Fundamentals of Condensed Matter (lecture 5)

Summary lecture 4

- Radial distribution function g(r)

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

- Expression for g(r) in terms of Z_N

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

- Compressibility relation

$$1 + 4\pi\rho \int_0^\infty h(r) r^2 dr = \rho k_B T \kappa_T$$

- Total correlation function

$$h(r) \equiv g(r) - 1$$

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** → **Today's lecture (5)**
- Relation g(r) with interactions and thermodynamics and recap

Today's lecture (5)

- Ornstein-Zernike relation
  - Direct correlation function
  - Fourier transform of Ornstein-Zernike
    - Link to thermodynamics, interactions, structure and scattering

- Scattering and microscopy experiments (on liquids)
  - Light scattering and Rayleigh ratio
  - Scattering by small, large and many large particles
  - The structure factor
  - Measuring structure factors and radial distribution functions

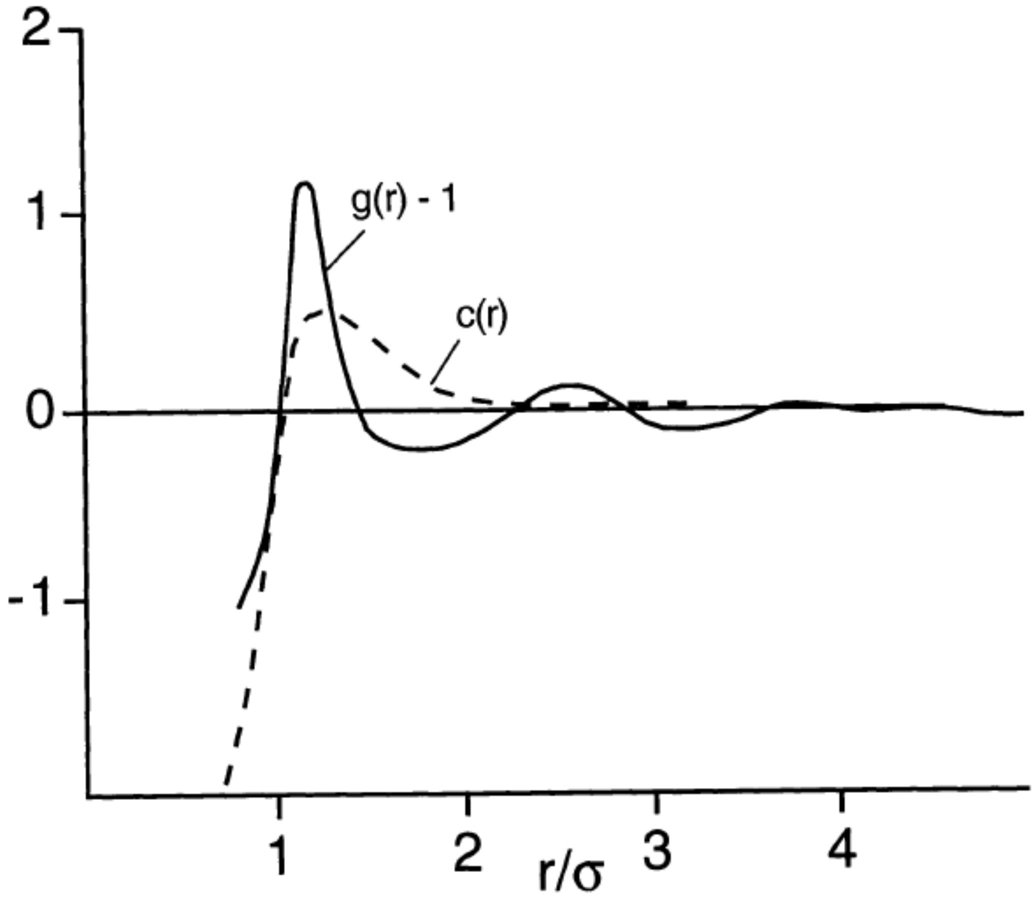
Orstein-Zernike equation

link pair potential to structure

Split total interaction in ***direct*** and ***indirect*** part

$$h_{12} = \underbrace{c_{12}}_{\textit{direct}\ \text{part}} + \rho \underbrace{\int d\tau_3 c_{13} h_{32}}_{\textit{indirect}\ \text{part}}$$

Direct correlation function *c*(*r*)



