Fundamentals of Condensed Matter
(lecture 6)

Summary lecture 5

- Ornstein-Zernike equation

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

- Fourier transform of Ornstein-Zernike

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

- Structure factor (scattering)

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

- Links Ornstein-Zernike and structure factor

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

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

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** → **Today, lecture (6)**

Today's lecture (6)

- Relation of g(r) with interactions and thermodynamics
  - Potential of mean force
  - Relation $g(r)$ and $\phi(r)$ at low densities
  - Average potential energy
  - Back to Van der Waals: internal energy

- Recap Liquids
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Potential of mean force *w(r)*

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

Related to probability that particle 1 is anywhere, any particle 2 at distance *r* from particle 1, irrespective of *N-2* other particles

$$w(r) = -k_B T \ln g(r)$$

Related to average force <*f(r)*> acting on particle 1, keeping 1 and 2 fixed (at distance *r*), irrespective of *N-2* other particles

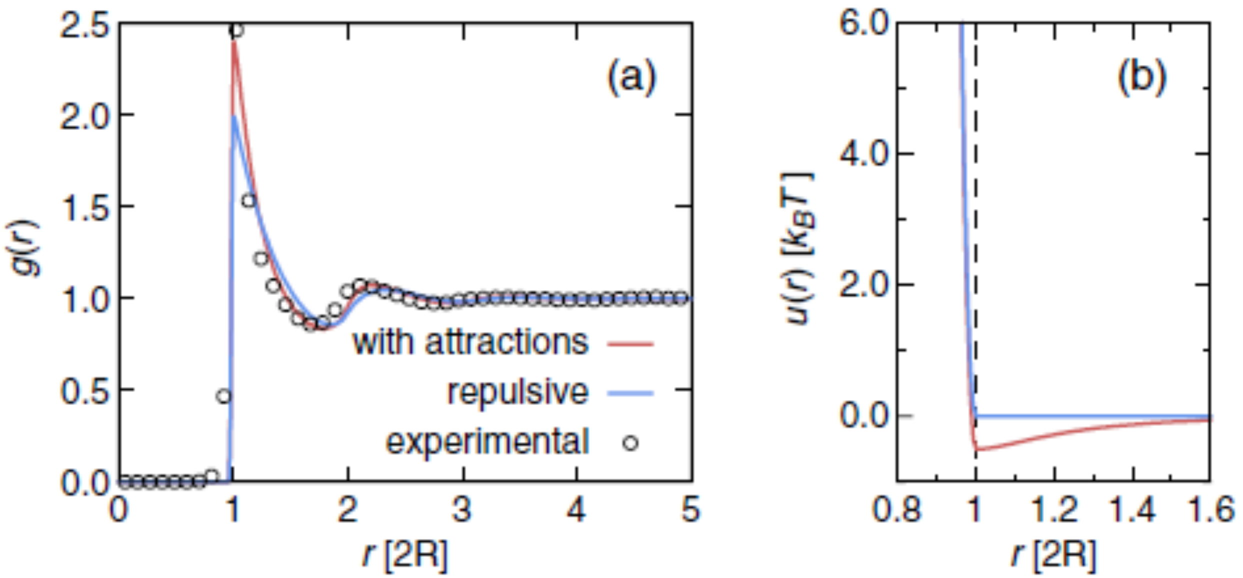
$$\langle f(r)\rangle = -\nabla_1 w(r)$$

Relation *g(r)* and pair potential *ϕ(r)* (at small *ρ*)

$$w(r) = -k_B T \ln g(r)$$

Limit of $\rho \to 0$

$$g(r) = e^{-\beta\phi(r)}$$



Thanks to Ivo Buttinoni (Duesseldorf)

[problem set: correspondence *g(r)* and *ϕ(r)*]

Average potential energy and *g(r)*

$$\langle U \rangle = 2\pi N\rho \int_0^\infty r^2 \phi(r) g(r) dr$$

More intuitively:

$$\langle U \rangle = \frac{N}{2} \int_0^\infty \phi(r) \cdot \underbrace{\rho g(r) 4\pi r^2 dr}_{\boxed{\text{average number of particles at distance } r \text{ from central particle}}}$$

