Fundamentals of Condensed Matter
(lecture 4)

Summary lecture 3

- Pairwise additivity

$$U_{tot} = \frac{1}{2}\sum_{i\neq j}\phi(r_{ij}) = \sum_{i>j}\phi(r_{ij})$$

- Second virial coefficient

$$B_2(T) = -2\pi\int_0^\infty \left(e^{-\beta\phi(r)} - 1\right) r^2 dr$$

- B2 for various model potentials
  - Hard spheres

$$B_2 = \frac{2\pi\sigma^3}{3}$$

  - Square well potential

$$B_2 = \frac{2\pi\sigma^3}{3}\left[1 - \left(\lambda^3 - 1\right)\left(e^{\beta\epsilon} - 1\right)\right]$$

  - Van der Waals

$$B_2 = b - \frac{a}{kT} \qquad a = -2\pi\int_\sigma^\infty \phi(r) r^2 dr$$

$$b = 2\pi\int_0^\sigma r^2 dr = \frac{2\pi\sigma^3}{3}$$

Content of the Liquids part (lectures 1-6)

- Recap thermodynamics and phase diagrams
- Recap statistical mechanics and classical statistical mechanics
- Second virial coefficient and model liquids
- **Structure of liquids and compressibility relation** $\longrightarrow$ **Today, lecture (4)**
- Ornstein-Zernike relation and link to (scattering) experiments
- Complex and biological fluids

Today’s lecture (4)

- Structure of liquids
  - Radial distribution function g(r)

- Compressibility equation
  - g(r) in terms of configuration integral
  - Fluctuations
  - Compressibility
  - Compressibility equation

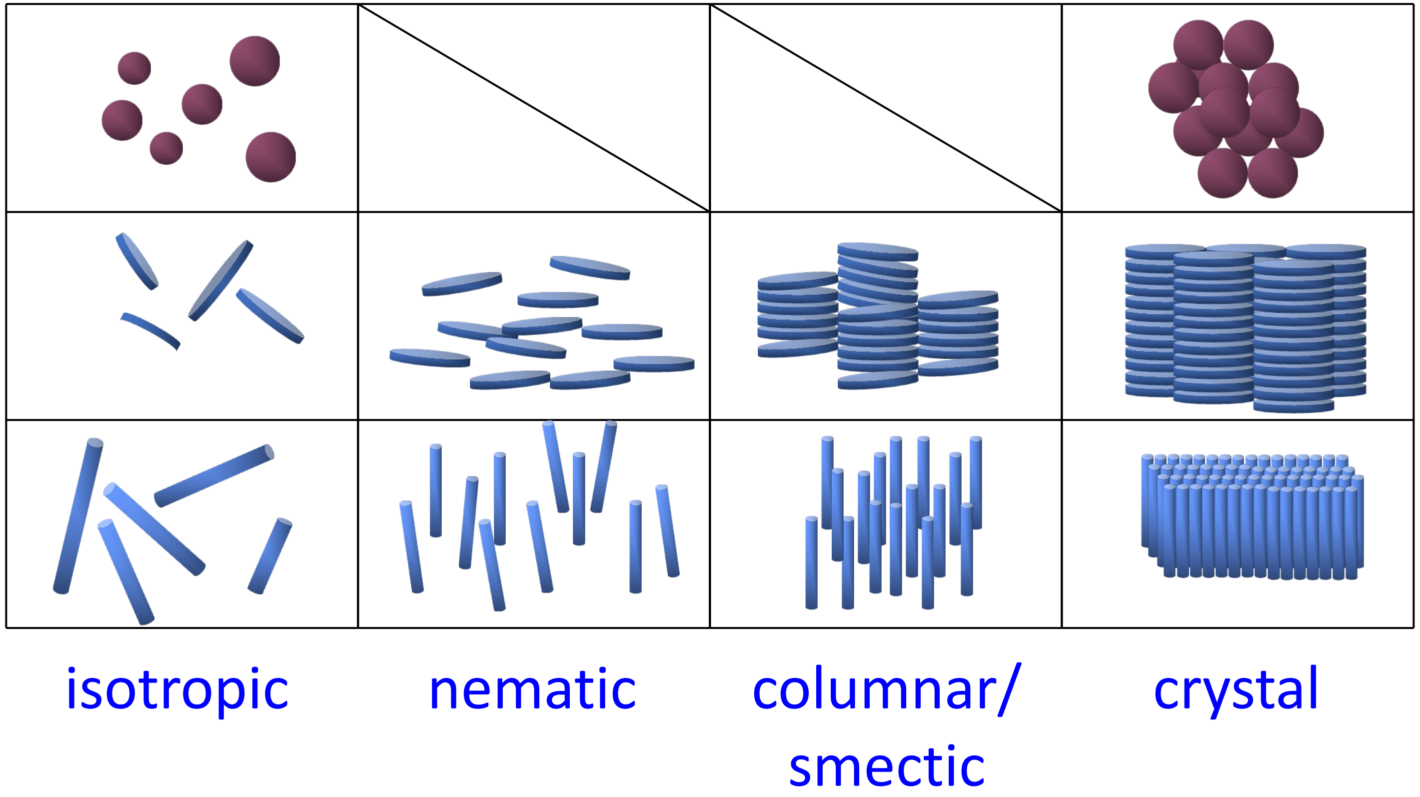
Why do liquids exist?

“Assume that a group of intelligent theoretical physicists had lived in closed buildings from birth such that they never had occasion to see any natural structures. ... They probably would predict the existence of atoms, of molecules, of solid crystals (…), of gases, but most likely not the existence of liquids.”

V.F. Weisskopf,
Trans. NY Acad. Sci. II 38, 202 (1977)

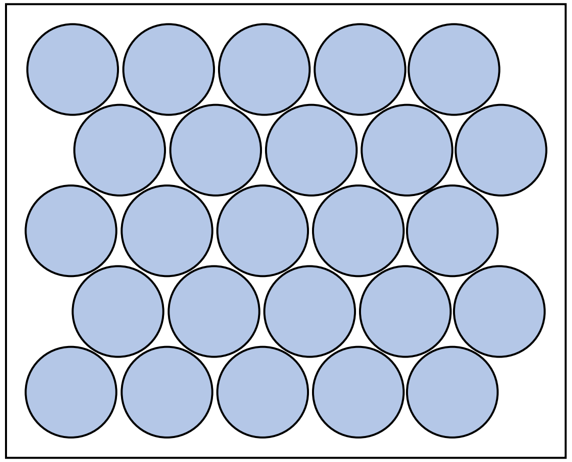
Structural knowledge is essential

(Complex) liquids: strong links between structure, thermodynamics and (pair) interactions