range $c(r)$ much shorter than $g(r)$ and $h(r)$, but similar to $\phi(r)$

Link structure and pair potential

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

Very difficult, non-linear integral equation

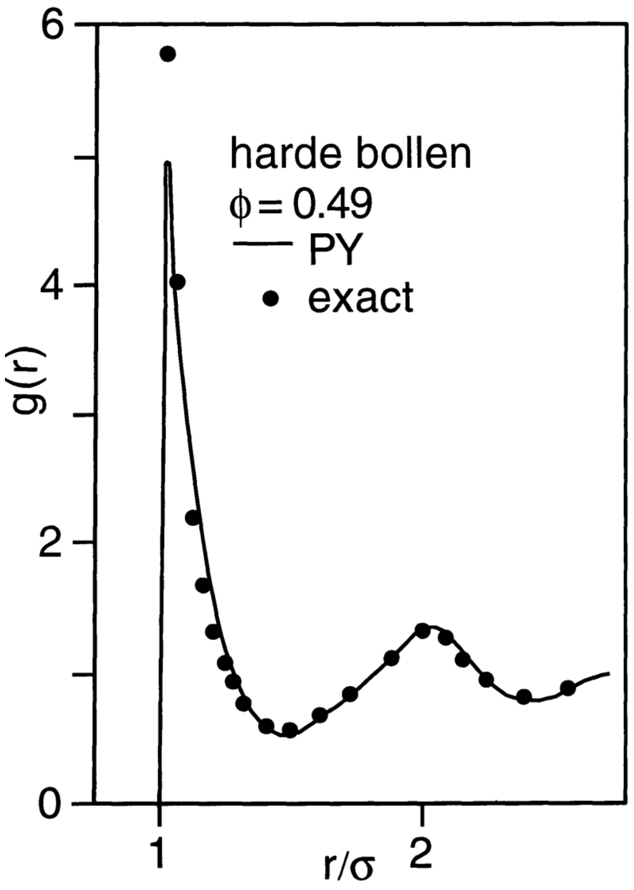
closure relations

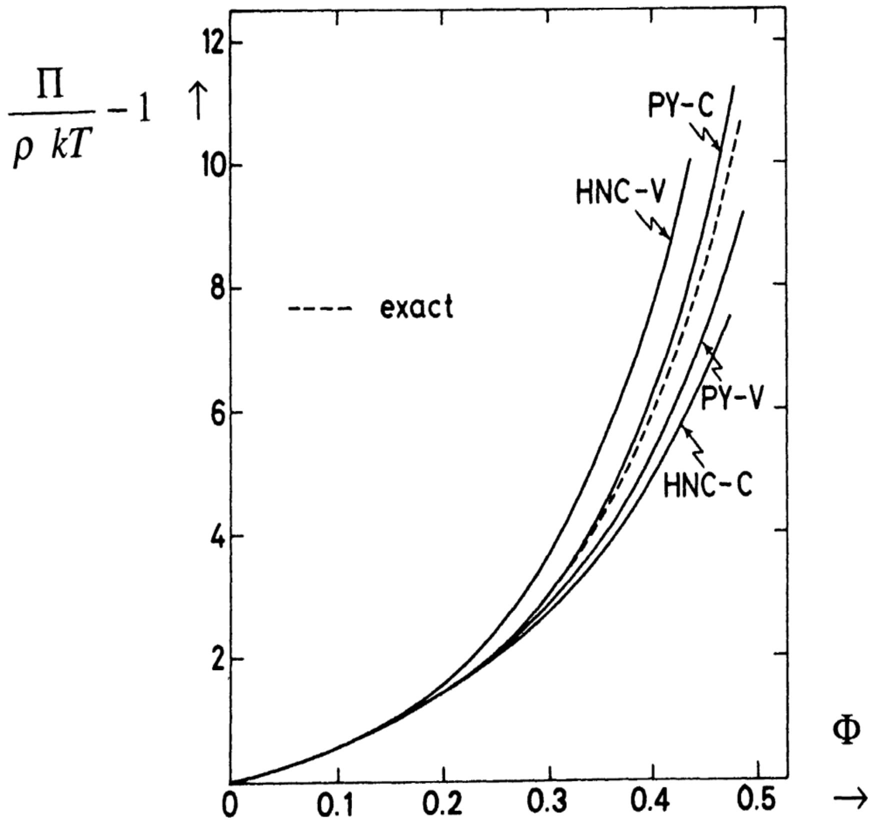
relate $c(r)$ to $\phi(r)$ and/or $h(r)$

$$c(r) = g(r)\left(1 - e^{\beta\phi(r)}\right)$$ Percus-Yevick

$$c(r) = -\beta\phi(r)$$ Mean Spherical Approximation

Results for hard spheres





Today's lecture (5)

- Ornstein-Zernike relation
  - Direct correlation function
  - **Fourier transform of Ornstein-Zernike**
    - **Link to thermodynamics, interactions, structure and scattering**

- Scattering and microscopy experiments (on liquids)
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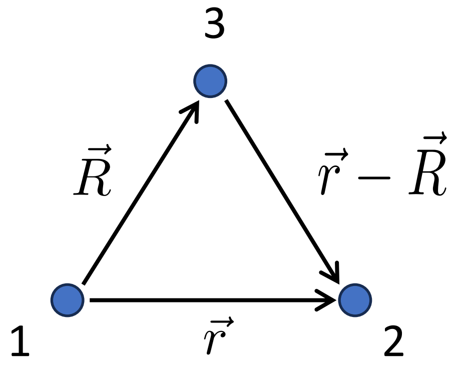
Fourier transform of Ornstein-Zernike equation

Links to scattering and compressibility

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



Fourier transform

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

Rearrange

$$1 + \rho\hat{h}(K) = \frac{1}{1 - \rho\hat{c}(K)}$$

$$1 + \rho\hat{h}(K) = S(K)$$ (structure factor *S(K)*, 2nd hour)

$$1 + \rho\hat{h}(K = 0) = \rho k_B T \kappa_T$$ (compressibility κ_T at $K = 0$)

Links between	
Thermodynamics	$\kappa_T = (1/\rho)\,(\partial\rho/\partial p)_T$
Structure	$h(r) = g(r) - 1$
Interactions	$c(r) \leftrightarrow \phi(r)$
Scattering	$1 + \rho\hat{h}(K) = S(K)$

