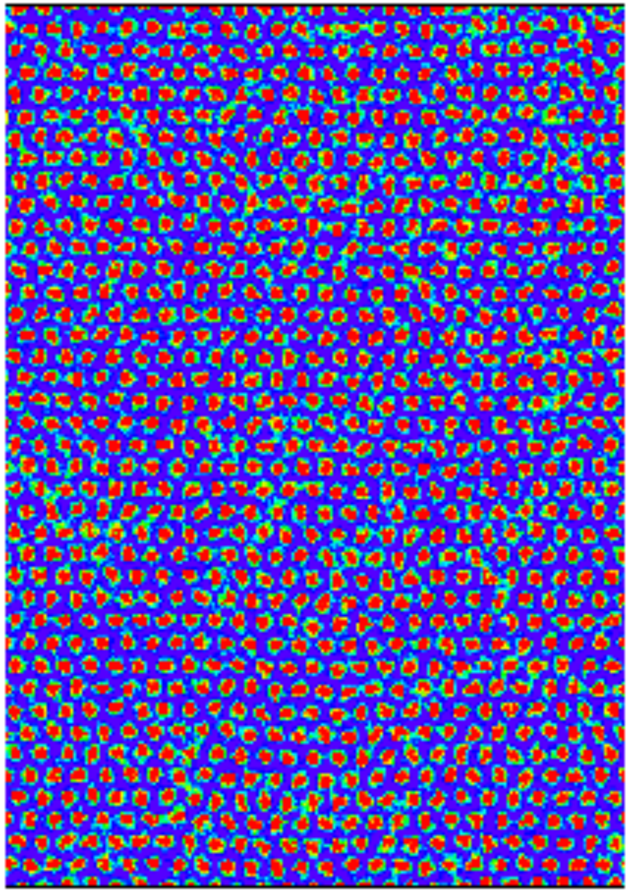
Electron Density
2d quantum electron Wigner crystal



