Lectures for the Nordita Winter School (Stockholm)
on

Condensed Matter Theory

Theory of freezing and non-equilibrium dynamics

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SFB TR6 Physics of Colloidal Dispersions in External Fields

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Outline:

1) Density functional theory of freezing: spheres

1.1 Phenomenological results

1.2 Independent treatment of the different phases

1.3 Unifying Microscopic theories

1.4 Phase diagrams of simple potentials

1.5 Density Functional Theory (DFT)

2) Brownian Dynamics and dynamical density functional theory

2.1 Brownian dynamics (BD)

2.2 Dynamical density functional theory (DDFT)

2.3 Hydrodynamic interactions

3) Density functional theory for rod-like particles

3.1 Statistical mechanics of rod-like particles

3.2 Simple models

3.3 Brownian dynamics of rod-like particles

1) Density functional theory of freezing: spheres

1.1) Phenomenological results:

experiments:

- liquids crystallize into periodic structures at low temperatures or/and high densities
- translational symmetry is broken
- one of the most important phase transitions in nature
- when does it happen?

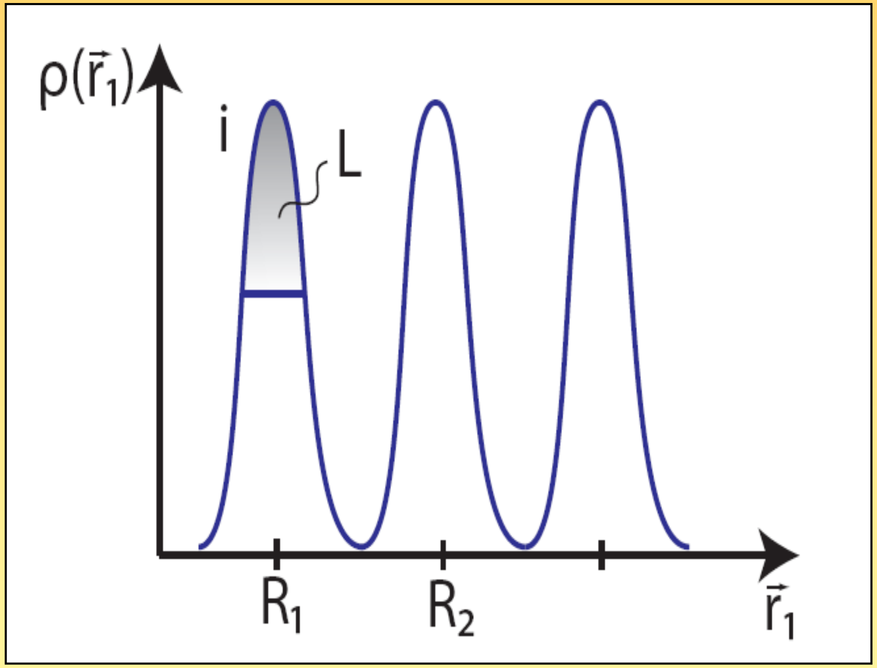
empirical facts:

i) **Lindemann-criterion of melting** (1910)

$$a = \rho^{-1/3} \;, \; u = \sqrt{\langle (\vec{r_i} - \vec{R}_i)^2 \rangle}$$ root mean square displacement

$\vec{R}_i$ lattice vectors

Lindemann parameter: $L = \frac{u}{a}$



computer simulation

hard spheres $L = 0.129$

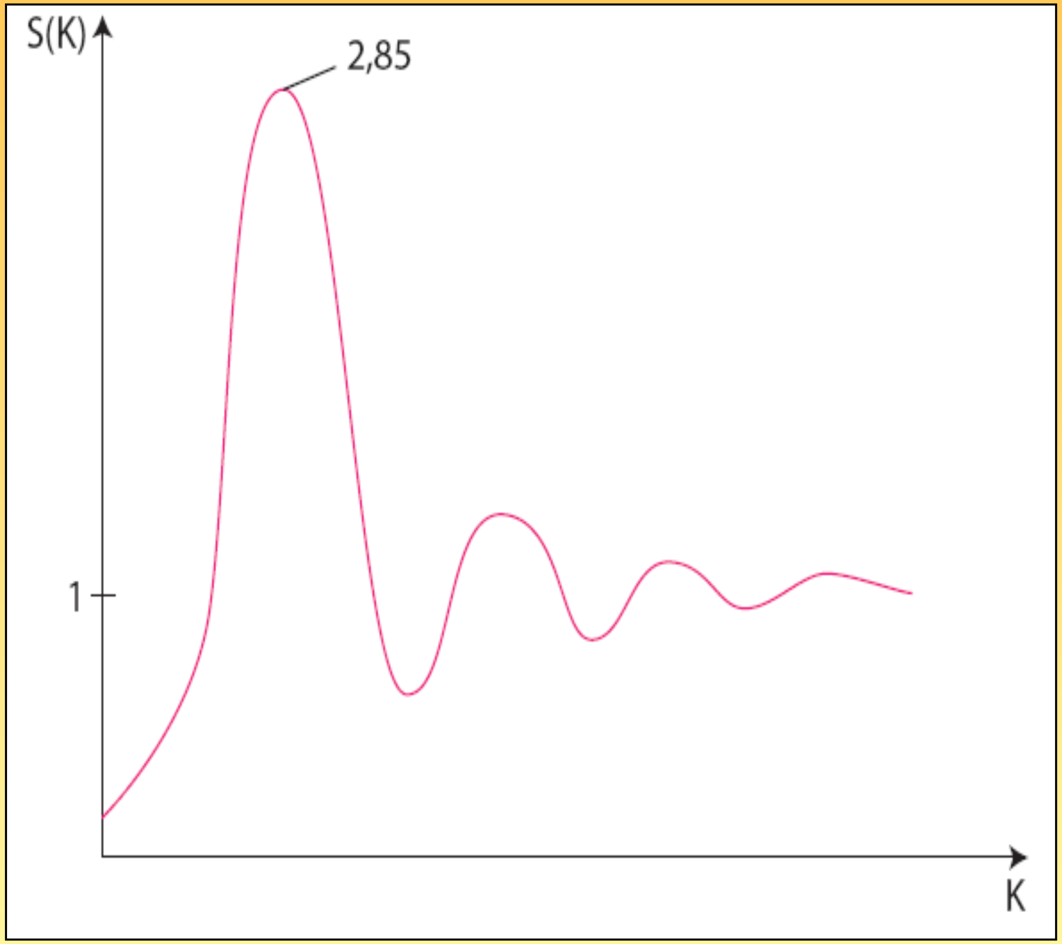
OCP $L = 0.18$

Yukawa interaction

criterion: $\text{solid melts, if } L \cong 0.1$ phenomenological rule

ii) Hansen-Verlet rule of freezing (1963)

at freezing, all $S(k)$ are similar



criterion:

liquid freezes, if the first maximum of $S(k)$ exceeds the value 2.85

→ confirmed for Yukawa, OCP, Lennard-Jones, etc...

1.2) Independent treatment of the different phases

(a) for the solid

impose a prescribed solid with lattice constant $\boxed{\mathrm{a}\ (\equiv \text{mean density } \rho)}$

harmonic lattice theory (phonons)

→ free energy of solid state: $\boxed{F_\mathrm{s}}$

$\boxed{T=0}$ lattice sum of potential energy per particle.

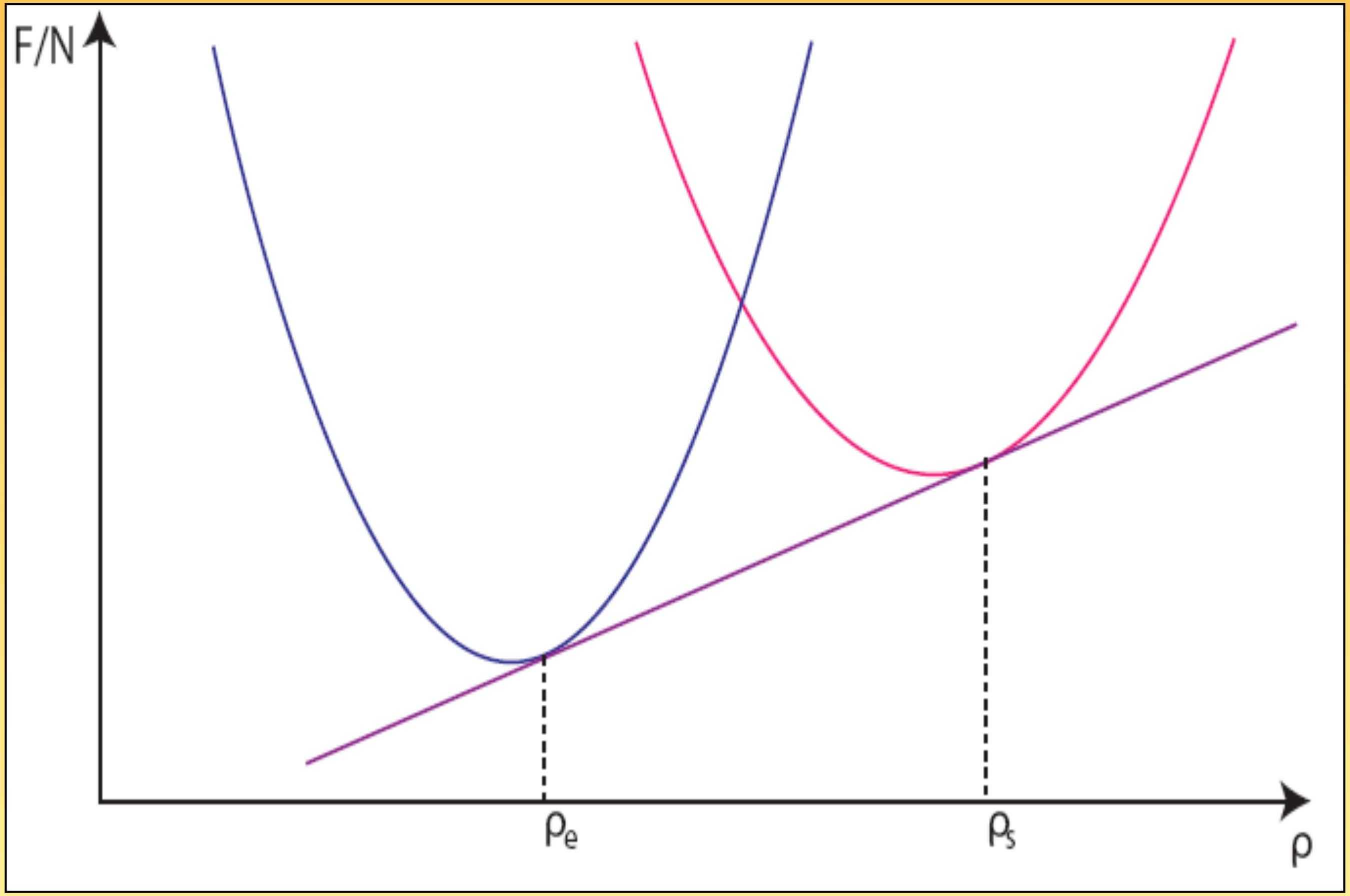
(b) for the liquid/fluid

liquid theory (e.g. HNC closure).

→ free energy of the liquid state.

Maxwell-double tangent construction

(ensures equality of pressure and chemical potentials in the different phases)



→ phase diagram (typically 1st order freezing)

1.3) Unifying Microscopic theories

i) **density functional theory** (in 3d)

based on liquid

solid ≡ condensation of liquid density modes

ii) **crystal-based theory** (in 2d) (Kosterlitz-Thouless)

defects in solid

liquid ≡ solid with an accumulation of defects

1.4) Phase diagrams of simple potentials

(known from computer simulations + theory)

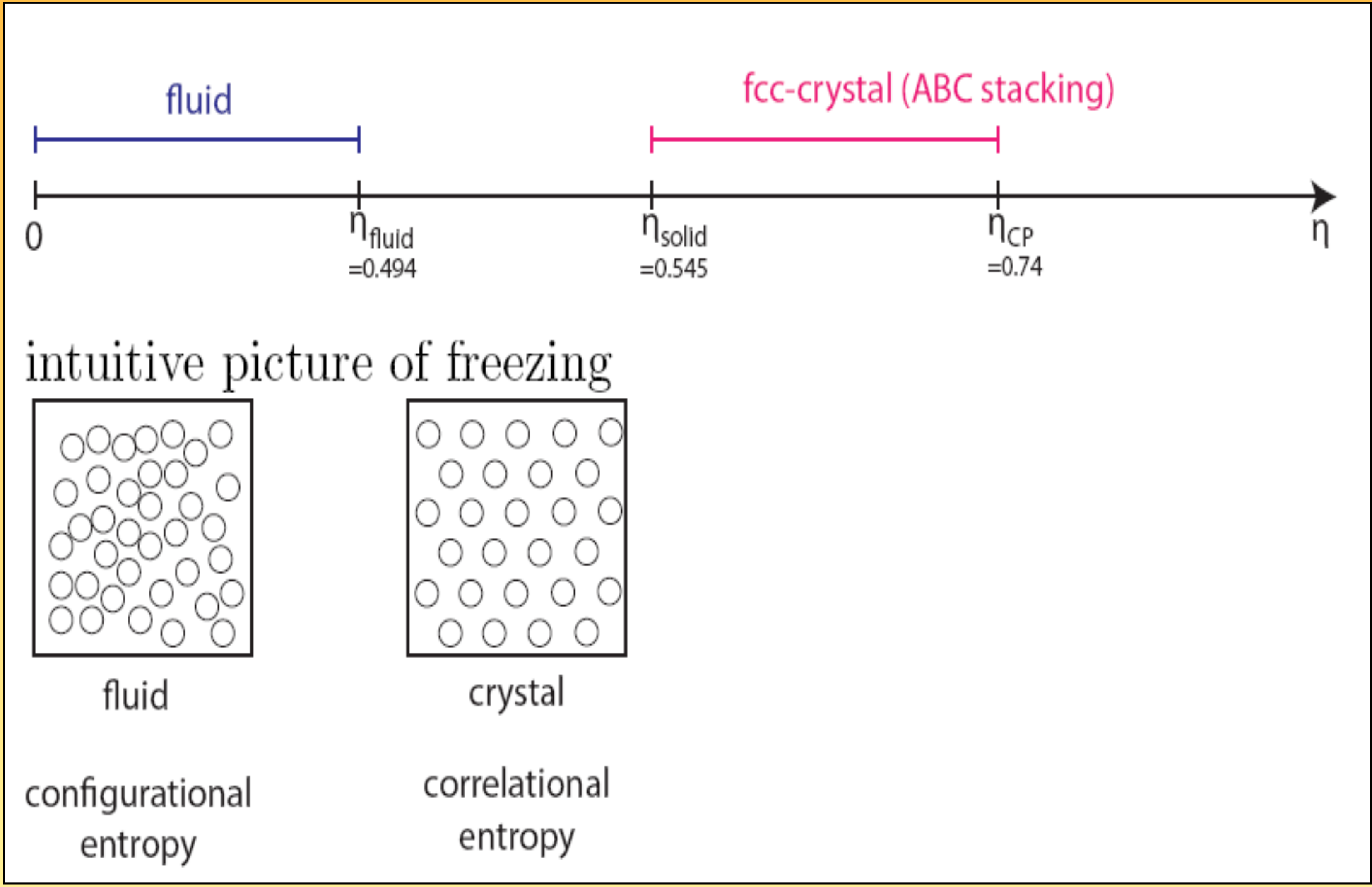
a) hard spheres

internal energy $U = \frac{3}{2} N k_B T$

averaged potential energy $\langle U_{\mathrm{pot}} \rangle = 0$

$F = U - TS$ there is only entropy, **packing effects**

phase diagram

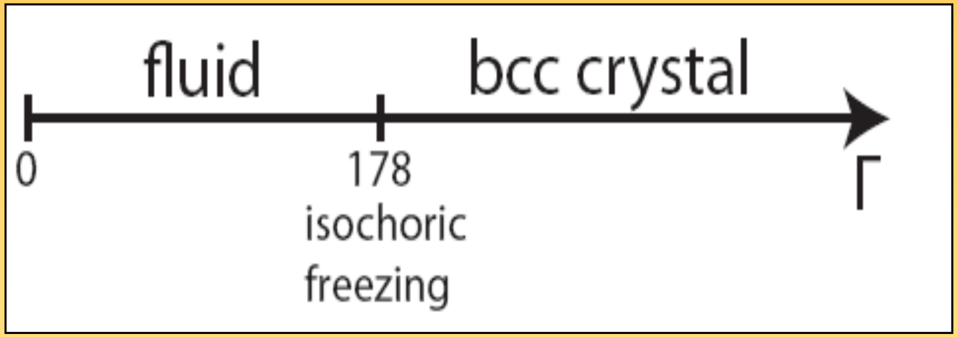


above freezing: $\eta > \eta_{solid}$ state with higher entropy (solid), has higher order

b) plasma (with neutralizing background)

only the combination $\Gamma = \frac{\sqrt[3]{\frac{4\pi\rho}{3}} V_0}{k_B T}$ determines correlations, phase diagram, etc.