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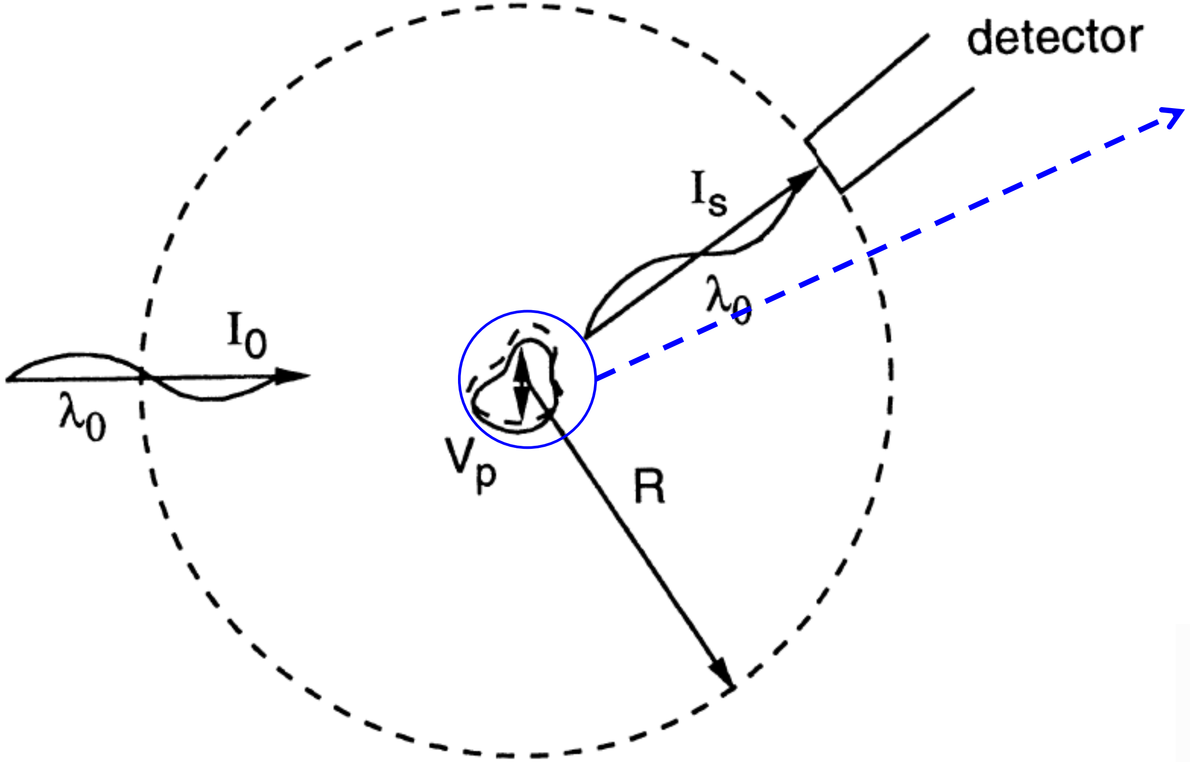
The electric field of light

$$\vec{E}\left(\vec{r},t\right) = \vec{E}_0 \cos\left(\omega t - \vec{k}\cdot\vec{r}\right)$$

wave vector (3D) $k \equiv |\vec{k}| = \dfrac{2\pi}{\lambda_0} \longleftarrow$ wavelength of light in vacuum

angular frequency $\omega = 2\pi\nu = \dfrac{2\pi c}{\lambda_0} = kc \longleftarrow$ speed of light

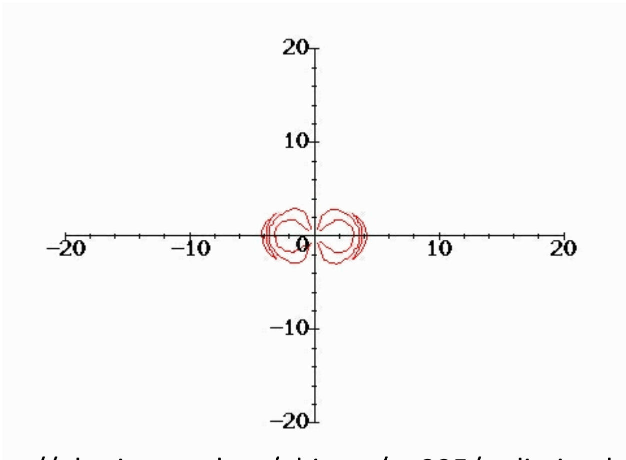
Origin of light scattering



oscillating electric dipoles

emits electromagnetic field

scattered light (λ_s=λ_0)



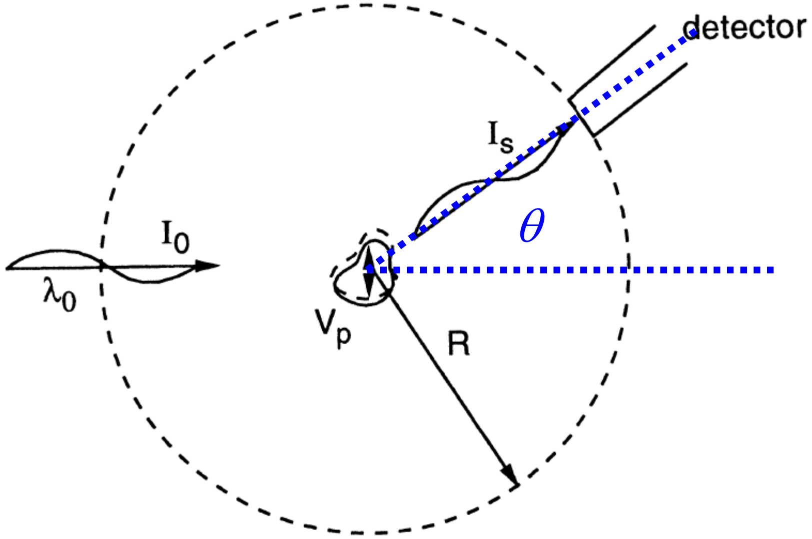
http://physics.usask.ca/~hirose/ep225/radiation.htm

Rayleigh ratio $R(\theta)$

θ: angle between incident and scattered light

$$R(\theta) \equiv \frac{I_S R^2}{I_0 V_S}$$

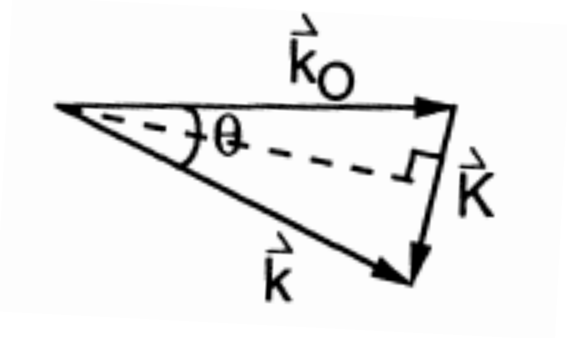
(per particle!)