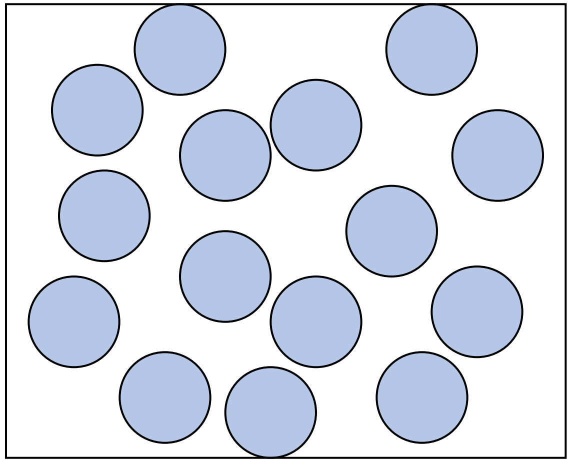


Structure of liquids

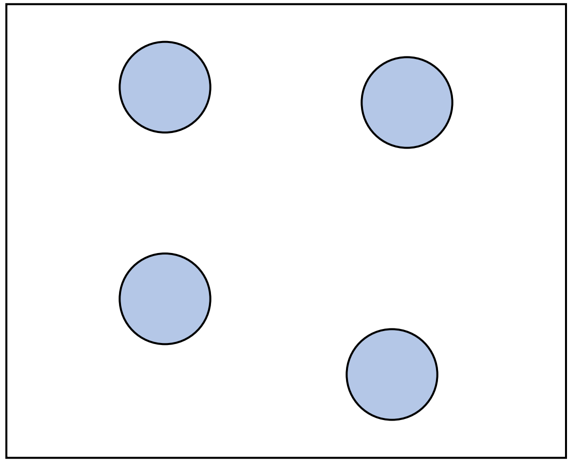
Crystal



Liquid



Gas



High density

Long range order

Vibrations at lattice site

A bit of both

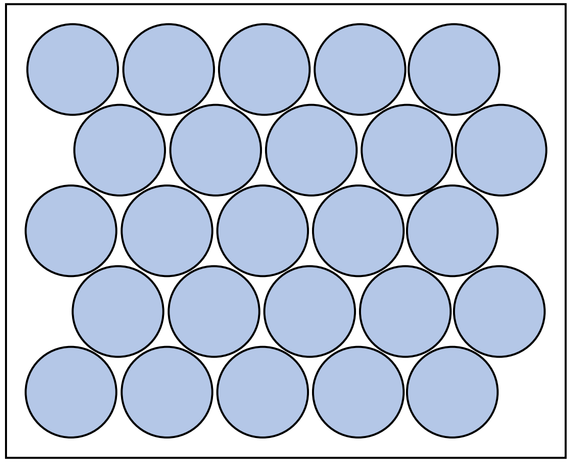
Low density

No order

Lots of movement

Reference structure for liquids?

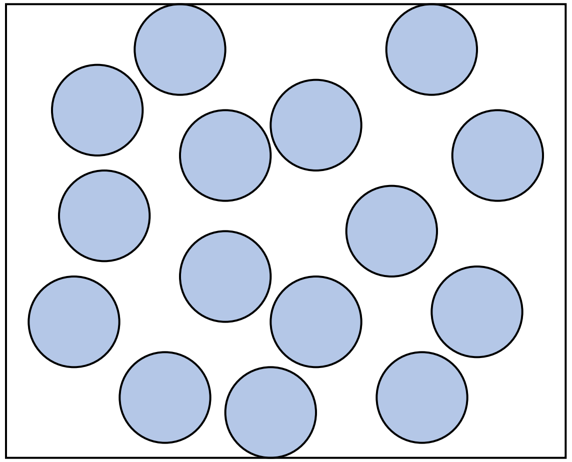
Crystal



Perfect crystals of independent atoms

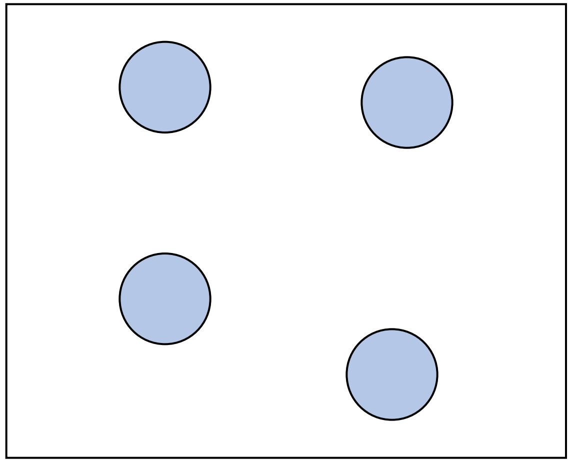
(Einstein crystal, see lecture 2 and problem set)

Liquid



?