Γ : coupling parameter



phase diagram

c) soft spheres

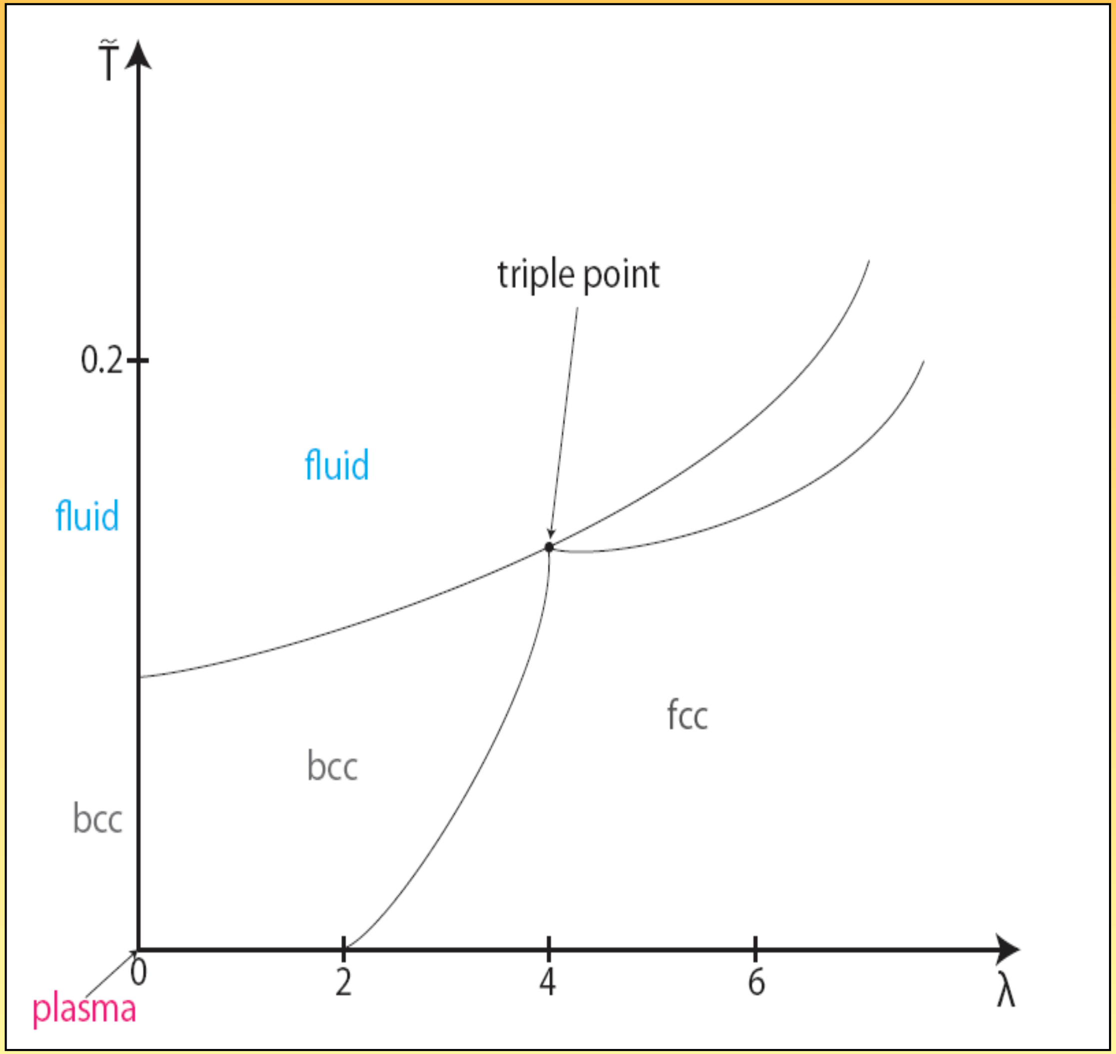
$$V(r) = V_0 \left(\frac{\sigma}{r}\right)^n$$

$n \gtrsim 6$ freezing into fcc lattice

$n \lesssim 6$ freezing into bcc lattice

d) Yukawa-system

$$V(r) = V_0 \cdot \frac{e^{-\kappa r}}{r}$$



only 2 reduced parameters:

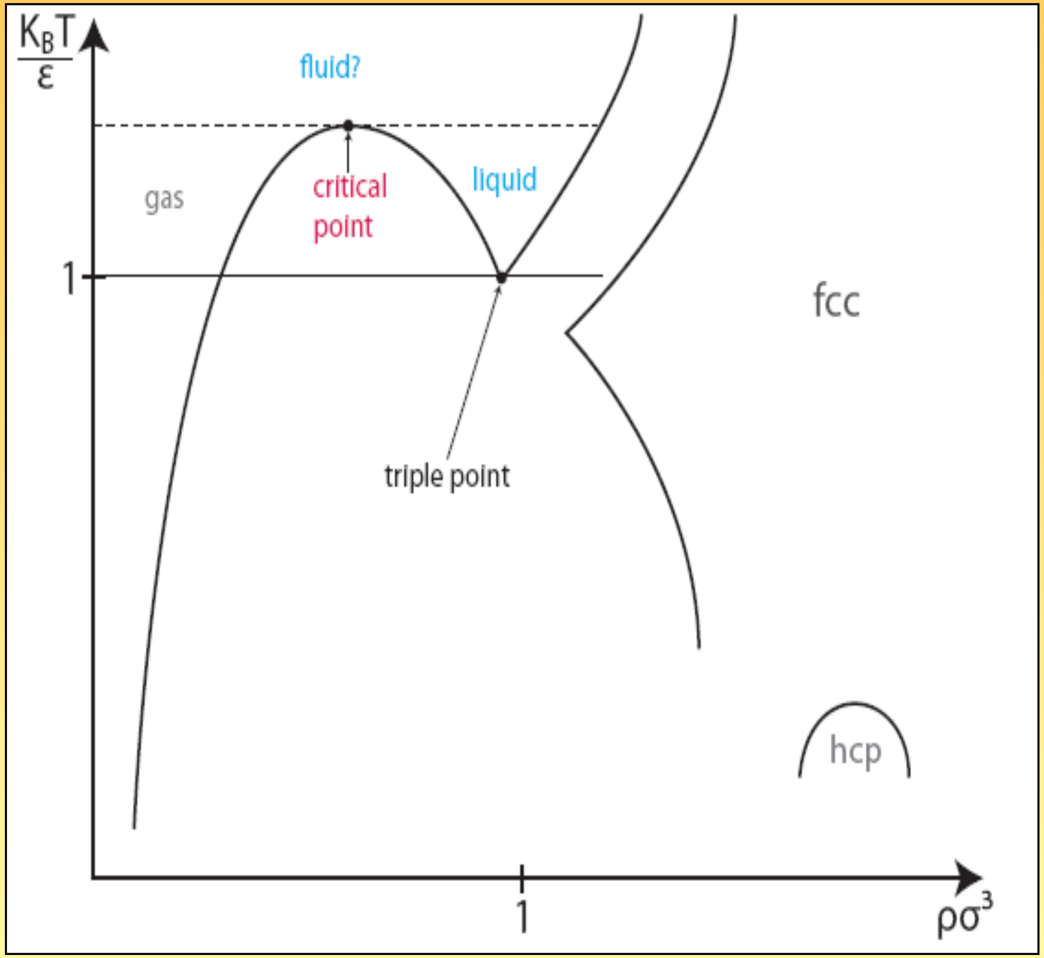
$$\lambda = \kappa \sqrt[3]{\frac{1}{\rho}}$$

$$\tilde{T} = \frac{k_B T}{V_0 \kappa} \lambda e^{\lambda}$$

e) Lennard-Jones-system

$$V(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

phase diagram:

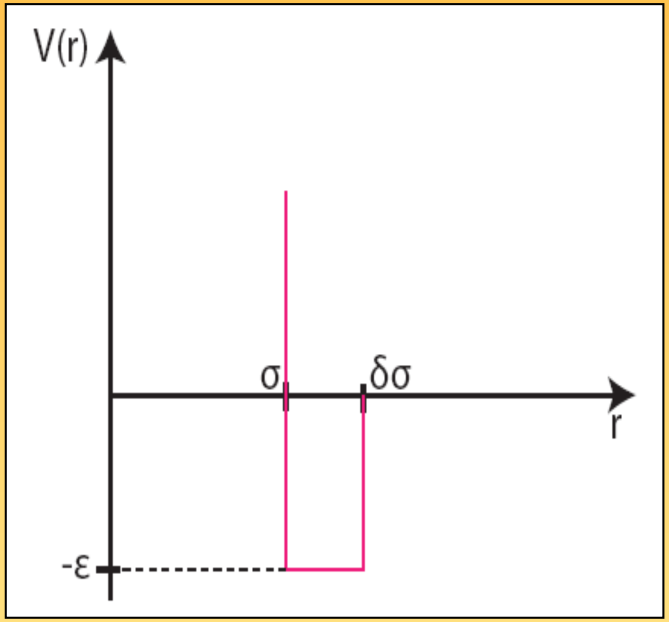


2 reduced parameters:

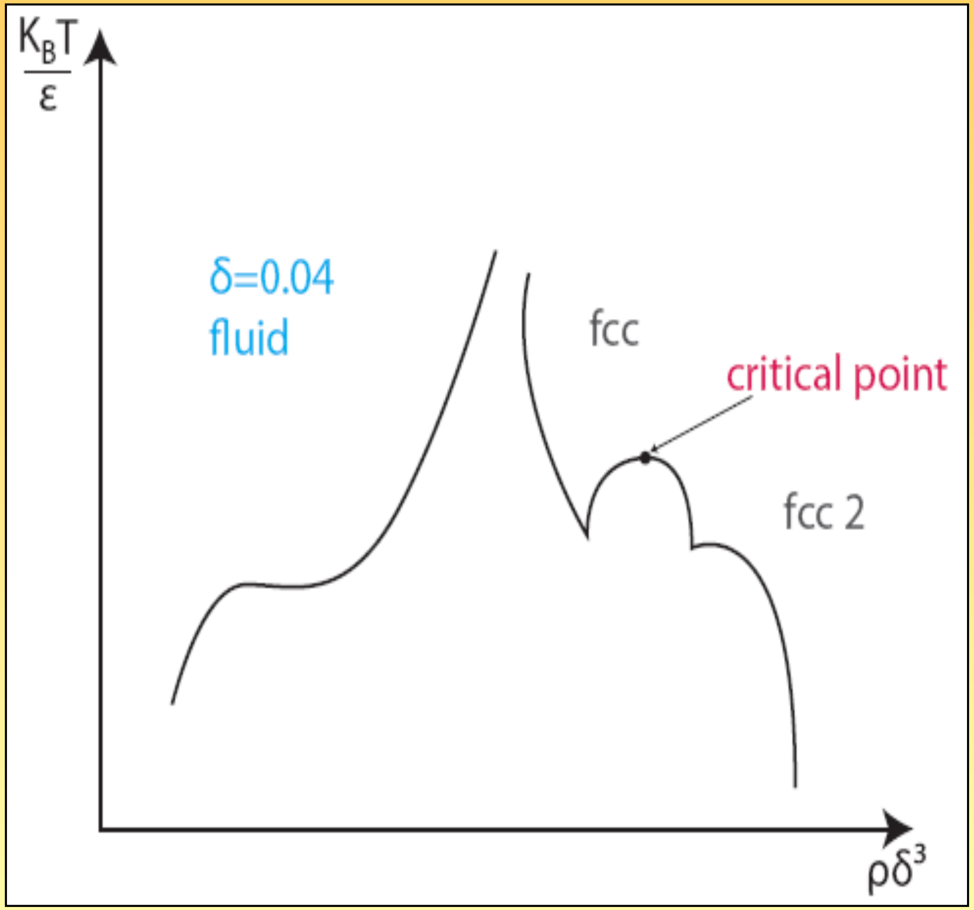
$$\frac{k_B T}{\epsilon}\ ,\ \rho\sigma^3$$

f) sticky hard spheres

$$V(r) = \begin{cases} \infty & r \leq \sigma \\ -\epsilon & \sigma \leq r \leq \sigma(1+\delta) \\ 0 & \text{elsewhere} \end{cases}$$



phase diagram:



$\delta \geq 0.25$ is needed to get a liquid

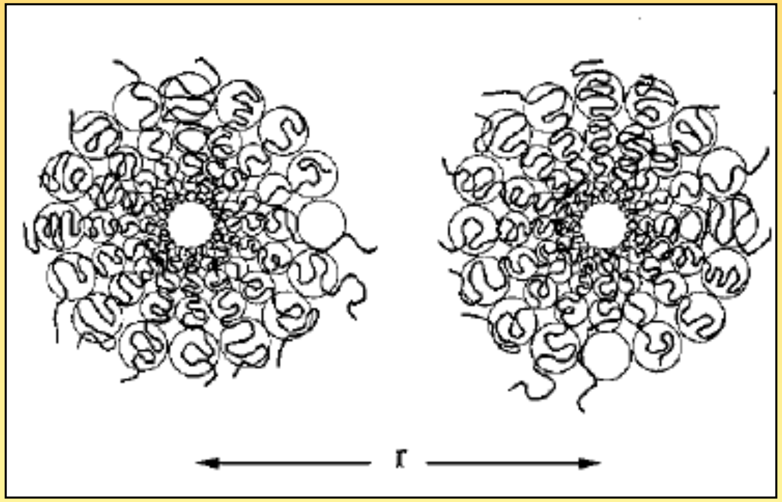
$\delta \leq 0.05$ is needed to get an iso-structural solid-solid transition

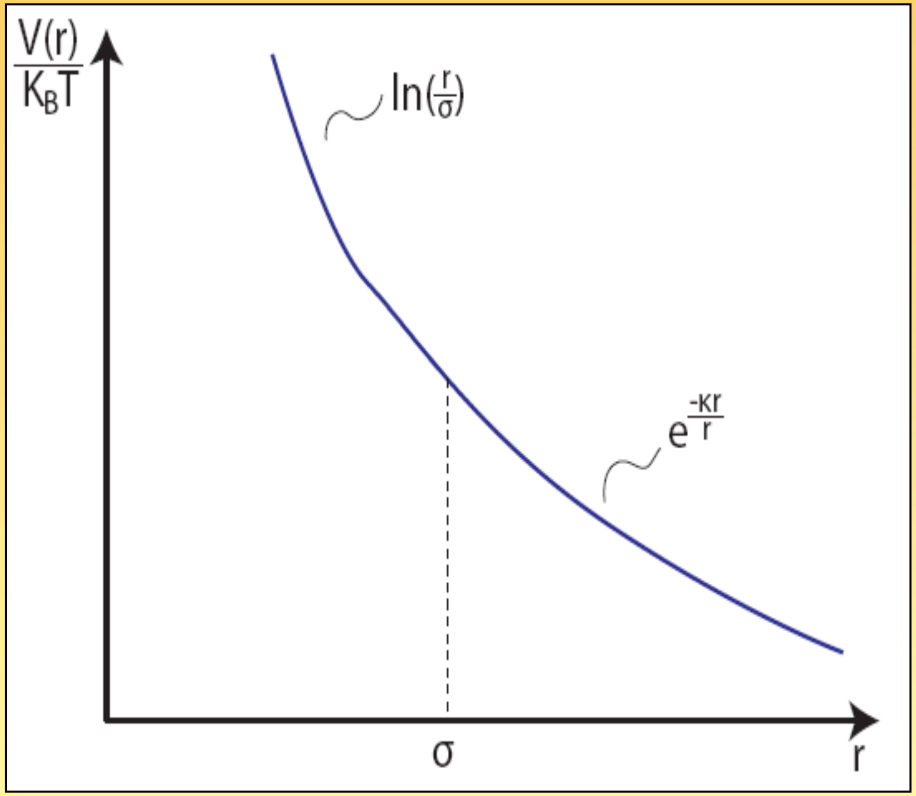
g) ultrasoft interactions

repulsive, realized for star polymers

exhibit “exotic“ stable solid lattices like bco, sc, A15, diamond, etc.

$$V(r) = \frac{5}{18} k_B T f^{3/2} \begin{cases} -\ln(\frac{r}{\sigma}) + \frac{1}{1+\sqrt{f}/2} & (r \leq \sigma), \\ \frac{\sigma}{1+\sqrt{f}/2} \frac{\exp[-\sqrt{f}(r-\sigma)/2\sigma]}{r} & (r > \sigma), \end{cases}$$





PRL 80, 4450 (1998)

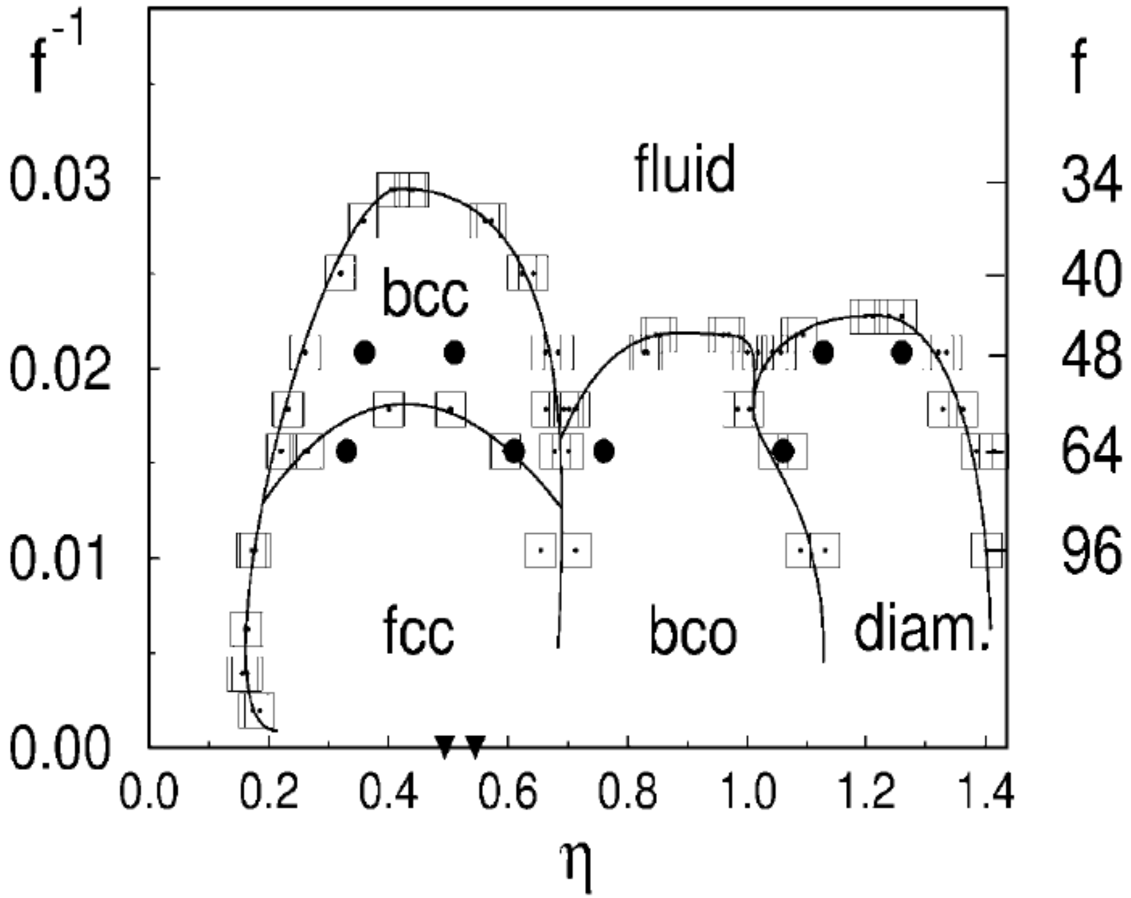


FIG. 1. The phase diagram of star polymer solutions for different arm numbers f versus packing fraction η. The squares and the circles indicate the phase boundaries as obtained from computer simulations and theory, respectively; lines are only guides to the eye. The statistical error of the simulations is of the order of the symbol size. The triangles indicate the freezing and melting point of hard spheres.