- independent of apparatus constants I_0, R and V_s (scattering volume)
- Rayleigh ratio: measure for intensity scattered light

Scattering vector *K*

$$\vec{K} \equiv \vec{k} - \vec{k}_0$$



$$|\vec{k}| = |\vec{k}_0| = k$$

(problem set)

$$K = \vec{K} = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \qquad K = \vec{K} = \frac{4\pi n}{\lambda_0} \sin\left(\frac{\theta}{2}\right)$$

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Scattering by small particles: Rayleigh scattering

$\lambda_0 \gg d$ *all charges oscillate in phase*

scattered intensity: $\frac{I_S}{I_0} \propto \frac{1}{\lambda_0^4}$

Almere, Netherlands, Photo by Jesper Albers

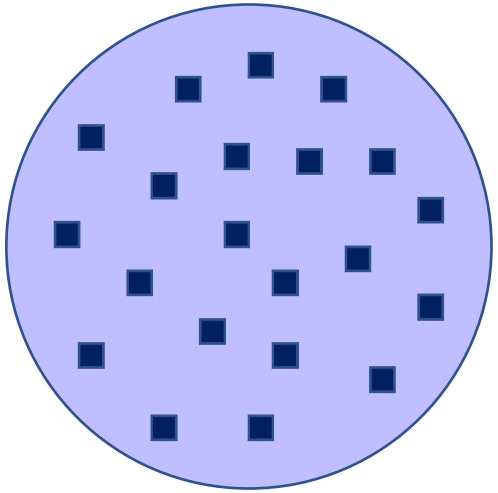
Tyndall effect

$$\lambda = \frac{\lambda_0}{n}$$

Scattering by large particles

$$\lambda_0 \leq d$$

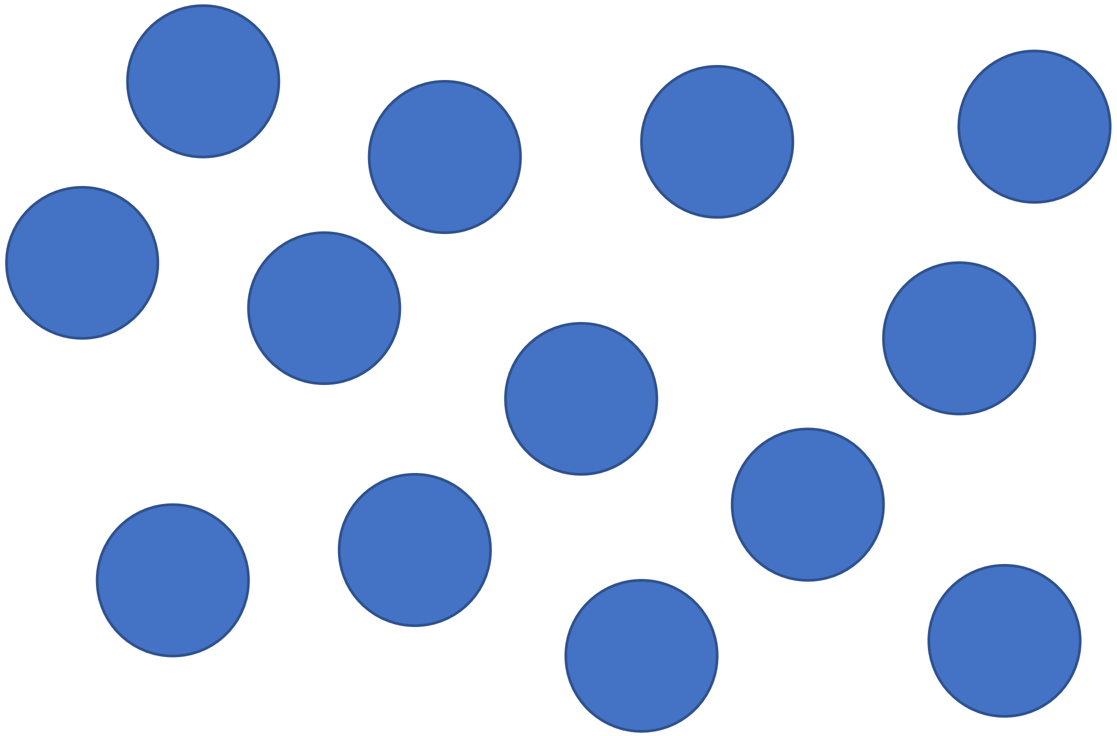
1. Particle = collection of Rayleigh scatterers
2. Spatial distribution of Rayleigh scatterers
3. Phase differences between scattered light
4. Interference → total scattered light