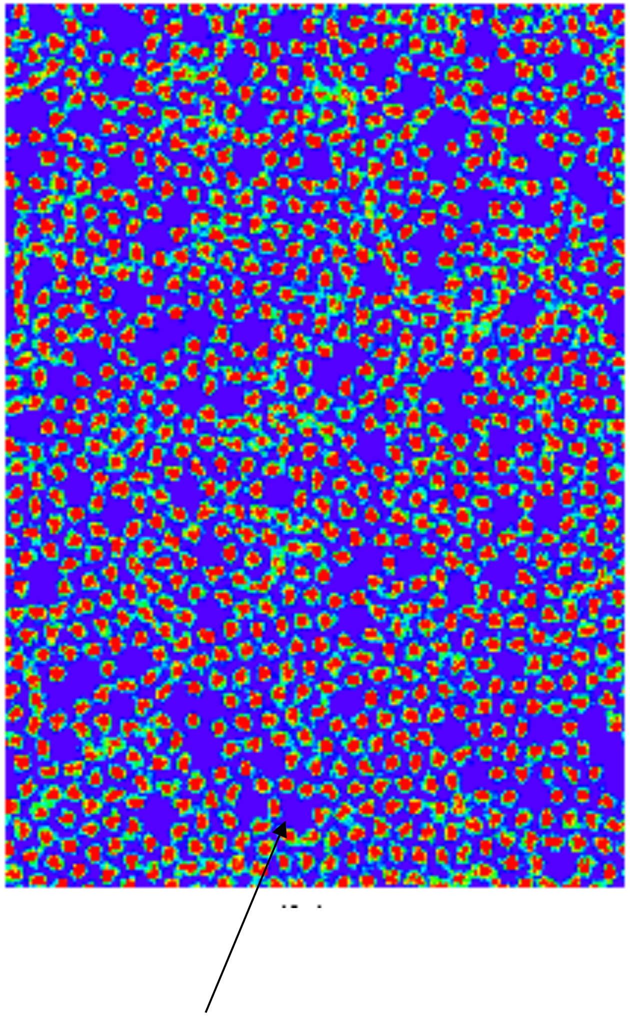


Contour levels are 0.0005,0.001,0.002,0.004,0.008

Snapshots of densities



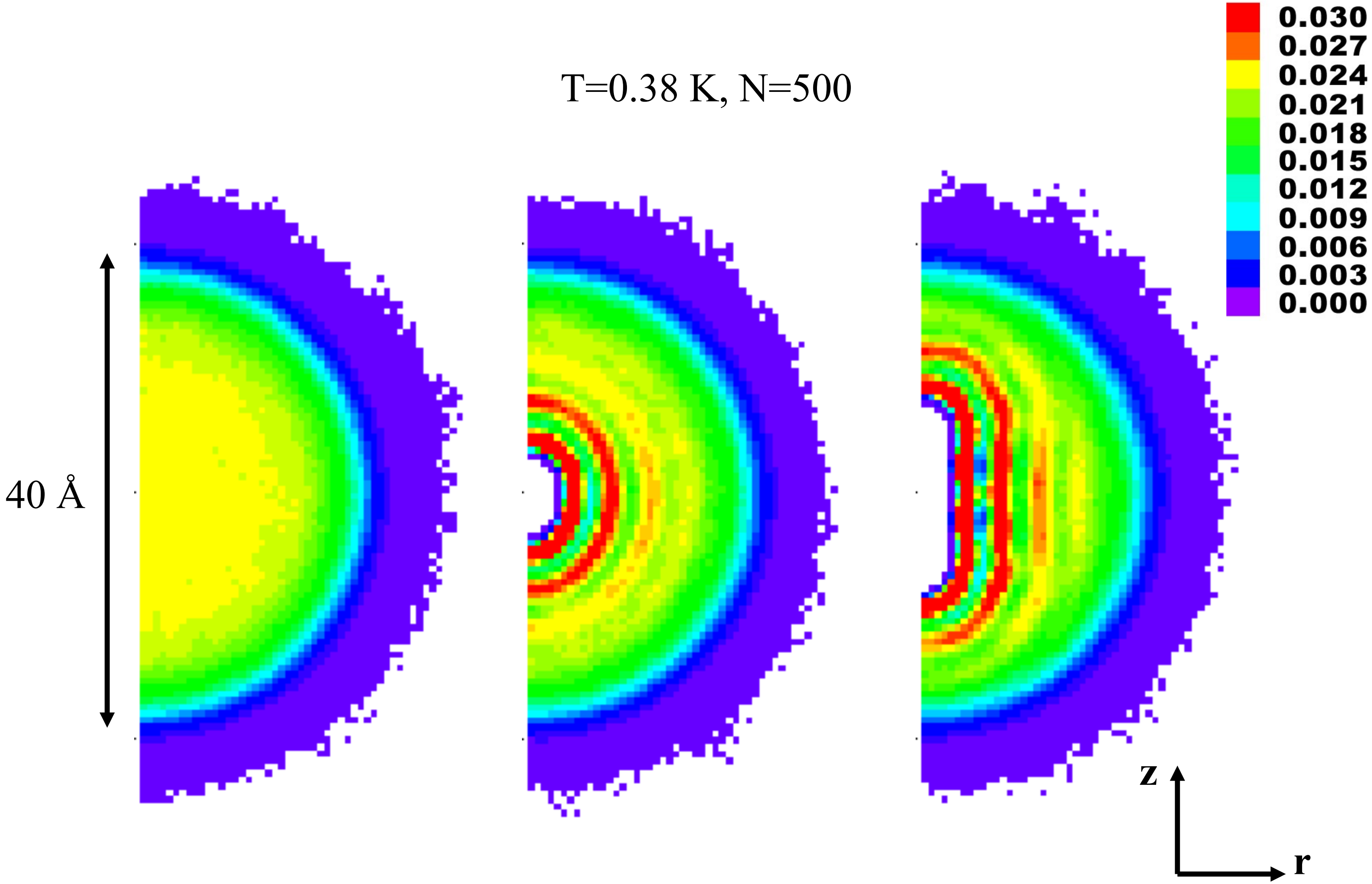
Liquid or crystal or glass?



Blue spots are defects

Density Distribution of ^{4}He+(HCN)$_x$ Droplets

T=0.38 K, N=500

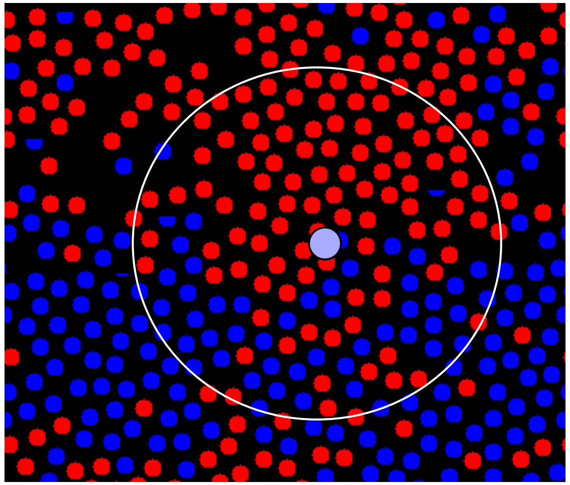


pure

1 HCN

3 HCN

Pair Correlation Function: g(r)
Radial distribution function (r.d.f.)
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?