PRL <u>82</u>, 5289 (1999)

h) penetrable potentials, e.g. Gaussian

$$v(r) = \varepsilon e^{-(r/\sigma)^2}$$

J. Phys.: Condens. Matter **12,** 5087 (2000)

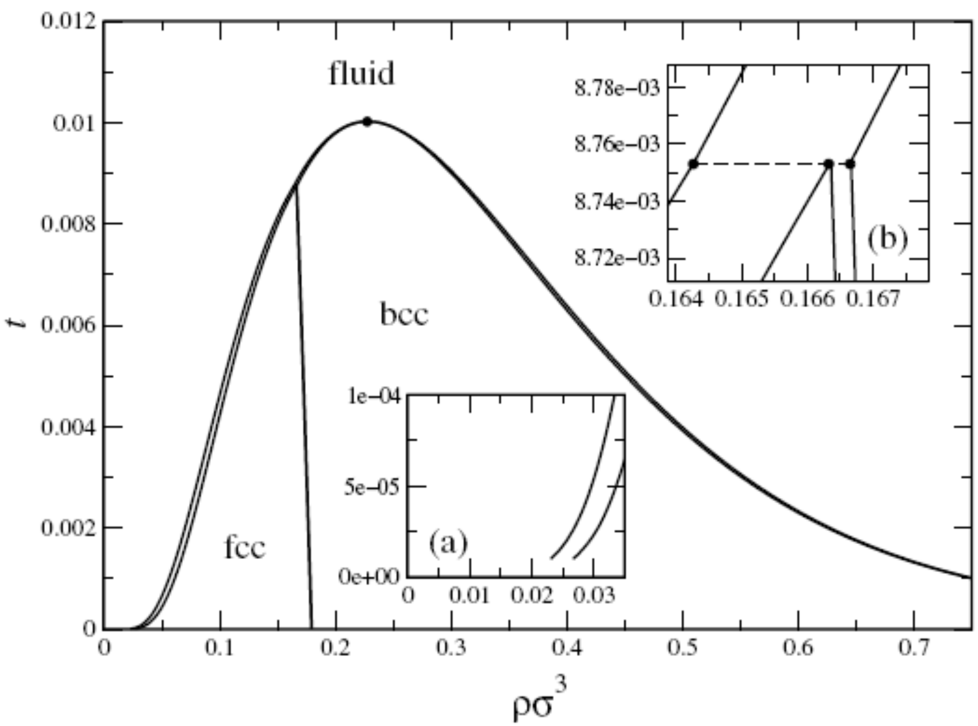


Figure 9. The phase diagram of the GCM obtained by the approach described in the text. The fcc–bcc coexistence lines are also double lines but they cannot be resolved on the scale of the figure because the fcc–bcc density gap is too small. The full dot marks the point at which the fluid–bcc coexistence curves turn around. The two insets show details of the phase diagram. (a) In the neighbourhood of zero densities and temperatures. (b) In the neighbourhood of the fluid–fcc–bcc triple temperature, with the dashed line denoting the triple line between these coexisting phases.

also possible: cluster crystals (if V(r) has non-positive Fourier transform)

1.5) Density Functional Theory (DFT)

See also: lectures of Martin Oettel

a) Basics

$$\left.\frac{\delta\Omega(T,\mu,[\rho])}{\delta\rho(\vec{r})}\right|_{\rho(\vec{r})=\rho_0(\vec{r})} = 0 \qquad \left.\frac{\delta\mathcal{F}(T,[\rho])}{\delta\rho(\vec{r})}\right|_{\rho(\vec{r})=\rho_0(\vec{r})} = \mu - V_{\text{ext}}(\vec{r})$$

Basic variational principle:

There exists a unique grand-canonical free energy-density-functional

$$\Omega(T,\mu,[\rho])) = \mathcal{F}(T,[\rho]) - \int \mathrm{d}^3\mathrm{r}(\mu - V_{ext}(\vec{r}))\rho(\vec{r})$$

which gets minimal for the equilibrium density $\rho_0(\vec{r})$

and then coincides with the real grandcanoncial free energy.

→ is also valid for systems which are inhomogeneous on a microscopic scale.

In principle, all fluctuations are included in an external potential which breaks all symmetries.

For interacting systems, in 3d, $\Omega(T,\mu,[\rho])$ is not known.

exceptions:

i) soft potentials in the high density limit, ideal gas (low density limit)

ii) 1d: hard rod fluid, exact Percus functional

strategy:

1) chose an approximation

2) parametrize the density field with variational parameters gas, liquid: $\rho(\vec{r}) = \rho$

solid: $\rho(\vec{r}) = \left(\frac{\alpha}{\pi}\right)^{-3/2} \sum_n \exp\left(-\alpha\left(\vec{r} - \vec{R}_n\right)^2\right)$

with $\left\{\vec{R}_n\right\}$ lattice vectors of bcc or fcc or ... crystals, spacing sets $\overline{\rho}$, vacancies?

α : variational parameter

Gaussian approximation for the solid density orbital is an excellent approximation

3) minimize $\Omega(T, \mu, [\rho])$ with respect to all variational parameters

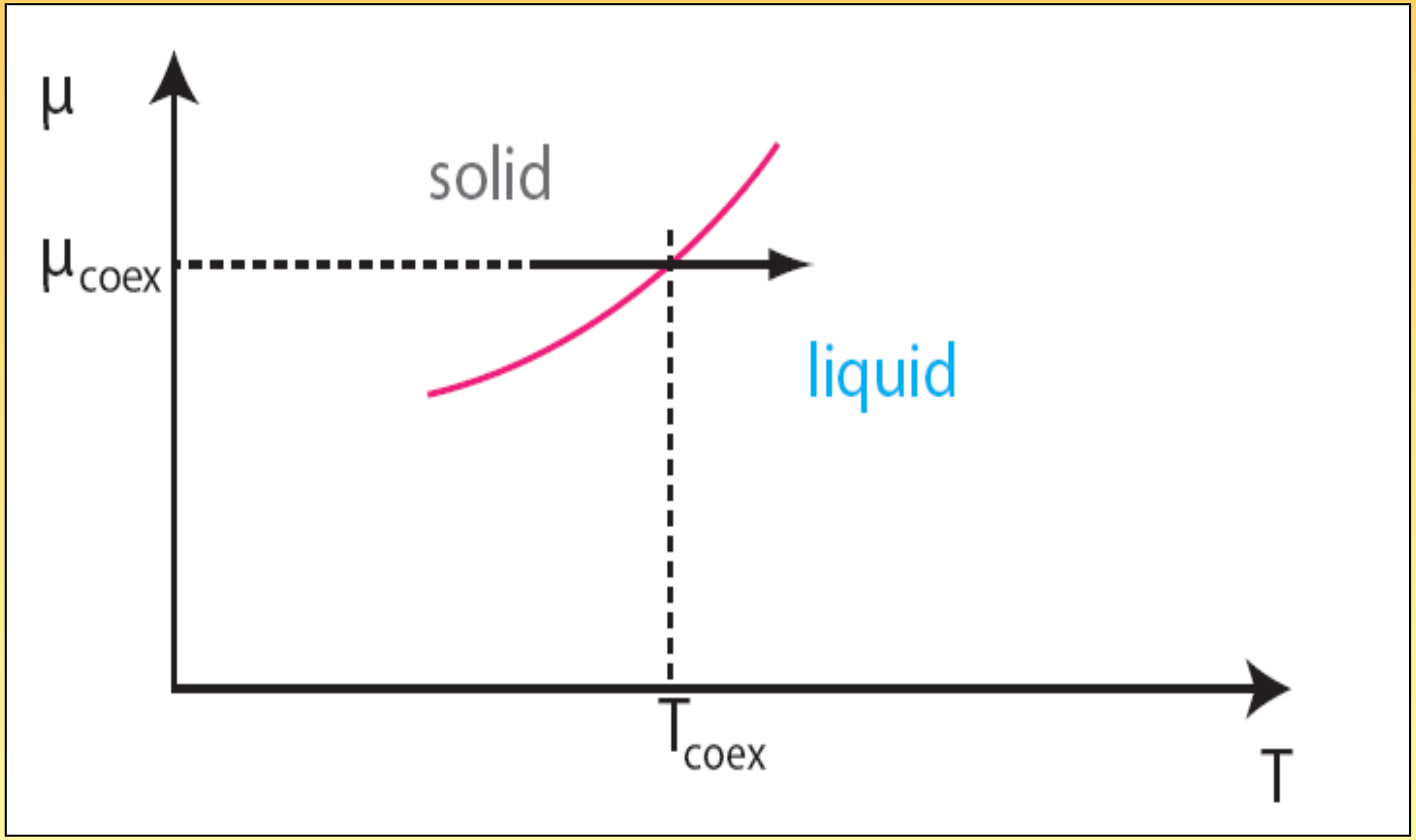
=> bulk phase diagram

EPL 22, 245 (1993)

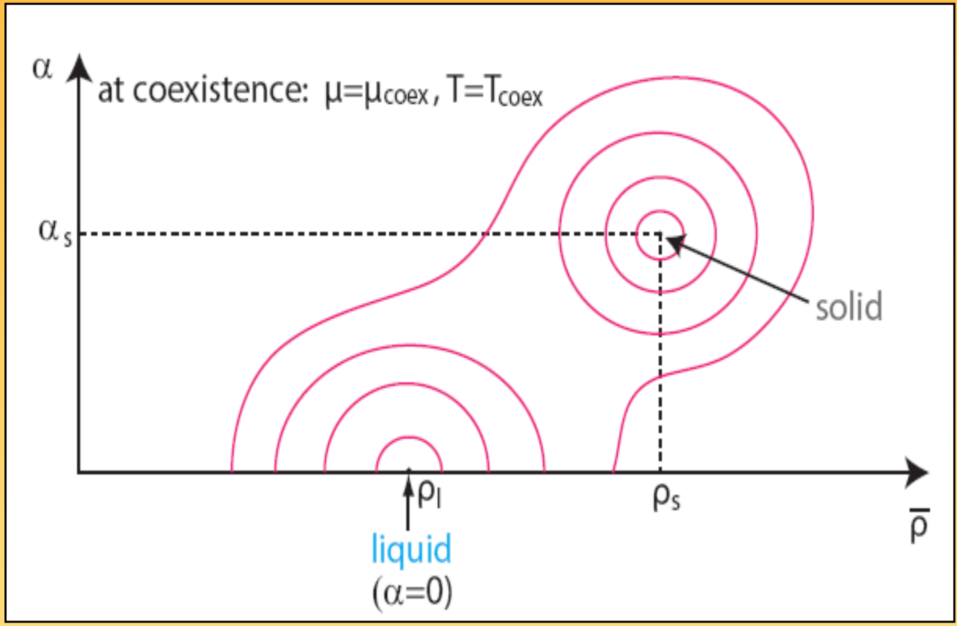
example:

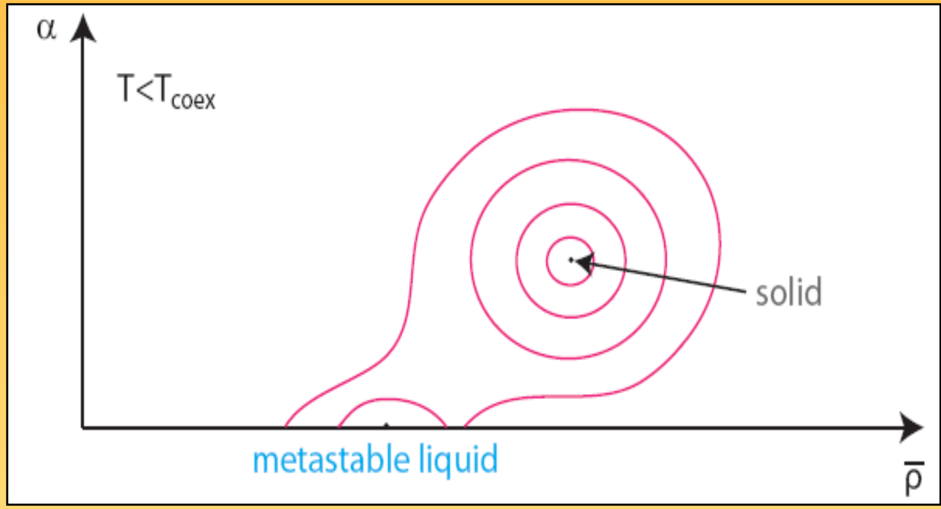
solid/liquid coexistence

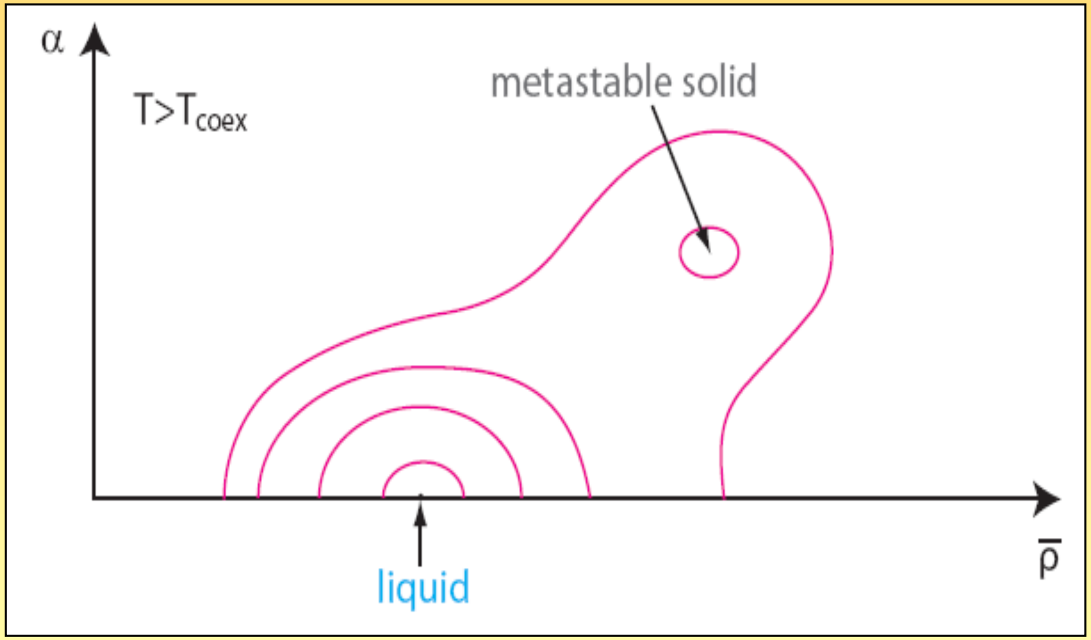
coexistence implies: $T, \mu, p = -\frac{\Omega}{V}$ are equal



contour plot of $\Omega(T, \mu, [\rho(\vec{r})]) = \Omega(T, \mu, \bar{\rho}, \alpha)$







Link to liquid state theory

$$c^{(2)}(\vec{r}-\vec{r}', T, \rho_0) = -\beta \left. \frac{\delta^2 \mathcal{F}_{exc}(T, [\rho])}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} \right|_{\rho_0}$$

↑

direct correlation function (from Ornstein-Zernike relation)

b) approximations for the density functional

1) ideal gas, $V(r) = 0$

$$\mathcal{F}(T,[\rho]) \equiv \mathcal{F}_{\mathrm{id}}(T,[\rho])$$

$$= k_B T \int \mathrm{d}^3 r \ \rho(\vec{r}) \left[\ln(\rho(\vec{r})\Lambda^3) - 1\right]$$

since
$$\Omega(T,\mu,[\rho]) = k_B T \int \mathrm{d}^3 r \ \rho(\vec{r}) \left(\ln(\rho(\vec{r})\Lambda^3) - 1\right)$$

$$+ \int \mathrm{d}^3 r \ (V_{\mathrm{ext}}(\vec{r}) - \mu)\, \rho(\vec{r})$$

$$0 = \left.\frac{\delta\Omega}{\delta\rho(\vec{r})}\right|_0 = k_B T \ln(\rho(\vec{r})\Lambda^3) + V_{\mathrm{ext}}(\vec{r}) - \mu$$

$$\rightsquigarrow \quad \rho_0(\vec{r}) = \frac{1}{\Lambda^3} \exp\left(-\frac{V_{\mathrm{ext}}(\vec{r}) - \mu}{k_B T}\right)$$

„generalized barometric law“

This is indeed the equilibrium density of an inhomogeneous gas.