Internal energy Van der Waals

Problem 4: internal energy: $E_{vdw} = \frac{3}{2}Nk_BT - a\frac{N^2}{V}$

$$E = E_{kin} + \langle U \rangle$$

problem set:

$$E = \frac{3}{2}Nk_BT + \underbrace{kT^2\left(\frac{\partial \ln Z_N}{\partial T}\right)_{N,V}}$$

$$\langle U \rangle = 2\pi N\rho \int_0^\infty r^2\phi(r)g(r)dr$$

Internal energy Van der Waals

Problem 4: internal energy: $E_{vdw} = \frac{3}{2}Nk_BT - a\frac{N^2}{V}$

Problem 9: pair potential: $\phi(r) = \begin{cases} \infty & r < \sigma \\ -\frac{A}{r^6} & r \geq \sigma \end{cases}$ $\phi(r) \ll k_BT \quad \rightarrow \quad \beta\phi(r) \ll 1$

Problem 9: Van der Waals parameters:

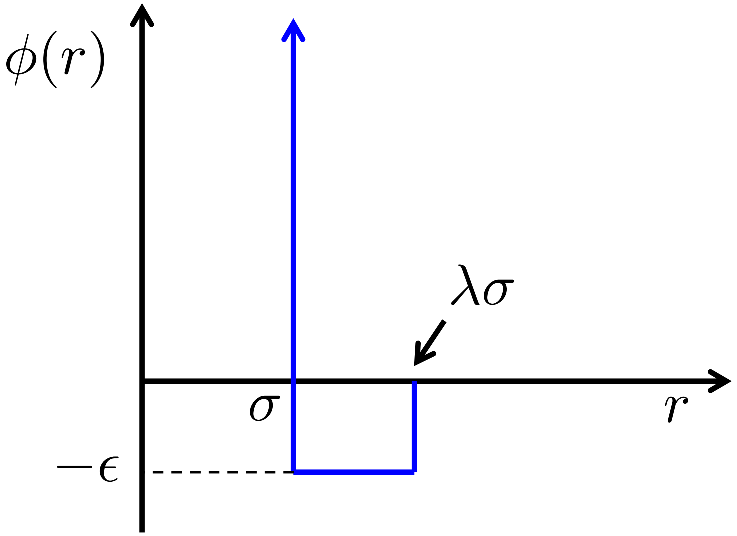
$$\begin{cases} a = -2\pi \int_\sigma^\infty \phi(r) r^2 dr \\ b = 2\pi \int_0^\sigma r^2 dr = \frac{2\pi\sigma^3}{3} \end{cases}$$

Problem set: mean potential energy square-well

$$\langle U \rangle = 2\pi N\rho \int_0^\infty r^2 \phi(r) g(r) dr$$

square well potential:

$$\phi(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \le r \le \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$



Three routes from *g(r)* to thermodynamics

$$k_B T \left(\frac{\partial \rho}{\partial p}\right)_T = 1 + 4\pi\rho \int_0^\infty (g(r) - 1) r^2 dr$$

(compressibility route)

$$E = \frac{3}{2} N k_B T + 2\pi N \rho \int_0^\infty \phi(r) g(r) r^2 dr$$

(caloric route)

$$p = \rho k_B T - \frac{2\pi\rho^2}{3} \int_0^\infty \phi'(r) g(r) r^3 dr$$

(virial route*)

* Not derived here $\left[\text{via } p = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = k_B T \left(\frac{\partial \ln Z_N}{\partial V}\right)_{N,T}\right]$

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Problem 7 (old exam question)

The classical configuration integral is given by

$$Z_N = \int ... \int e^{-\beta U(\tau_1,...,\tau_N)} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N,$$

where $U(\tau_1, ..., \tau_N)$ is the total potential energy and $\beta = 1/(k_B T)$.

a) Explain what is meant by *pair-wise additivity* and give the corresponding expression for U in terms of the pair potential between particles i and j, $\phi(r_{ij}) = \phi_{ij}$.

b) Use your above expression for U in terms of ϕ_{ij} within the pair-wise additivity approximation together with the definition of the Mayer f-function, $f_{ij} \equiv e^{-\beta\phi_{ij}} - 1$, to show that Z_N can be written as

$$Z_N = \int ... \int \prod_{i>j}^{N} (1 + f_{ij}) \, \mathrm{d}\tau_1 ... \mathrm{d}\tau_N.$$

c) Explain the significance of the Mayer f-function in performing the integrals in Z_N. Include in your answer a sketch of a realistic/reasonable pair potential ϕ_{ij} and the corresponding Mayer f-function f_{ij}.