Gas

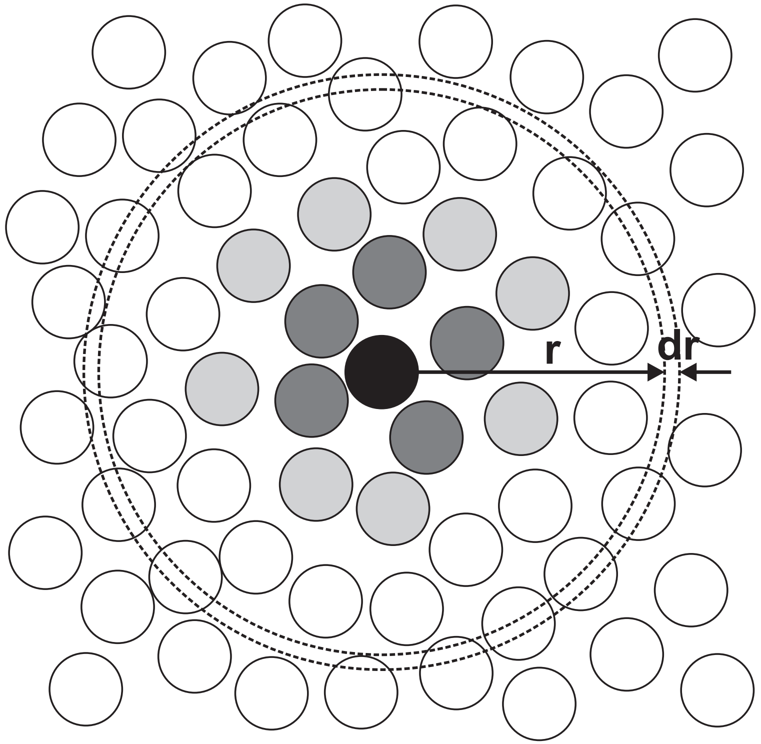


Perfect gas

Quantifying the structure of liquids

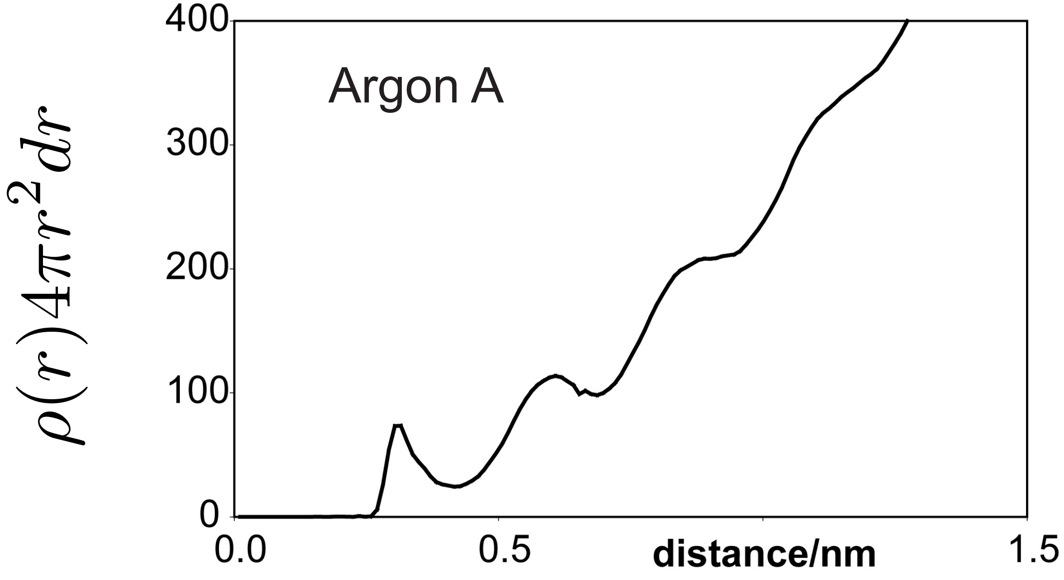
average number density

$$\rho = \frac{N}{V}$$



average number of particles between r and r+dr

$$\rho(r)4\pi r^2 dr$$



Quantifying the structure of liquids

average number density

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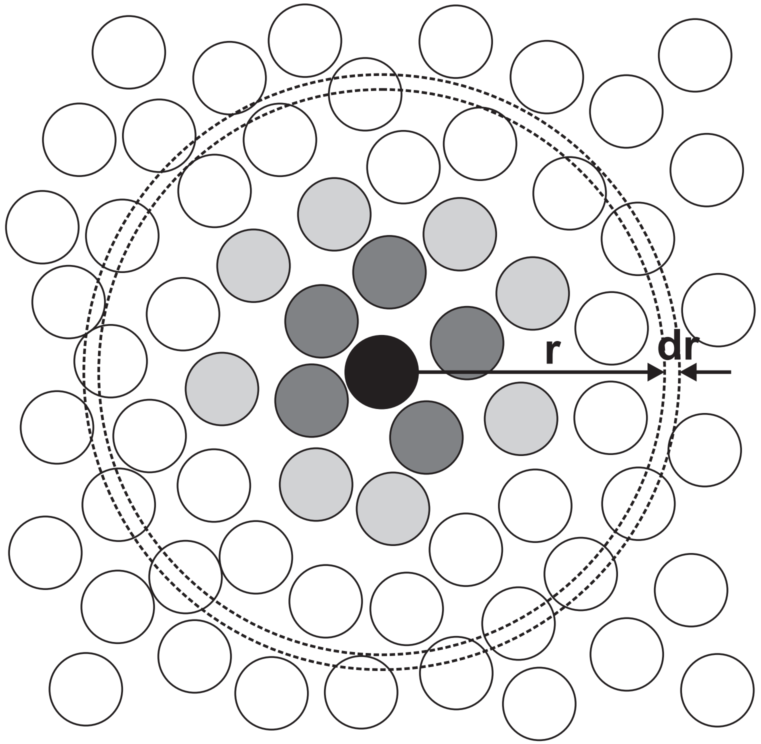
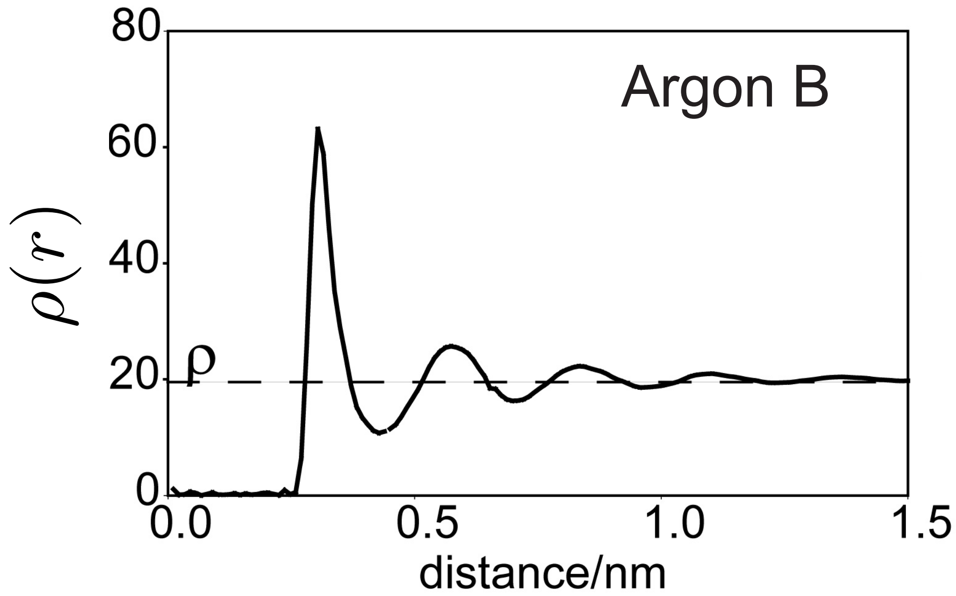


