

## Lesson 3: From structure factors to interatomic potential

- ✓ Summary on general properties of  $S(k)$  and  $g(r)$
- ✓ Basic Elements of theory of structure. Total energy and state equation calculation
- ✓ Hierarchy of equations, definition of potential of mean force
- ✓ Structure factors, equation of state and phase transitions in special cases
- ❖ Perfect gas: classical and quantum regime
  - ❖ “real gas” vs Lennard Jones systems
  - ❖ Hard spheres
  - ❖ Towards the long range
  - ❖ Hints on charged systems

# Structure of liquids – module of the course “structure of matter”

## Elastic scattering in a nutshell

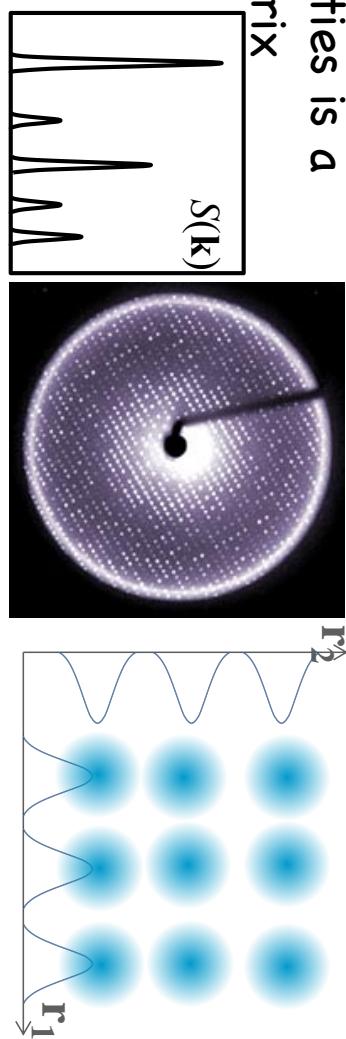
**General formula for elastic scattering**

$$\frac{I(\mathbf{k})}{nf^2} - N\delta_{0,\mathbf{k}} = S(\mathbf{k}) = 1 + \frac{1}{N} \int \rho_2(\mathbf{r}, \mathbf{r}') e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} d\mathbf{r} d\mathbf{r}' - N\delta_{0,\mathbf{k}}$$

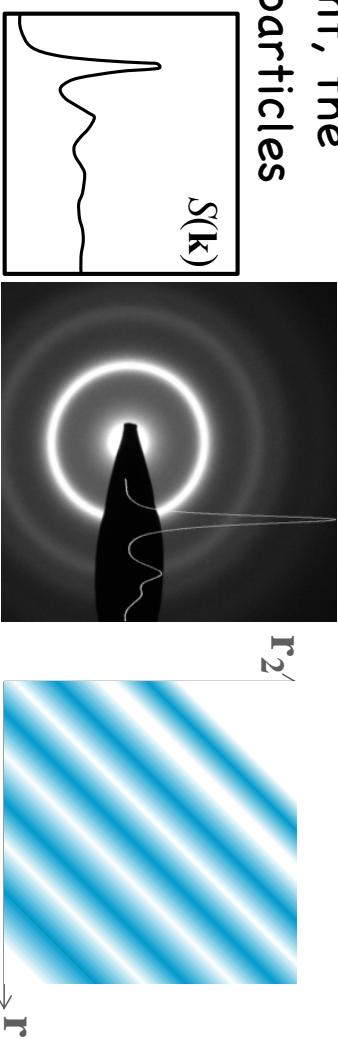
The scattering intensity is proportional to the FT of the 2 particles density

**Crystal:** The product of single particles densities is a good approximation for the total density matrix

$$S(\mathbf{k}) \approx \frac{1}{N} \int \rho(\mathbf{r}') \rho(\mathbf{r}) e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} d\mathbf{r} d\mathbf{r}'$$



**Liquid:** The single particle density is a constant, the pair distribution function dominates the two particles density



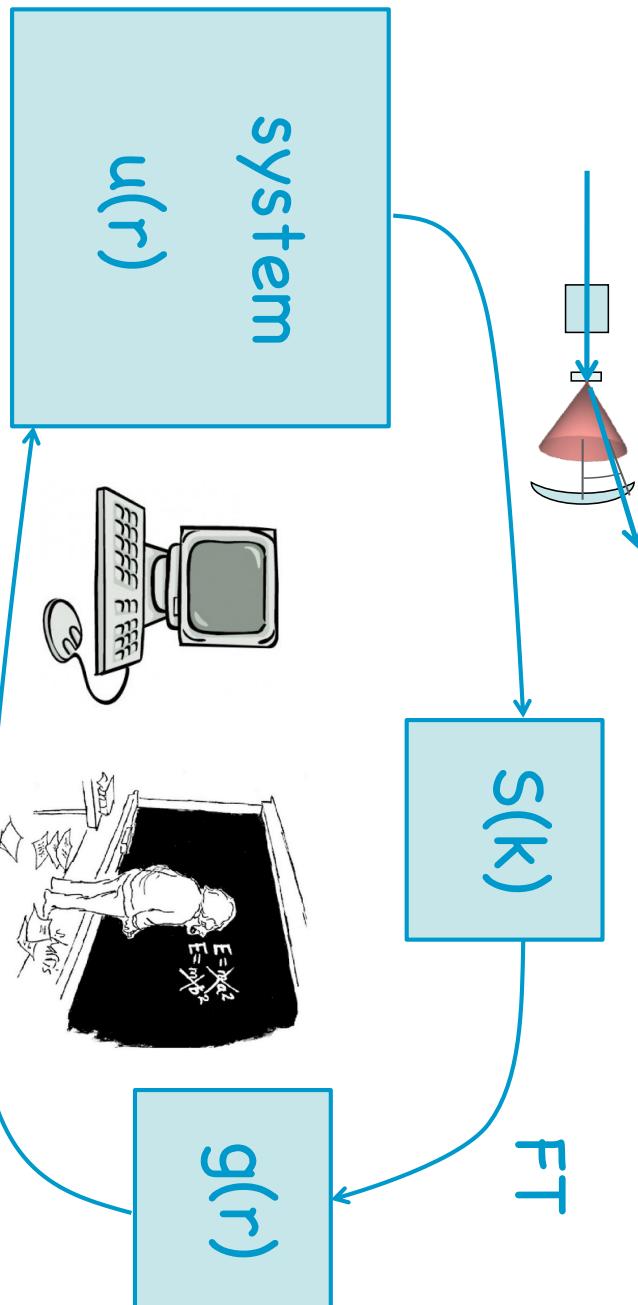
$$S(\mathbf{k}) = 1 + \frac{1}{N} \rho^2 \int [g(|\mathbf{r} - \mathbf{r}'|) - 1] e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} d\mathbf{r} d\mathbf{r}'$$

$$\rho(\mathbf{r}) = \left\langle \sum_i \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle \quad \text{single particle density}$$

$$\rho_2(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i,j} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') \right\rangle \quad \text{2-particles density}$$

# Structure of liquids – module of the course “**structure of matter**”

Now we know how to measure the fluid structure through elastic scattering  $S(k)$ ...  
... and how to relate it to the 2-particles probabilities and distribution function  $g(r)$   
... But a fundamental connection is missing. How is  $g(r)$  related to the interparticle potential  $u(r)$ ?



**Theory:** the  $u(r) \leftrightarrow g(r)$  relation is evaluated by means of many body theories, and analytical or numerical calculations. This approach has a small or null computational cost, but often requires approximations to handle many body interactions

**Computer simulations:** an set of particles is simulated with a user defined  $u(r)$  and the resulting  $g(r)$  is evaluated after sufficiently long runs. Similar to an experiment, but with  $u(r)$  is an input and therefore known. The  $g(r) \leftrightarrow u(r)$  dependency can be analyzed varying at will  $u(r)$ . This approach is limited only by the actual computer power, and gives insight only upon data analysis and elaboration

# Structure of liquids – module of the course “structure of matter”

$S(q)$  and  $g(r)$  are uniquely related. What about  $g$  and the inter atomic potential  $u$ ? Are them uniquely related?

$$S(q) = 1 + \rho \int [g(r) - 1] e^{-iqr} dr$$

Let's have a system of particles interacting with a two body potential  $u(r) = u(|\mathbf{r}_1 - \mathbf{r}_2|)$ . Obviously  $u$  uniquely determines  $g$ .

But is the opposite true? Does any pair distribution function  $g$  corresponds to a unique pair potential  $u$ ?

The answer is yes:  $u(r)$  and  $g(r)$  are in one-to-one correspondence in the following conditions

- ✓ At thermodynamic equilibrium
- ✓ If in the system rigorously only two-particle forces act
- ✓ Of course two potentials differing by a constant give the same  $g(r)$

The proof proceeds quite straightforwardly using the minimum principle for free energies with respect to probability distributions (similar to that of the one-to-one correspondence of  $n(r)$  to  $u(r)$  in DFT)

The existence of  $u(r)$  for any  $g(r)$  is not guarantee, however direct numerical inversion procedures exist, which converge to the  $u(r)$  when conditions are satisfied

# Structure of liquids – module of the course “structure of matter”

## Connection between structure and interactions: internal energy

- ✓ We consider now a simple monoatomic fluid with only pair-potentials interactions

- ✓ The average value of the total potential energy is

$$\langle U \rangle = \frac{1}{Z} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \sum_{i < j} u(r_{ij}) \exp(-\sum_{i < j} u(r_{ij}) / kT)$$

The integral is decomposed  $N(N-1)/2$  identical terms. The part depending on the couples involved in  $u(\mathbf{r}-\mathbf{r}')$  is factorized, and the remaining one would be in principle an integral over  $N-2$  coordinates

$$= \frac{N(N-1)}{2} \int d\mathbf{r} d\mathbf{r}' u(|\mathbf{r} - \mathbf{r}'|) \left[ \frac{\int d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp(-\sum_{i < j} u(r_{ij}) / kT) \delta(\mathbf{r} - \mathbf{r}_1) \delta(\mathbf{r}' - \mathbf{r}_2)}{Z} \right]$$

$$= \frac{N(N-1)}{2} \int d\mathbf{r} d\mathbf{r}' u(|\mathbf{r} - \mathbf{r}'|) g(|\mathbf{r} - \mathbf{r}'|) \rho^2 \frac{(N-2)!}{N!}$$

$$= \frac{1}{2} \rho^2 V \int u(r) g(r) 4\pi r^2 dr$$

$$\bar{\rho}_2(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i \neq j} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') \right\rangle$$

The final result could be guessed from the beginning: in a system described by a simple pair potential, the potential energy can be written in terms of the pair potential itself weighted by the pair distribution function. Therefore, the internal energy of a classical monoatomic fluid of particles interacting with a body potential is

$$E = \frac{3}{2} NkT + \frac{N}{2} \rho \int u(r) g(r) 4\pi r^2 dr$$

March&Tosi Atomic dynamics in liquids, cap 1, pag 3-4

Ideal part

# Structure of liquids – module of the course “structure of matter”

## Connection between structure and interactions: equation of state

$$E = \frac{3}{2} NkT + \frac{N}{2} \rho \int u(r) g(r) 4\pi r^2 dr \rightarrow C_V = \frac{3}{2} Nk + \frac{N}{2} \rho \int u(r) \frac{\partial g(r)}{\partial T} 4\pi r^2 dr$$

Ideal part

### Internal energy

### Specific heat

- ✓ A similar procedure applied to the virial theorem (for confined systems)  $2\langle K \rangle = -\sum_i \mathbf{F}_i \cdot \mathbf{r}_i$  leads to

Contribution of the pressure → Contribution of internal forces

$$\frac{2}{2} \frac{3}{2} NkT = \boxed{3\rho V} + \boxed{\frac{N}{2} \rho \int r \frac{\partial u(r)}{\partial r} g(r) dr}$$

Generalization of the equation of state of perfect gases

Equation of state of monoatomic simple fluids

$$\rightarrow p = \rho kT - \frac{\rho^2}{6} \int r \frac{\partial u(r)}{\partial r} g(r) dr$$

Exercises:

1. Prove that  $-\sum_i \mathbf{F}_i \cdot \mathbf{r}_i = 3\rho pV$  if only pressure forces exist. Hint: pass from the sum to the integral, assume for simplicity a gas in a sphere, and uniform pressure on the surface of the sphere (force is null except on the surface). The proof can be easily generalized to any shape surface provided the containing force is orthogonal to the surface
2. See what happens in the equation of state if  $u(r) \propto r^n$ . Hint: rewrite the virial theorem in terms of the average potential energy for polynomial force laws)

$$\lim_{k \rightarrow 0} S(k) = \rho k T K_T$$

Ornstein – Zernike relation

# Structure of liquids – module of the course “structure of matter”

Connection between structure and interactions:

**Summary: what do we know in general?**

$$E = \frac{3}{2} NkT + \frac{N}{2} \rho \int u(r) g(r) 4\pi r^2 dr \rightarrow C_V = \frac{3}{2} Nk + \frac{N}{2} \rho \int u(r) \frac{\partial g(r)}{\partial T} 4\pi r^2 dr$$