$g(r) = < \Sigma_{i<j} \delta (r - [r_i - r_j]) > (2\rho/N^2)$

- In practice, the delta-function is replaced by *binning*: one makes 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!

Algorithm for g(r)

```
! Loop over all pairs of atoms.
     do i=2,natoms
       do j=1,i-1
!Compute distance between i and j.
         r2 = 0
    do k=1,ndim
           dx(k) = r(k,i) - r(k,j)
!Periodic boundary conditions.
         if(dx(k).gt. ell2(k)) dx(k) = dx(k)-ell(k)
         if(dx(k).lt.-ell2(k)) dx(k) = dx(k)+ell(k)
           r2 = r2 + dx(k)*dx(k)
         enddo
!Only compute for pairs inside radial cutoff.
         if(r2.lt.rcut2) then
          index=sqrt(r2)*dr_inverse
          g(index)=g(index)+1
            endif
       enddo
     enddo
```

All of this is the same.
Do g(r) while F is calculated!

How do we choose dr_inverse?

New code

Also need to normalize and output at the end of a block.

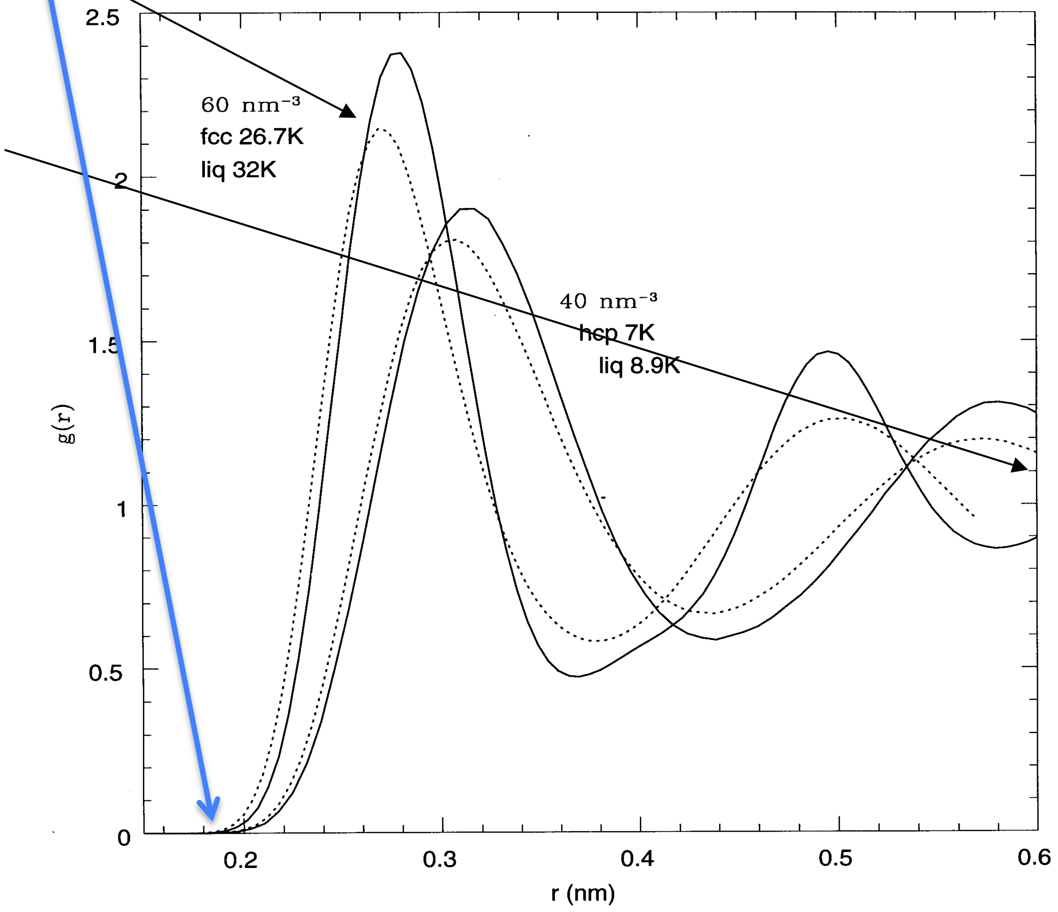
Example: g(r) in liquid and solid helium