radially averaged number density

$$\rho(r)$$



Quantifying the structure of liquids

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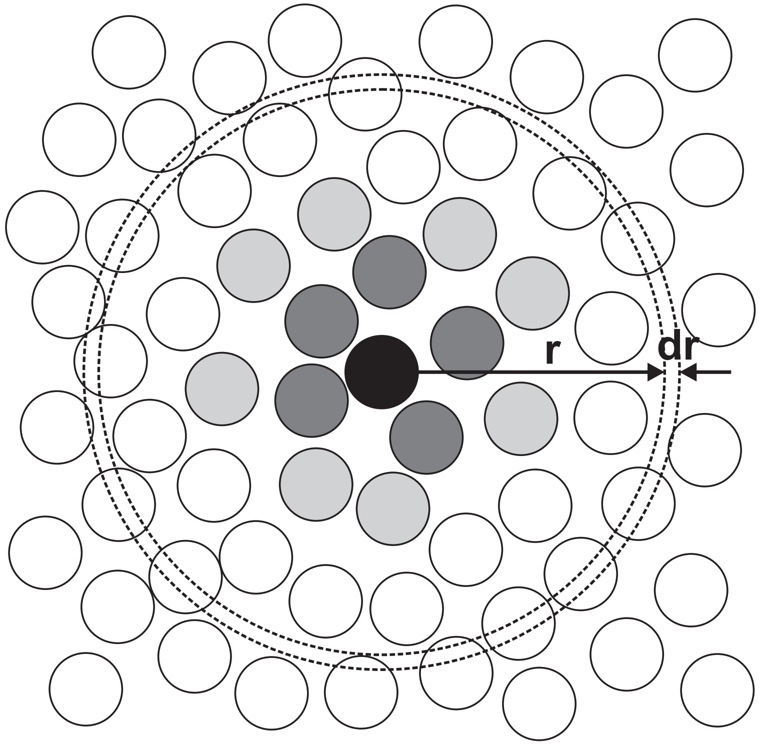
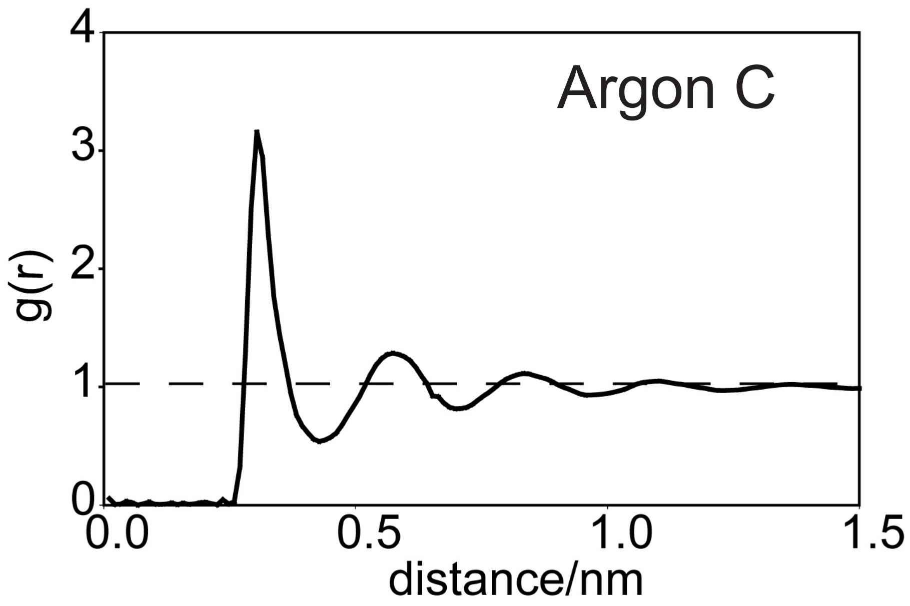
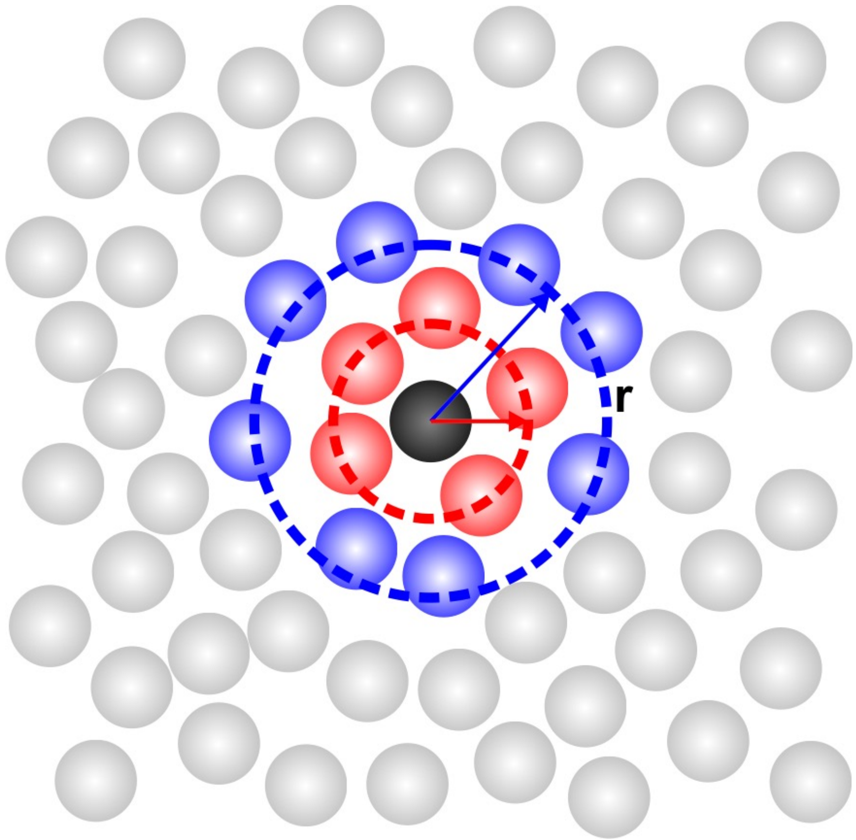