**Internal energy**

**Specific heat**

$$p = \rho kT - \frac{\rho^2}{6} \int r \frac{\partial u(r)}{\partial r} g(r) dr \quad \text{Equation of state}$$

$$\lim_{k \rightarrow 0} S(k) = \rho kT K_T$$

**Compressibility**

$$\frac{p}{\rho kT} = 1 \pm \frac{\rho \lambda^3(T)}{4\sqrt{2}(2s+1)} \quad \lambda = \sqrt{\frac{h^2}{3mKT}}$$

Ideal quantum gases, first order correction to the perfect gas

The pressure increases for fermions, decrease for bosons

- ✓ Everything is function of  $g(r)$  (or  $S(k)$ ) AND  $u(r)$
- ✓ We also know that the relationship  $u(r) \rightleftharpoons g(r)$  is unique

- ✓  $S(k)/g(r)$  can be derived from the corresponding  $u(r)$  by means of **computer simulations**: a system of  $N$  particles interacting with the user-defined  $u(r)$  is put in a simulation box in given conditions, a simulation is run to thermalize the system and  $g(r)/S(k)$  are numerically evaluated. This is a **numerical experiment**, with the advantage that the user can decide any kind of potential (which is not allowed in reality) and the disadvantage that the computation cost limits the size of the system and brings numerical uncertainty

- ✓ Finding the  $g(r)-u(r)$  relation “analytically” can “resolve” the system completely (at least in equilibrium conditions) and give more physical insight

# Structure of liquids – module of the course “structure of matter”

Connection between structure and interactions:

**Summary: what do we know in general?**

$$E = \frac{3}{2} NkT + \frac{N}{2} \rho \int u(r) g(r) 4\pi r^2 dr \rightarrow C_V = \frac{3}{2} Nk + \frac{N}{2} \rho \int u(r) \frac{\partial g(r)}{\partial T} 4\pi r^2 dr$$

**Internal energy**      **Specific heat**

$$p = \rho kT - \frac{\rho^2}{6} \int r \frac{\partial u(r)}{\partial r} g(r) dr \quad \text{Equation of state}$$

$$\lim_{k \rightarrow 0} S(k) = \rho kT K_T$$

**Compressibility**

- ✓ Everything is function of  $g(r)$  (or  $S(k)$ ) AND  $u(r)$
- ✓ We also know that the **relationship  $u(r) \rightleftharpoons g(r)$  is unique**
- ✓  $S(k)/g(r)$  can be derived from the corresponding  $u(r)$  by means of **computer simulations**
- ✓ Finding in general the  **$u(r) \rightleftharpoons g(r)$  relationship** means to solve a many body problem, i.e. give a “Theory of structure”. This is possible only approximately.

**Next:**

We will see some approximate structure theories for liquids and apply them to some simple cases.

# Structure of liquids – module of the course “structure of matter”

**Connection between structure and interactions:  $g(r)$  vs  $u(r)$**

- We start back from the definition of the pair distribution function

$$\bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2) = \left\langle \sum_{i \neq j} \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \right\rangle \xrightarrow{\text{fluid}} \bar{\rho}_2(|\mathbf{r}_1 - \mathbf{r}_2|) = \rho^2 g(|\mathbf{r}_1 - \mathbf{r}_2|) =$$

Statistical average over the  
 classical grand canonical ensemble  
 Separation of momentum and  
 coordinate space integration

$$= \sum_{N=2} \frac{1}{Z_N N!} \int \prod_{I,J} d\mathbf{r}_I d\mathbf{p}_J e^{-[K(\{\mathbf{p}_J\}) + U(\{\mathbf{r}_I\})]/kT} \sum_{i \neq j} \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j)$$

$$\rho^2 g(|\mathbf{r}_1 - \mathbf{r}_2|) = \frac{1}{\Xi} \sum_{N=2} \frac{z^N}{(N-2)!} \int e^{-U(\mathbf{r}_1, \dots, \mathbf{r}_N)/kT} d\mathbf{r}_3 \cdots d\mathbf{r}_N$$

Integrating out the two Dirac deltas only  
 an integral over  $\mathbf{r}_3 \dots \mathbf{r}_N$  remains

The identity of particles is used, bringing  $N(N-1)$  equals integral which reduces the  $N!$  at denominator to  $(N-2)!$

**Fugacity**

$$z = \left( \frac{m k T}{2 \pi \hbar^2} \right)^{3/2} e^{\mu/kT}$$

$$\Xi = \sum_{N=0} \frac{z^N}{N!} \int e^{-U(\mathbf{r}_1, \dots, \mathbf{r}_N)/kT} d\mathbf{r}_1 \cdots d\mathbf{r}_N$$

Grand canonical partition  
 function

# Structure of liquids – module of the course “structure of matter”

Connection between structure and interactions:  $g(r)$  vs  $u(r)$

$$\rho^2 g(|\mathbf{r}_1 - \mathbf{r}_2|) = \frac{1}{\Xi} \sum_{N=2} \frac{Z^N}{(N-2)!} \int e^{-U(\mathbf{r}_1, \dots, \mathbf{r}_N)/kT} d\mathbf{r}_3 \cdots d\mathbf{r}_N$$

Integrating out the two Dirac deltas only  
an integral over  $\mathbf{r}_3 \dots \mathbf{r}_N$  remains

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i>j} u(|\mathbf{r}_i - \mathbf{r}_j|) = u(|\mathbf{r}_1 - \mathbf{r}_2|) + \sum_{i=3} u(|\mathbf{r}_1 - \mathbf{r}_i|) + \text{terms independent from } \mathbf{r}_1$$

Taking the gradient of first equation with respect to  $\mathbf{r}_1$

$$\rho^2 \nabla_{\mathbf{r}_1} g(|\mathbf{r}_1 - \mathbf{r}_2|) = -\frac{1}{kT} \nabla_{\mathbf{r}_1} u(|\mathbf{r}_1 - \mathbf{r}_2|) \frac{1}{\Xi} \sum_{N=2} \frac{Z^N}{(N-2)!} \int e^{-U(\mathbf{r}_1, \dots, \mathbf{r}_N)/kT} d\mathbf{r}_3 \cdots d\mathbf{r}_N$$

This is the definition  
of  $\rho^2 g(r)$

$$-\frac{1}{kT} \frac{1}{\Xi} \sum_{N=2} Z^N \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-U(\mathbf{r}_1, \dots, \mathbf{r}_N)/kT} \sum_{i=3} \nabla_{\mathbf{r}_1} u(|\mathbf{r}_1 - \mathbf{r}_i|)$$

This contributes with  $N-2$  equal integrals  
which can be evaluated with e.g. with

$$\langle \rho_3(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \rangle = \left\langle \sum_{i,j,k} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') \delta(\mathbf{r}_k - \mathbf{r}'') \right\rangle \xrightarrow{\text{fluid}} \rho^3 g_3(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$$

Using then the definition of the third  
order distribution function (the  
obvious 3-body extension of the  $g$ ),  
this leads to

$$\rho^3 g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{1}{\Xi} \sum_{N=3} \frac{Z^N}{(N-3)!} \int e^{-U(\mathbf{r}_1, \dots, \mathbf{r}_N)/kT} d\mathbf{r}_4 \cdots d\mathbf{r}_N$$

which finally leads to

$$\nabla_{\mathbf{r}_1} g(|\mathbf{r}_1 - \mathbf{r}_2|) = -\frac{g(|\mathbf{r}_1 - \mathbf{r}_2|)}{kT} \nabla_{\mathbf{r}_1} u(|\mathbf{r}_1 - \mathbf{r}_2|) - \frac{\rho}{kT} \int d\mathbf{r}_3 \nabla_{\mathbf{r}_1} u(|\mathbf{r}_1 - \mathbf{r}_3|) g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

# Structure of liquids – module of the course “structure of matter”

## Connection between structure and interactions: $g(r)$ vs $u(r)$

Using the fluid isotropy one can finally write (March&Tosi Chapt 2)

$$\nabla g(r) = -\frac{g(r)}{kT} \nabla u(r) - \frac{\rho}{kT} \int d\mathbf{r}' \nabla u(r') g_3(\mathbf{r}, \mathbf{r}')$$

That is: the pair potential  $u(r)$  is related to the structure  $g(r)$  by means of the three particles distribution function!

### What do we learn from this?

- ✓ The connection between interaction and structure is recursive: to evaluate  $g(r)$  we need  $g_3$ ; to evaluate  $g_3$  as a function of  $u$  we need the four particles function and so on (infinite hierarchy) ⇒ **the many body problem is very complex!!**
- ✓ All the many body structure theories are more or less complex approximation to close the above eqn, alternative to the exact numerical solution by means of simulations
- ✓ However, the **zeroth order of this chain** already gives some physical insight. Let's rewrite the equation in the equivalent form

$$\frac{\nabla g(r)}{g(r)} = \nabla [\ln(g(r))] = -\nabla \frac{u(r)}{kT} - \frac{\rho}{kT g(r)} \int d\mathbf{r}' \nabla u(r') g_3(\mathbf{r}, \mathbf{r}')$$

$$\text{or } \nabla [\ln(g(r)) + \frac{u(r)}{kT}] = -\frac{\rho}{kT g(r)} \int d\mathbf{r}' \nabla u(r') g_3(\mathbf{r}, \mathbf{r}')$$

If the third and subsequent order correlations is negligible

That is, in case of negligible 3-body correlations the equation is **exactly and trivially closed**: the pair distribution follows the **pair potential driven Boltzmann law!** This is somehow intuitive: a particle is more probably found at the distance from another where there is a well of the pair potential

$$g(r) = e^{-\frac{u(r)}{kT}} \quad \text{or} \quad u(r) = -kT \ln(g(r))$$

# Structure of liquids – module of the course “structure of matter”

## Connection between structure and interactions: potential of mean force

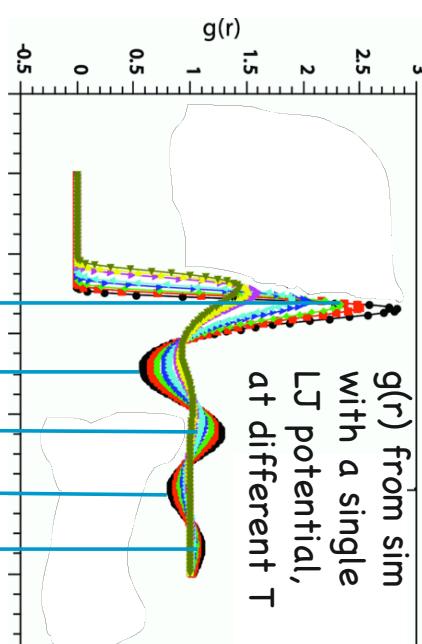
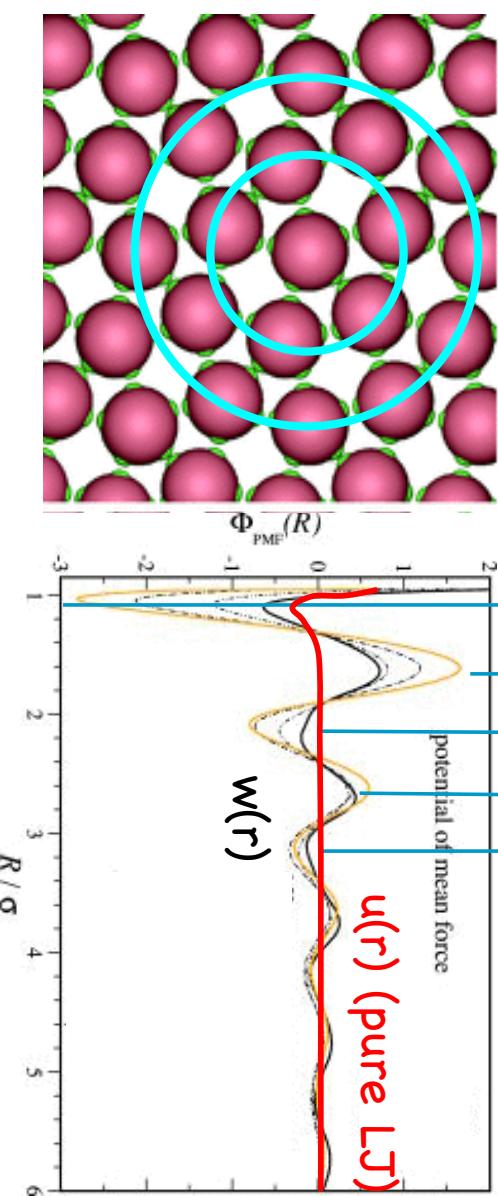
$g(r) = e^{-\frac{u(r)}{kT}}$  In general this equation holds only in the conditions where the higher order correlations and the  $-kT \ln()$  operation is called the “Boltzmann inversion” (BI)  
are not relevant (e.g. at large distances, for diluted gases etc)

$$g(r) = e^{-\frac{w(r)}{kT}} \quad \text{or} \quad w(r) = -kT \ln(g(r))$$

However, without losing generality, one can write  
and the  $-kT \ln()$  operation is called the “Boltzmann inversion” (BI)  
 $w(r)$  is the so-called **potential of mean force (PMF)**.  $w(r)$  can be similar to  $u(r)$ , the two differing by a complex correction depending on the  $g_3$ .