Interference due to scattering within a particle

Form factor *P(K)*

Scattering by many large particles: structure factor



Interference due to scattering by different particles

Structure factor *S(K)*

Rayleigh ratio for scattering in concentrated systems

$$R(\vec{K}) = \underbrace{R(K \to 0)}\underbrace{P(K)}\underbrace{S(\vec{K})}$$

R(K → 0): forward scattering

Interference due to scattering within a particle

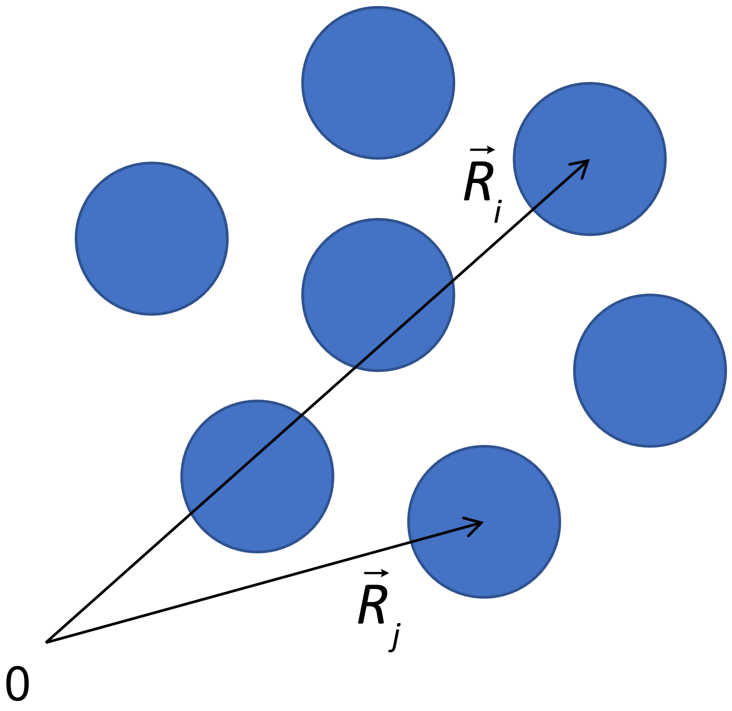
Form Factor ***P(K)***

Interference due to scattering by different particles

Structure Factor ***S(K)***

Structure factor for concentrated systems

$$R(\vec{K}) = R(K \to 0)P(K)S(\vec{K})$$



with

structure factor *S(K)*

$$S(\vec{K}) = \frac{1}{N}\left\langle \sum_{i,j} e^{i\vec{K}\cdot(\vec{R}_i - \vec{R}_j)} \right\rangle$$

Interference due to scattering by different particles

S(K) for homogeneous systems (like liquids)

$$S(K) = 1 + \rho \int [g(r) - 1]\, e^{i\vec{K}\cdot\vec{r}} d\vec{r}$$

For very dilute systems:

$$g(r) \rightarrow 1$$
$$S(K) \rightarrow 1$$

Link between *S(K)*, *h(r)* and *c(r)*

$$S(K) = 1 + \rho \underbrace{\int [g(r) - 1]\, e^{i\vec{K}\cdot\vec{r}} d\vec{r}}_{\text{Fourier transform of } h(r)}$$

$$= 1 + \rho \hat{h}(K)$$

$$= \frac{1}{1 - \rho \hat{c}(K)}$$

- *S(K)* is related to the Fourier transform of the total correlation function *h(r) = g(r) -1*
- … and also to the Fourier transform of the direct correlation function *c(r)*

Link between *S(K)* and thermo at *K* → 0

$$S(K) = 1 + \rho \int [g(r) - 1]\, e^{i\vec{K}\cdot\vec{r}} d\vec{r}$$

$$S(K \to 0) = 1 + \rho \int h(r) d\vec{r}$$

Combine with compressibility relation (from lecture 4):

$$\begin{aligned} S(K \to 0) &= \rho k_B T \kappa_T \\ &= k_B T \left(\frac{\partial \rho}{\partial p} \right)_T \end{aligned}$$

Links structure factor and statistical mechanics

<u>Ornstein-Zernike and scattering provide link between</u>

- Thermodynamics: compressibility κ_T
- Structure: total correlation function *h(r)*
- Interactions: direct correlation function *c(r)*
- Experiments (and simulations): structure factor *S(K)*

$$\boxed{\begin{aligned} S(K) &= 1 + \rho \int \left[g(r) - 1 \right] e^{i\vec{K}\cdot\vec{r}} d\vec{r} \\ &= 1 + \rho \hat{h}(K) \\ &= \frac{1}{1 - \rho \hat{c}(K)} \end{aligned}}$$

$$\boxed{\begin{aligned} S(K \to 0) &= 1 + \rho \int h(r) d\vec{r} \\ &= \rho k_B T \kappa_T \\ &= k_B T \left(\frac{\partial \rho}{\partial p} \right)_T \end{aligned}}$$

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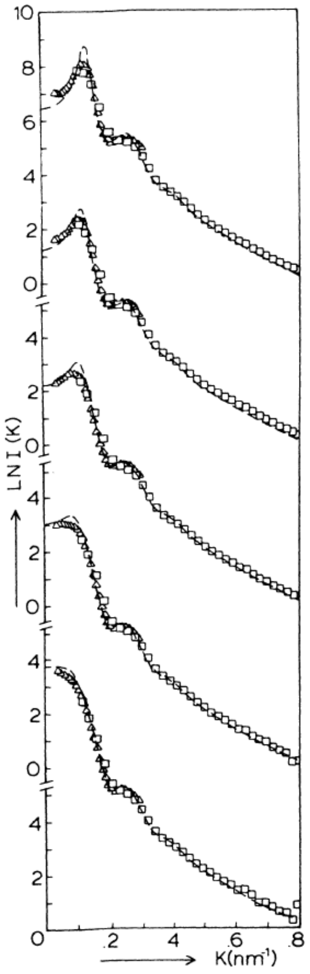
Example: equation of state for hard spheres