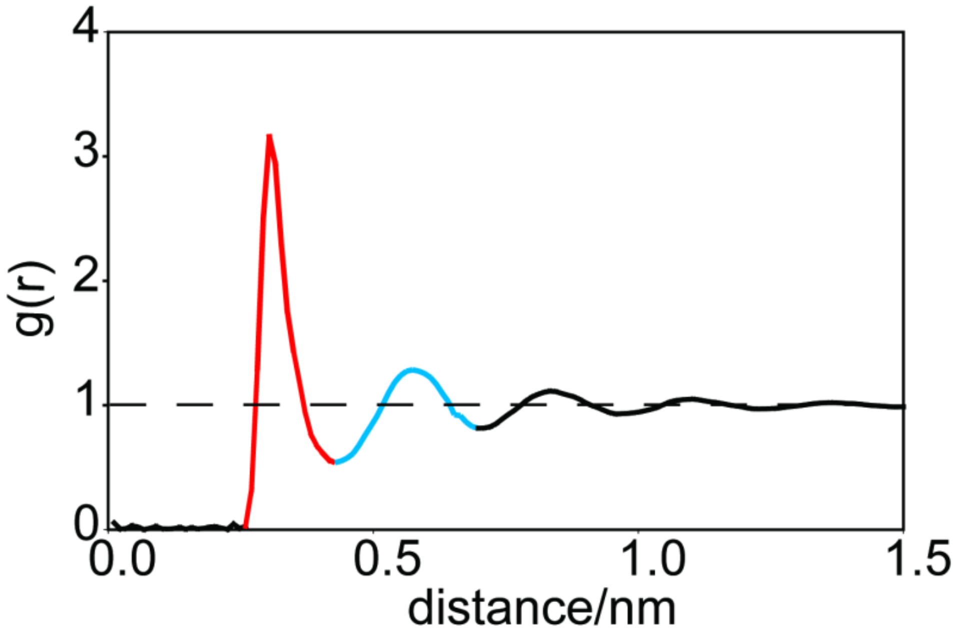
radial distribution function

$$g(r) = \frac{\rho(r)}{\rho}$$



Coordination shells

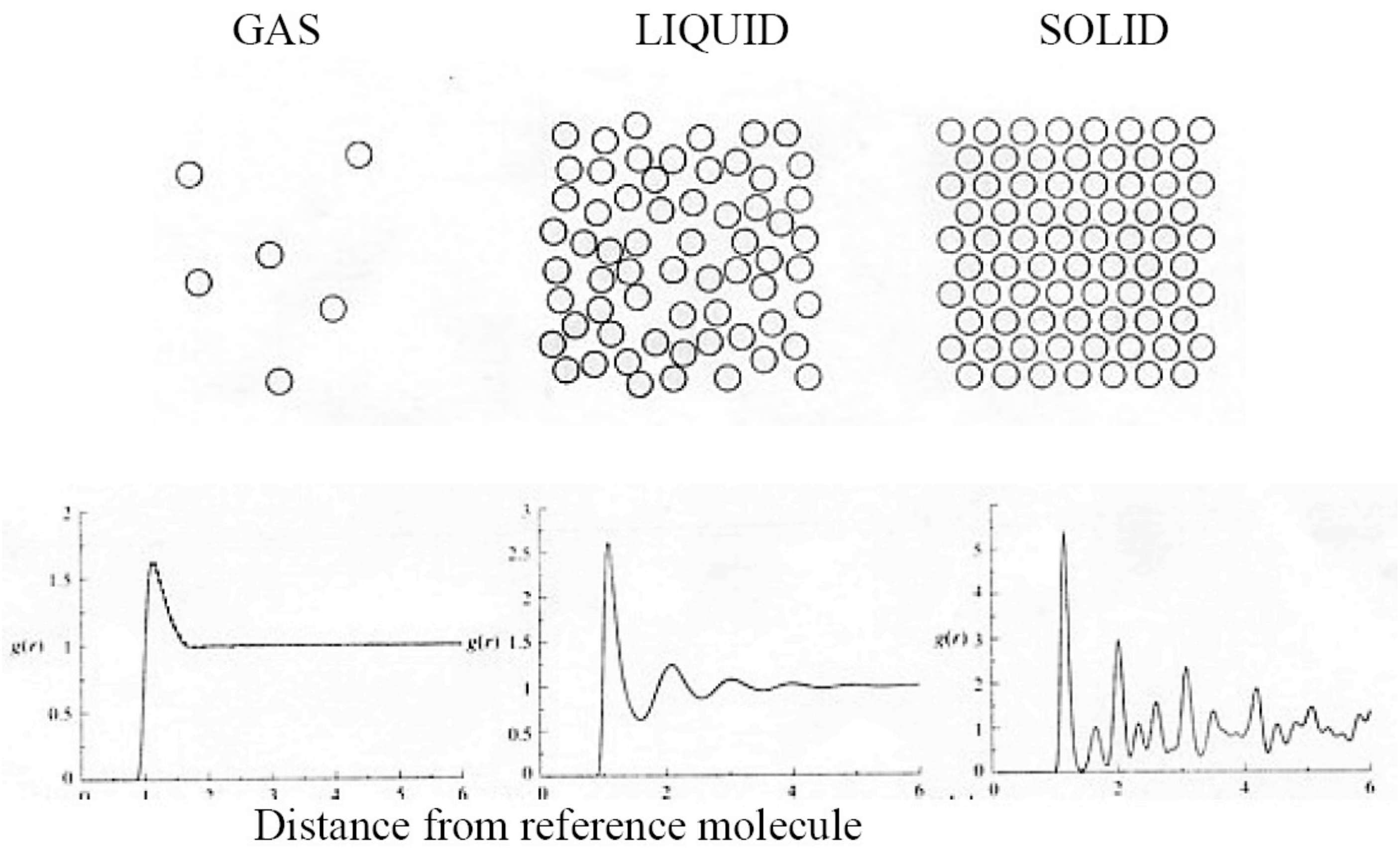




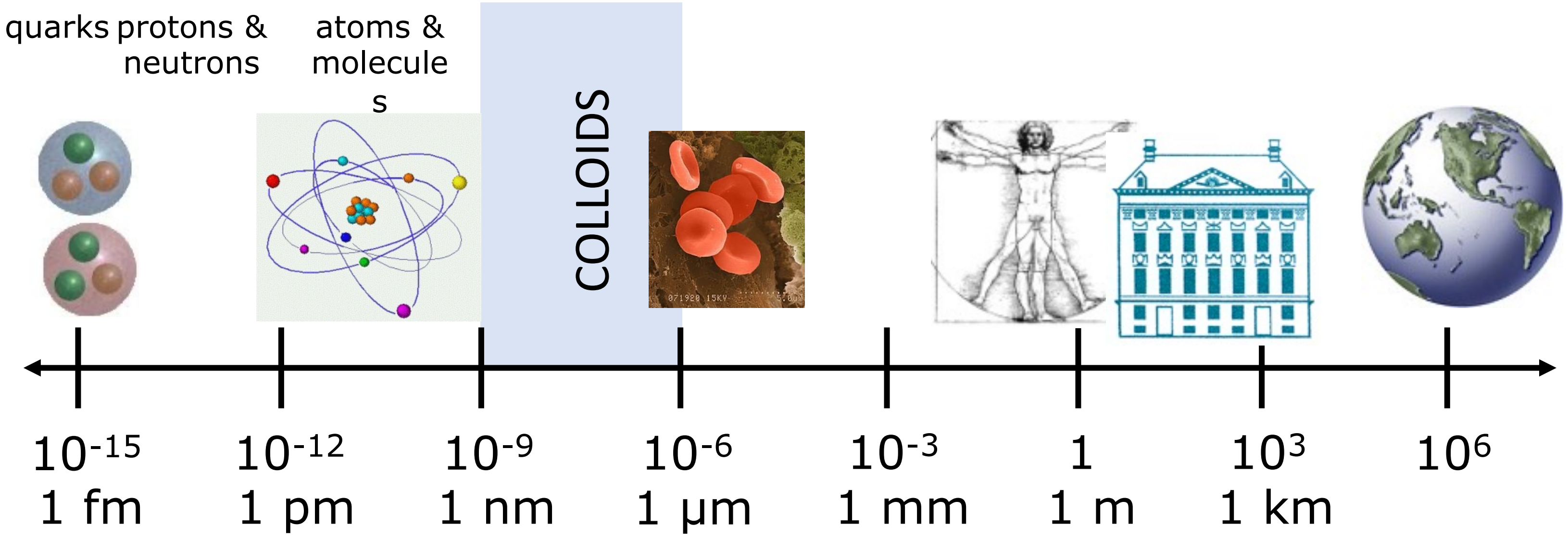
average number of particles between r and r+dr

$$\rho(r)4\pi r^2 dr = \rho g(r)4\pi r^2 dr$$

Gas, liquid and crystal g(r)



Intermezzo: Colloids



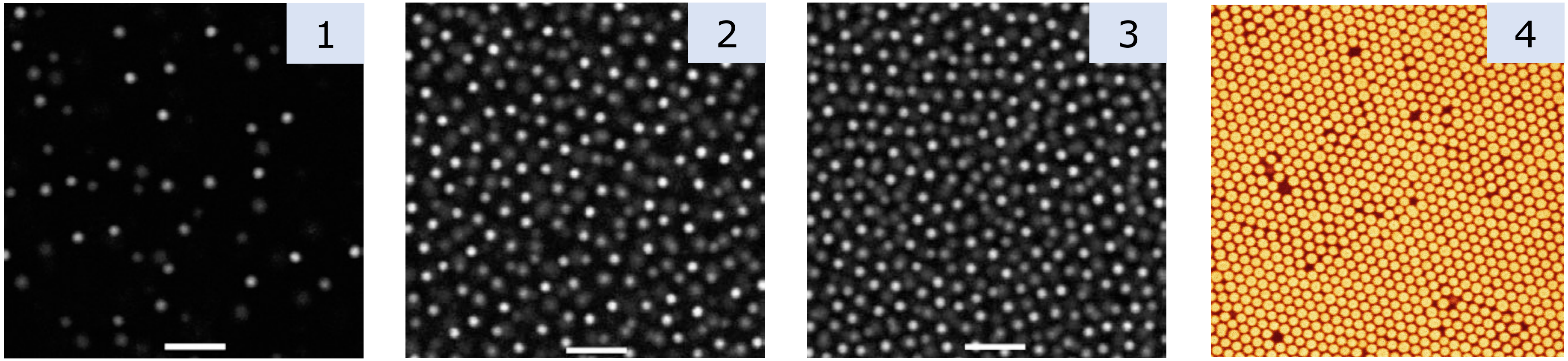
Same statistical thermo → Similar phase behaviour

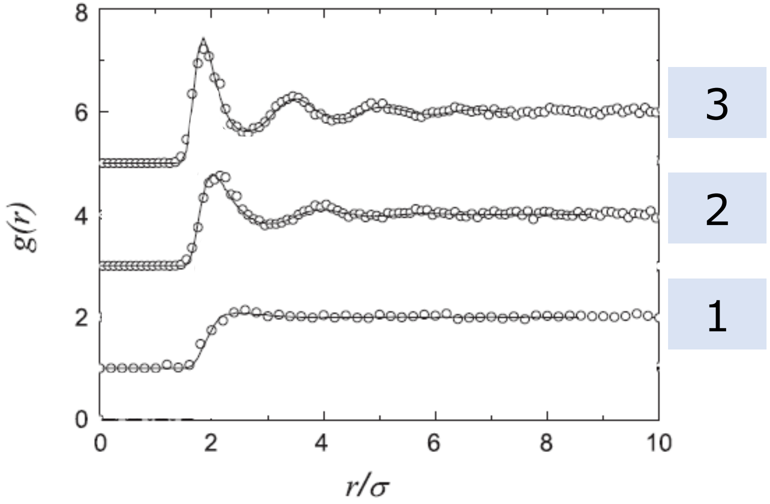
Colloids = (huge) “model atoms”