**Example: Lennard Jones fluid**

- ✓ The Boltzmann inversion converts maxima in minima and vice versa, and produces divergences when  $g(r)$  vanishes
- ✓ The potential of mean force is oscillating and therefore different from the bare LJ potential
- ✓ The additional minima present in the PMF are the expression of the **cooperative effects of many body interactions**: shells of neighbors form and stabilize each other. The PMF is expression of the probability of finding a particle even at distance different from the potential well of LJ



BI

# Structure of liquids – module of the course “structure of matter”

## Connection between structure and interactions: Born-Green closure

$$\nabla_{\mathbf{r}_1} g(|\mathbf{r}_1 - \mathbf{r}_2|) = -\frac{g(|\mathbf{r}_1 - \mathbf{r}_2|)}{kT} \nabla_{\mathbf{r}_1} u(|\mathbf{r}_1 - \mathbf{r}_2|) - \frac{\rho}{kT} \int d\mathbf{r}_3 \nabla_{\mathbf{r}_1} u(|\mathbf{r}_1 - \mathbf{r}_3|) g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

- ✓ While this is an exact result, we need a “closure” expressing  $g_3$  as a function of  $g$  and/or  $u$
- ✓ One popular approximation is the so-called “superposition approximation” (Kirkwood, 1935), assuming that the three body correlation can be approximated with a chain of two body correlations

$$g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g(|\mathbf{r}_1 - \mathbf{r}_2|) g(|\mathbf{r}_2 - \mathbf{r}_3|) g(|\mathbf{r}_1 - \mathbf{r}_3|)$$

from which one gets the **Born-Green** formula, that is a closed system from which the connection  $g \leftrightarrow u$  is established

Guide lines for the **derivation of BG formula**:

- ✓ Use the superposition approximation
- ✓ Use the liquid isotropy and change variables:  
 $r_2 - r_1 = r$ ,  $r_3 - r_2 = r'$ ,  $r_3 - r_1 = r' - r$   
 Substitute  $g(r) \rightarrow g(r)-1 = h(r)$  in the right hand side integral thanks to the null “spherical average” (The integrals including  $\nabla u(r)$  times a radial function is null because  $u$  depends only on  $|\mathbf{r}|$ )
- ✓ This substitution is useful because the hole function is well behaved (i.e. vanishes) at large  $r$

- ✓  $E(x)$  is a support function in the BG theory, with the following properties:

- If  $g \sim 1$  (e.g. at large  $x$ ) one has  $E(x) = -u(x)/kT$ .  $E = 0$  for the ideal gas
- Using thermodynamic derivatives it can be shown that  $FT[E](k=0) = \bar{E}(0) = 2[1 - p/\rho kT]$

**REMARK:**

in this form, the relation  $u(r) \approx g(r)$  is **closed**, and can be solved, at least numerically

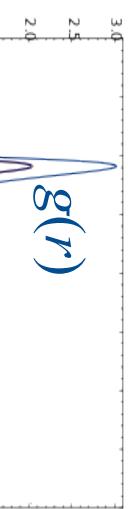
# Structure of liquids – module of the course “structure of matter”

## Connection between structure and interactions

Summary of useful structure functions and their names and definition of the direct correlation function  $c(r)$

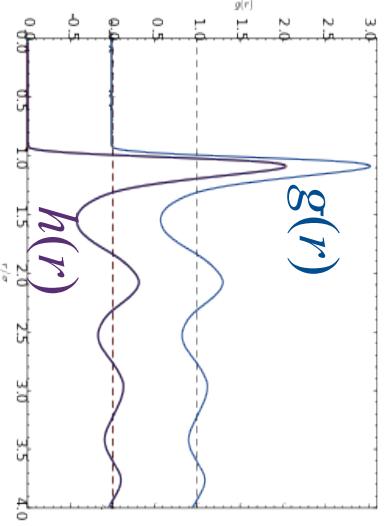
Direct space

$g(r)$	pair distribution function
$h(r) = g(r) - 1$	hole function or total correlation function



$$c(r) = h(r) + \rho \int d\mathbf{r}' h(\mathbf{r}') c(|\mathbf{r} - \mathbf{r}'|)$$

direct correlation function



Asymptotic behavior

$$h(r \rightarrow \infty) = 0$$

Fourier space

$$S(k) = 1 + \bar{h}(k) \quad \text{Structure factor}$$

$$\bar{h}(k) = \frac{\bar{c}(k)}{1 - \bar{c}(k)}$$

$\bar{c}(k) = \frac{\bar{h}(k)}{1 + \bar{h}(k)} = \frac{S(k) - 1}{S(k)} = 1 - \frac{1}{S(k)}$

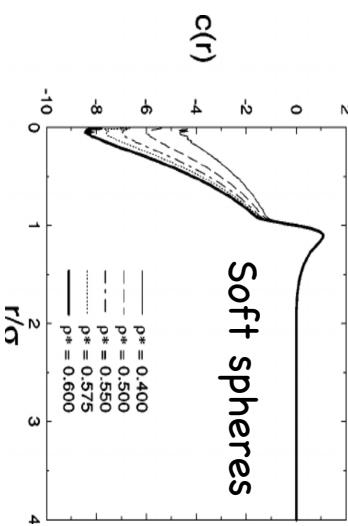
Equivalent relationship all derived from the definition of  $c$ ,  $h$  and  $S$

$$\int h(r) d\mathbf{r} = S(0) - 1 = \rho k T K_T - 1 = \begin{cases} 0 & \text{perfect gas} \\ -1 & \text{uncompressible fluid; the hole integrates to one particle} \end{cases}$$

$$\int c(r) d\mathbf{r} = \bar{c}(0) = 1 - 1/\rho k T K_T$$

null for perfect gas, can assume all negative values, the more negative, the more incompressible

$c$ ,  $h$ ,  $g$  and  $S$  all include the same information, which can be obtained even directly from experiment. Once one of this functions is available, all the others are available as well.



# Structure of liquids – module of the course “structure of matter”

Pair correlation g(r), h(r), c(r)	Structure factor S(k), S(0), c(k)	Internal energy	Equation of state	“Force equation”
$h(r)=g(r)-1$ $h(r)=c(r)+\rho \int d\mathbf{r}' h(r') c( \mathbf{r}-\mathbf{r}' )$	$S(k) = 1 + \bar{h}(k)$ $S(0) = \rho k T K_T$ $\bar{c}(k) = \frac{\bar{h}(k)}{1 + \bar{h}(k)} = 1 - \frac{1}{S(k)}$	$E = \frac{3}{2} N k T + \frac{N}{2} \rho \int u(r) g(r) d\mathbf{r}$ $C_V = \frac{3}{2} N k + \frac{N}{2} \rho \int u(r) \frac{\partial g}{\partial T}(r) d\mathbf{r}$	$p = \rho k T - \frac{\rho^2}{6} \int r \frac{\partial u(r)}{\partial r} g(r) d\mathbf{r}$ $= - \frac{\rho}{k T g(r)} \int d\mathbf{r} \nabla u(r) g_3(\mathbf{r}, \mathbf{r}')$	$\sqrt{[\ln(g(r)) + \frac{u(r)}{kT}]}$
$g(r)=1$ $h(r)=0$ $c(r)=0$	$S(k)=1$ $k_T=1/\rho k T$ $c(k)=0$	$E = \frac{3}{2} N k T$ $C_V = \frac{3}{2} N k$	$p = \rho k T$	$u(r)=0$
Perfect gas				

What's next? Short ranged potentials



Soft spheres   Model for colloids



Lennard-Jones fluid Model for noble gases.

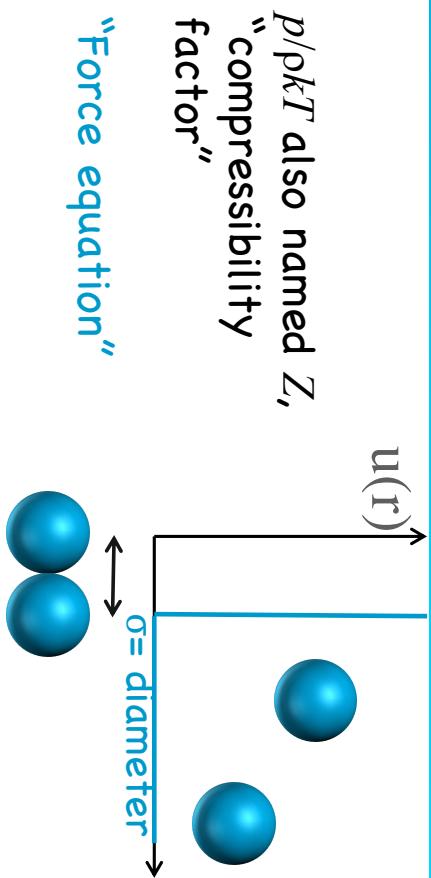
Additional parameter  $\epsilon$  (attractive well depth)

# Structure of liquids – module of the course “structure of matter”

## The hard spheres system

$$\frac{P}{\rho kT} = 1 - \frac{\rho}{6} \int r \frac{\partial(u(r)/kT)}{\partial r} g(r) dr \quad \text{State equation}$$

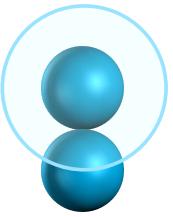
$$\ln g(r) + \frac{u(r)}{kT} = \rho \int_{r-r'}^{\infty} g(r') - 1 dr' \int g(x) \frac{\partial(u(x)/kT)}{\partial x} dx \quad \text{“Force equation”}$$



- ✓ The interaction  $u(r)$  depends on a single parameter  $\sigma$  (the sphere diameter)
- ✓ The Force equation depends on  $u$  only in the combination  $u/kT$ , but  $C \times u(r) = u(r)$
- ✓ Because  $\sigma$  is the scale length of the system it is expected that all quantities are conveniently expressed as a function of  $x=r/\sigma$  and of the density expressed through the packing fraction  $\eta = \rho(4/3)\pi R^3 = \pi \rho \sigma^3 / 6 = \rho V$  (sometimes named  $\phi$ )
- ✓  $g(r)$  is identically null for  $r < \sigma$  and  $u$  is null for  $r > \sigma$ , but  $u$  and its derivative diverge at  $r = \sigma$  therefore the calculation of those integrals is not trivial

However...

- ✓ Consider the first the state equation. The right hand side derives for the calculation of the virial of forces. In the ideal case, this reduces to the virial of the external pressure brings the term  $\rho V$ . The hard spheres are “ideal” (i.e. non interacting) until they come in touch. Therefore in first approximation one might infer that the correction to the ideal gas equation is the substitution of  $V$  to  $V-b$ , being  $b$  the co-volume, i.e. the excluded volume of a particle coming in contact with another. This is  $8\pi$  the volume of a single sphere but it must be divided by 2 because it is shared between two spheres. Therefore the final result is  $V$  to  $V-4V$  and  $\frac{P}{\rho kT} = \frac{1}{1-4\eta}$



# Structure of liquids – module of the course “structure of matter”

## The hard spheres system

$$\frac{p}{\rho kT} = 1 - \frac{\rho}{6} \int r \frac{\partial(u(r)/kT)}{\partial r} g(r) dr \quad \text{State equation}$$

$$\frac{p}{\rho kT} = \frac{1}{1-4\eta} = \frac{1}{1-\frac{2\pi\sigma^3}{3}\rho}$$

The approximation is valid until the two-particles contacts prevail over multi-particle contacts, i.e. for low density, small  $\eta$ ...