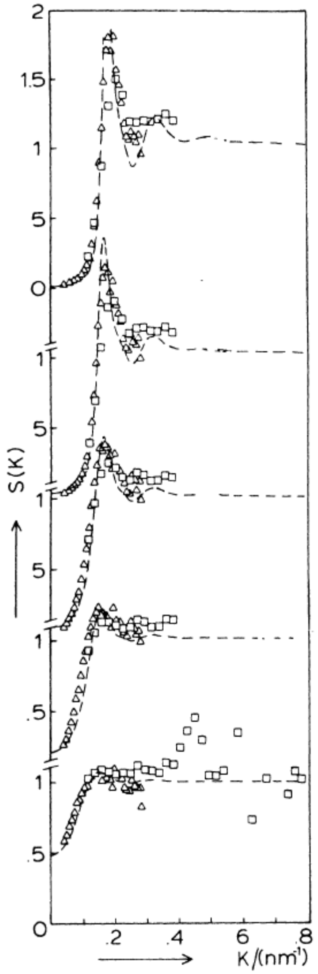
$$I(K) \propto P(K)S(K)$$

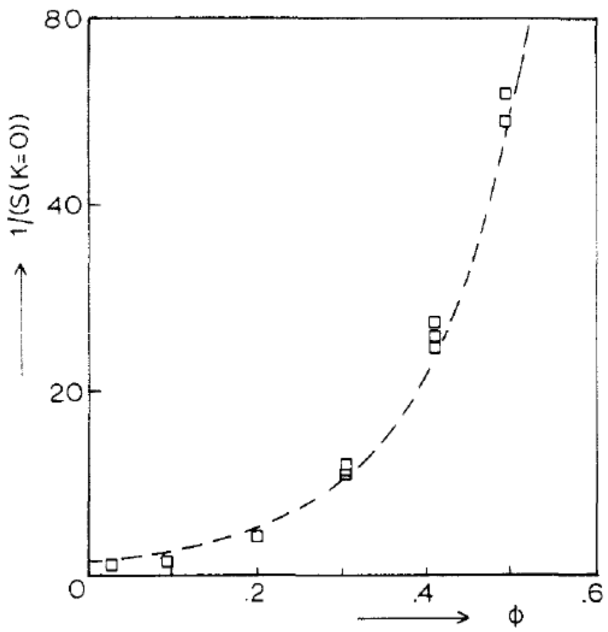
$$S(K) \propto \frac{I(K)}{P(K)}$$

$$\frac{1}{S(K \to 0)} \propto \frac{1}{\kappa_T} \propto \left(\frac{\partial p}{\partial \rho}\right)_T$$