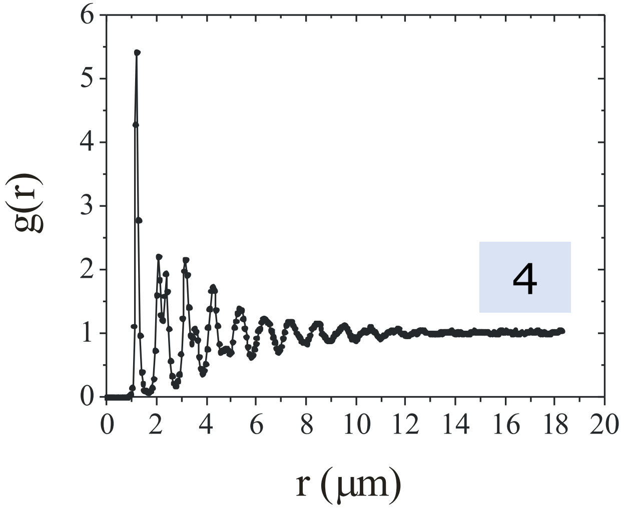
3rd year BSc course ‘Soft Matter’ by Evan Spruijt and RD

Colloidal gas,liquid and crystal g(r)

What you see is what you get: picture ↔ g(r)







Paddy Royall et al, J Phys.: Condens. Mater, 15, S3581 (2003)

RPAD et al, Langmuir, 20, 658 (2004)