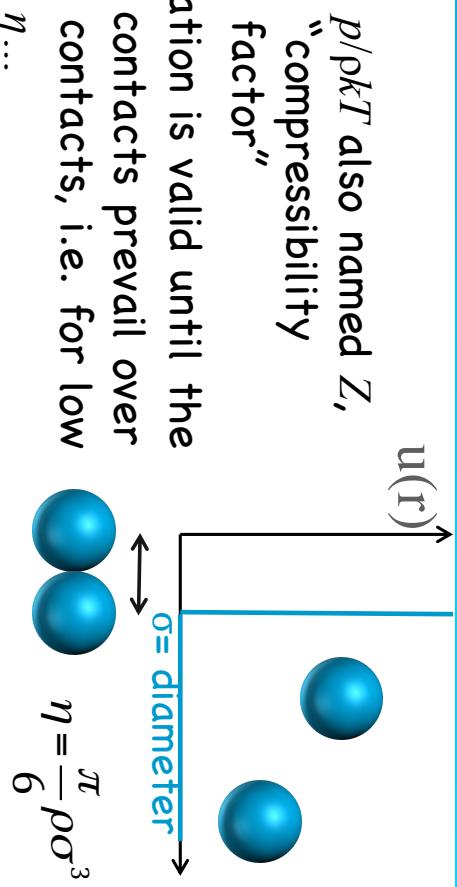
$$\frac{p}{\rho kT}$$

HS, diluted

ideal gas

- ... but computer simulations show that the hard-sphere systems can exist also at higher densities than  $\eta=1/4$ !
- ✓  $g(r)$  is exactly null for  $r < \sigma$ , but it is  $\neq 1$  for  $r < \sigma \Rightarrow$  the correlations are present even at distances where the interaction is exactly null!
- ✓  $g$  is discontinuous at  $r=\sigma$
- ✓ At low densities  $g(r)$  and  $S(k)$  tends to 1
- ✓ At large densities the compressibility decreases

$p/\rho kT$  also named  $Z$ ,  
“compressibility factor”



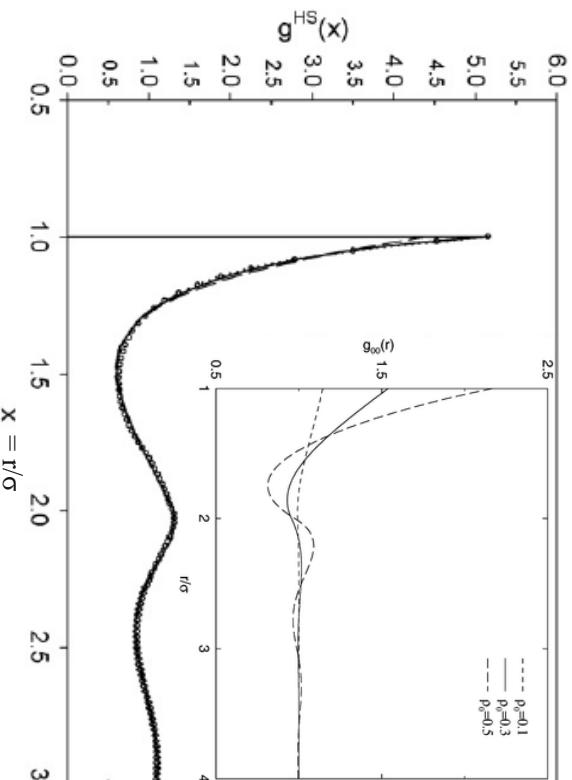
$$\eta = 1/4 \\ \rho = 3/(2\pi\sigma^3)$$

$$p/kT$$

$$\rho, \eta$$

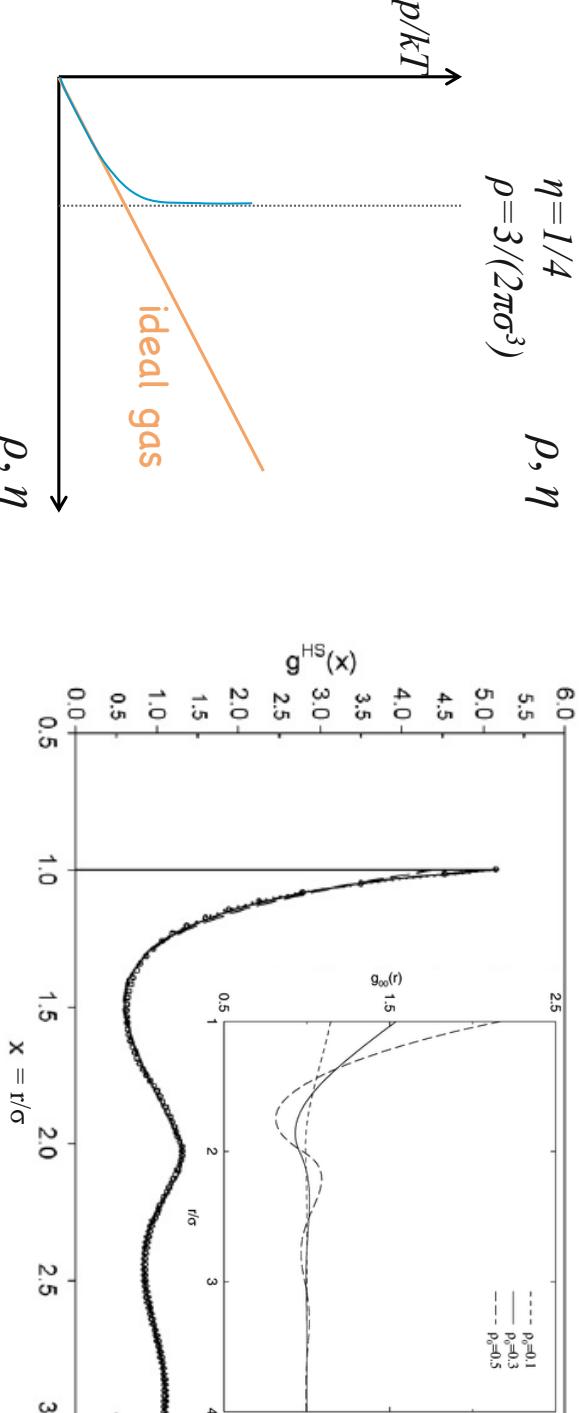
$$p/kT$$

$$\rho, \eta$$



$$\rho, \eta$$

ideal gas



# Structure of liquids – module of the course “structure of matter”

## The hard spheres system

$$\frac{P}{\rho kT} = 1 - \frac{\rho}{6} \int r \frac{\partial(u(r)/kT)}{\partial r} g(r) dr \quad \text{State equation}$$

$$\frac{P}{\rho kT} = \frac{1}{1 - 4\eta} = \frac{1}{1 - \frac{2\pi\sigma^3}{3}\rho} \approx 1 + 4\eta + 16\eta^2 + \dots$$

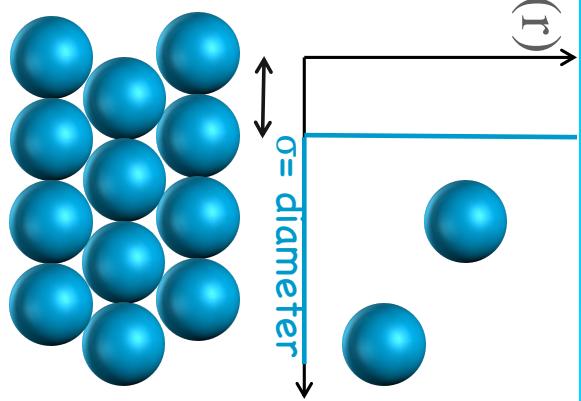
**Very diluted gas**

What happens at very high concentrations?

Will the system prefer to orderly pack (i.e. **crystallize**) or to remain disordered?

Closed packing density (FCC or HCP crystals):  $\eta_c = \frac{\pi\sqrt{2}}{6} \approx 0.74$      $\rho_c = \frac{\sqrt{2}}{\sigma^3}$

In proximity of the critical crystal density, the compressibility goes to zero, while the pressure has to diverge since it is not possible to compress the system beyond the closed packed conformation



But what happens in the intermediate range, where the dilute gas approximation does not work?

Better theories are needed than the heuristic co-volume approximation, and/or simulations

$p/\rho kT$  also named  $Z$ ,  
“compressibility  
factor”

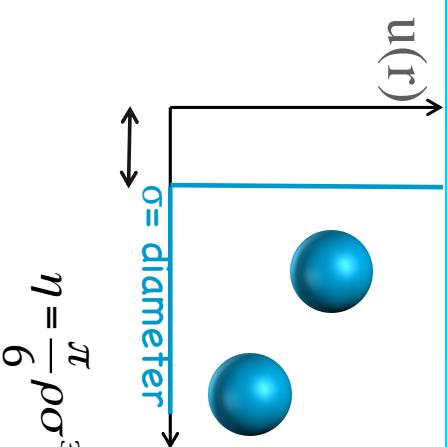
# Structure of liquids – module of the course “structure of matter”

## The hard spheres system

$$\frac{p}{\rho kT} = 1 - \frac{\rho}{6} \int r \frac{\partial(u(r)/kT)}{\partial r} g(r) d\mathbf{r} \quad \text{State equation}$$

$$\ln g(r) + \frac{u(r)}{kT} = \rho \int_{r-r'}^{\infty} g(x) \frac{\partial(u(x)/kT)}{\partial x} dx \quad \text{“Force equation”}$$

$p/\rho kT$  also named  $Z$ ,  
“compressibility factor”



$$\eta = \frac{\pi}{6} \rho \sigma^3$$

Abe approximation (also “hypernetted chain”)  
 $w(r) = -kT \ln g(r)$  Def of Potential of mean force  $w$

$$\ln g(r) + \frac{u(r)}{kT} = \rho \int_{r-r'}^{\infty} dr' h(r') \left[ \int g(x) \frac{\partial((u-w)/kT)}{\partial x} dx - \int_{r-r'}^{\infty} \frac{\partial g(x)}{\partial x} dx \right] =$$

$$\xrightarrow[g(r) \sim 1 \text{ in the first integral}]{} \rho \int_{r-r'}^{\infty} dr' h(r') \left[ \frac{w(r-r') - u(r-r')}{kT} + h(r-r') \right]$$

Core of Abe approx:  $g(r)$  is set to its non interacting particle value within the integral. The correlations are accounted for correctly in the regions where  $g(r)$  is near to 1. Abe approx leads to

$$c(r) = \frac{w(r) - u(r)}{kT} + h(r) = - \left[ \ln g(r) + \frac{u(r)}{kT} \right] + h(r)$$

$$\ln g(r) + \frac{u(r)}{kT} = \rho \int d\mathbf{r}' h(r') c(r-r')$$

Abe is equivalent to set  $E(r)=c(r)$  in the state eqn

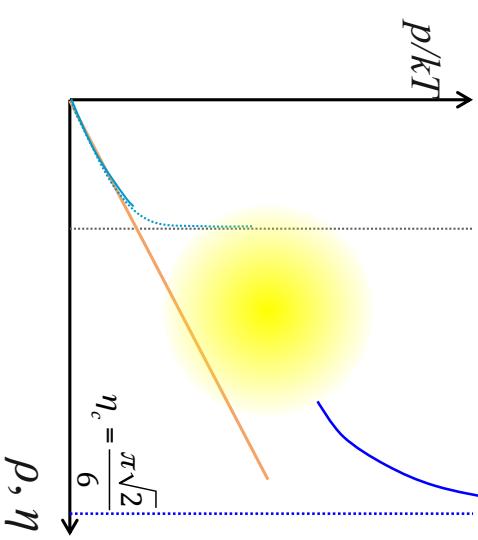
$$h(r) - c(r) = - \frac{w(r) - u(r)}{kT} \xrightarrow[r \rightarrow \infty]{} c(r) \approx -\frac{u(r)}{kT}$$

Direct correlation function

Long range limit

$$h(r) \approx -\frac{w(r)}{kT}$$

Total correlation function



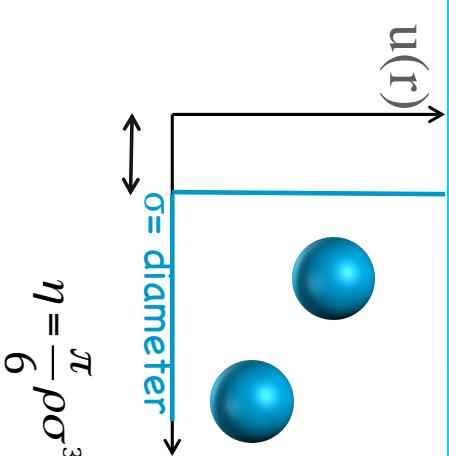
# Structure of liquids – module of the course “structure of matter”

## The hard spheres system

$$\frac{P}{\rho kT} = 1 - \frac{\rho}{6} \int r \frac{\partial(u(r)/kT)}{\partial r} g(r) d\mathbf{r} \quad \text{State equation}$$

$$\ln g(r) + \frac{u(r)}{kT} = \rho \int_{r-r'}^{\infty} (g(r') - 1) dr' \int_{r-r'}^{\infty} g(x) \frac{\partial(u(x)/kT)}{\partial x} dx \quad \text{“Force equation”}$$

$p/\rho kT$  also named  $Z$ ,  
“compressibility factor”



Abe approximation (also “hypernetted chain”)

$$w(r) = -kT \ln g(r) \quad \text{Def of Potential of mean force } w$$

$$h(r) = c(r) + \rho \int d\mathbf{r}' h(r') c(r-r') \quad \text{Definition of direct correlation function}$$

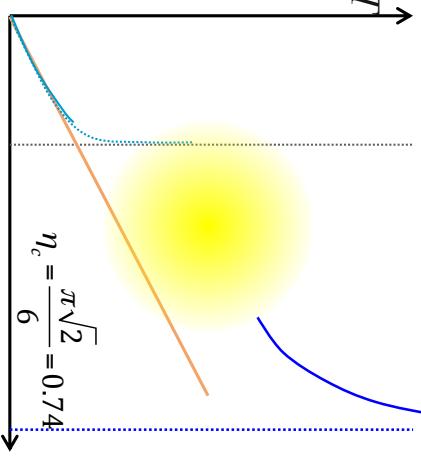
$$h(r) - c(r) = -\frac{w(r) - u(r)}{kT} \rightarrow \begin{cases} c(r) \approx -\frac{u(r)}{kT} & \text{Direct correlation function} \\ h(r) \approx -\frac{w(r)}{kT} & \text{Total correlation function} \end{cases}$$