Increasing volume fraction

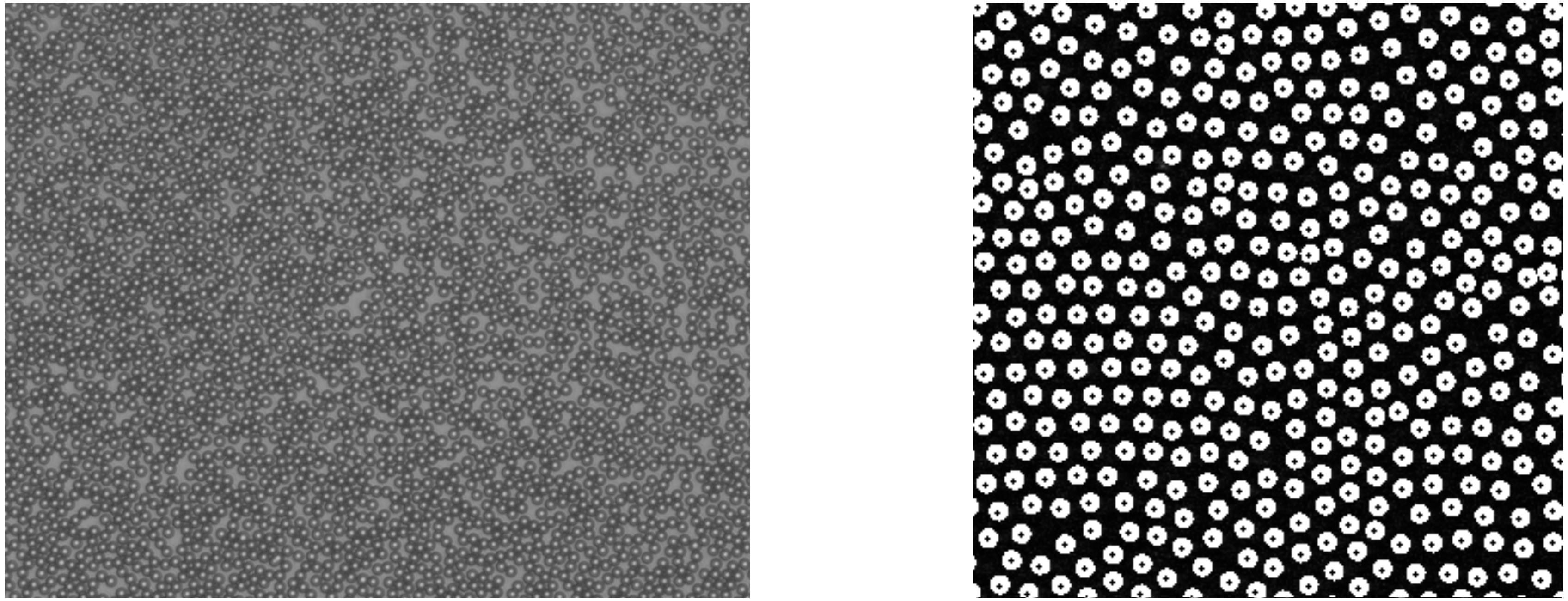




C.G. de Kruif, W.J. Briels, R.P. May, A. Vrij, Langmuir 4 (1988) 668-676

Actually … microscopy also works …

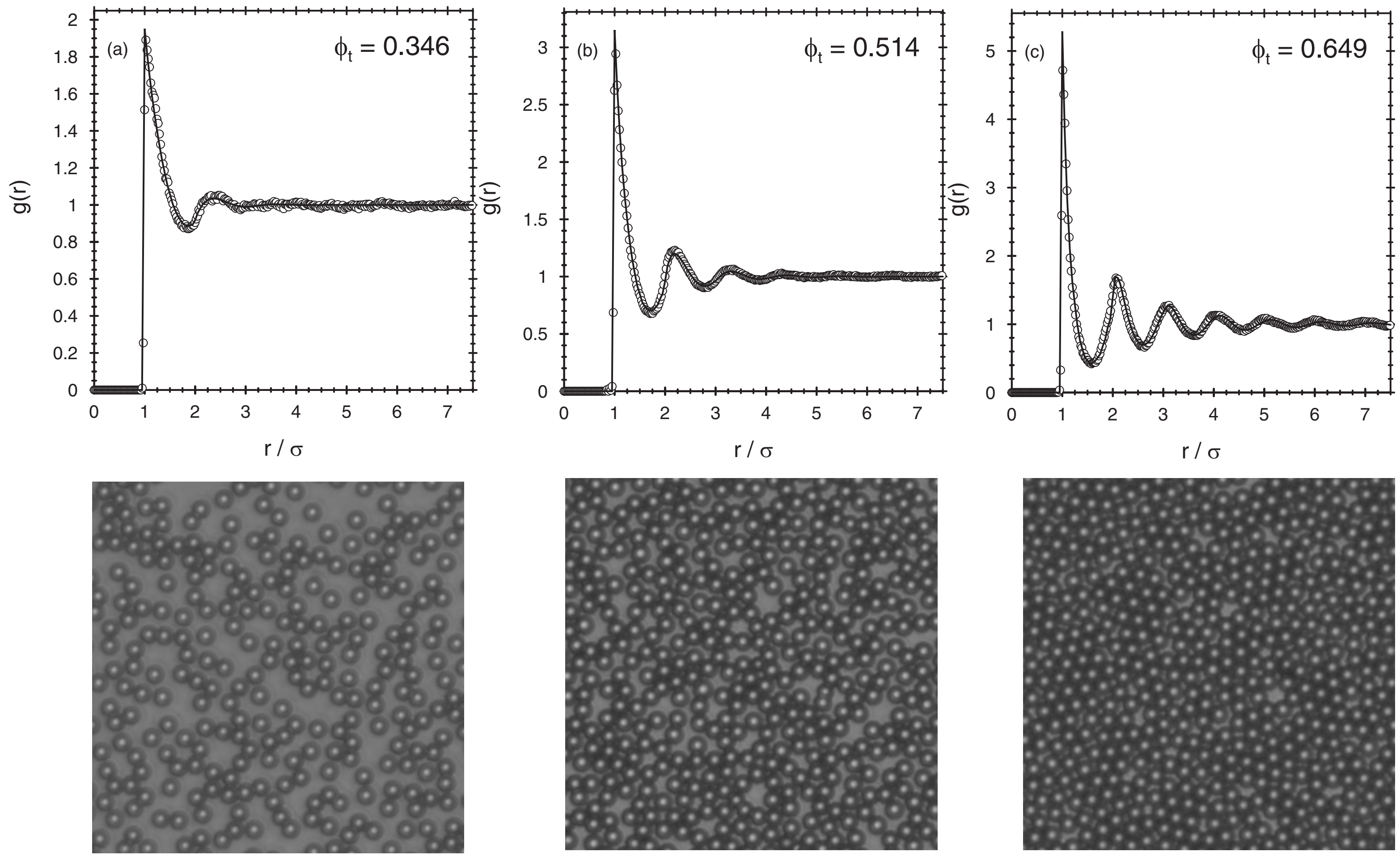
… for colloidal liquids!



We know all the single particle coordinates … so we can *directly* compute *g(r)* and *S(K)*

$$g(r) = \frac{1}{\rho}\left\langle \frac{1}{N}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\delta\left(\vec{r}-\vec{r}_j+\vec{r}_i\right)\right\rangle \qquad S(\vec{K}) = \frac{1}{N}\left\langle \sum_{i,j} e^{i\vec{K}\cdot(\vec{R}_i-\vec{R}_j)}\right\rangle$$