2) in the interacting case, $V(r) \neq 0$:

$\mathcal{F}(T,[\rho]) =: \mathcal{F}_{\mathrm{id}}(T,[\rho]) + \mathcal{F}_{\mathrm{exc}}(T,[\rho])$ defines the excess free energy functional $\mathcal{F}_{\mathrm{exc}}(T,[\rho])$

approximations on different levels

1) LDA, local density approximation:

$$\mathcal{F}_{\text{exc}}(T,[\rho]) \cong \int \mathrm{d}^3r \; f_{\text{exc}}(T,\rho(\vec{r}))$$

where $f_{\text{exc}}(T,\rho)$ is the excess free energy density in a homogeneous (bulk) system, input, valid only for small inhomogeneites

2) LDA + mean field:

$$\mathcal{F}_{\text{exc}}(T,[\rho]) = \int \mathrm{d}^3r \left[f_{\text{exc}}(T,\rho(\vec{r})) - \frac{1}{2} V_0 \rho^2(\vec{r}) \right]$$

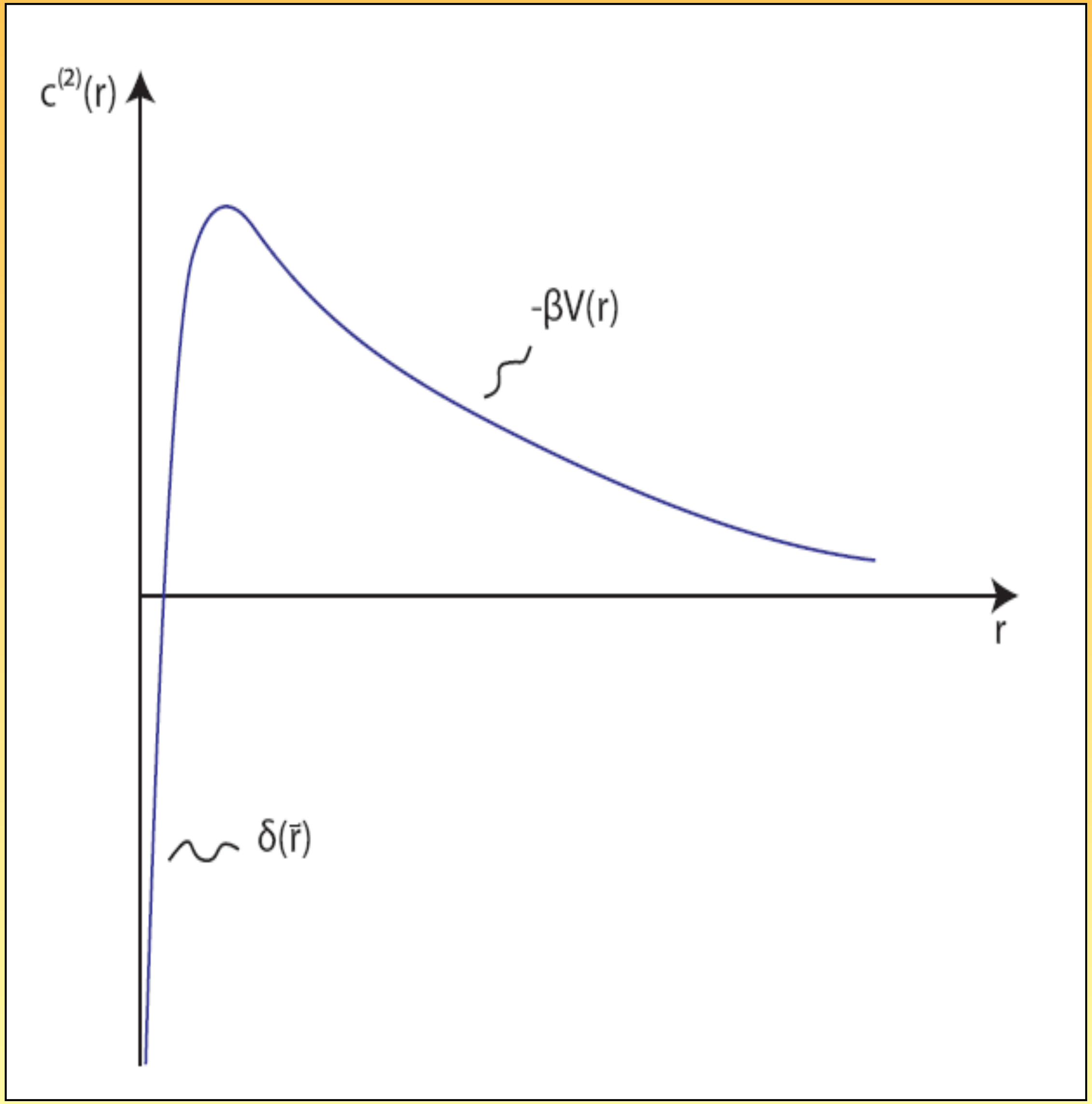
$$+\frac{1}{2}\int \mathrm{d}^3r \int \mathrm{d}^3r' \; V(|\vec{r}-\vec{r}'|)\rho(\vec{r})\rho(\vec{r}')$$

with $V_0 = \int \mathrm{d}^3r V(r)$

=> homogeneous limit is respected valid for "moderate" inhomogeneites, but not for density variations on the microscopic scale

$$c^{(2)}(\vec{r},\vec{r}^{\,'}) = -\beta\frac{\partial^2 f_{\mathrm{exc}}(T,\rho(\vec{r}))}{\partial\rho^2}\delta(\vec{r}-\vec{r}^{\,'}) + \beta V_0\delta(\vec{r}-\vec{r}^{\,'}) - \beta V(\vec{r})$$

(DH approx.)



3) Ramakrishnan-Yussouf (RY) 1979

$$\mathcal{F}_{\text{exc}}(T,[\rho]) \cong -\frac{k_B T}{2}\int \mathrm{d}^3r \int \mathrm{d}^3r' \; \underbrace{c^{(2)}(|\vec{r}-\vec{r}'|, \overbrace{\bar{\rho}}^{\text{reference}}, T)}_{\text{input}}(\rho(\vec{r})-\bar{\rho})(\rho(\vec{r}')-\bar{\rho})$$

is reproducing the direct correlation function

$c^{(2)}(r,\bar{\rho},t)$ exactly at $\rho = \bar{\rho}, T$

results in a solid-fluid transition (for hard spheres)

4) **Weighted density approximation (WDA)** Curtin & Ashcroft, 1985

$$\mathcal{F}_{\text{exc}}(T,[\rho]) = \int \mathrm{d}^3 r \ \rho(\vec{r})\Psi(T,\tilde{\rho}(\vec{r}))$$

Ψ : free energy per particle; $\tilde{\rho}$: weighted density

$$\tilde{\vec{\rho}} = \int \mathrm{d}^3 r' \ w(|\vec{r}-\vec{r}'|,\tilde{\rho}(\vec{r}),T)\rho(\vec{r}')$$

determine $w(r,\rho,T)$ such that

$$-\frac{1}{k_B T}\frac{\delta^2 \mathcal{F}_{\text{exc}}}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}\bigg|_{\bar{\rho}} = c^{(2)}(|\vec{r}-\vec{r}'|,T,\bar{\rho})$$ for all $\bar{\rho}$

$\rightsquigarrow$ WDA yields excellent data for hard sphere freezing, etc. problem with WDA: overlapping hard sphere configurations are not excluded

5) Rosenfeld functional (for hard spheres)

(fundamental measure theory (FMT))

$$\frac{\mathcal{F}_{\text{exc}}[\rho]}{k_B T} = \int \mathrm{d}^3 r \ \Phi[\{n_\alpha(\vec{r})\}]$$

$\alpha = 0, 1, 2, 3, V_1, V_2$ geometrical measures

with $n_\alpha(\vec{r}) = \int \mathrm{d}^3 r' \ w^{(\alpha)}(\vec{r} - \vec{r}\,')\rho(\vec{r}\,')$

6 weight functions:

$$
\begin{aligned}
w^{(0)}(\vec{r}) &= \frac{w^{(2)}(\vec{r})}{\pi\sigma^2} \quad , \sigma : \\
w^{(1)}(\vec{r}) &= \frac{w^{(2)}(\vec{r})}{2\pi\sigma} \\
w^{(2)}(\vec{r}) &= \delta\left(\frac{\sigma}{2} - r\right) \\
w^{(3)}(\vec{r}) &= \Theta\left(\frac{\sigma}{2} - r\right) \\
w^{(V_1)}(\vec{r}) &= \frac{\vec{w}^{(V_2)}(\vec{r})}{2\pi\sigma} \\
w^{(V_2)}(\vec{r}) &= \frac{\vec{r}}{r}\delta\left(\frac{\sigma}{2} - r\right)
\end{aligned}
$$

hard sphere diameter

and

$$
\begin{aligned}
\Phi &= \Phi_1 + \Phi_2 + \Phi_3 \\
\Phi_1 &= -n_0 \ln(1 - n_3) \\
\Phi_2 &= \frac{n_1 n_2 - \vec{n}_{v_1} \cdot \vec{n}_{v_2}}{1 - n_3} \\
\Phi_3 &= \frac{\frac{1}{3} n_2^3 - n_2(\vec{n}_{v_2} \cdot \vec{n}_{v_2})}{8\pi(1 - n_3)^2}
\end{aligned}
$$

functional survives dimensional crossover

3D→2D→1D→0D

PRE 55, 4245 (1997)

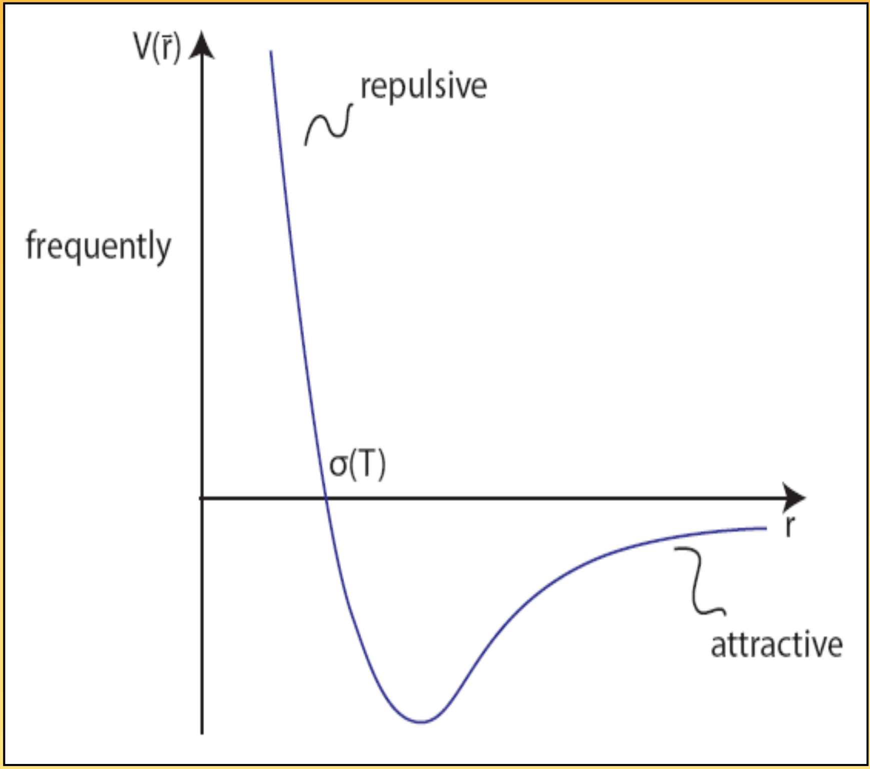
advantages

- excludes overlapping hard sphere configurations
- yields $\text{PY } c^{(2)}(r,\rho)$ as output
- excellent data for hard sphere freezing

results, hard spheres

	ρ fluid σ^3	ρ solid σ^3	L (: Lindemann)
computer simulations	0.94	1.04	0.129
RY	0.97	1.15	0.06
WDA	0.92	1.04	0.10
Rosenfeld	0.94	1.03	0.101

6) Hard sphere pertubation theory



$$V(r) = \underbrace{V_{\text{rep}}(r)}_{\text{short-ranged}} + \underbrace{V_{\text{attr}}(r)}_{\text{long-ranged}} \qquad \text{(WCA)}$$

approximate $V_{\text{rep}}(r)$ by a hard sphere potential with an effective diameter

$$\sigma(T) = \int_0^\infty \mathrm{d}r \, \left(1 - e^{-\beta V_{\text{rep}}(r)}\right)$$

(Barker, Henderson)

then
$$\mathcal{F}_{\text{exc}}(T,[\rho]) \cong \mathcal{F}^{\text{HS}}_{\text{exc}}(T,[\rho])\Big|_{\sigma=\sigma(T)}$$

$$+\frac{1}{2}\int \mathrm{d}^3r \int \mathrm{d}^3r' \, \rho(\vec{r})\rho(\vec{r}\,') \underbrace{V_{\text{attr}}(|\vec{r}-\vec{r}\,'|)}_{\text{mean field}}$$

$\rightsquigarrow$ good phase diagram for Lennard-Jones (LJ)

2) Brownian Dynamics and dynamical density functional theory

2.1) Brownian dynamics (BD)

literature: M.Doi, S.F. Edwards, "Theory of Polymer Dynamics", Oxford, 1986

colloidal particles will be randomly kicked by the solvent

Smoluchowski picture

Brownian motion is diffusion. $\rho(\vec{r}, t)$ time-dependent density field of the particle(s)

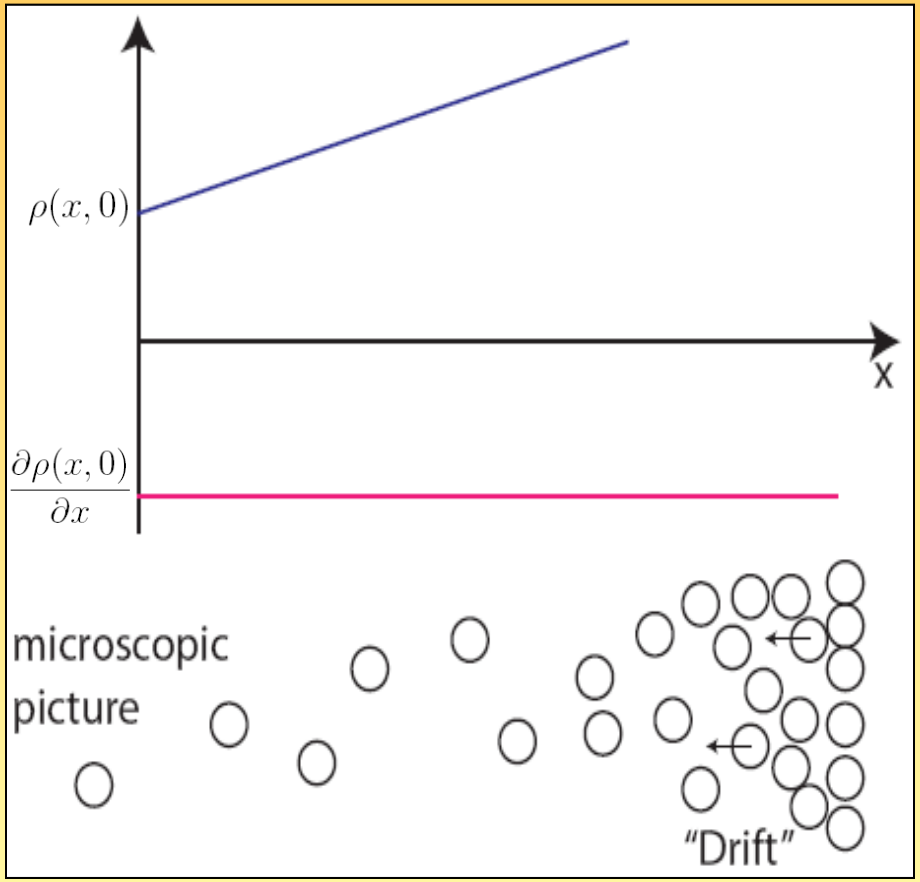
Fick´s law

current density

$$\vec{j}(\vec{r},t) = -D\vec{\nabla}\rho(\vec{r},t)$$

$D :$ phenomenological diffusion coefficient

example:



mass conservation → continuity equation

$$\frac{\partial\rho(\vec{r},t)}{\partial t} + \vec{\nabla}\vec{j}(\vec{r},t) = 0$$

→ combined with Fick´s law:

$$\frac{\partial\rho(\vec{r},t)}{\partial t} = D\Delta\rho(\vec{r},t)$$

diffusion equation

This is valid for free particles with a given intial density $\rho(\vec{r}, t = 0)$.