Problem 12 (old exam question)

The compressibility equation is given by

$$1 + 4\pi\rho \int_0^\infty h(r) r^2 \mathrm{d}r = \rho k_B T \kappa_T, \qquad \text{Eq. 1}$$

where $\rho = \frac{N}{V}$ is the number density, $h(r) \equiv g(r) - 1$ the total correlation function and $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ the isothermal compressibility.

(a) Show that the isothermal compressibility can be rewritten as

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

Problem 12 (old exam question)

The second virial coefficient is given by

$$B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta\phi(r)} - 1\right) r^2 \mathrm{d}r, \qquad \text{Eq. 2}$$

where $\phi(r)$ is the interaction pair potential as a function of the separation r and $\beta = 1/(k_B T)$.

(b) In the limit of small ρ we can assume that the radial distribution function $g(r) = \exp(-\phi(r)\beta)$. Use this to show that in the low density limit the compressibility equation can be written in terms of B_2 as

$$1 - 2\rho B_2 = k_B T \left(\frac{\partial \rho}{\partial p}\right)_T .$$

(c) Show that for small ρ this can be approximated as

$$\left(\frac{\partial p}{\partial \rho}\right)_T = k_B T \left(1 + 2\rho B_2 + \ldots\right).$$

and, hence, obtain an expression for the pressure. Comment on your answer.

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From thermo and (classical) stat mech ...

$$p = k_B T \left(\rho + B_2\rho^2 + B_3\rho^3 + \ldots\right)$$

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}n$$

$$Q_{class} = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} Z_N$$

$$Z_N = \int \cdots \int e^{-\beta U(x_1,\ldots,z_N)} d\tau_1 \cdots d\tau_N$$

$$A = -k_B T \ln Q$$

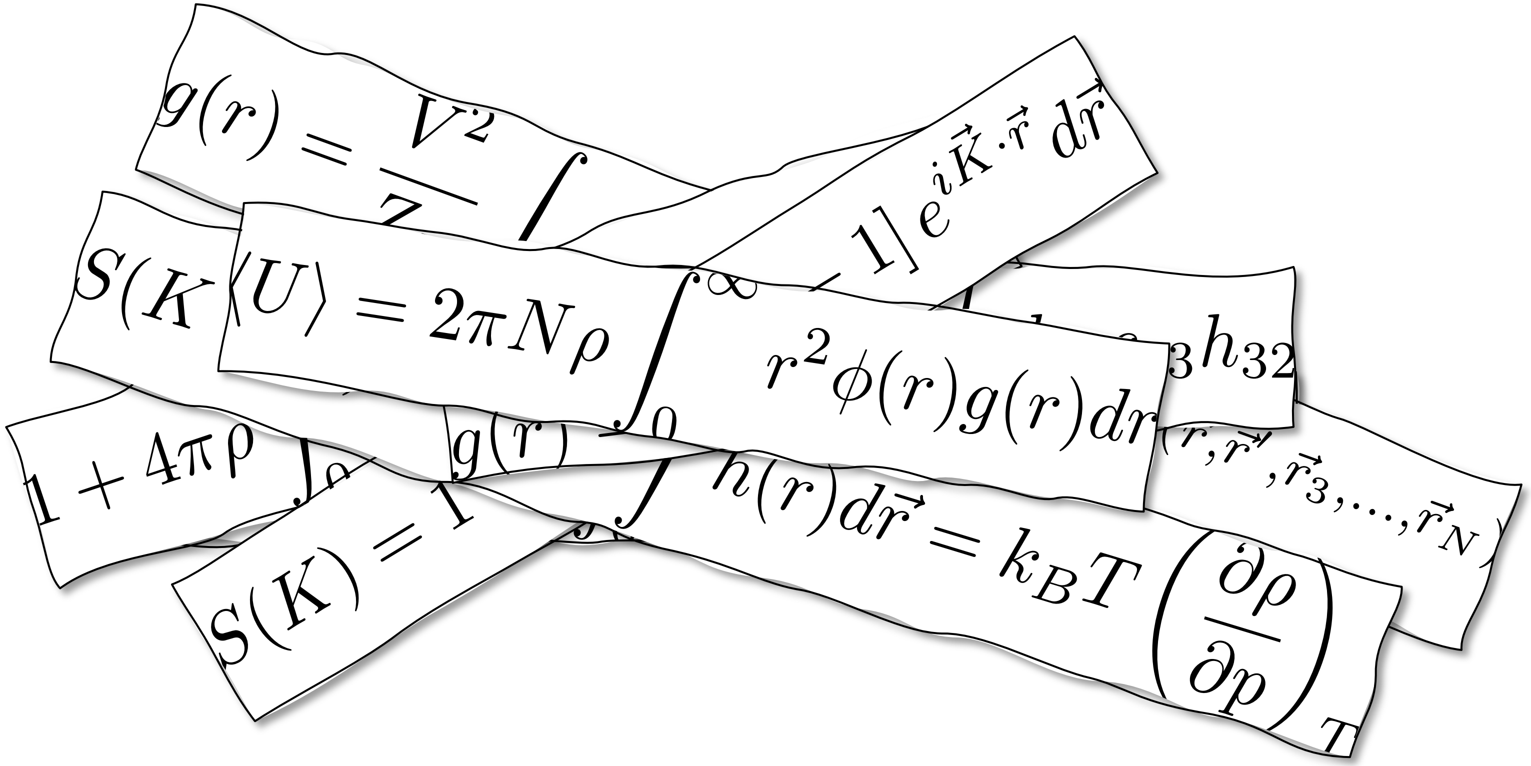
$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