- ***Exclusion hole around the origin***
- ***First peak*** is at inter-particle spacing. (shell around the particle)

- **Only can go out to r < L/2**

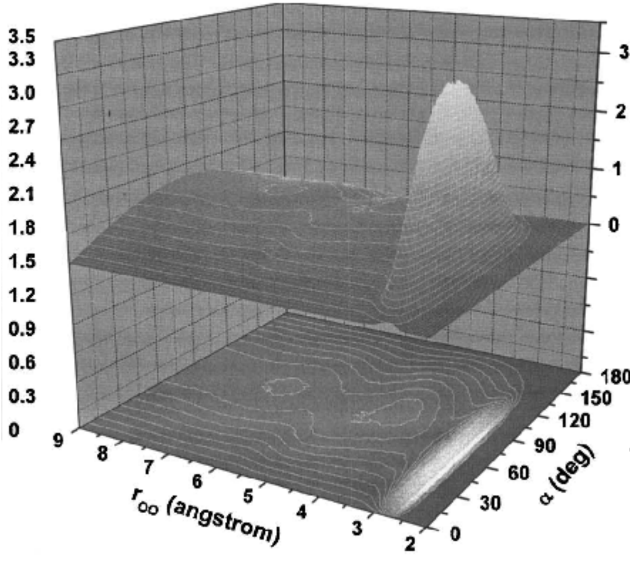
in periodic boundary conditions without bringing in images.