With an external potential $V_{\text{ext}}(\vec{r})$, there is the force

$\vec{F} = -\vec{\nabla} V_{\text{ext}}(\vec{r})$ acting on the particles

→ drift velocity $\vec{v}_{\text{D}}$ of the particles resp. an additional current density $\vec{j}_{\text{D}} = \rho \vec{v}_{\text{D}}$

assumption: totally overdamped motion

$$\rightarrow \vec{v}_{\text{D}} = \frac{\vec{F}}{\zeta} = -\frac{1}{\zeta} \vec{\nabla} V_{\text{ext}}(\vec{r})$$

ζ : friction coefficient

remark: for a sphere (radius R) in a viscous solvent, Stokes equation yields:

$$\zeta = 6\pi \eta_{\text{s}} R$$

η_s : shear viscosity

total current density

$$\vec{j} = -D\vec{\nabla}\rho(\vec{r},t) - \rho(\vec{r},t)\frac{1}{\zeta}\vec{\nabla}V_{\text{ext}}(\vec{r})$$

in equilibrium:

i) $$\rho(\vec{r},t) = \rho^{(0)}(\vec{r}) = A\exp(-\beta V_{\text{ext}}(\vec{r}))$$

ii) the total current has to vanish, i.e.:

$$0 = -D \underbrace{\vec{\nabla}\rho^{(0)}(\vec{r})}_{-\beta A\exp(-\beta V_{\text{ext}}(\vec{r}))\vec{\nabla}V_{\text{ext}}(\vec{r})} - \overbrace{\rho^{(0)}(\vec{r})}^{A\exp(-\beta V_{\text{ext}}(\vec{r}))} \frac{1}{\zeta}\vec{\nabla}V_{\text{ext}}(\vec{r})$$

→ $$D = \frac{k_B T}{\zeta}$$

Stokes-Einstein-relation

(special case for fluctuation-dissipation-theorem)

hence $$\vec{j} = -\frac{1}{\zeta}(k_B T\vec{\nabla}\rho + \rho\vec{\nabla}V_{\text{ext}})$$

→ continuity equation $$\frac{\partial\rho(\vec{r},t)}{\partial t} = \frac{1}{\zeta}(k_B T\Delta\rho(\vec{r},t) + \vec{\nabla}(\rho(\vec{r},t)\vec{\nabla}V_{\text{ext}}(\vec{r})))$$

Smoluchowski equation

Diffusion in phase space

$\rightarrow$ non-interacting particles

$w(\vec{r},t)$ is probability to find a particle at positio $\vec{r}$ and time t

$\rightarrow$ normalized: $\int \mathrm{d}^3 r \;\; w(\vec{r},t) = 1$

$w(\vec{r},t)$ is identical to $\rho(\vec{r},t)$ except normalization:

$$\rightarrow \quad w(\vec{r},t) = \frac{\rho(\vec{r},t)}{\int \mathrm{d}^3 r \rho(\vec{r},t)} = \frac{1}{N}\rho(\vec{r},t)$$

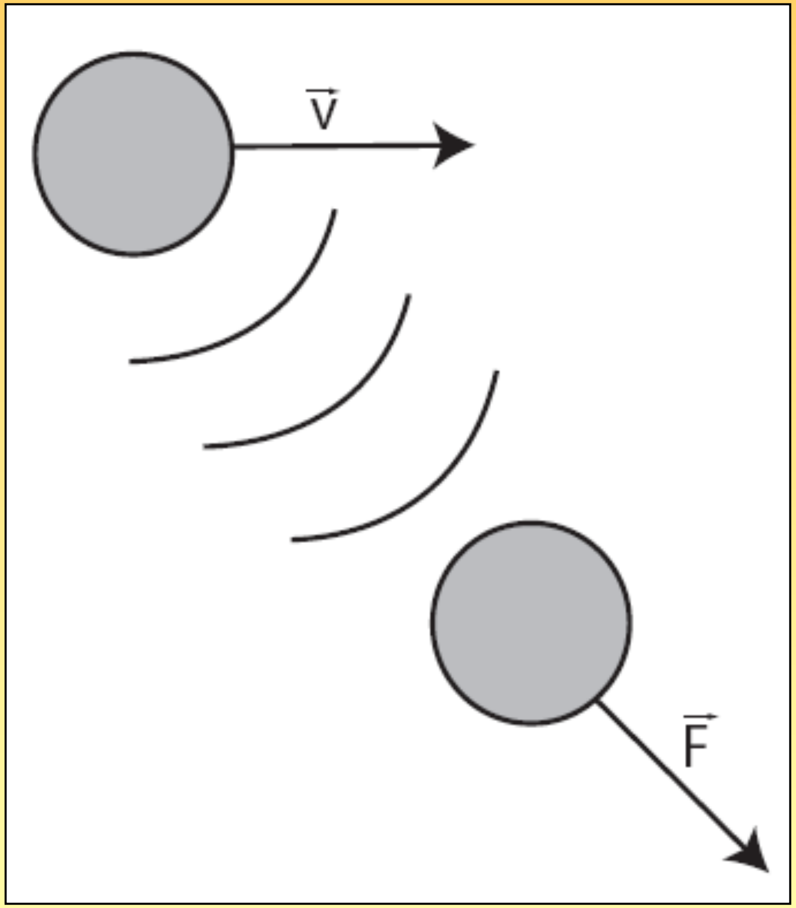
$$\rightarrow \quad \frac{\partial w}{\partial t} = \frac{1}{\zeta}(k_B T \Delta w - \vec{\nabla}(w \cdot \vec{\nabla} V_{\mathrm{ext}}))$$

Smoluchowski-equation (Focker-Planck-equation) now: **<u>N interacting particles</u>**

$$\{\vec{r}_i\} = \{\vec{r}_1, \cdots \vec{r}_N\}$$

more compact notation: (analogue for all other vectors)

$$\{x_i\} = \{\vec{r}_i\} = \{\underbrace{x_1, x_2, x_3}_{\vec{r}_1}, \underbrace{x_4, x_5, x_6}_{\vec{r}_2}, \cdots, \underbrace{x_{3N-2}, x_{3N-1}, x_{3N}}_{\vec{r}_N}\}$$



velocity of particle induces
flow of solvent

→ (force) / movement of other particle

→ hydrodynamic interaction

linear relation between $\vec{v}_\alpha$ and $\vec{F}$

$$v_{\alpha,i} = \sum_{j=1}^{3N} L_{ij}(\{x_n\})\vec{F}_j \qquad , \vec{F}_j = -\frac{\partial}{\partial x_j} \underbrace{U_{\text{tot}}}_{V_{\text{ext}}+V}$$

L_{ij} : mobility matrix, calculated from Navier-Stokes-eq.

One can show:

- $L_{ij} = L_{ji}$
- $\sum_{ij} F_i F_j L_{ij} > 0 \text{ for all } F_{i,j} \neq 0$ positive definite

probability density $w(\{\vec{r}_i\}, t)$ for interacting particles with equation:

$$\frac{\partial w}{\partial t} = -\sum_{n=1}^{3N} \frac{\partial}{\partial x_n}(v_{\text{tot},n} w)$$

with

$$v_{\text{tot},n} = \sum_{m=1}^{3N} L_{mn} \frac{\partial}{\partial x_m}(k_B T \ln w + U_{\text{tot}})$$

→ generalized Smoluchowski equation for interacting particles

One can write: $\frac{\partial w}{\partial t} = \mathcal{O} w$

$$\mathcal{O} = \sum_{n,m=1}^{3N} \frac{\partial}{\partial x_n} L_{nm} (k_B T \frac{\partial}{\partial x_m} + \frac{\partial U_{\text{tot}}}{\partial x_m})$$

$\mathcal{O}$: Smoluchowski operator (compare Liouville operator)

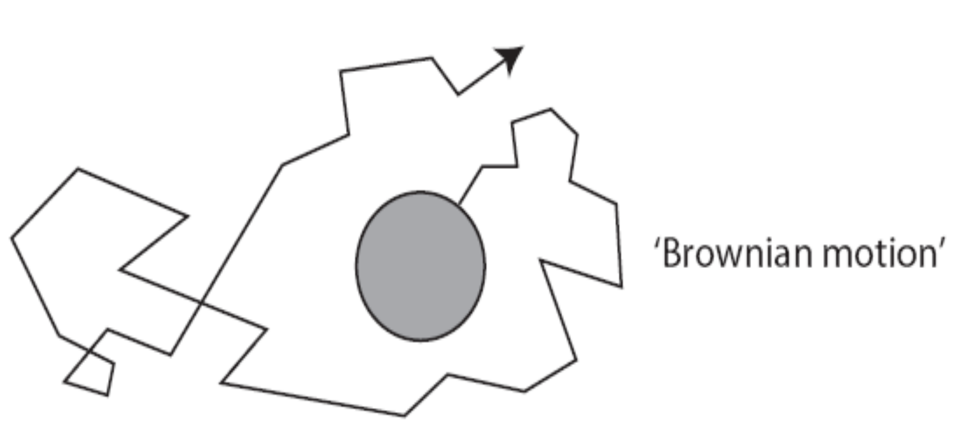
often: $L_{nm} = \frac{1}{\zeta} \delta_{nm}$

(no hydrodynamic interactions,
good for low packing fractions $\eta \leq 0.01$)

Langevin-picture

Smoluchowski-picture: $w(\{\vec{r}_i\}, t)$ with diffusion dynamics

Langevin-picture: stochastic trajectories in real-space



First, we consider only one particle

in an external potential $V_{\rm ext}(\vec{r})$

with random force $\vec{f}(t)$

$$\underbrace{\cancel{m}\ddot{\vec{r}}}_{\downarrow} + \underbrace{\zeta\dot{\vec{r}}}_{\text{friction}} = -\vec{\nabla}V_{\rm ext}(\vec{r}) + \vec{f}(t) \qquad (*)$$

→ stochastic differential equation:

assume: system overdamped $(m\ddot{\vec{r}} \ll \zeta\dot{\vec{r}})$

$\vec{f}(t)$ comes from random kicks of the solvent

probability distribution for $\vec{f}(t) : \psi[\vec{f}(t)]$

observable $A(x(t))$: **strategy**

1) solve (*) for a given $\vec{f}(t)$ 2) average $\vec{f}(t)$ with $\psi[\vec{f}(t)]$

(in principal functional integral)

Now: $\vec{f}(t)$ is Gaussian distributed

$$\begin{aligned} \langle \vec{f}(t) \rangle &= 0 \\ \langle f_i(t) f_j(t') \rangle &= 2\zeta k_B T \delta_{ij} \delta(t - t') \qquad , i, j = 1 \cdots 3 \\ (\text{i.e.: } \psi[\vec{f}(t)] &\propto \exp(-\frac{1}{4\zeta k_B T} \int \mathrm{d}t \ f^2(t))) \end{aligned}$$

$$\frac{\partial w}{\partial t} = D \Delta w$$

Equivalence of Langevin and Smoluchowski picture for interacting particles (no hydrodynamic interactions)

with hydrodynamic interactions(HI.):

L_{nm} depends on $\{x_j\}$

The Smoluchowski equation (**) is obtained from the following Langevin equations:

$$\dot{x}_n(t) = \sum_{m=1}^{3N} L_{nm} \left(-\frac{\partial U_{\text{total}}}{\partial x_m} + f_m(t) \right) + \underbrace{k_B T \sum_{m=1}^{3N} \frac{\partial L_{nm}}{\partial x_m}}_{\text{additional term}}$$

2.2) Dynamical density functional theory (DDFT)

1) Derivation from the Smoluchowski equation

(Archer, Evans, J.Chem.Phys. 121, 4246 (2004))

recall Smoluchowski equation for the N-particle density

$$w(\vec{r}_1, \ldots, \vec{r}_N, t) \equiv w(\vec{r}^N, t) \quad , \quad \vec{r}^N = \{\vec{r}_1, \ldots, \vec{r}_N\}$$

no HI.

$$\frac{\partial w}{\partial t} = \hat{O} w = \frac{1}{\zeta} \sum_{i=1}^{N} \vec{\nabla}_i \cdot [k_B T \vec{\nabla}_i + \vec{\nabla}_i \underbrace{U_{\text{total}}(\vec{r}^N, t)}_{\text{time dependent}}] w$$

$$U_{\text{total}}(\vec{r}^N, t) = \sum_{i=1}^{N} \underbrace{V_{\text{ext}}(\vec{r}_i, t)}_{\text{time dependent}} + \sum_{\substack{i,j=1 \\ i<j}}^{N} V(|\vec{r}_i - \vec{r}_j|)$$

idea: integrate out degrees of freedom

integration yields

$$\rho(\vec{r}_1, t) = N \int \mathrm{d}^3 r_2 \ldots \int \mathrm{d}^3 r_N \;\; w(\vec{r}^N, t)$$

2-particle density:

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2, t) = N(N-1) \int \mathrm{d}^3 r_2 \ldots \int \mathrm{d}^3 r_N \;\; w(\vec{r}^N, t)$$

integrating the **Smoluchowski equation** with $N \int \mathrm{d}^3 r_2 \ldots \int \mathrm{d}^3 r_N$:

$$\begin{aligned} \Rightarrow \frac{\partial}{\partial t}\rho(\vec{r}_1, t) \;\; = \;\; & N \cdot \int \mathrm{d}^3 r_2 \ldots \int \mathrm{d}^3 r_N \{ \sum_{i=1}^{N} (k_B T \Delta_i w(\vec{r}^N, t) \\ & + \vec{\nabla}_i (\vec{\nabla}_i V_{\mathrm{ext}}(\vec{r}_i, t) w(\vec{r}^N, t))) \\ & + \sum_{\substack{i=1 \\ i<j}}^{N} \vec{\nabla}_i (\vec{\nabla}_i (V(|\vec{r}_i - \vec{r}_j|) w(\vec{r}^N, t))) \} \end{aligned}$$

now:

1)

$$N \int \mathrm{d}^3 r_2 \quad \dots \quad \int \mathrm{d}^3 r_N \sum_{i=1}^{N} k_B T \Delta_i w(\vec{r}^N, t) = k_B T \Delta_1 \rho(\vec{r}_1, t)$$

$$+N \int \mathrm{d}^3 r_2 \dots \int \mathrm{d}^3 r_N k_B T \sum_{i=2}^{N} \Delta_i w(\vec{r}^N, t)$$

$$= \quad k_B T \Delta_1 \rho(\vec{r}_1, t)$$

$$+ \sum_{i=2}^{N} N k_B T \int \mathrm{d}^3 r_i \vec{\nabla}_i \underbrace{(\vec{\nabla}_i \int \mathrm{d}^3 r_2 \dots \int \mathrm{d}^3 r_N \; w(\vec{r}^N, t))}_{f(\vec{r}_1, \vec{r}_i, t)}$$

$$\text{Gauss:} \int_S \mathrm{d}^2 f_i \vec{\nabla}_i f(\vec{r}_1, \vec{r}_i, t) = 0$$

$$= \quad k_B T \Delta_1 \rho(\vec{r}_1, t) + \sum_{i=2}^{N} N k_B T \underbrace{\int \mathrm{d}^3 r_i \vec{\nabla}_i (\vec{\nabla}_i (f(\vec{r}_1, \vec{r}_i, t)))}_{=0}$$

2)

$$N \int \mathrm{d}^3 r_2 \quad \ldots \quad \int \mathrm{d}^3 r_N \sum_{i=1}^{N} \vec{\nabla}_i (\vec{\nabla}_i V_{\mathrm{ext}}(\vec{r}_i, t) w(\vec{r}^N, t))$$

$$= \quad N \int \mathrm{d}^3 r_2 \ldots \int \mathrm{d}^3 r_N \vec{\nabla}_1 (\vec{\nabla}_1 V_{\mathrm{ext}}(\vec{r}_1, t)) w(\vec{r}^N, t) + 0$$

$$= \quad \vec{\nabla}_1 ((\vec{\nabla}_1 V_{\mathrm{ext}}(\vec{r}_1, t)) \rho(\vec{r}_1, t))$$

3)

$$N\int \mathrm{d}^3r_2 \quad \dots \quad \int \mathrm{d}^3r_N \sum_{\substack{i,j=1\\ i<j}}^{N} \vec{\nabla}_i\cdot(\vec{\nabla}_i V(|\vec{r}_i-\vec{r}_j|))w(\vec{r}^N,t)$$

$$= \quad N\int \mathrm{d}^3r_2\dots\int \mathrm{d}^3r_N \vec{\nabla}_1(\sum_{j=2}^{N}\vec{\nabla}_1 V(|\vec{r}_1-\vec{r}_j|)w(\vec{r}^N,t))$$

$\vec{r}^N$ is symmetric in coordinates, set $j=2$

$$= \quad N(N-1)\vec{\nabla}_1\int \mathrm{d}^3r_2\vec{\nabla}_1 V(|\vec{r}_1-\vec{r}_2|)\int \mathrm{d}^3r_3$$

$$\dots\int \mathrm{d}^3r_N \; w(\vec{r}^N,t)$$

$$= \quad \int \mathrm{d}^3r_2\vec{\nabla}_1(\vec{\nabla}_1 V(|\vec{r}_1-\vec{r}_2|))\rho^{(2)}(\vec{r}_1,\vec{r}_2,t)$$

$$\begin{aligned}\rightarrow \zeta\frac{\partial}{\partial t}\rho(\vec{r}_1,t) = \quad & k_BT\Delta_1\rho(\vec{r}_1,t)+\vec{\nabla}_1(\rho(\vec{r}_1,t)\vec{\nabla}_1 V_{\mathrm{ext}}(\vec{r}_1,t)) \\ & +\vec{\nabla}_1\int \mathrm{d}^3r_2 \; \rho^{(2)}(\vec{r}_1,\vec{r}_2,t)\vec{\nabla}_1 V(|\vec{r}_1-\vec{r}_2|)\end{aligned}$$

in equilibrium, necessarily $\frac{\partial\rho(\vec{r}_1,t)}{\partial t}=0$

i.e.

$$0 = \vec{\nabla}(k_B T \vec{\nabla}\rho(\vec{r},t) + \rho(\vec{r},t)\vec{\nabla}V_{\text{ext}}(\vec{r},t) + \int d^3r' \ \rho^{(2)}(\vec{r},\vec{r}',t)\vec{\nabla}V(|\vec{r}-\vec{r}'|))$$

$$= \vec{\nabla}\underbrace{(k_B T \vec{\nabla}\rho(\vec{r}) + \rho(\vec{r})\vec{\nabla}V_{\text{ext}}(\vec{r}) + \int d^3r' \ \rho^{(2)}(\vec{r},\vec{r}')\vec{\nabla}V(|\vec{r}-\vec{r}'|))}_{=\text{ const, must vanish for } r\to\infty}$$

$$\Rightarrow 0 = k_B T \vec{\nabla}\rho(\vec{r}) + \rho(\vec{r})\vec{\nabla}V_{\text{ext}}(\vec{r}) + \int d^3r' \ \rho^{(2)}(\vec{r},\vec{r}')\vec{\nabla}V(|\vec{r}-\vec{r}'|)$$