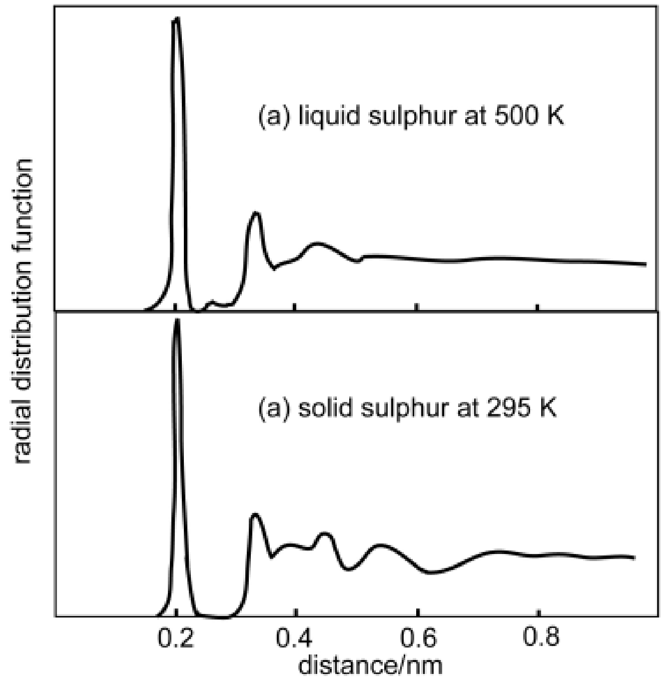
g(r) of atoms and molecules

Mono-atomic liquids → “particle-picture” applies

Molecular liquids → “particle-picture” may fail

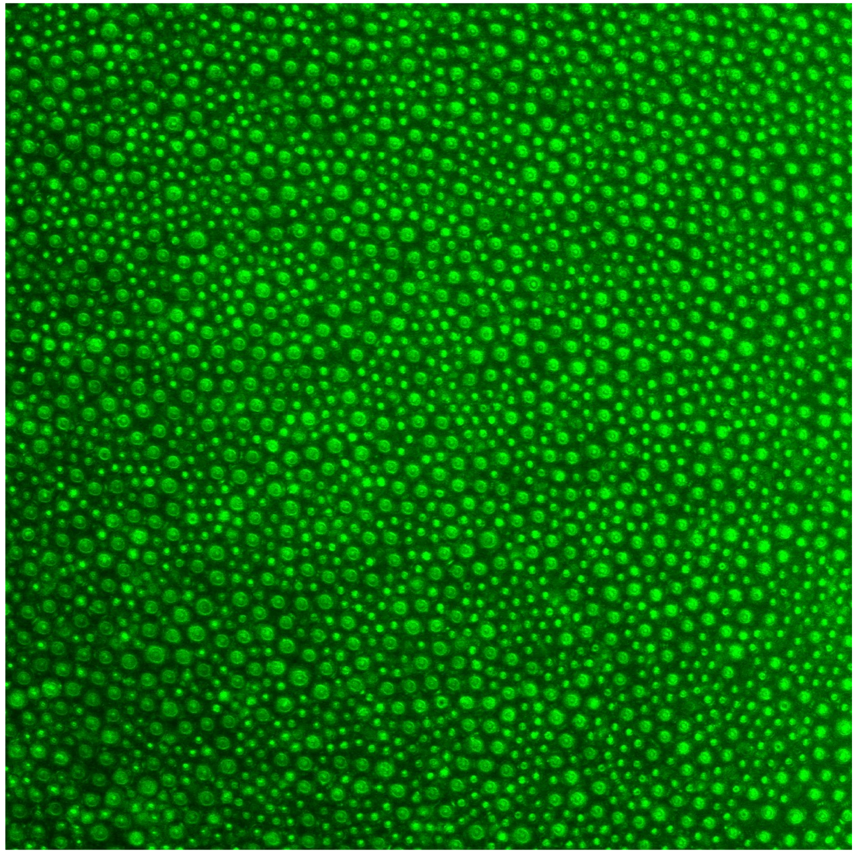
Example: Sulfur S_8

- ‘intra-ring’ S-S distance
- ‘inter-ring’ S-S distance



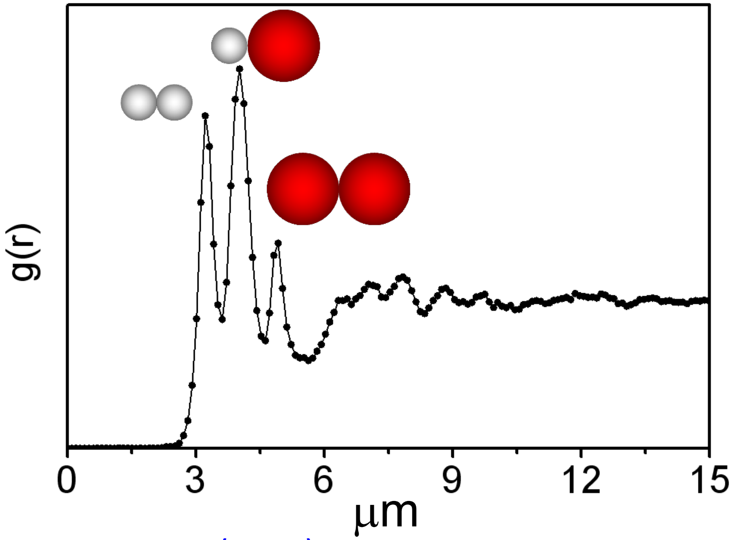
g(r) of mixtures

Simplest mixture: binary system of large and small hard spheres

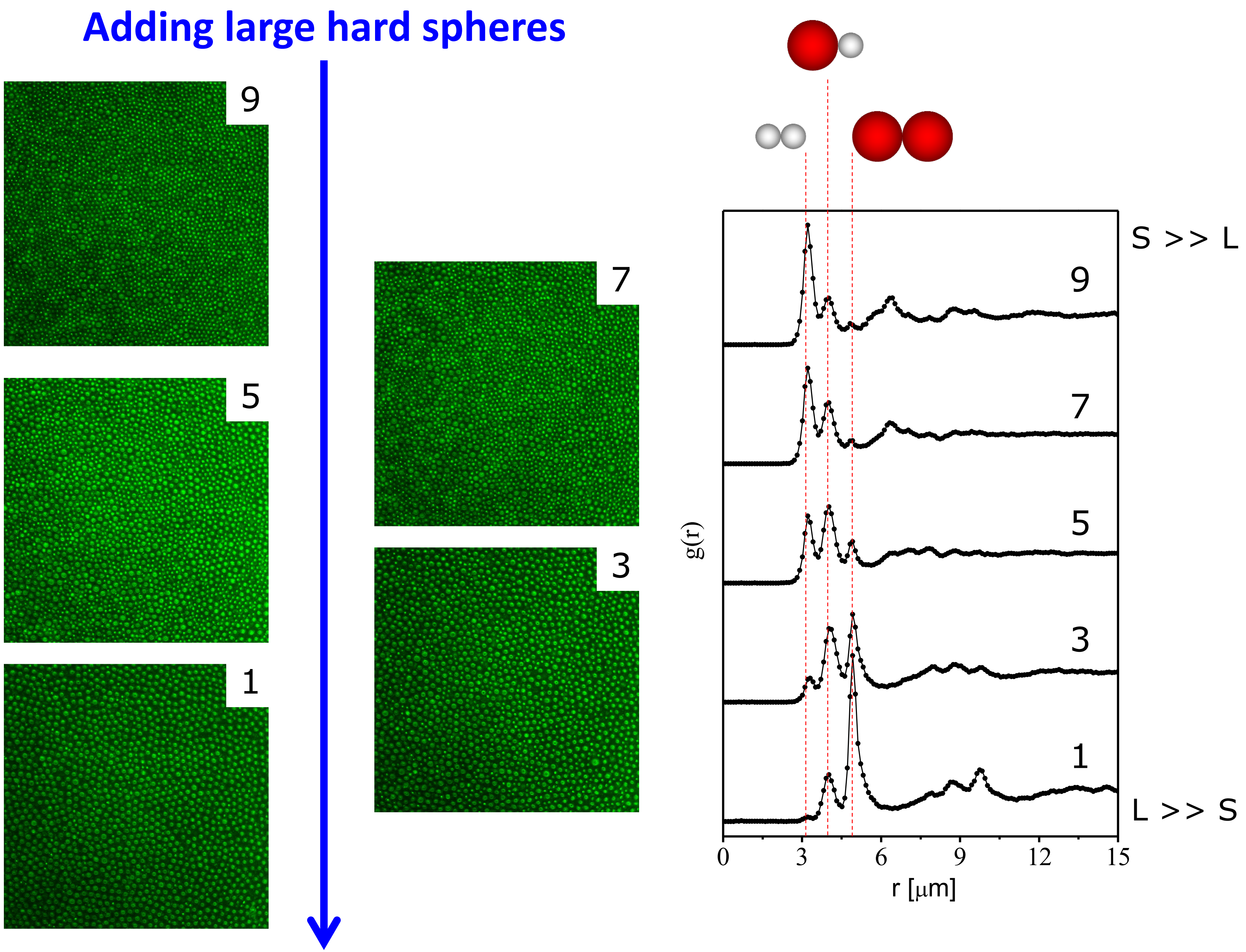


185 x 185 μm² (again colloids)

$$g(r) \begin{cases} g_{SS}(r) \\ g_{SL}(r) \text{ (and } g_{LS}(r)) \\ g_{LL}(r) \end{cases}$$



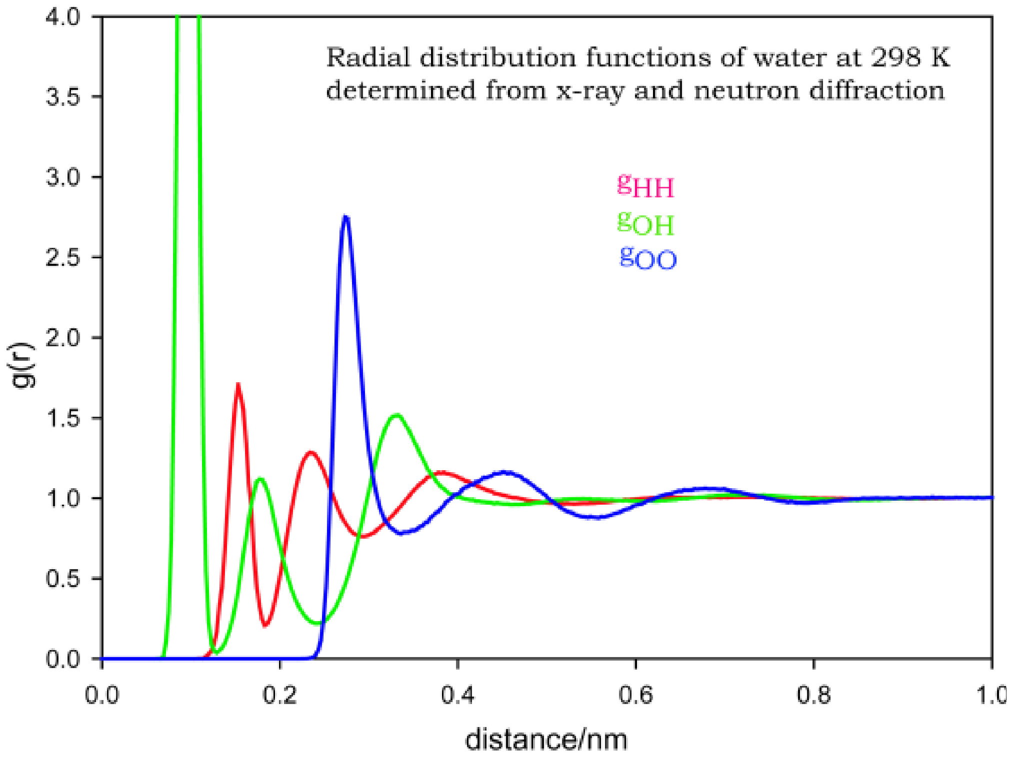
J. Baumgartl et al, Phys. Rev. Lett., 98, 198303 (2007)


Adding large hard spheres
9
5
1
7
3
g(r)
r [μm]
0
3
6
9
12
15
S >> L
L >> S

Molecular ‘binary’ g(r): H_2O

`partial radial distribution functions’ for water

$$g_{H_2O}(r) \begin{cases} g_{HH}(r) \\ g_{OH}(r) \\ g_{OO}(r) \end{cases}$$



radial distribution functions can be directly measured (lecture 5)

Today's lecture (4)

- Structure of liquids
  - Radial distribution function g(r)

- **Compressibility equation**
  - g(r) in terms of configuration integral
  - Fluctuations
  - Compressibility
  - Compressibility equation

Compressibility relation

link between structure [g(r)] and thermodynamics [κ_T]

interactions!!