… to relations between:

- Thermodynamics: $p, B_2(T), \kappa_T, \langle U \rangle, E$
- Structure: $g(r), h(r), S(K)$
- Interactions: $\phi(r), c(r)$
- Experiments: $S(K), g(r)$

for liquids (and imperfect gases)



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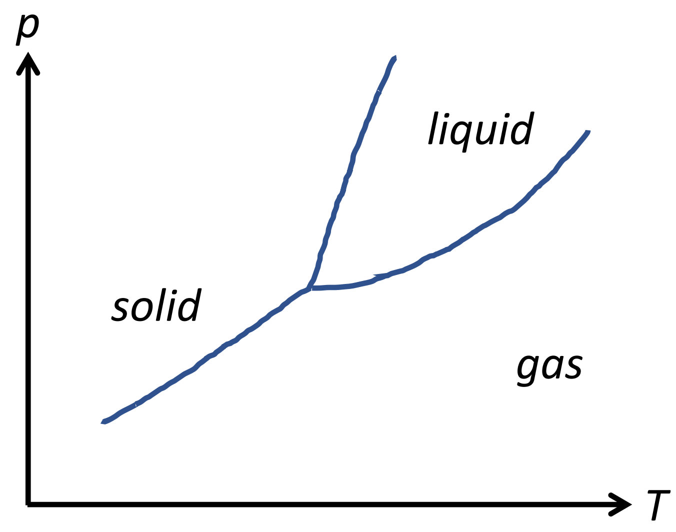
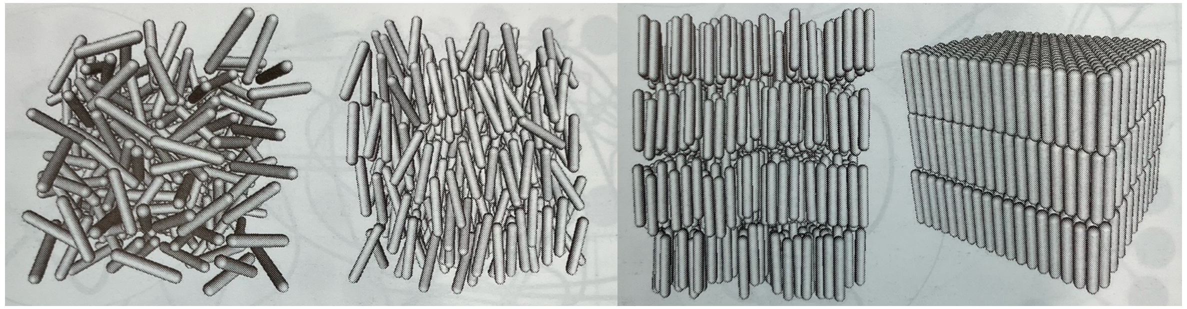
From simple to complex fluids*