- Crystal shows up as shoulders

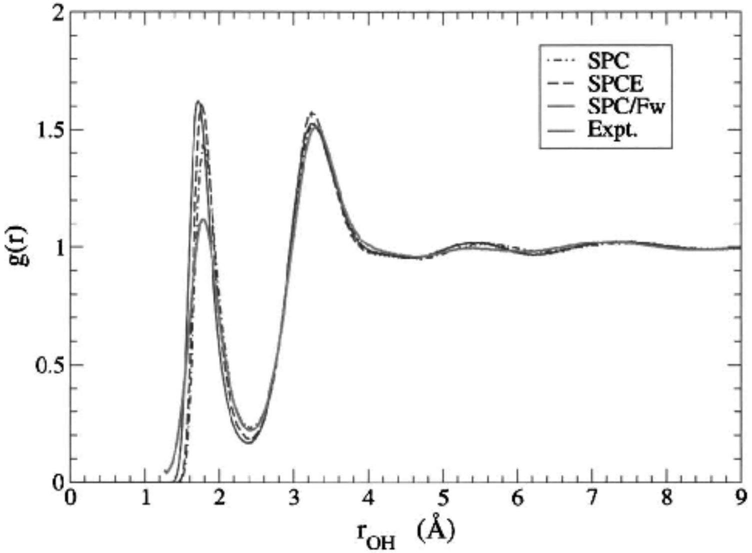


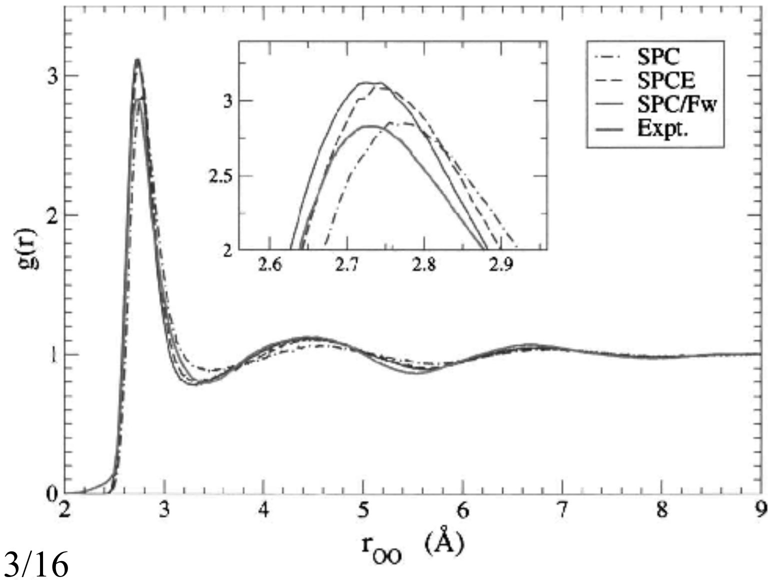
Pair correlation in water

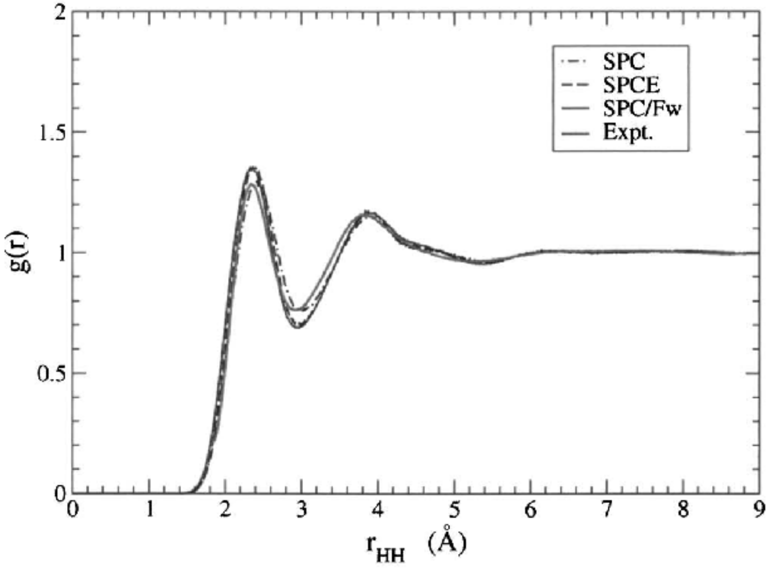
SPC J. Chem. Phys. **124**, 024503 (2006)