The problem with hard core potentials is that all functions oscillate fast near the core region. Percus Yevick closure defines an effective potential returning the correct long range limit and regularizing functions near the core region.

$$c(r) \stackrel{\text{def}}{=} -\frac{u_{\text{eff}}(r)}{kT} = g(r)[1 - e^{u(r)/kT}] = e^{-w(r)/kT} - e^{-[w(r)-u(r)]/kT}$$

- ✓ PY gives an analytical expression of  $c(r)$  (null for  $r>\sigma$ , polynomial for  $r<\sigma$ ) and for  $g(r)$ ,  $h(r)$  etc.
- ✓ PY gives explicit expressions for the state equation

- ✓ PY is very good up to densities much larger than the dilute gas state equations
- March&Tosi, chapter 2, sec2.5; additionally, only for the brave ones: A. Mulero, et al, PCCP 2001, 3, 4991 and Rintoul et al, PRE 1998 58 532



$\rho, \eta$

$p/kT$

# Structure of liquids – module of the course “structure of matter”

## The hard spheres system

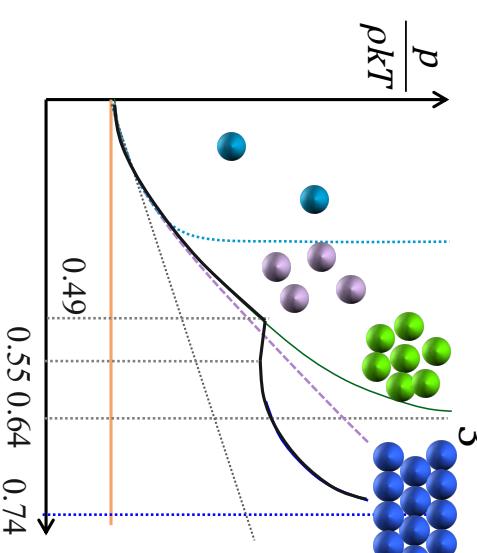
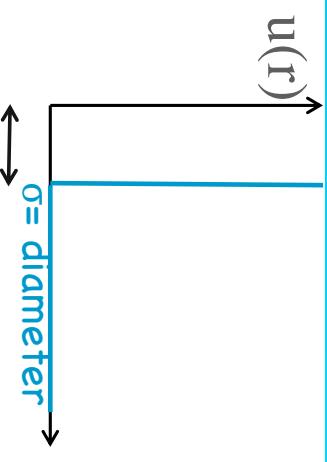
$$\frac{p}{\rho kT} = 1 - \frac{\rho}{6} \int r \frac{\partial(u(r)/kT)}{\partial r} g(r) dr \quad \text{State equation}$$

$$\frac{p}{\rho kT} = \frac{1}{1-4\eta} = \frac{1}{1-\frac{2\pi\sigma^3}{3}\rho} \quad \text{Very diluted gas}$$

$$\frac{p}{\rho kT} = \frac{1+\eta+\eta^2}{(1-\eta)^3} \approx 1+4\eta+10\eta^2 + \dots \quad \text{Percus Yevick}$$

$$\eta = \frac{\pi}{6} \rho \sigma^3$$

$p/\rho kT$  also named  $Z$ ,  
“compressibility  
factor”



The “exact” state equation of the disordered phase (obtained with computer simulation) however, has an asymptote at  $\eta \sim 0.64$ .

In the simulations, the system is forced to be disordered i.e. in a random phase. What happens between the two lines?

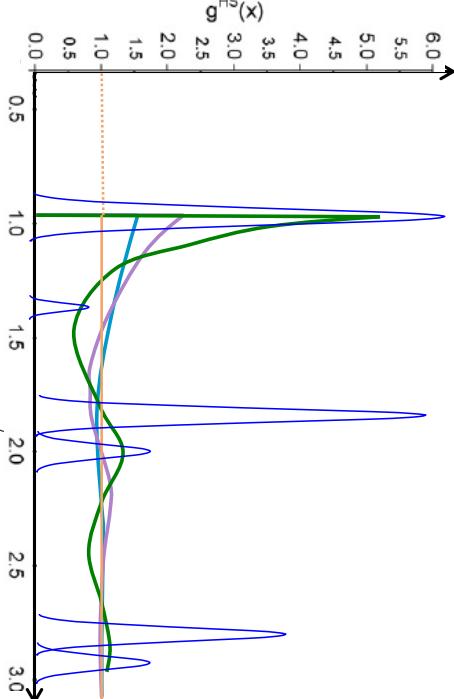
### Crystallization/melting!

✓ The very diluted HS gas exists at low densities and its  $g(r)$  is near to that of the ideal gas

✓ The PY approx is good at higher densities

✓ Better approximations or simulations can represent the super-dense random phase (glass?) which however has a maximum density of ~0.64

✓ However, crystallization occurs earlier, at  $\eta \sim 0.49-0.55$ , and the FCC crystal has a higher density. The change in density upon crystallization is discontinuous (1<sup>st</sup> order phase transition)



# Structure of liquids – module of the course “structure of matter”

## The Lennard Jones fluid

$$\frac{p}{\rho kT} = 1 - \frac{\rho}{6} \int r \frac{\partial(u(r)/kT)}{\partial r} g(r) dr \quad \text{State equation}$$

$$\frac{p}{\rho kT} = \frac{1}{1 - 4\eta} = \frac{1}{1 - \frac{2\pi\sigma^3}{3}\rho} \quad p(1 - 4\eta) = \rho kT \quad \text{diluted gas} \sim \text{hard spheres}$$

The Lennard Jones potential includes an attractive tail through a single new parameter  $\varepsilon$

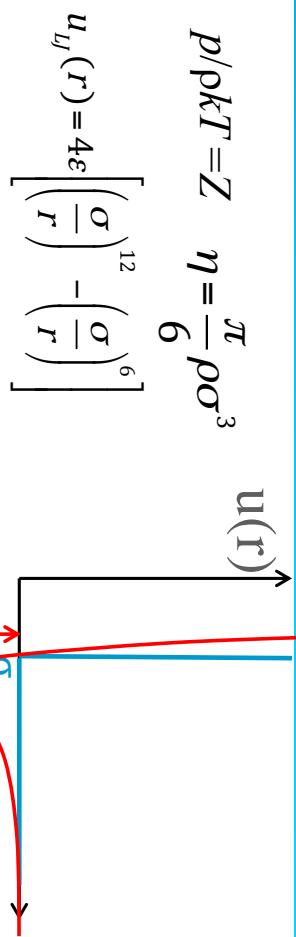
We might consider the LJ system as a **perturbation to the HS system** parameterized by  $\varepsilon$ . (This is rigorously true only for a potential composed by LJ for  $r > \sigma$  and an infinite wall for  $r < \sigma$ ). Then it is reasonable to write That is, the **van der Waals gas state equation**.

The original heuristic argument for deriving this equation relies on the fact that the attractive interaction reduces the pressure exerted by the particles on the walls. This effect is proportional to number of particles as is the normal pressure effect, but for each particle it depends on the number of particles from which it is surrounded, therefore depends on the square of density.

The general form of the state equation allows us to calculate the parameter  $a$ , being related to the **virial of the internal forces**. Guidelines for the calculation:

- assume that the “divergent part” of the integral due to the hard core is already included in  $\rho_{HS}$ . The integral in the state equation can be only for  $r > \sigma$  and put equal to  $-a\rho^2$ .
- also assume that  $g(r) \sim 1$  in the relevant region of integration (PY approx).

In these conditions the integral can be explicitly calculated, and one has the **explicit form for the state equation of van der Waals gases**



$$p/\rho kT = Z \quad \eta = \frac{\pi}{6} \rho \sigma^3$$

$$u_{LJ}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

# Structure of liquids – module of the course “structure of matter”

# The Lennard Jones fluid

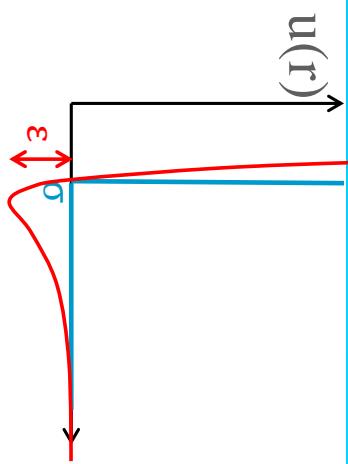
$$\frac{p}{\rho kT} = \frac{1}{1 - 4\eta} = \frac{1}{1 - \frac{2\pi\sigma^3}{3}\rho}$$

$$p(1 - 4\eta) = \rho kT$$

diluted gas ~hard spheres

$$p/\rho kT = Z$$

$$\eta = \frac{\pi}{6} \rho \sigma^3$$



$$\frac{P}{kT} = \frac{\rho}{1-b\rho} - A(T)\rho^2 \quad b = 4V = \frac{2\pi}{3}\sigma^3 \quad A = \frac{a}{kT} = \frac{16\pi}{9}\frac{\varepsilon}{kT}\sigma^3$$

✓ (Classical) ideal gases have

✓ Hard spheres system (no attraction, only **hard core repulsion**) have a “**fluid**” (disordered, no distinction between gas and liquid) phase and a **crystal phase**

✓ phase and a crystal phase  
Van der Waals liquid and

✓ Van der Waals (hard core)

repulsion + short range

repulsion + short-range attraction) have a crystal

diffusion) have a crystal fluid phase above the

**critical point ( $\varepsilon/kT \gtrsim 1.26$ )**

**critical point ( $\varepsilon/kT \gtrsim 1.26$ )  
and crystal+liquid+gas**

and **crystalliquid+gas** below the critical point

below the critical point

## 1. The repulsive core

includes the crystal phases

includes the crystal plastic

produces the liquid phase

# Structure of liquids – module of the course “structure of matter”

## The Lennard Jones fluid

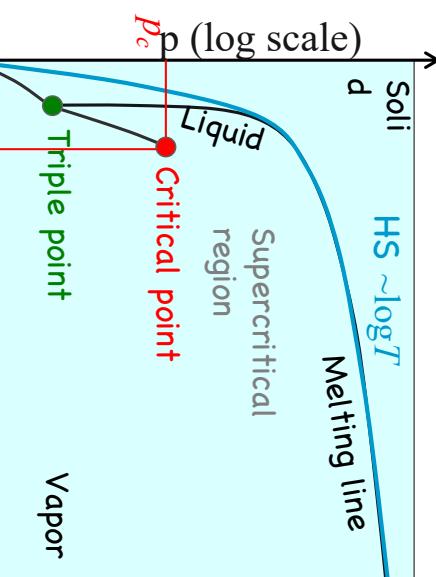
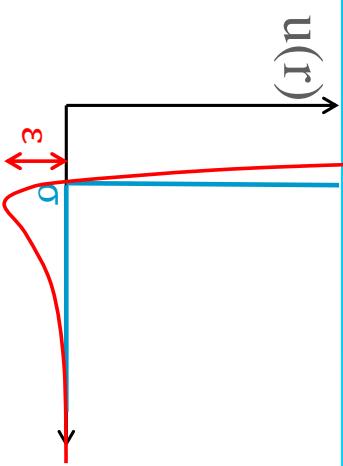
$$p/\rho kT = Z \quad \eta = \frac{\pi}{6} \rho \sigma^3$$

$$\frac{p}{\rho kT} = \frac{1}{1 - 4\eta} = \frac{1}{1 - \frac{2\pi\sigma^3}{3}\rho}$$

$p(1 - 4\eta) = \rho kT$       **diluted gas ~hard spheres**

$$\frac{p}{kT} = \frac{\rho}{1 - b\rho} - A\rho^2 \quad b = 4V = \frac{2\pi}{3}\sigma^3 \quad A = \frac{a}{kT} = \frac{16\pi}{9} \frac{\epsilon}{kT} \sigma^3$$

**van der Waals fluid**



**Critical point:** pressure and temperature at which liquid and gas have the same density  $\rho_c$   
Below the critical point  $\rho$  is discontinuous across the liquid vapor transition line

At the **triple point**, liquid and vapor coexist with solid

As  $\epsilon \rightarrow 0$ , the critical points tend to 0, merging into the triple one and then pushing it to 0 too.