Simple fluids



- *Simple one-component substance*
- *Small, quasi-spherical molecules*

Complex fluids



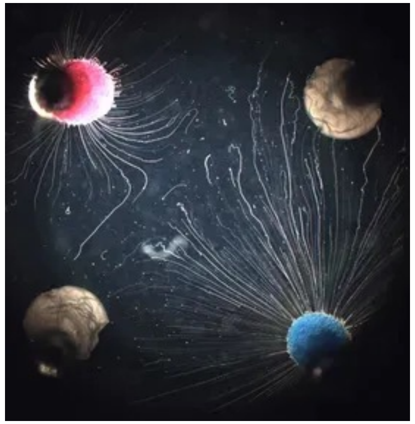
Thanks to Peter Bolhuis (now UvA)

- *Complex interactions (dipoles, H-bonding, ...)*
- *Multicomponent systems*
- *Non-spherical substances: liquid crystals*
- *Macromolecular systems: polymers*
- *Multi-phase systems: colloidal suspensions*

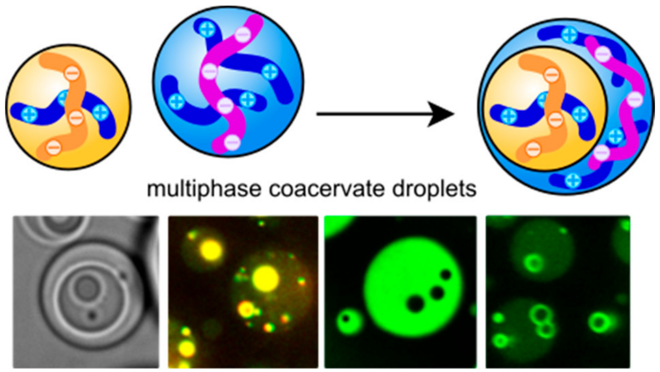
* Basic concepts for simple and complex liquids, Jean-Louis Barrat and Jean-Pierre Hansen, Cambridge University Press (2003)

A few examples of complex fluids work in the IMM

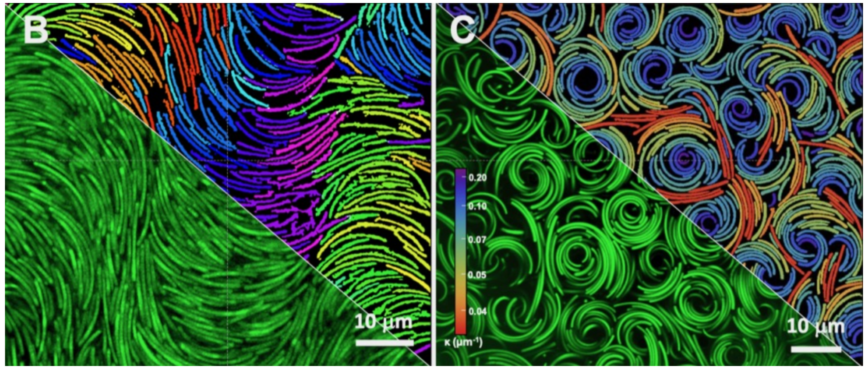
- *Polymer solutions*
- *Emulsions*
- *Liquid crystals*
- *Surfactant solutions*
- *Colloidal fluids*
- *Biological fluids*
- *...*