α is angle between dipoles



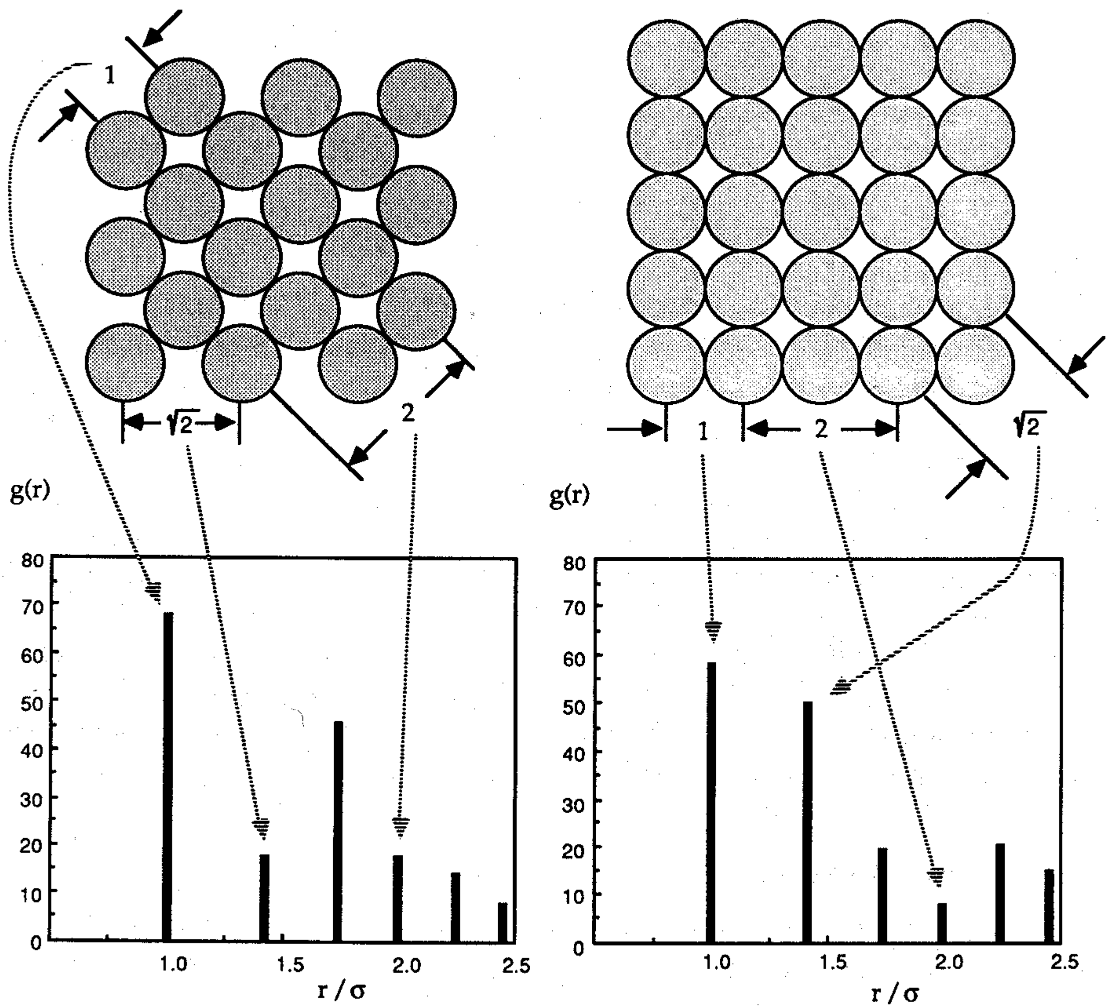




g(r) for fcc and bcc lattices

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

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

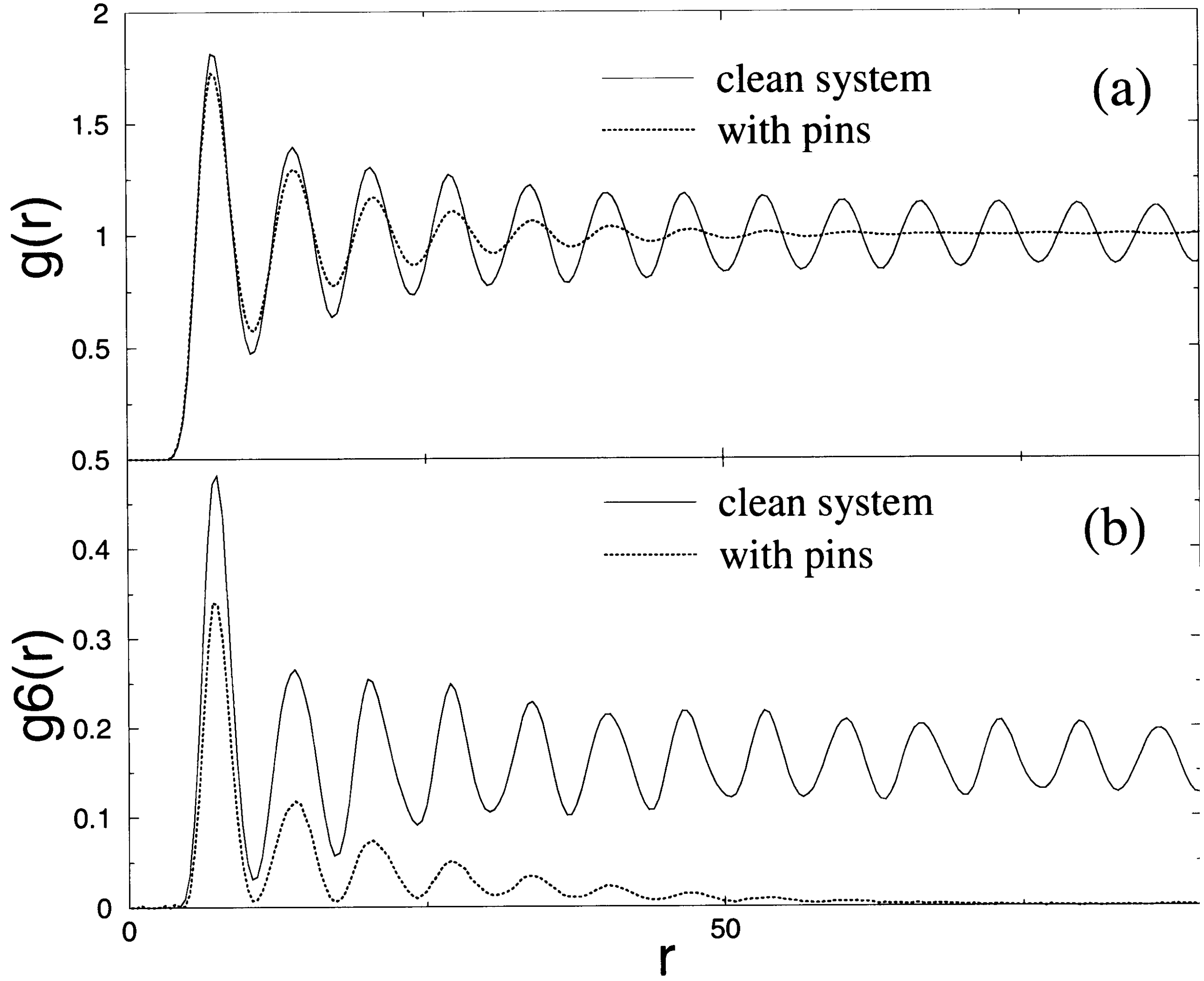


(a) face-centered cubic lattice

(b) simple cubic lattice

J. Haile, MD simulations

2D vortex lattice



The (Static) Structure Factor: S(k)

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

$$S(\mathbf{k}) = \begin{cases} \dfrac{1}{N}\left\langle \left|\rho_{\mathbf{k}}\right|^2 \right\rangle \quad \text{where} \quad \rho_{\mathbf{k}} = \sum_{i=1}^{N} e^{i\mathbf{k}\mathbf{r}_i} \\ 1 + \rho \int_{\Omega} d\mathbf{r} e^{i\mathbf{k}\mathbf{r}} \left[g(\mathbf{r}) - 1 \right] \qquad (*) \end{cases}$$

- Problems with (*): Need to ***extend g(r) to infinity and calculate 3D g(r).***

Why is S(k) important?