(Yvon, Born, Green hierarchy YBG)

in equilibrium, DFT says:

$$\frac{\delta \mathcal{F}}{\delta \rho(\vec{r})} = \mu - V_{\text{ext}}(\vec{r}) \quad , \quad \mathcal{F} = \mathcal{F}_{\text{id}} + \mathcal{F}_{\text{exc}}$$
$$= k_B T \ln(\Lambda^3 \rho(\vec{r})) + \frac{\delta \mathcal{F}_{\text{exc}}}{\delta \rho(\vec{r})}$$

apply

$$\vec{\nabla} : \vec{\nabla} V_{\text{ext}}(\vec{r}) + k_B T \underbrace{\vec{\nabla} \ln(\Lambda^3 \rho(\vec{r}))}_{\frac{1}{\rho(\vec{r})} \vec{\nabla} \rho(\vec{r})} + \vec{\nabla} \frac{\delta \mathcal{F}_{\text{exc}}}{\delta \rho(\vec{r})} = 0$$

combined with YBG: $\rightsquigarrow$

$$\int \mathrm{d}^3 r' \ \rho^{(2)}(\vec{r}, \vec{r}\,') \vec{\nabla} V(|\vec{r} - \vec{r}\,'|) = \rho(\vec{r}) \vec{\nabla} \cdot \frac{\delta \mathcal{F}_{\text{exc}}[\rho]}{\delta \rho(\vec{r})}$$

We postulate that this argument holds also in nonequilibrium. In doing so, non-equilibrium correlations are approximated by equilibrium ones at the same $\rho(\vec{r}, t)$ (via a suitable $V_{\text{ext}}(\vec{r})$ in equilibrium)

hence:

$$\zeta \frac{\partial \rho(\vec{r},t)}{\partial t} = \vec{\nabla}\Big(k_B T \vec{\nabla}\rho(\vec{r},t) + \rho(\vec{r},t)\vec{\nabla}V_{\mathrm{ext}}(\vec{r},t) + \rho(\vec{r},t)\vec{\nabla}\frac{\delta \mathcal{F}_{\mathrm{exc}}}{\delta\rho(\vec{r},t)}\Big)$$

$$\zeta \frac{\partial \rho(\vec{r},t)}{\partial t} = \vec{\nabla}\rho(\vec{r},t)\vec{\nabla}\frac{\delta\Omega[\rho]}{\delta\rho(\vec{r},t)}$$

DDFT

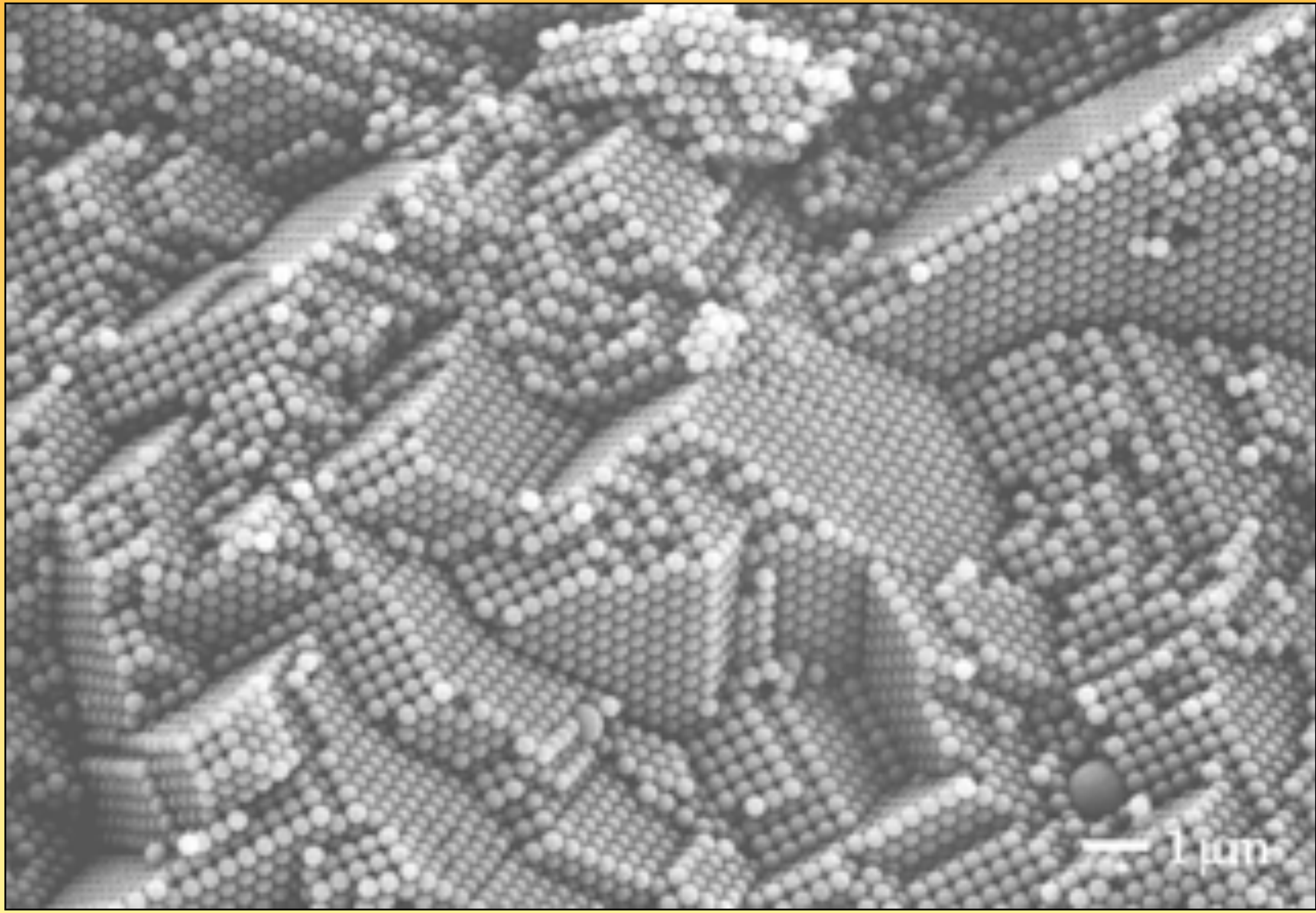
applications:

– time-dependent external potentials

DDFT makes very good approximations for the dynamical density fields. even for freezing, glass transitions, crystal growth when tested against BD computer simulations

example: dynamics of freezing, crystal growth

colloidal dispersions



colloidal particles

(from A. Imhof and D. Pine)

Equilibrium

&

Non-equilibrium

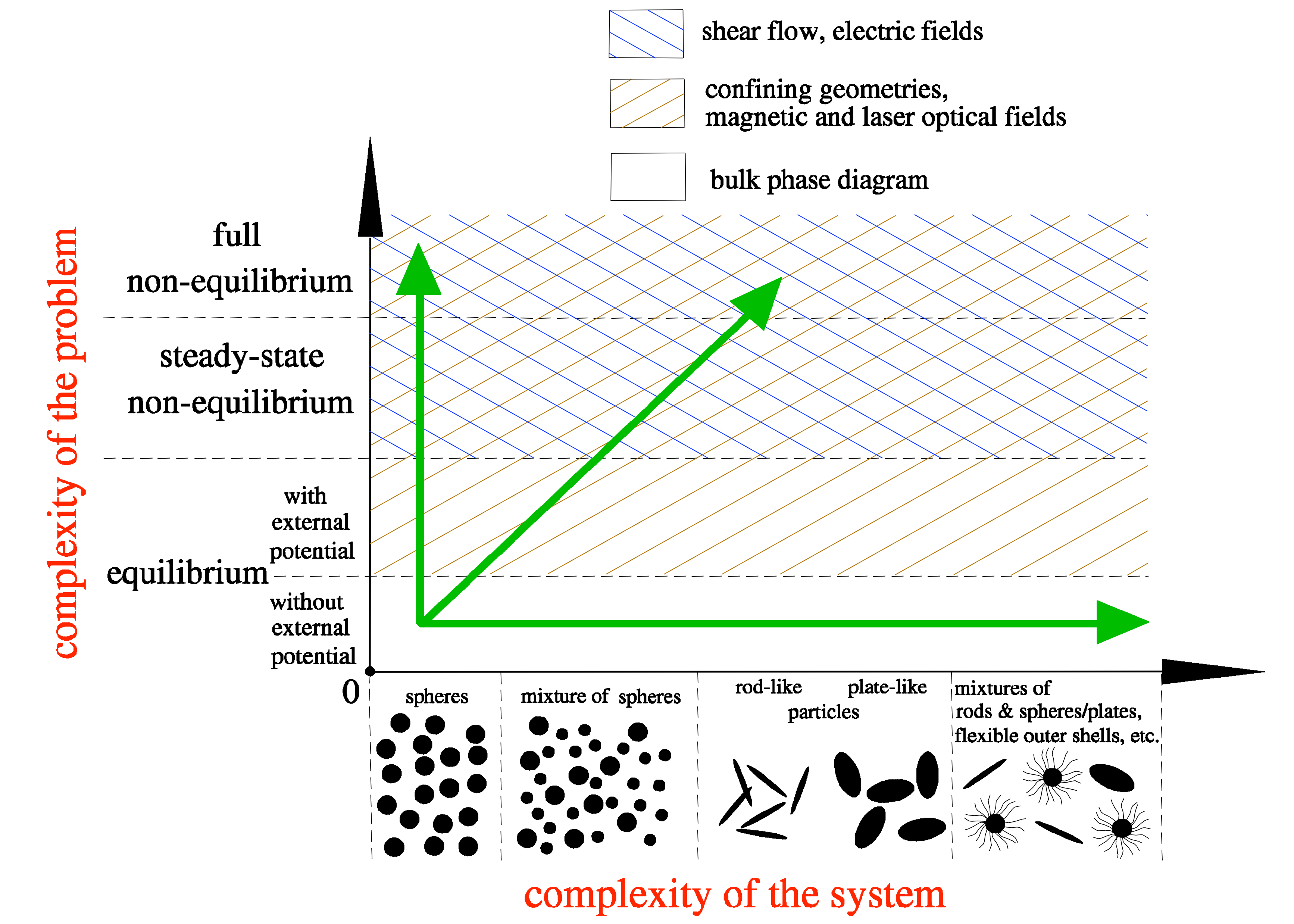
in colloidal dispersions

excellent model systems

phase transformation Kinetics
(crystallization, glass transition, homogeneous and heterogeneous nucleation)

plus an external field (shear, gravity, electric, laser-optical, walls etc.)

The road map of complexity

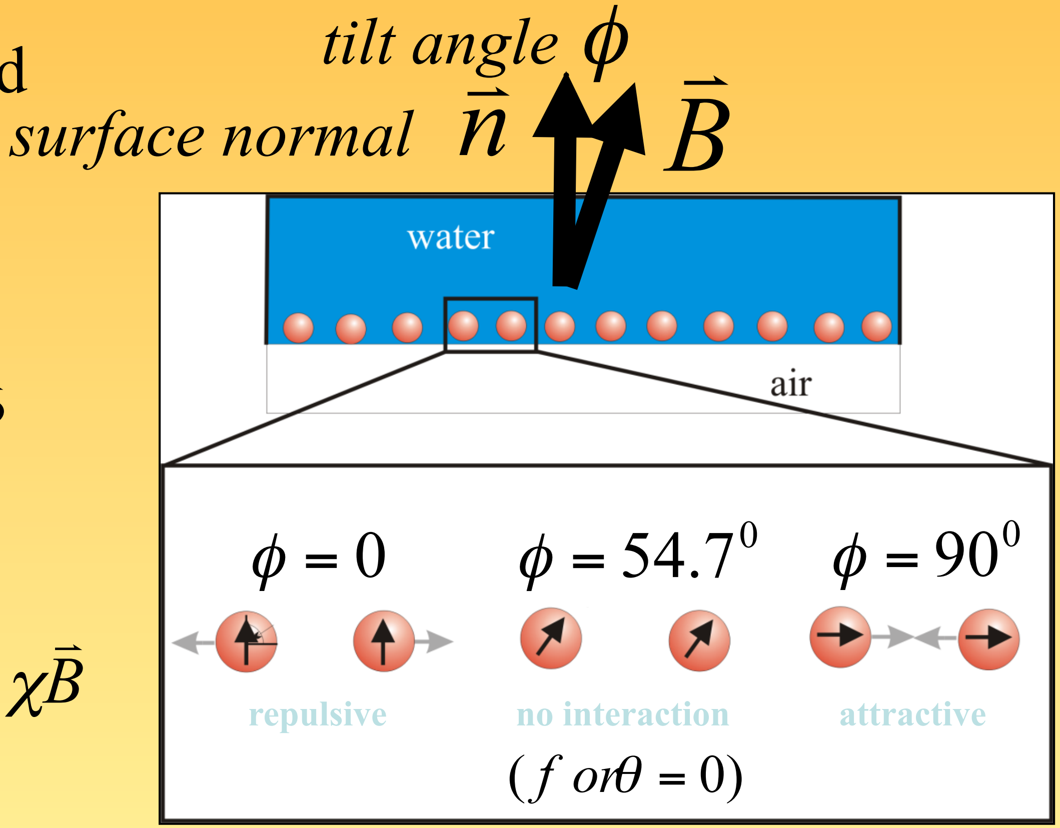


H. Löwen, Journal of Physics: Condensed Matter 13, R415 (2001)

Colloids - controlled by an external magnetic field

- spherical colloids confined to water/air interface
- superparamagnetic due to Fe_2O_3 doping
- external magnetic field $\vec{B}$
  - ⇨ induced dipole moments $\vec{m} = \chi \vec{B}$

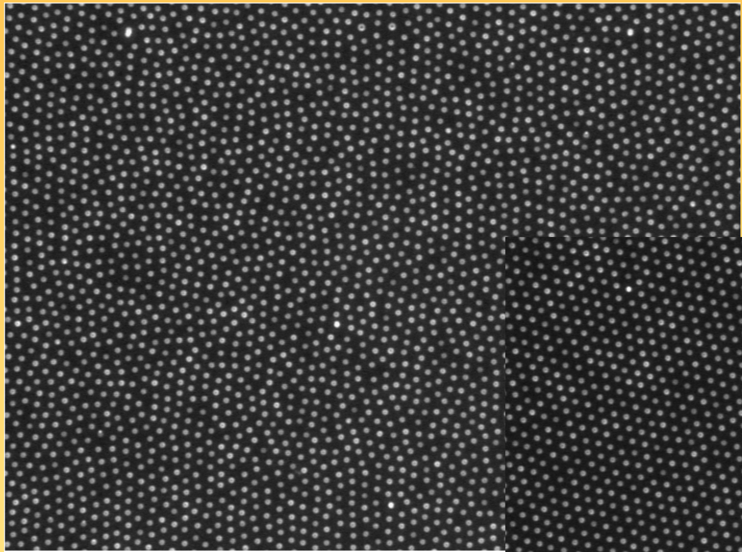
⇨ tunable interparticle potential



$$u(\vec{r}) = u_{HS} + \frac{m^2}{2}\frac{1}{r^3}(1 - 3\cos^2\phi\ \cos^2\theta)$$

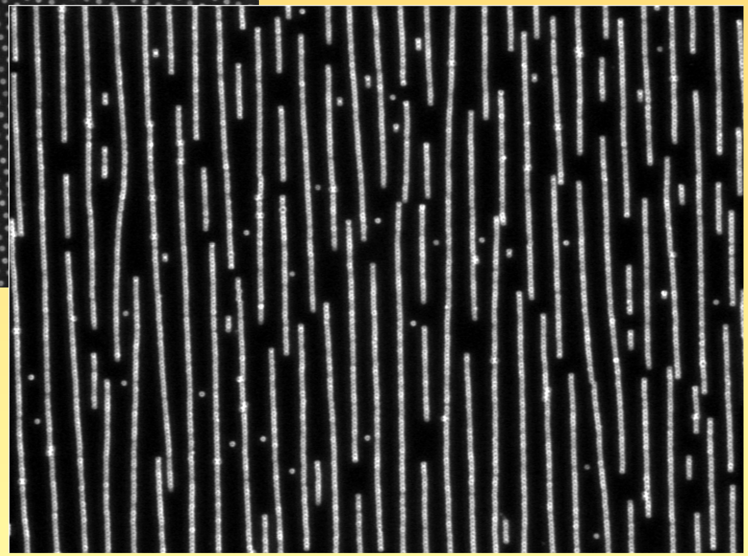
$$\theta = \measuredangle(\vec{r}, \vec{B}_{\parallel})$$

particle configurations for different fields



← $\vec{B}$ perp. to surface, liquid

in-plane $\vec{B}$
↓



↗

$\vec{B}$ perp. to surface, crystal

(P. Keim, G. Maret et al)

Crystal growth at externally imposed nucleation clusters

Idea: impose a cluster of fixed colloidal particles
(e.g. by optical tweezer)

Does this cluster act as a nucleation seed for further crystal growth?

cf: homogeneous nucleation: the cluster occurs by thermal fluctuations, here we prescribe them

How does nucleation depend on cluster size and shape?