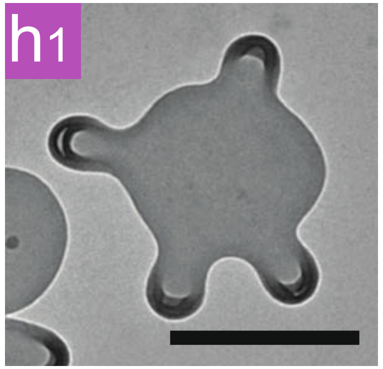
Peter Korevaar Lab



Spruijt Lab



Dullens Lab

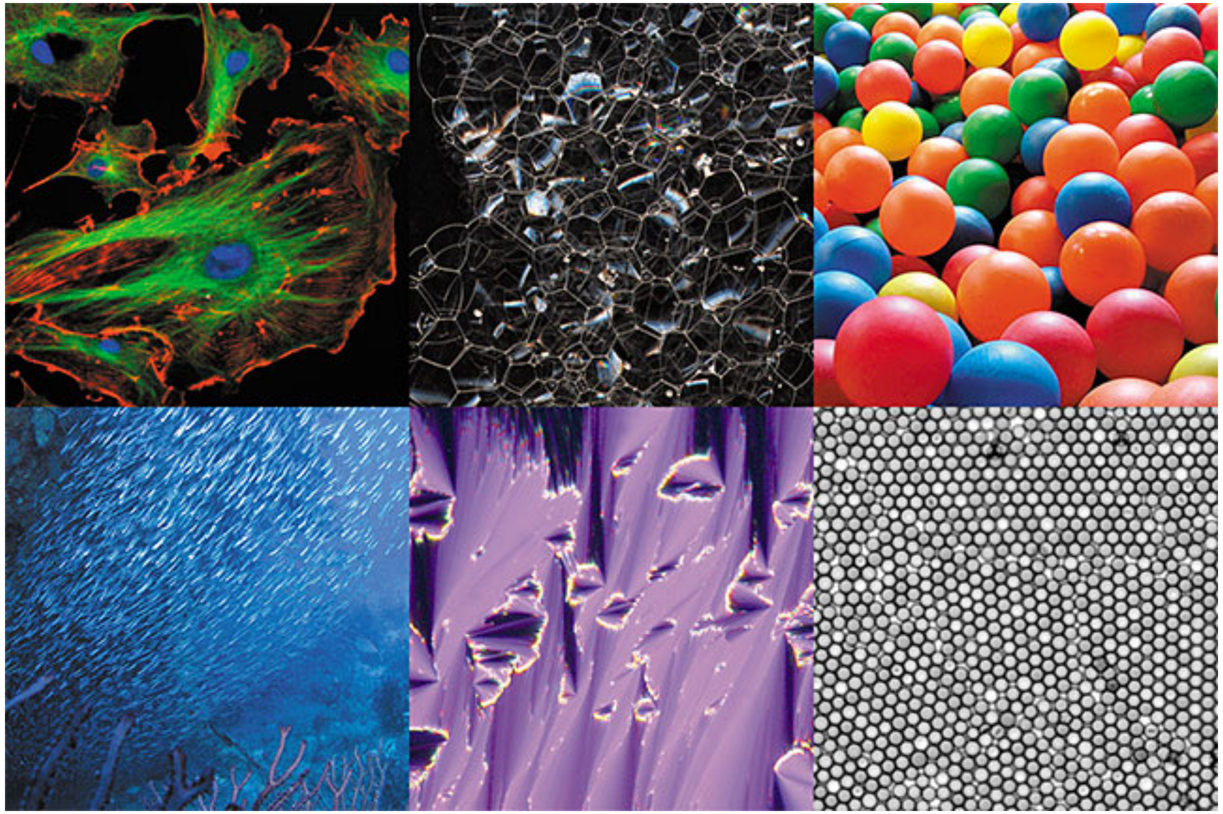


Wilson Lab

Also other groups: HFML (Peter Christianen), IMM (Eeftens Lab, Huck Lab, Hansen Lab, Kouwer Lab, ...)

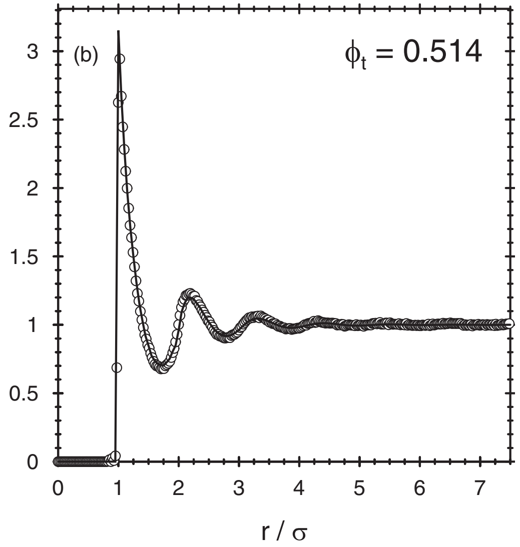
From simple liquids to colloids and soft matter