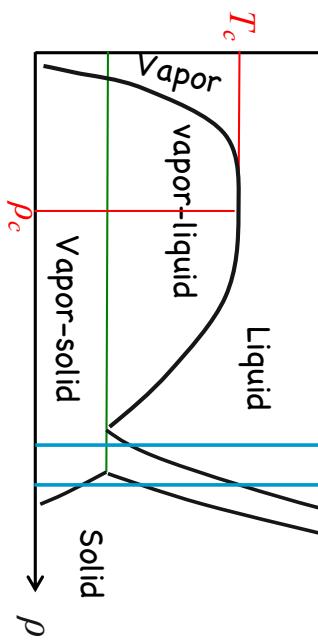
$$KT_c = \frac{64}{81}\epsilon \approx 0.79\epsilon$$

$$\eta_c = \frac{1}{12} \rightarrow \rho_c = \frac{1}{2\pi\sigma^3}$$

$$p_c = \frac{4}{27\pi\sigma^3}\epsilon = \frac{8}{27}\rho_c\epsilon$$

$$\frac{p_c\rho_c}{kT_c} = \frac{3}{8}$$

In the **hard spheres system** the crystallization occurs when  $\rho\sigma^3 \sim 0.5$  and  $p/\rho kT$  is independent from  $T \Rightarrow p_c \sim \text{const} \rho_c \sigma^3 \times kT$   
Both triple and critical point disappear



# Structure of liquids – module of the course “structure of matter”

## The Lennard Jones fluid

$$p/\rho kT = Z \quad \eta = \frac{\pi}{6} \rho \sigma^3$$

$$\frac{p}{\rho kT} = \frac{1}{1 - 4\eta} = \frac{1}{1 - \frac{2\pi\sigma^3}{3}\rho}$$

$$p(1 - 4\eta) = \rho kT$$

diluted gas ~hard spheres

$$\frac{p}{kT} = \frac{\rho}{1 - b\rho} - A\rho^2 \quad b = 4V = \frac{2\pi}{3}\sigma^3 \quad A = \frac{a}{kT} = \frac{16\pi}{9} \frac{\epsilon}{kT} \sigma^3$$

van der Waals fluid

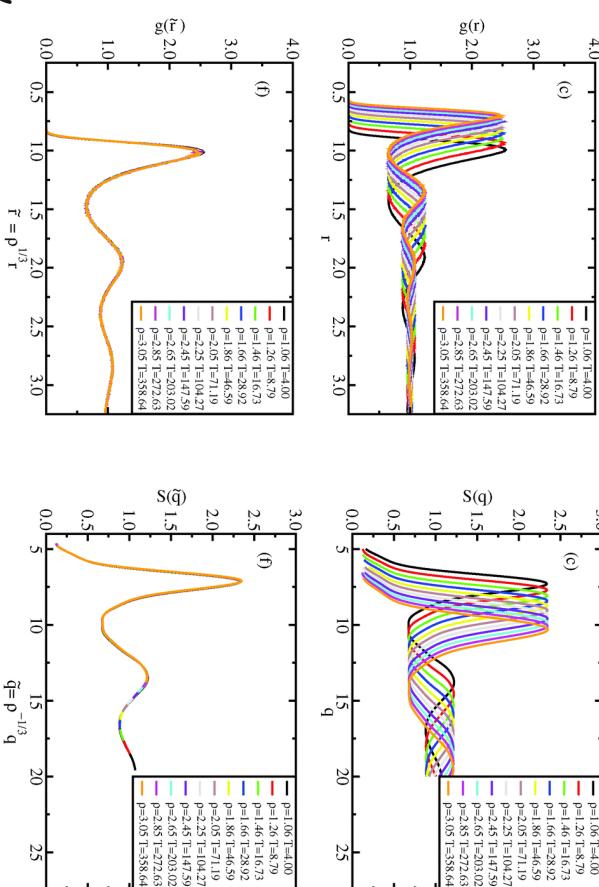
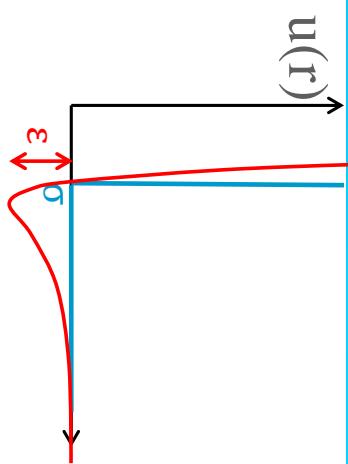
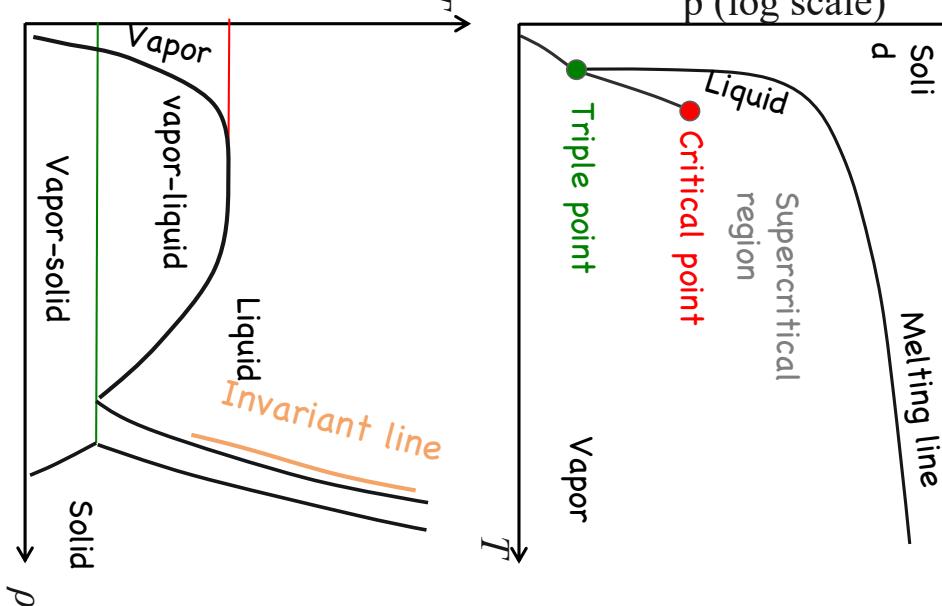
$$\ln g(r) + \frac{u(r)}{kT} = \rho \int_{r-r'}^{\infty} (g(r') - 1) dr' \int_{r-r'}^{\infty} g(x) \frac{\partial(u(x)/kT)}{\partial x} dx$$

The decoupled (BG) form of the force equation is parameter independent if written as a function of the

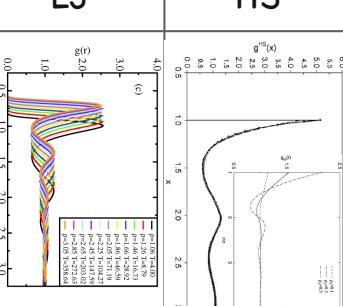
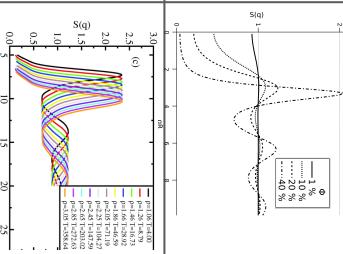
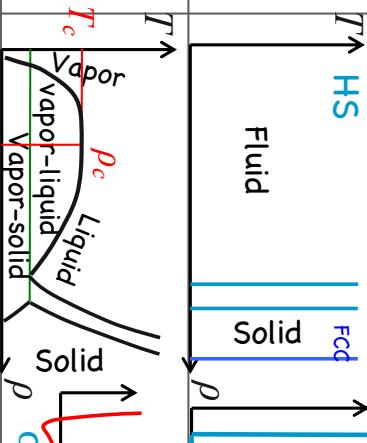
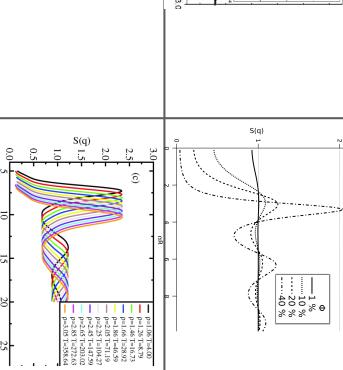
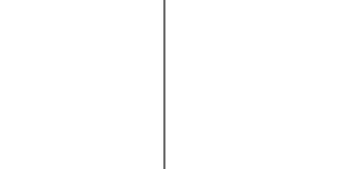
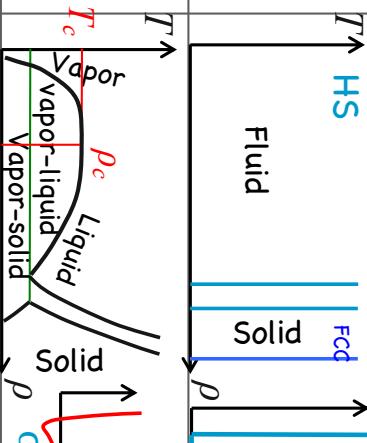
reduced units  
 $u \rightarrow u/kT$  and  $r \rightarrow r\rho^{1/3}$ .

This implies that invariant lines exist in the phase diagram along which  $g(r)$  and  $S(k)$  are invariant when expressed in reduced units. For the LJ system the invariance lines can be evaluated analytically

The freezing line is (approximately) one of those.



# Structure of liquids – module of the course “structure of matter”

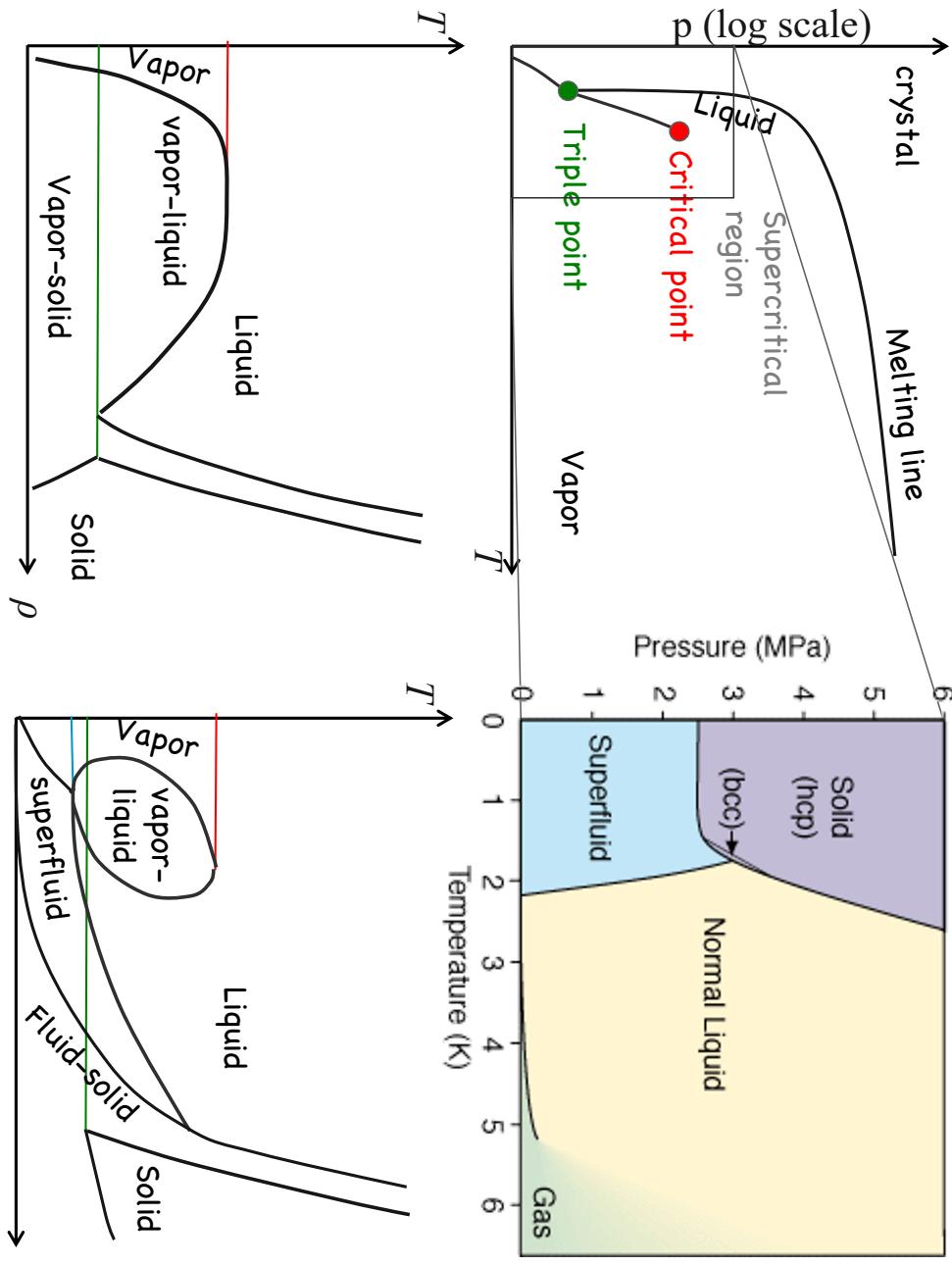
	Pair correlation $g(r), h(r), c(r)$	Structure factor $S(k), S(0), c(k)$	Internal energy, phase diagram, $u(r)$	Equation of state	“Force equation”
general	$h(r)=g(r)-1$ $h(r)=c(r)+\rho \int dr' h(r') c( \mathbf{r}-\mathbf{r}' )$	$S(k) = 1 + \bar{h}(k)$ $S(0) = \rho k T K_T$ $\bar{c}(k) = \frac{\bar{h}(k)}{1 + \bar{h}(k)} = 1 - \frac{1}{S(k)}$	$E = \frac{3}{2} N k T + \frac{N}{2} \rho \int u(r) g(r) d\mathbf{r}$ $C_V = \frac{3}{2} N k + \frac{N}{2} \rho \int u(r) \frac{\partial g}{\partial T}(r) d\mathbf{r}$	$p = \rho k T - \frac{\rho^2}{6} \int r \frac{\partial u(r)}{\partial r} g(r) d\mathbf{r}$ $= - \frac{\rho}{k T g(r)} \int d\mathbf{r} \nabla u(r) g_3(\mathbf{r}, \mathbf{r}')$	$\sqrt{[\ln(g(r)) + \frac{u(r)}{kT}]} =$ $(\rho T g(r))^{\frac{1}{2}}$
Ideal gas	$g(r)=1$ $h(r)=0$ $c(r)=0$	$S(k)=1$ $k_T=1/\rho k T$ $c(k)=0$	$E = \frac{3}{2} N k T$ $C_V = \frac{3}{2} N k$	$p = \rho k T$	$u(r)=0$
HS				$\frac{p}{\rho k T} = \begin{cases} \frac{1}{1-4\eta} & \text{at low dens} \\ f(\eta), \eta = \pi / 6\rho\sigma^3 & \end{cases}$	Solvable by approx theories such as Percus-Yevick
J				$\frac{p}{\rho k T} = \begin{cases} \frac{1}{1-b\rho} + a\rho^2 & \text{low dens} \\ f(T, \rho) & \end{cases}$	Solvable by approx theories (PY) Invariant lines