I. **Find expression for radial distribution function in terms of Z_N**

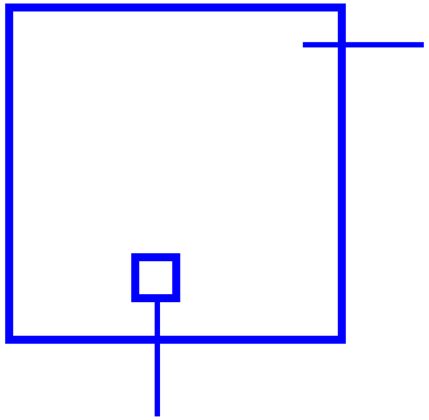
II. Use expression for *g(r)* to quantify fluctuations

Related to the isothermal compressibility κ_T

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$$

$$\rho = \frac{N}{V}$$

I. Expression for *g(r)* $= \dfrac{\rho(r)}{\rho}$



N, V, T

$d\tau$

in the limit of

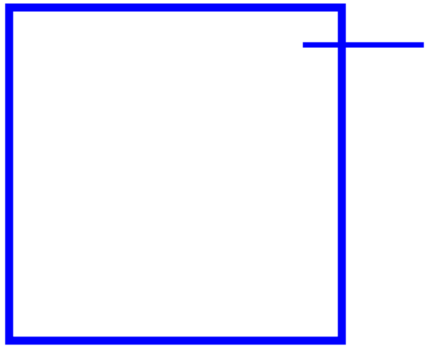
$N, V \to \infty$ & $\dfrac{N}{V} = \rho$

Average number of particles in $d\tau$?

$\langle N \rangle$ in $d\tau$ = probability that a particle is in $d\tau$ $\qquad \rho d\tau$

$\langle N(r) \rangle$ in $d\tau$ = probability that a particle is at distance r in $d\tau$ $\qquad \rho(r) d\tau$

I. Expression for *g(r)* $= \dfrac{\rho(r)}{\rho}$



N, V, T

in the limit of

$N, V \to \infty$ & $\dfrac{N}{V} = \rho$

probability to find certain configuration

$$\left.\begin{array}{l} 1 \text{ at } \vec{r}_1 \text{ in } d\tau_1 \\ 2 \text{ at } \vec{r}_2 \text{ in } d\tau_2 \\ \quad \cdots \\ N \text{ at } \vec{r}_N \text{ in } d\tau_N \end{array}\right\} \to \frac{e^{-\beta U(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)}}{Z_N} d\tau_1 d\tau_2 \cdots d\tau_N$$

Configuration integral

$$Z_N = \int \cdots \int e^{-\beta U(x_1,\ldots,z_N)} d\tau_1 \cdots d\tau_N \quad \to \quad Z_N = \int_V d\tau_1 \int_V d\tau_2 \cdots \int_V d\tau_N e^{-\beta U(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)}$$

I. Expression for *g(r)* … cont'd

$$g(r) = \frac{V^2}{Z_N} \int_V d\tau_3 \cdots \int_V d\tau_N e^{-\beta U(\vec{r},\vec{r}',\vec{r}_3,\ldots,\vec{r}_N)}$$

in the limit of $N, V \to \infty$ & $\dfrac{N}{V} = \rho$

Compressibility relation

link between structure [g(r)] and thermodynamics [κ_T]

interactions!!

I. Find expression for radial distribution function in terms of Z_N

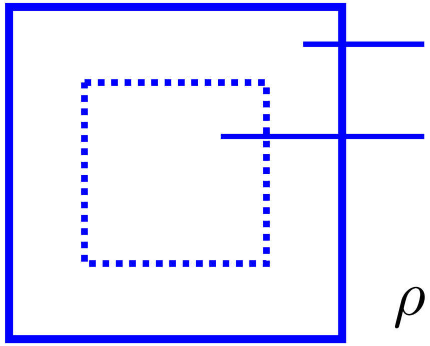
II. Use expression for *g(r)* to quantify fluctuations

Related to the isothermal compressibility κ_T

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$$

$$\rho = \frac{N}{V}$$

II. Fluctuations (grand-canonical ensemble)



N, V, T

n, v, T

$$\rho = \frac{N}{V} = \frac{\langle n \rangle}{v}$$

Fluctuations in *n* → Variance

$$\langle n^2 \rangle - \langle n \rangle^2 = \rho^2 k_B T v \kappa_T \; {}^*$$

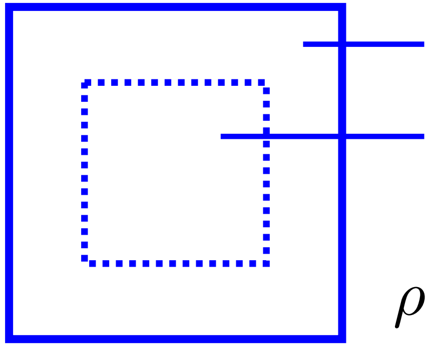
with compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$$

Calculate $\langle n^2 \rangle - \langle n \rangle^2$ using expression for *g(r)* …

* not derived here

Fluctuations … cont'd



N, V, T

n, v, T

$$\rho = \frac{N}{V} = \frac{\langle n \rangle}{v}$$

Define

$$q(\vec{r}) = \begin{cases} 1 & \text{if} \quad \vec{r} \in v \\ 0 & \text{if} \quad \vec{r} \notin v \end{cases}$$

Counts number of particles in *v*

$$\sum_{i=1}^{N} q(\vec{r}_i) = n$$

Calculate $\langle n^2 \rangle - \langle n \rangle^2$ Start with $\langle n^2 \rangle$

Fluctuations … cont'd … cont'd

$$\langle n^2 \rangle = \langle n \rangle + \rho^2 v \int d\tau \, [g(r) - 1] + \langle n \rangle^2$$

total correlation function: $h(r) \equiv g(r) - 1$

Compressibility relation

we obtained: $$\langle n^2\rangle - \langle n\rangle^2 = \langle n\rangle + \rho^2 v \int h(r)d\tau$$

started with: $$\langle n^2\rangle - \langle n\rangle^2 = \rho^2 k_B T v \kappa_T$$

$$\boxed{\begin{aligned} 1 + \rho \int h(r)d\tau &= \rho k_B T \kappa_T \\ 1 + 4\pi\rho \int_0^\infty h(r) r^2 dr &= \rho k_B T \kappa_T \end{aligned}}$$

Link between ***structure*** and ***thermodynamics***

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$$

See also problem set

Next lecture: Ornstein-Zernike relation

- Link between ***interaction potential*** and ***structure***

$$h_{12} = c_{12} + \rho \int d\tau_3 c_{13} h_{32}$$

or

$$\hat{h}(k) = \hat{c}(k) + \rho \hat{c}(k) \hat{h}(k)$$

- Link with (scattering) experiments

Content of the Liquids part (lectures 1-6)

- Recap thermodynamics and phase diagrams
- Recap statistical mechanics and classical statistical mechanics
- Second virial coefficient and model liquids
- Structure of liquids and compressibility relation
- **Ornstein-Zernike relation and link to (scattering) experiments** → **Next lecture (5)**
- Complex and biological fluids