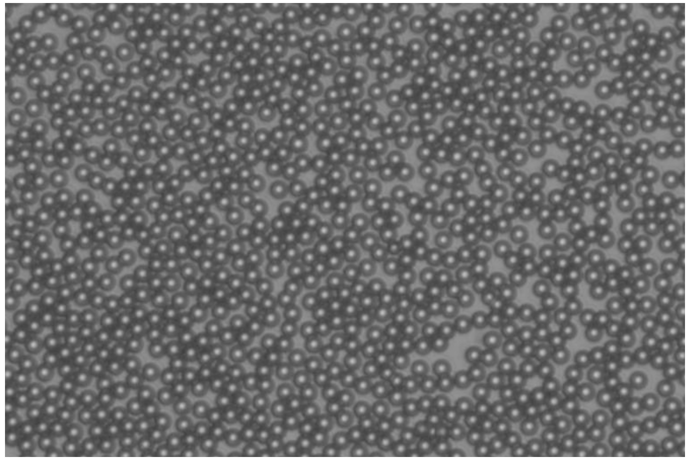
*R. Evans, D. Frenkel, M. Dijkstra, Phys. Today **72**, 38 (2019)*

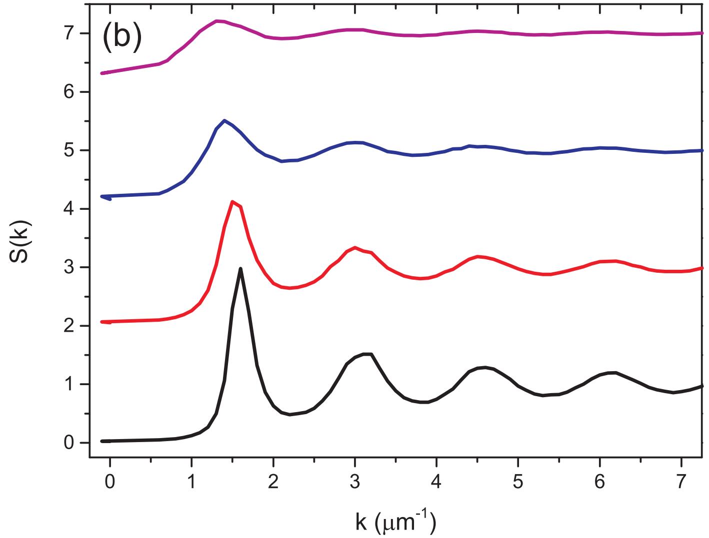


“Colloids provide a crucial link between simple liquids and complex fluids and soft matter.”

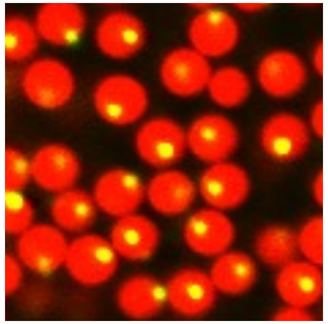
Colloids provide a crucial link between simple liquids and complex fluids and soft matter

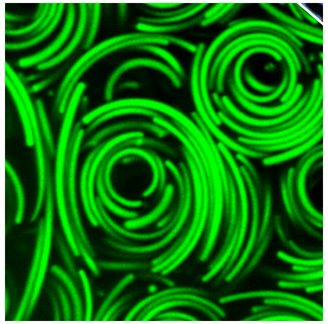


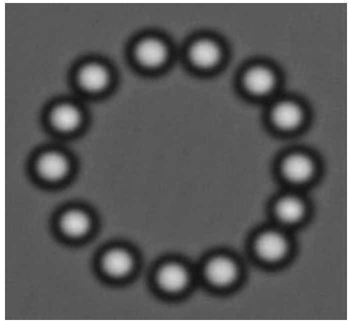


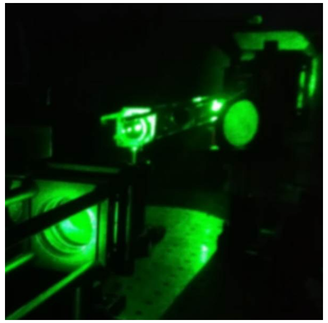


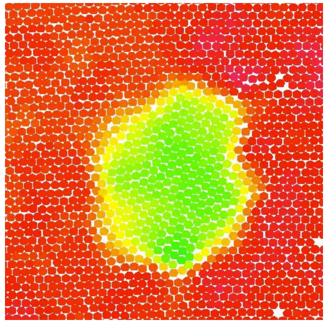
... we cook them, we look at them and tweez them ...











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