- Measured in neutron and X-ray scattering experiments.
- Provide a direct test of the assumed potential.
- Use to see the state of a system **(much more precise than g(r))**

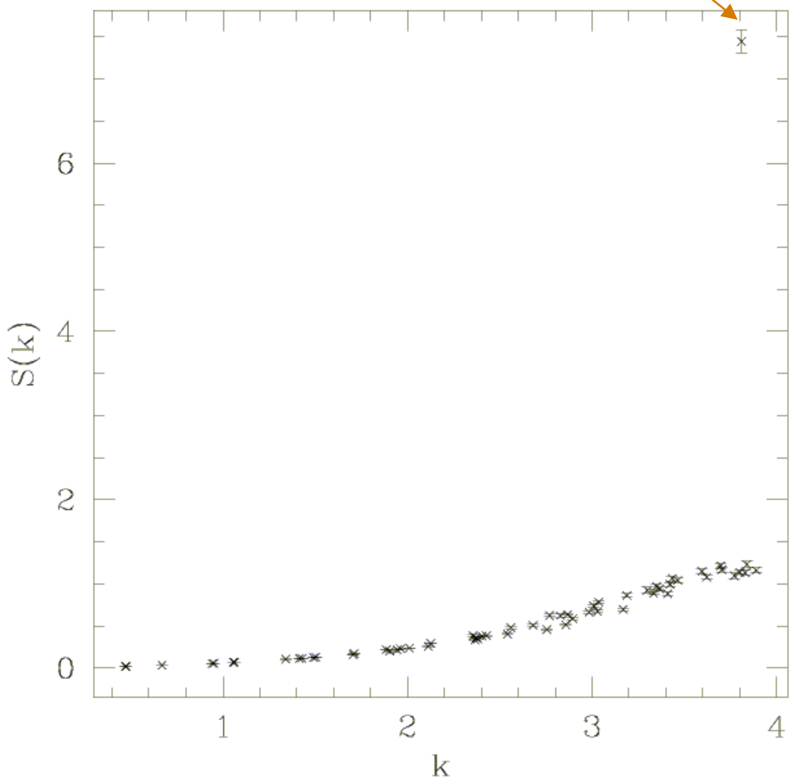
  Is it a liquid, solid, glass, gas ?
- Order parameter in a solid is ρ_G where G is a particular wavevector.