# Structure of liquids – module of the course “structure of matter”

Before going forward:

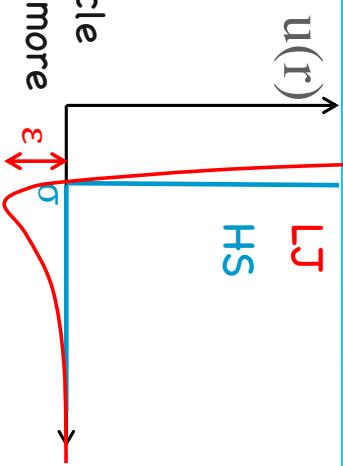
What happens in the quantum regime?

- ✓ The value of  $\epsilon$  in e.g. He is very small  $\rightarrow T_{c,p}$  are pushed towards 0
- ✓ Normally, a crystal melts when thermal fluctuations are larger than inter-particle distance, but at very low  $T$  quantum fluctuations influence the crystal stability more than thermal fluctuations and  $T$  has a minor role in the crystal/gas transition
- ✓ Conversely, the superfluid phase appears



Without going into the details the qualitative phase diagram is very complex, so it is the state equation  $p=p(T,p)$  e.g. infinite compressibility...

The BEC is driven by the boson nature of the particles, but it is also influenced by the presence of a finite hard core, because of which the particles cannot be treated exactly as “ideal”



# Structure of liquids – module of the course “structure of matter”

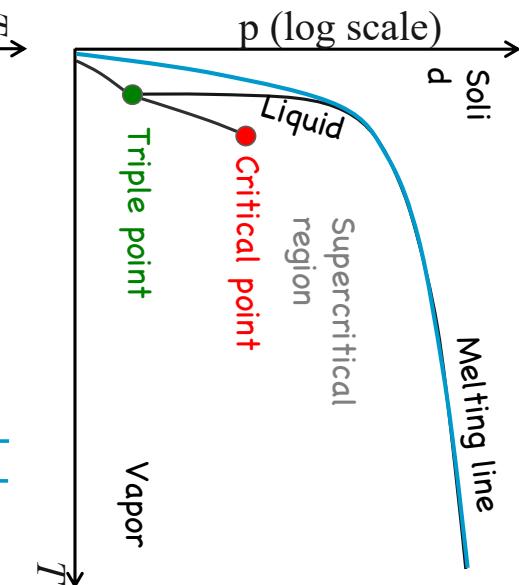
## The role of the range: colloids

Going back to classical regime, when  $\varepsilon \rightarrow 0$  one gets back the HS system, the triple and critical point disappear and only the solid-fluid transition is present. This is an effect of the reduction of the attractive tail which stabilizes the liquid phase

However, the interaction strength can be decreased not only decreasing  $\varepsilon$  but also **decreasing the range of the interaction**.

In fact, as the range of attraction becomes smaller of 10-30% of the  $\sigma$  value, the triple point disappear and only two phases (fluid and crystal) are stable, as if the system was always supercritical

However, the critical point does not entirely disappear: a metastable “fluid-fluid” phase appear within the vapor-solid coexistence region



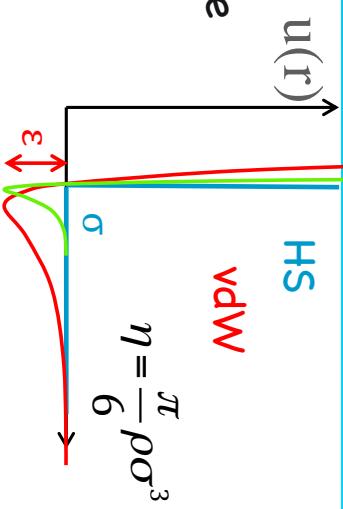
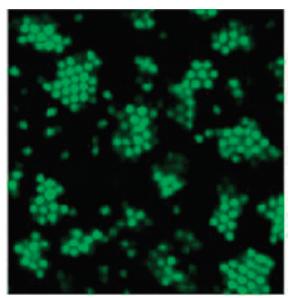
In this state, “nucleation” occurs, i.e. the formation of (disordered) aggregates of particles separated by large portion of vacuum

→ **colloidal behavior**

These models are useful to represent large particles interactions (proteins, besides colloids)

**And what about very large range interactions?**

If these are attractive, nothing really different happens, only the critical points move to larger temperatures, because the condensed phase is stabilized. However, very long range attractive interactions are rare in condensed matter)



# Structure of liquids – module of the course “structure of matter”

## Long range repulsion: the Wigner crystal

Let's consider for completeness the extreme case of the pure Coulomb potentials: electrons on an inert positive background. The potential is very long range, but at the same time  $\sigma=0$  (no repulsive hard core). Therefore the classical fluid-crystal transition is pushed towards very large (or infinite?) densities.

In addition the **attraction is absent**, therefore it is to be expected that the liquid phase is also absent

However, in the 30ties Wigner (1934) showed that organizing electrons in a regular lattice can realize a gain in the exchange energy, until fluctuations are so large that the crystal order is disrupted.

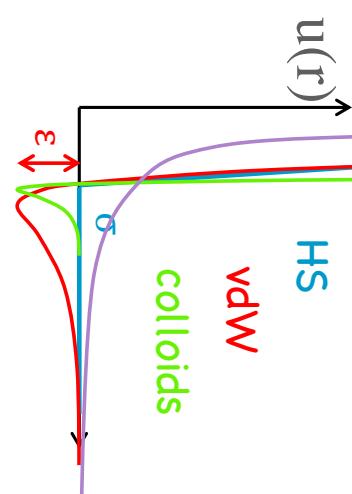
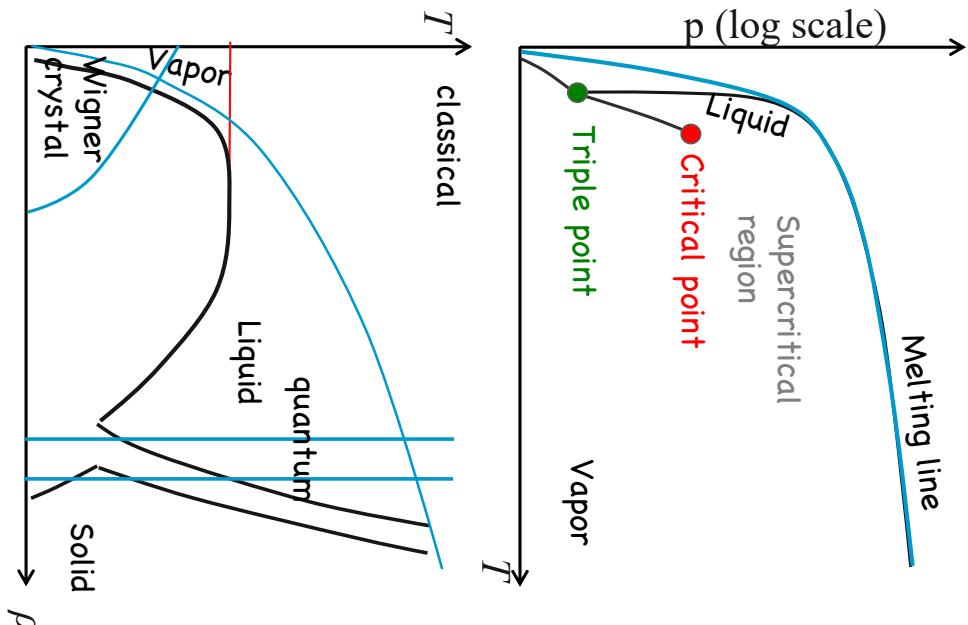
Fluctuations depends on temperature in the classical regime. The line that separates quantum from classical regime (comparing the thermal wavelength with the interparticle distance) is  $T \propto \hbar^2/m \rho^{2/3}$

In the quantum regime, also the quantum fluctuations come into play, which energy depends on  $k_F^{-2} \sim \rho^{2/3}$

The crystallization/melting in the quantum regime results from an interplay between the kinetic energy and the exchange energy, and occurs when the inter-electron separation reaches a fixed value, which is  $\sim 100$  atomic units, corresponding to the density of about  $10^{18} \text{ el/cm}^3$  (for comparison, the density of a classical fluid at crystallization is normally  $\sim 10^{24} \text{ cm}^{-3}$ )

Therefore Wigner crystallization occurs at very small densities and low temperatures

Wigner, E. (1934). "On the Interaction of Electrons in Metals". Physical Review. 46 (11): 1002–1011. Bibcode:1934PhRv...46.1002W. doi:10.1103/PhysRev.46.1002.



# Structure of liquids – module of the course “structure of matter”

## Long range interactions

Going back to classical regime, however, in the presence of Coulomb interaction, the previous approximations do not work, because the approx  $g(r) \sim 1$  and  $u(r) \sim 0$  work only at very large distances. We then go back to the starting force equation within the **superposition approximation**

$$\nabla_{\mathbf{r}_1} g(|\mathbf{r}_1 - \mathbf{r}_2|) = -\frac{g(|\mathbf{r}_1 - \mathbf{r}_2|)}{kT} \nabla_{\mathbf{r}_1} u(|\mathbf{r}_1 - \mathbf{r}_2|) - \frac{\rho}{kT} \int d\mathbf{r}_3 \nabla_{\mathbf{r}_1} u(|\mathbf{r}_1 - \mathbf{r}_3|) g(|\mathbf{r}_1 - \mathbf{r}_2|) g(|\mathbf{r}_2 - \mathbf{r}_3|) g(|\mathbf{r}_1 - \mathbf{r}_3|)$$

and we consider the structure functions in the fourier space

$$\rho g(r) = \frac{1}{N} \left\langle \sum_{i \neq j} \delta(r - (r_i - r_j)) \right\rangle \xrightarrow{FT} S(k) = \frac{1}{N} \left\langle \bar{\rho}(k) \bar{\rho}(-k) \right\rangle$$

i.e. as we know from the beginning, the elastic scattering function is related to the FT of the particle density **fluctuations (squared)**

$$\bar{\rho}(k) = F T [ \sum_i \delta(\mathbf{r} - \mathbf{r}_i) ] = \sum_i \exp(i k \mathbf{r}_i)$$

Combining the two equations one gets

$$S(k) = 1 + \frac{1}{Nk^2} \sum_{k'} \frac{\bar{u}(k')}{kT} \langle \bar{\rho}(k) \bar{\rho}(k') \bar{\rho}(k+k') \rangle \mathbf{k} \cdot \mathbf{k}'$$

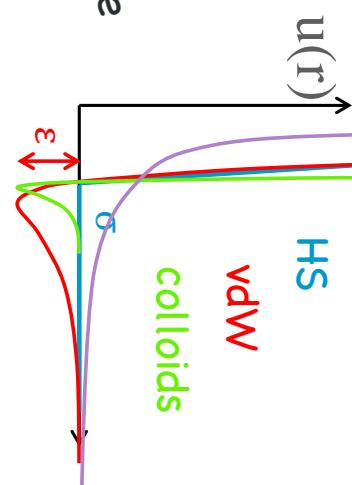
**Random Phase Approximation (RPA):** it is assumed that in the above formula, because of destructive interference among different  $k$ s fluctuations, only the term  $\mathbf{k}' = -\mathbf{k}$  of the sum survives. (valid in the long wavelength limit). With this assumption and using the  $S(k)$  definition one gets

$$S(k) = \frac{1}{1 + \rho \bar{u}(k) / kT} \quad \rightarrow \quad \bar{c}(k) = -\frac{\rho \bar{u}(k)}{kT} \quad \rightarrow$$

The same result of Abe theory in asymptotic limit is assumed at any length

$$c(r) = -\frac{u(r)}{kT}$$

**RPA** closes the equations for  $S$  (or  $c$ ) in the Fourier space. From  $S(k)$  (or  $c(k)$ ) all the other structure functions can be evaluated. RPA is an approximate “global” theory valid in any range of  $r$ , but needing that the **inter-particle potential is Fourier-transformable and weak**. This is not true for hard core potentials such as LJ or hard spheres.