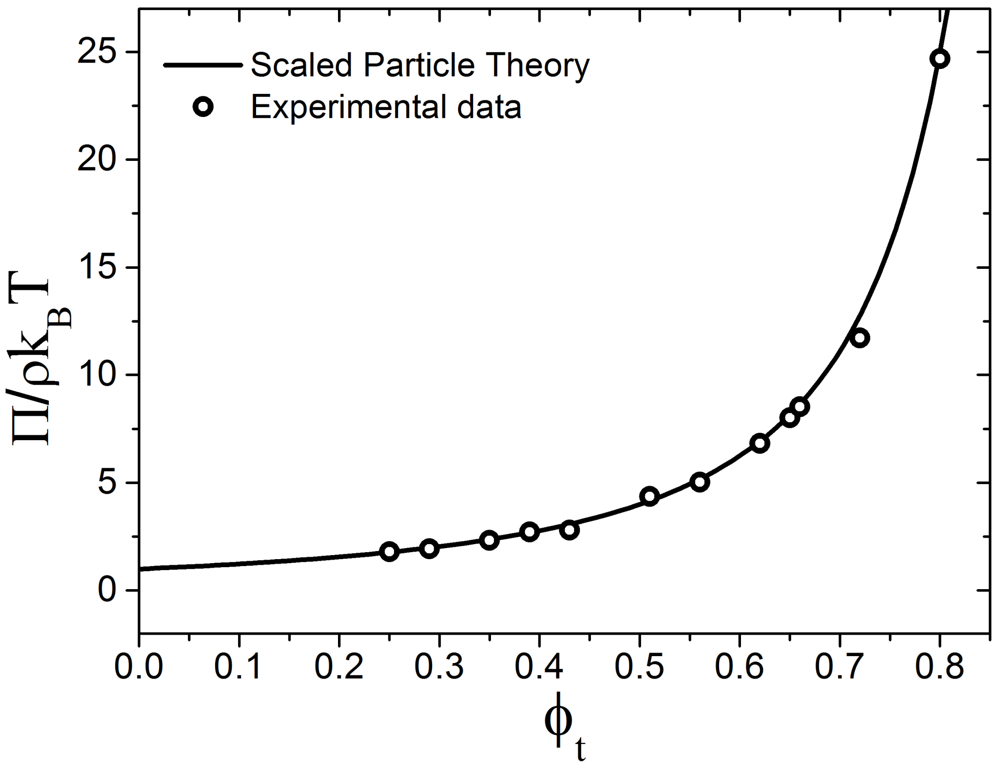
Radial distribution function



A.L. Thorneywork, R. Roth, D.G.A.L. Aarts and R.P.A. Dullens, J. Chem. Phys. (2014)

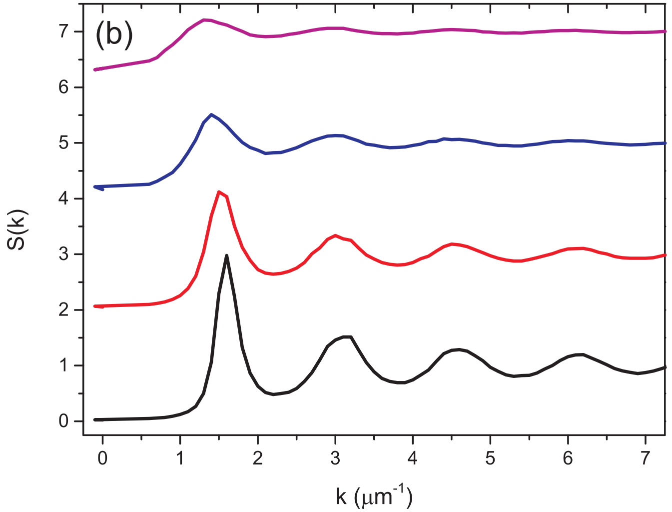
Equation of state from *g(r)*

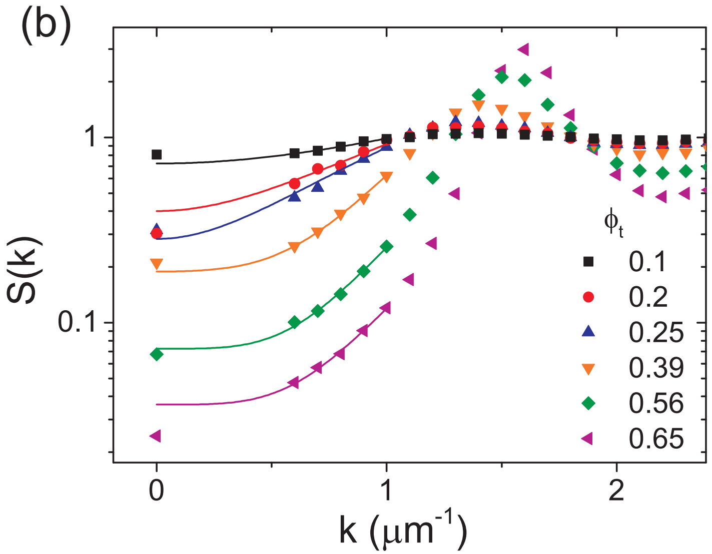
For (2D) hard spheres: $$p = \rho k_B T \left[1 + 2\phi g(r = \sigma)\right]$$



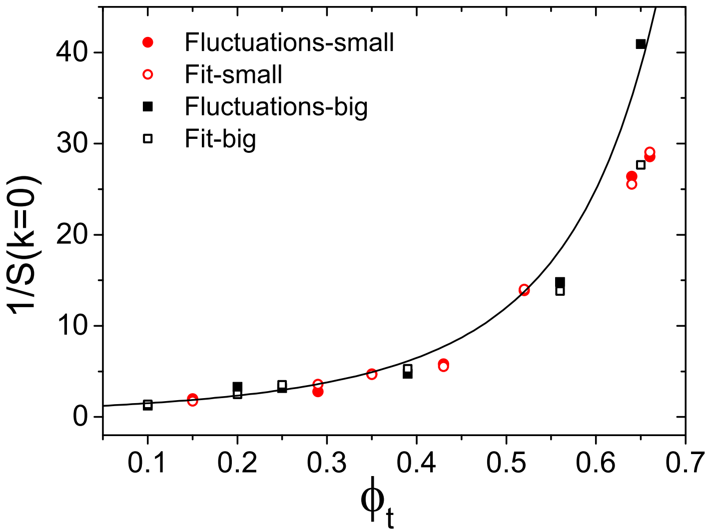
A.L. Thorneywork, R. Roth, D.G.A.L. Aarts and R.P.A. Dullens, J. Chem. Phys. (2014)

Structure factors





$$\frac{1}{S(K \to 0)} \propto \frac{1}{\kappa_T} \propto \left(\frac{\partial p}{\partial \rho}\right)_T$$



A.L. Thorneywork, S. Schnyder, D.G.A.L. Aarts, J. Horbach, R. Roth and R.P.A. Dullens, Mol. Phys. (2018)

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 *
- **Relation g(r) with interactions and thermodynamics and recap** → **Next lecture (6)**

* Problems 13 – 15 of problem set 3 are associated to lecture 5