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

- 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*

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

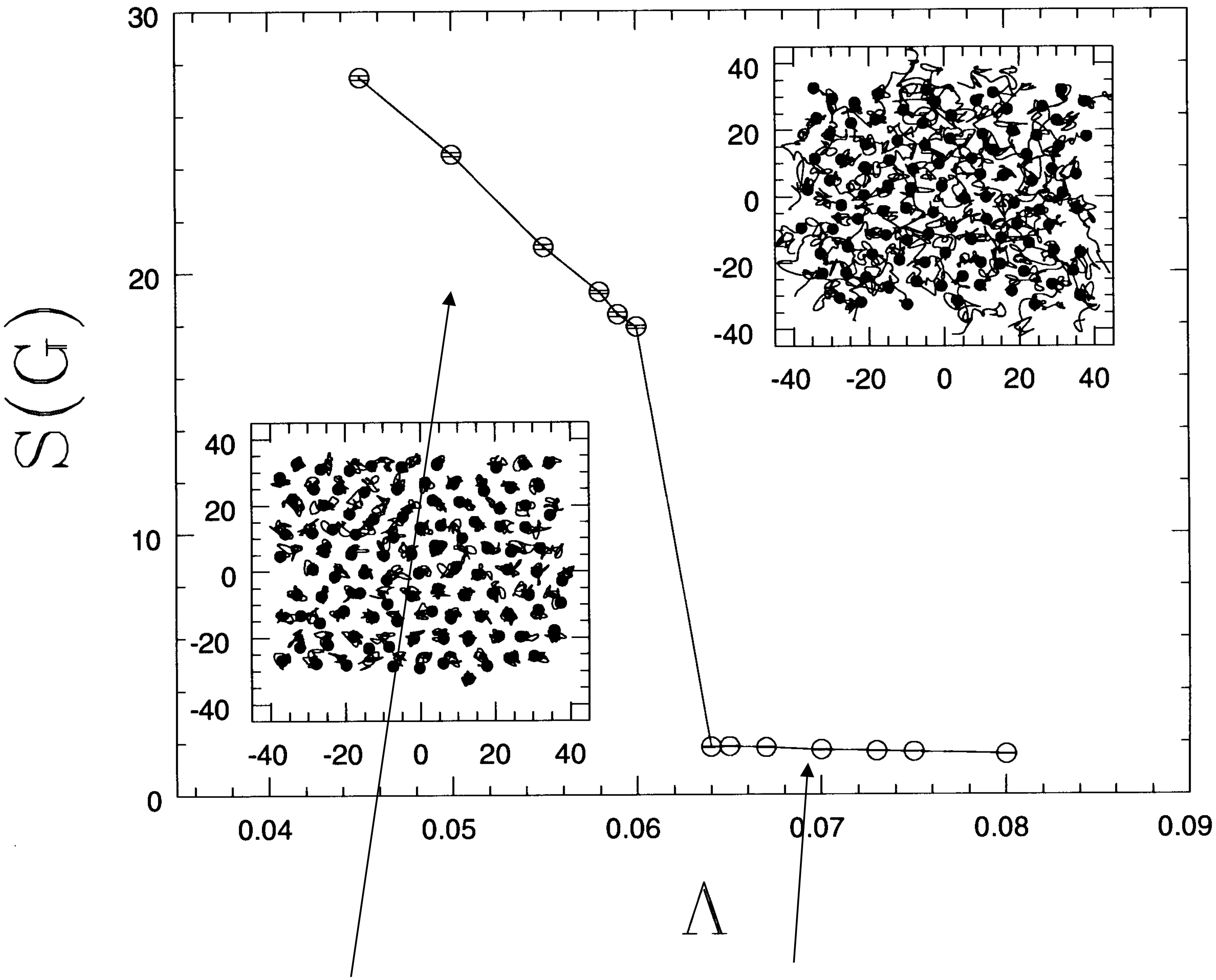
- To tell a liquid from a crystal, see how S(G) scales as the system is enlarged. *In a solid, S(G) will have peaks that scale with the number of atoms*.


Bragg peak

- The compressibility is given by:

$$\chi_T = \frac{S(0)}{k_B T \rho}$$

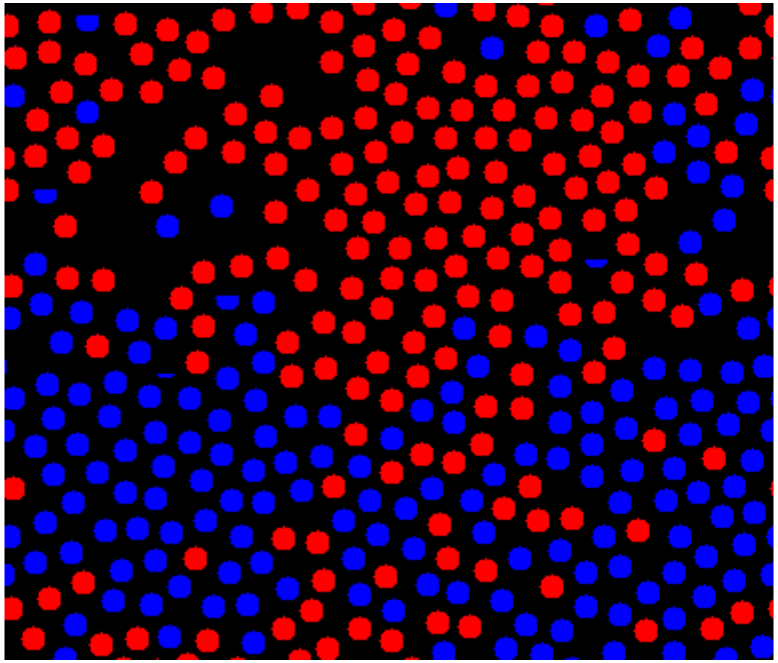
- **We can use this to detect a liquid-gas transition: the compressibility should diverge as k → 0**



Crystal

liquid

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



What is the order parameter for a glass?

How to distinguish it from a liquid or from a crystal?

Next time: dynamical correlations

Homework due on Thursday.