# Structure of liquids – module of the course “structure of matter”

## Long range interactions

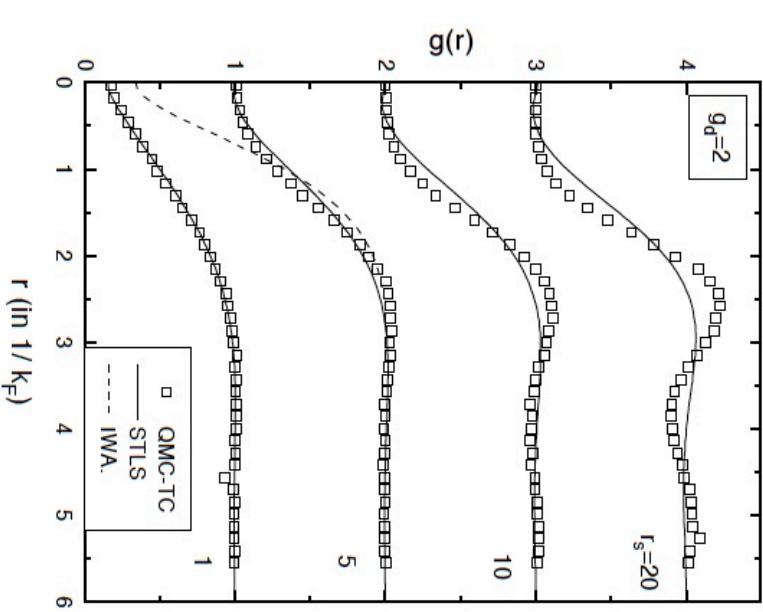
As a result, RPA produces the following approximation for structure functions

$$S(k) = \frac{1}{1 + \rho \bar{u}(k) / kT} \quad \rightarrow \quad \bar{c}(k) = -\frac{\rho \bar{u}(k)}{kT} \quad \rightarrow \quad c(r) = -\frac{u(r)}{kT}$$

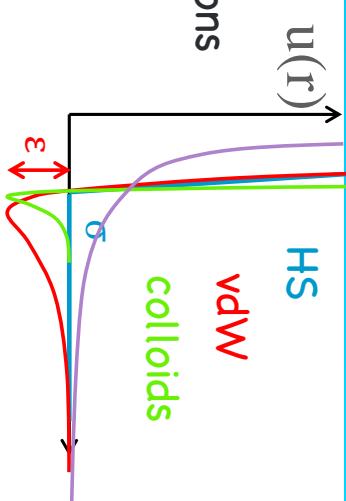
RPA is a closure, all the quantities can be calculated at least numerically.

RPA is only the first step in a development in the response functions: it can be shown that in RPA the system respond to the local field generated by the particles (electron) cloud with the response function of the ideal system.

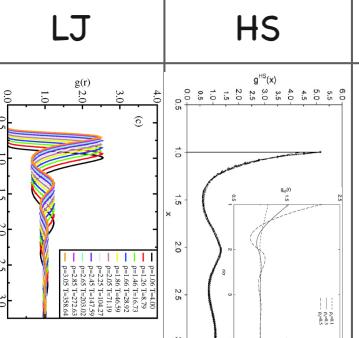
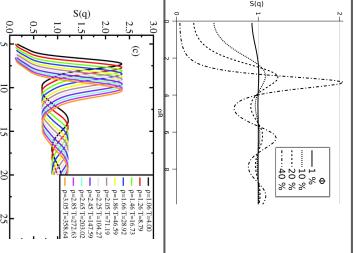
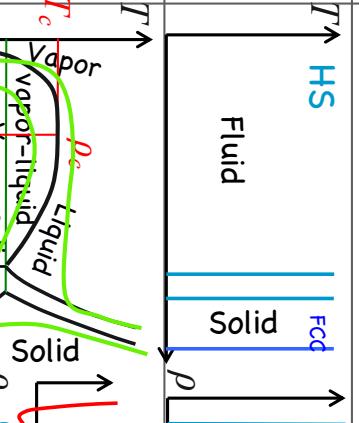
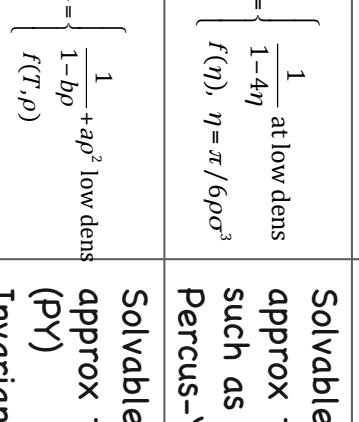
Clearly, RPA is very rough for short range/hard-core potentials, because it assumes that Abe limit is valid everywhere, while this is a very bad assumption in the hard core region.



The Coulomb potential diverges for short  $r$ , therefore RPA is bad even for coulomb interactions. However it is globally better than for other potentials because it catches the long range limit, which for the Coulomb case produces the predominant effects.



# Structure of liquids – module of the course “structure of matter”

	Pair correlation g(r), h(r), c(r)	Structure factor S(k), S(0), c(k)	Internal energy, phase diagram, u(r)	Equation of state	“Force equation”
general	$h(r) = g(r) - 1$ $h(r) = c(r) + \rho \int d\mathbf{r}' h(r') c( \mathbf{r} - \mathbf{r}' )$	$S(k) = 1 + \bar{h}(k)$ $S(0) = \rho k T k_B$ $\bar{c}(k) = \frac{\bar{h}(k)}{1 + \bar{h}(k)} = 1 - \frac{1}{S(k)}$	$E = \frac{3}{2} N k T + \frac{N}{2} \rho \int u(r) g(r) d\mathbf{r}$ $C_V = \frac{3}{2} N k + \frac{N}{2} \rho \int u(r) \frac{\partial g}{\partial T}(r) d\mathbf{r}$	$p = \rho k T - \frac{\rho^2}{6} \int r \frac{\partial u(r)}{\partial r} g(r) d\mathbf{r}$ $= -\frac{\rho}{k T g(r)} \int d\mathbf{r} \nabla u(r) g_3(\mathbf{r}, \mathbf{r})$	$\sqrt{[\ln(g(r)) + \frac{u(r)}{kT}]}$ $= -\frac{\rho}{k T g(r)} \int d\mathbf{r} \nabla u(r) g_3(\mathbf{r}, \mathbf{r})$
Ideal gas	$g(r) = 1$ $h(r) = 0$ $c(r) = 0$	$S(k) = 1$ $k_T = 1/\rho k T$ $c(k) = 0$	$E = \frac{3}{2} N k T$ $C_V = \frac{3}{2} N k$	$p = \rho k T$	$u(r) = 0$
LJ				$\frac{p}{\rho k T} = \begin{cases} \frac{1}{1-4\eta} & \text{at low dens} \\ f(\eta), \eta = \pi / 6\rho\sigma^3 & \end{cases}$	Solvable by approx theories such as Percus-Yevick
Coulomb	RPA	$\bar{c}(k) = -\frac{\rho \bar{u}(k)}{k T}$		$\frac{p}{\rho k T} = \begin{cases} \frac{1}{1-b\rho} + a\rho^2 & \text{low dens} \\ f(T_c, \rho) & \end{cases}$	RPA long wavelength limit

## Summary

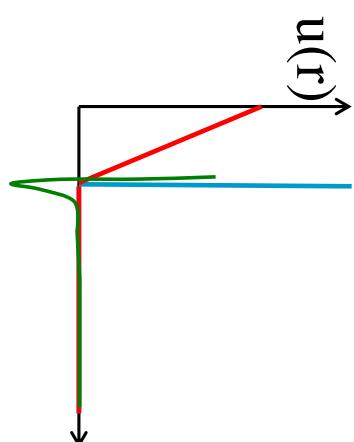
- ✓ PY works for short ranged hard core potentials (e.g. hard spheres or shifted LJ)
- ✓ RPA works for long ranged potential without an hard core
- ✓ Abe works for the long range part, where it returns the correct asymptotic behavior  $c(r) = -u(r)/kT$  the condition of validity is  $h^2 < |c|$

# Structure of liquids – module of the course “structure of matter”

## Connection between structure and interactions

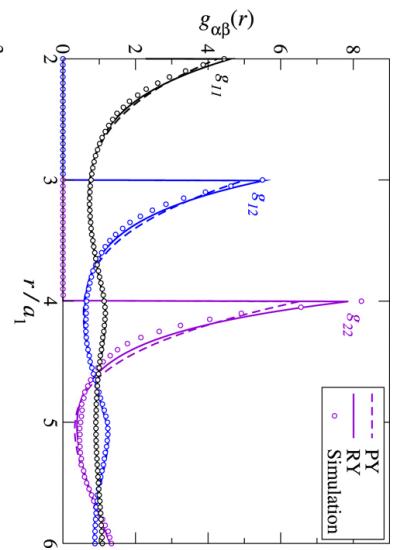
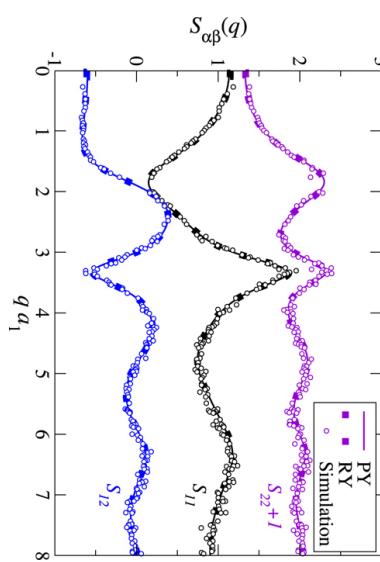
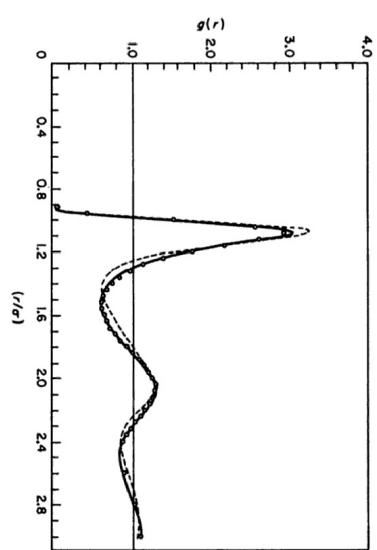
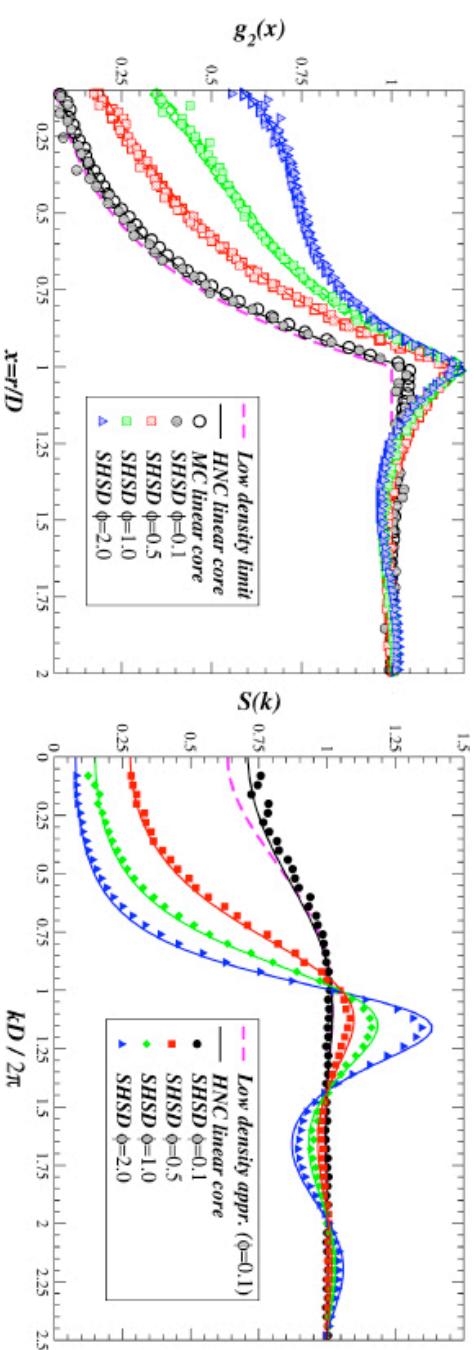
### Approximate liquid theories: comparison

- ✓ PY works very well for hard core potentials (e.g. hard spheres). In practice, structure functions are basically indistinguishable from simulations



- ✓ With LJ potential PY works quite well on average, except for small errors in the location of peaks and wells

### ✓ HNC (or Abe) works well for spheres with soft core



- ✓ RPA is not generally used for hard core liquids. However, in the standard form or some variants is often used for the Coulomb liquids, where the long range of the interaction makes the behavior of the system being dominated by potentials at all distances, making global theories with similar weights at all distances working better.