(S. van Teeffelen, C.N. Likos, H. Löwen, PRL, 100,108302 (2008))

DDFT, equilibrium functional by Ramakrishnan-Yussouff

(S. van Teeffelen et al, EPL 75, 583 (2006); J. Phys.: Condensed Matter, 20, 404217 (2008))

2d $\quad V(r) = \frac{u_0}{r^3}$ (magnetic colloids with dipole moments)

coupling parameter $\quad \Gamma = u_0 \rho^{3/2} / k_B T$

equilibrium freezing for $\quad \Gamma = \Gamma_f = 36$

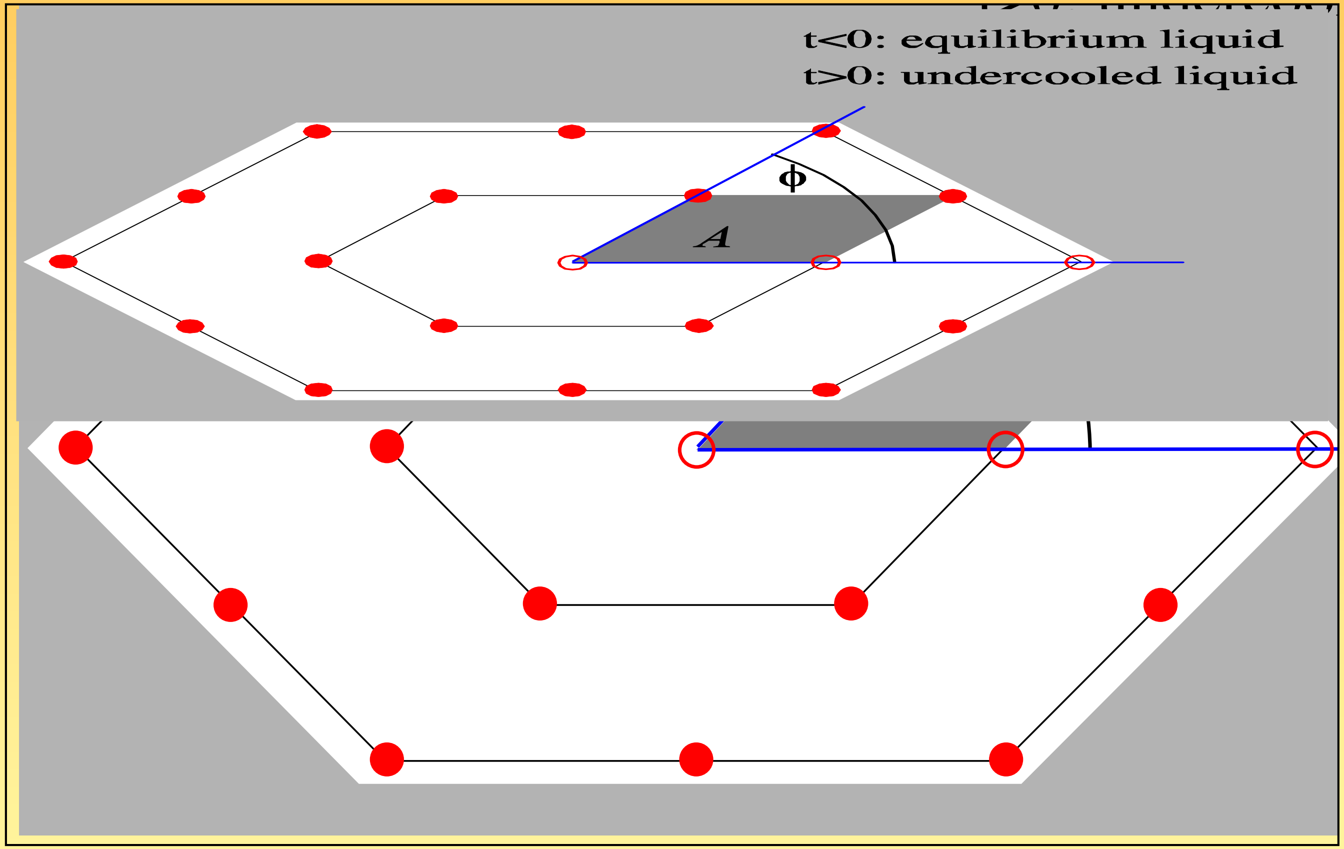
procedure

a) particles in an external trapping potential $V_{ext}(\vec{r})$ at high temperatures ($\Gamma = 10 < \Gamma_f$) for t <0

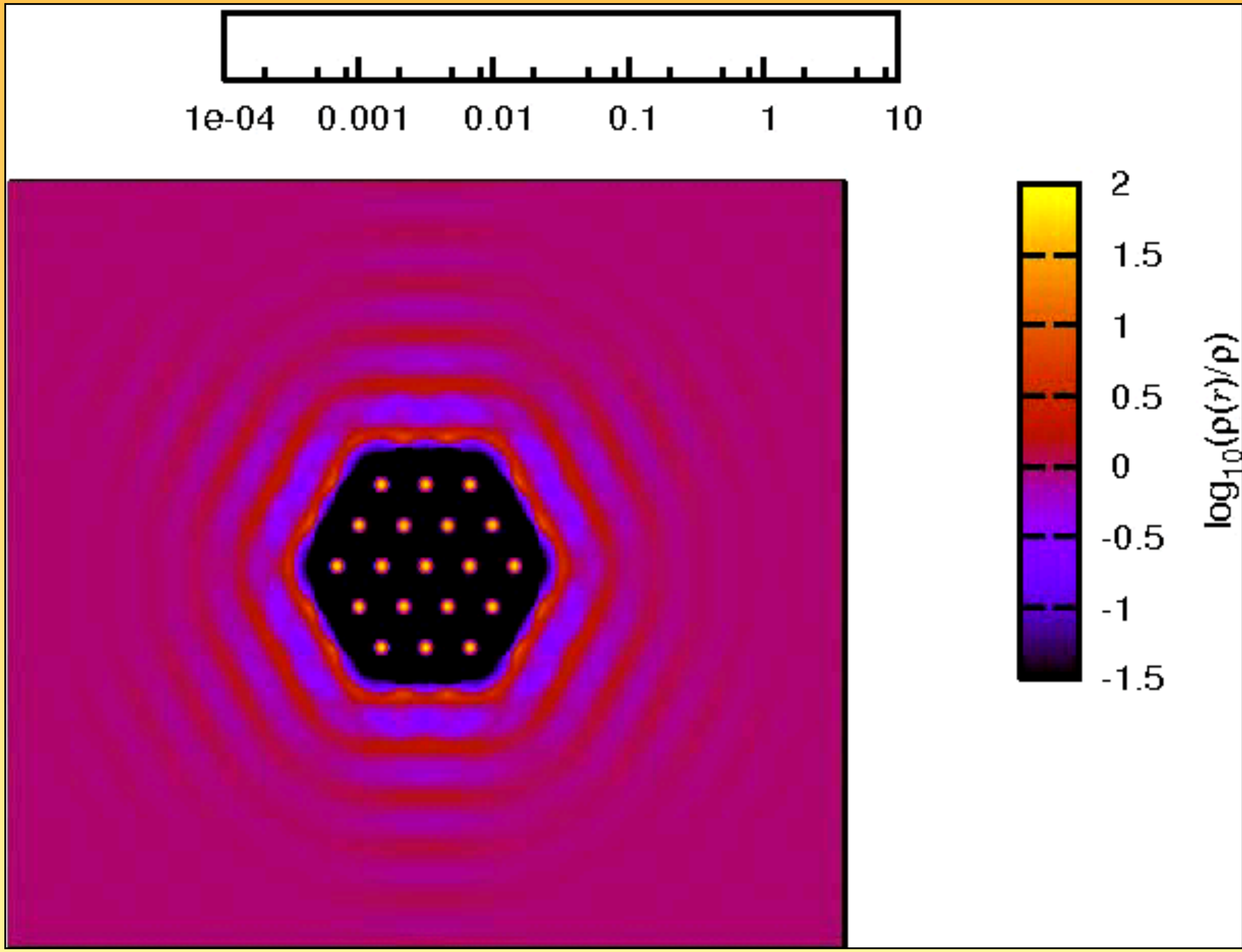
b) release $V_{ext}(\vec{r})$ and decrease T instantaneously for t >0 (enhance Γ towards Γ =63)

imposed nucleation seed

cut-out of a rhombic crystal with N=19 particles

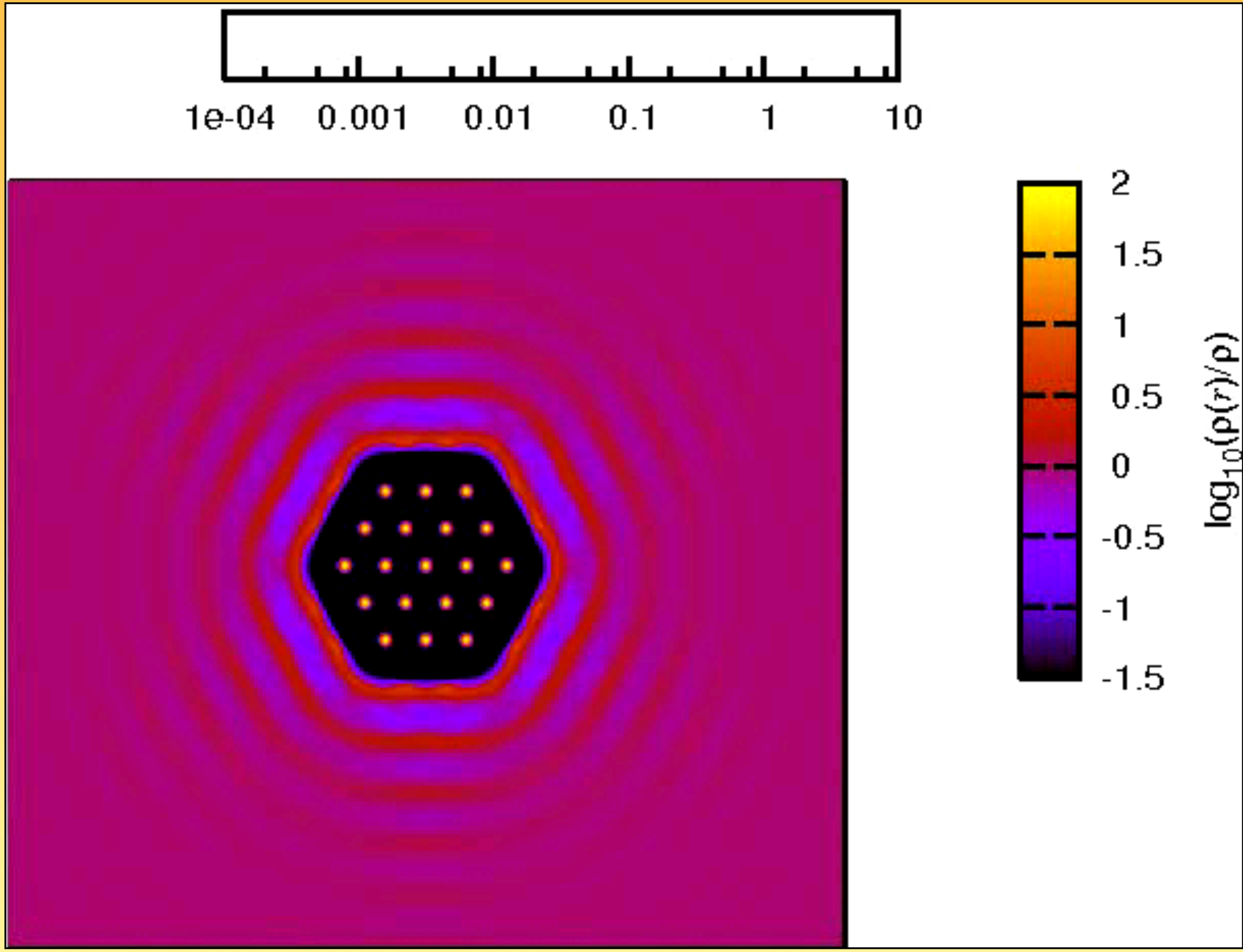


nucleation + growth



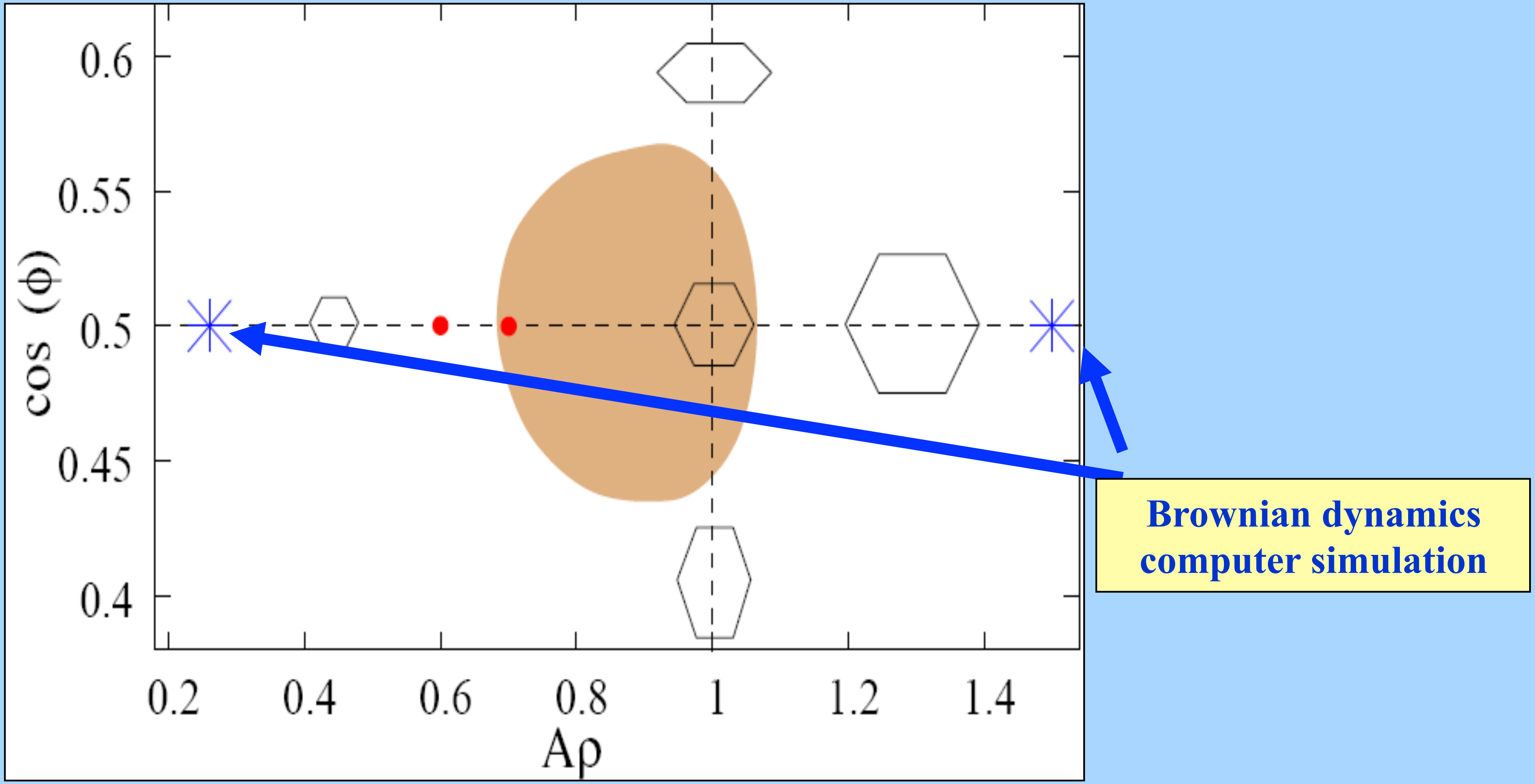
$\phi = 60^0$ $A\rho = 0.7$

no nucleation



$\phi = 60^0$ $A\rho = 0.6$

„island“ for heterogeneous nucleation in $(\cos\phi, A\rho)$ space.

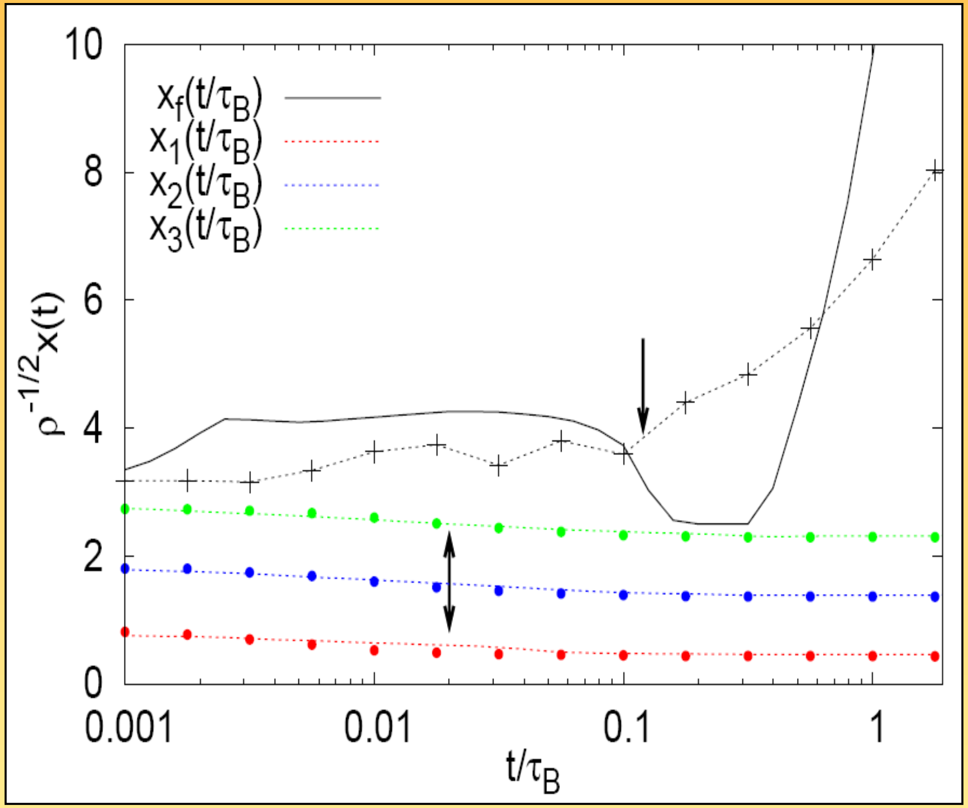


strongly asymmetric in A

symmetric in ϕ

Two stage process: **- sub-Brownian time: relaxation to “ideal“ crystal positions**

- Brownian time: crystal growth

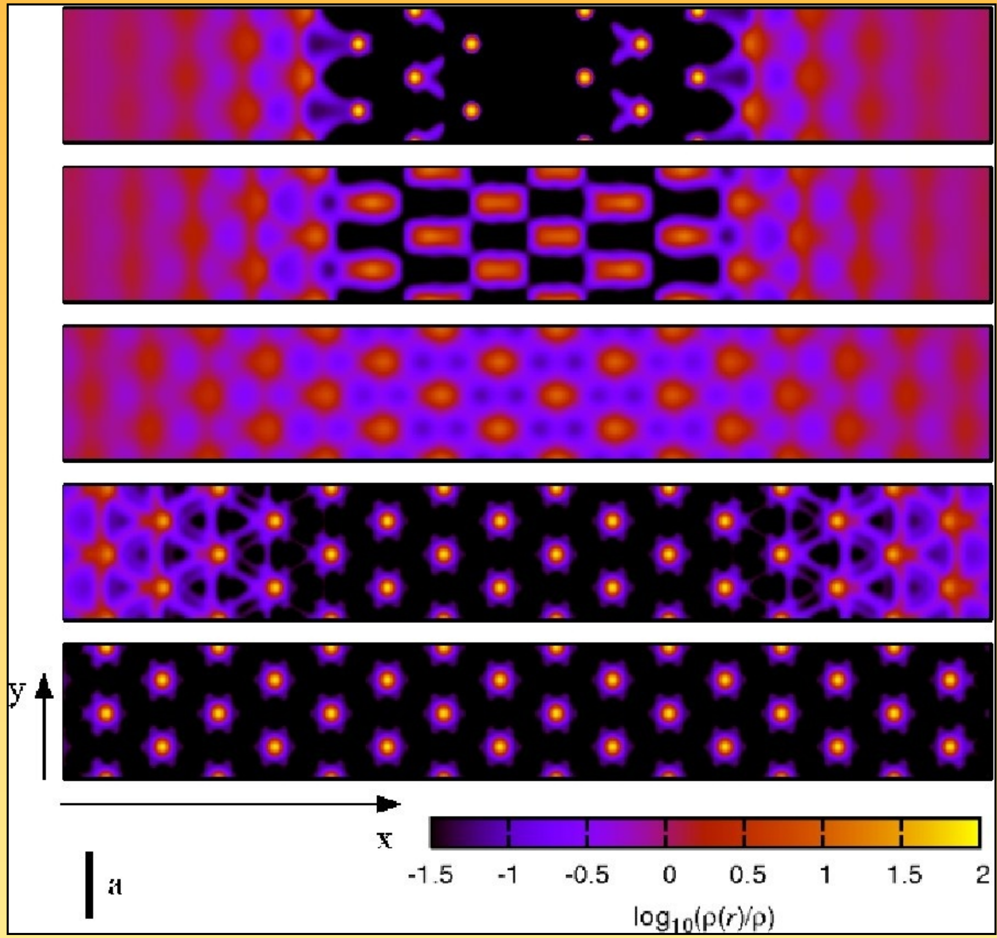


Time evolution of the position of the linear array‘s three rows of crystalline particles $x_i(t)$ and the position of the **crystal front** $x_f(t)$ as a function of time.

Dynamical density functional theory results are compared against **Brownian dynamics** simulation data.

The arrows indicate the typical time scales on which the **relaxation** is occurring and on which the crystal growth sets in, respectively.

Two linear arrays separated by an empty core



- Snapshots of the central region of the **dimensionless density field** $\rho(r,t)/\rho$ of a linear hollow nucleus of two times three infinite rows of **hexagonally crystalline particles** at times t/r_B= 0, 0.01, 0.1, 0.63, 1.0 (from top to bottom). Note that the images display twice the system's central region of dimensions $L_x/4x2L_y$ for better visiblity.

2.3) Hydrodynamic interactions

How does $L_{nm}(\{x_j\})$ look like explicitely?

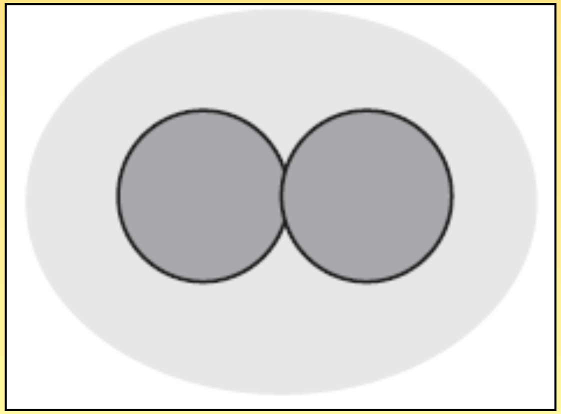
Solve Stokes/Navier-Stokes equations, difficult **problems:**

1) $L_{nm}(\{x_j\})$ is long-ranged

H.I are important for volume fractions

2) H.I. have **many-body character**, pair expansion only possible at low concentrations

3) H.I. have quite different near-field behaviour. They are divergent, lubrication



standard approximations:

$$\vec{v}_n = \sum_{m=1}^{N} \bar{\bar{H}}_{nm} \vec{F}_m$$

each quantity $\bar{\bar{H}}_{nm}$ is a 3 × 3 matrix

R_H : hydrodynamic radius

η_s : shear viscosity of solvent

0) **no H.I.** $H_{nm} = \mathbb{1} \frac{\delta_{nm}}{\zeta}$, $\zeta = 6\pi\eta_s R_H$

1) **Oseen-Tensor** $H_{nm} = \frac{\mathbb{1}}{\zeta}$

$$\bar{\bar{H}}_{nm} = \bar{\bar{H}}(\underbrace{\vec{r}_n - \vec{r}_m}_{\vec{r}})$$

with Oseen tensor

$$\bar{\bar{H}}(\vec{r}) = \frac{1}{8\pi\eta_s}(\mathbb{1} + \hat{r} \otimes \hat{r})\frac{1}{r} \quad , \quad \hat{r} = \frac{\vec{r}}{r}$$

far field term, long ranged of H.I.

$\otimes$: dyadic product or tensor product

$$\begin{aligned} \rightarrow \vec{a} &= (a_1, a_2, a_3) = (a_i) \\ \vec{b} &= (b_1, b_2, b_3) = (b_i) \\ (\vec{a} \otimes \vec{b})_{ij} &= a_i b_j \qquad 3 \times 3 \text{ matrix} \end{aligned}$$

2) Rotne-Prager-tensor

$$H_{nn} = \frac{\mathbb{1}}{\zeta} \quad , \quad H_{nm} = \bar{\bar{H}}_{RP}(\vec{r}_n - \vec{r}_m)$$

with $$\bar{\bar{H}}_{RP}(\vec{r}) = D_0(\underbrace{\frac{3}{4}\frac{R_H}{r}[\mathbb{1} + \hat{r} \otimes \hat{r}]}_{\text{Oseen}} + \frac{1}{2}\frac{R_H^3}{r^3}[\mathbb{1} - 3\hat{r} \otimes \hat{r}])$$

3) higher-order expansions

4) triplet contributions (Beenaker, Mazur)

DDFT for hydrodynamic interactions

(M. Rex, H. Löwen, Phys. Rev. Letters **101**, 148302 (2008))

starting point: Smoluchowski equation

total potential energy

$$\frac{\partial P(\vec{r}^N, t)}{\partial t} = \sum_{i,j=1}^{N} \vec{\nabla}_i \cdot \bar{\bar{H}}_{ij}(\vec{r}^N) \cdot \left[\vec{\nabla}_j + \vec{\nabla}_j \frac{U(\vec{r}^N, t)}{k_B T} \right] P(\vec{r}^N, t)$$

$\bar{\bar{H}}_{ij}(\vec{r}^N)$ configuration-dependent mobility tensor which describes hydrodynamic interactions

two particle approximation:

$$H_{ij}(\vec{r}^N) \approx D_0 \left(\mathbb{1}\delta_{ij} + \delta_{ij} \sum_{i \neq j} \omega_{11}(\vec{r}_i - \vec{r}_e) + (1 - \delta_{ij}) \omega_{12}(\vec{r}_i - \vec{r}_e) \right)$$

Rotne-Prager expression

$$\omega_{11}(\vec{r}) = 0$$

$$\omega_{12}(\vec{r}) = \frac{3}{8}\frac{\sigma_H}{r}(\bar{\bar{1}} + \hat{\vec{r}} \otimes \hat{\vec{r}}) + \frac{1}{16}(\frac{\sigma_H}{r})^3(1 - 3\hat{\vec{r}} \otimes \hat{\vec{r}}) + 0((\frac{\sigma_H}{r})^7)$$

Integrating Smoluchowski equation (Archer, Evans, 2004)

$$\frac{k_B T}{D_0}\frac{\partial \rho(\mathbf{r},t)}{\partial t} = \nabla_{\mathbf{r}} \cdot \Bigg\{ \rho(\mathbf{r},t)\nabla_{\mathbf{r}}\frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r},t)} + \int \mathrm{d}\mathbf{r}' \; \rho^{(2)}(\mathbf{r},\mathbf{r}',t)\boldsymbol{\omega}_{11}(\mathbf{r}-\mathbf{r}') \cdot \nabla_{\mathbf{r}} \frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r},t)} + \int \mathrm{d}\mathbf{r}' \; \rho^{(2)}(\mathbf{r},\mathbf{r}',t)\boldsymbol{\omega}_{12}(\mathbf{r}-\mathbf{r}') \cdot \nabla_{\mathbf{r}'} \frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r}',t)} \Bigg\}.$$

Possible closure

$$\rho^{(2)}(\mathbf{r},\mathbf{r}',t) = \left(1 + c^{(2)}(\mathbf{r},\mathbf{r}')\right)\rho(\mathbf{r},t)\rho(\mathbf{r}',t) + \rho(\mathbf{r}',t)\int \mathrm{d}\mathbf{r}'' \ \left((\rho^{(2)}(\mathbf{r},\mathbf{r}'',t) - \rho(\mathbf{r},t)\rho(\mathbf{r}'',t))c^{(2)}(\mathbf{r}'',\mathbf{r}')\right)$$

with $$c^{(2)}(\mathbf{r},\mathbf{r}') = \frac{-\beta\,\delta^2 \mathcal{F}_{\mathrm{exc}}[\rho]}{\delta\rho(\mathbf{r},t)\delta\rho(\mathbf{r}',t)}$$

easier: $$\rho^{(2)}(\mathbf{r},\mathbf{r}',t) \approx \rho(r,t)\rho(r',t)g(|\mathbf{r}-\mathbf{r}'|,\bar{\rho})$$

suitably averaged density

Application:

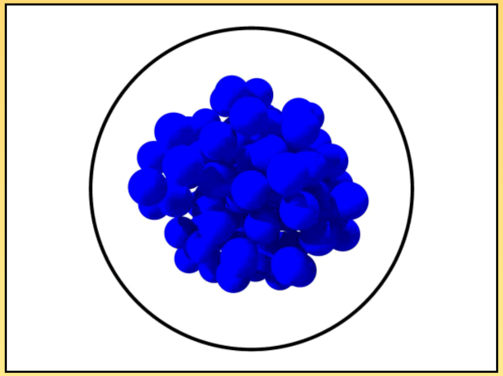
colloids in an oscillating trap

$$V_{\text{ext}}(r,t) = V_1 \left(\frac{r}{R_1}\right)^4 + V_2 \cos(2\pi t/\tau) \left(\frac{r}{R_2}\right)^2$$

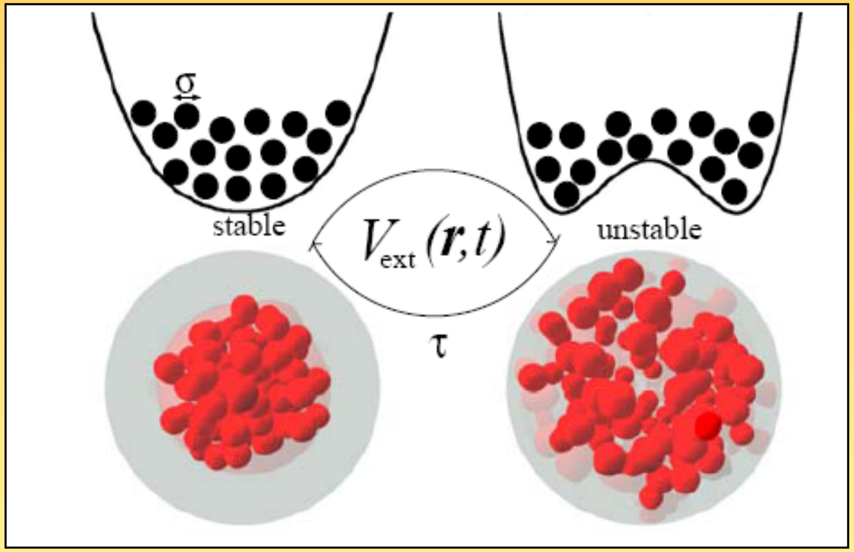
$R_1 = 4\sigma,\ R_2 = \sigma$

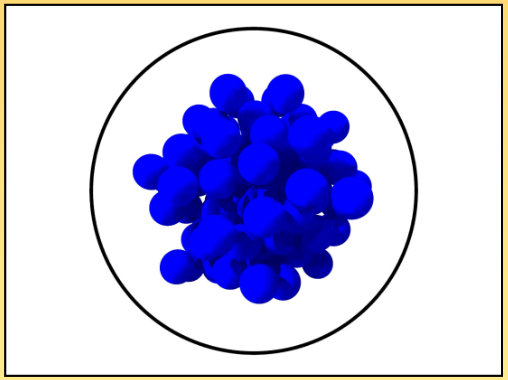
$V_1 = 10k_BT,\ V_2 = k_BT$

$\tau = 0.5\tau_B,\ \tau_B = \sigma^2 / D_0$



(H)

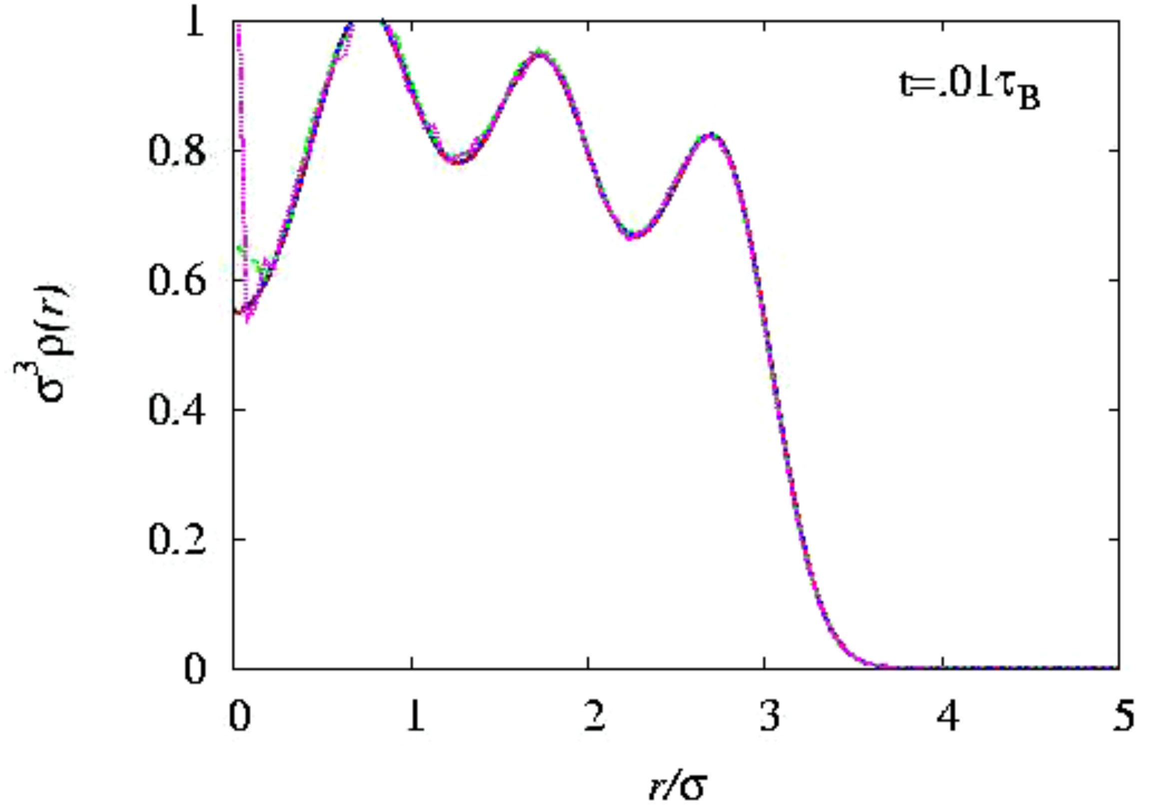




(N)

hard spheres with interaction diameter $\sigma = \frac{4}{3}\sigma_H$

the breathing mode

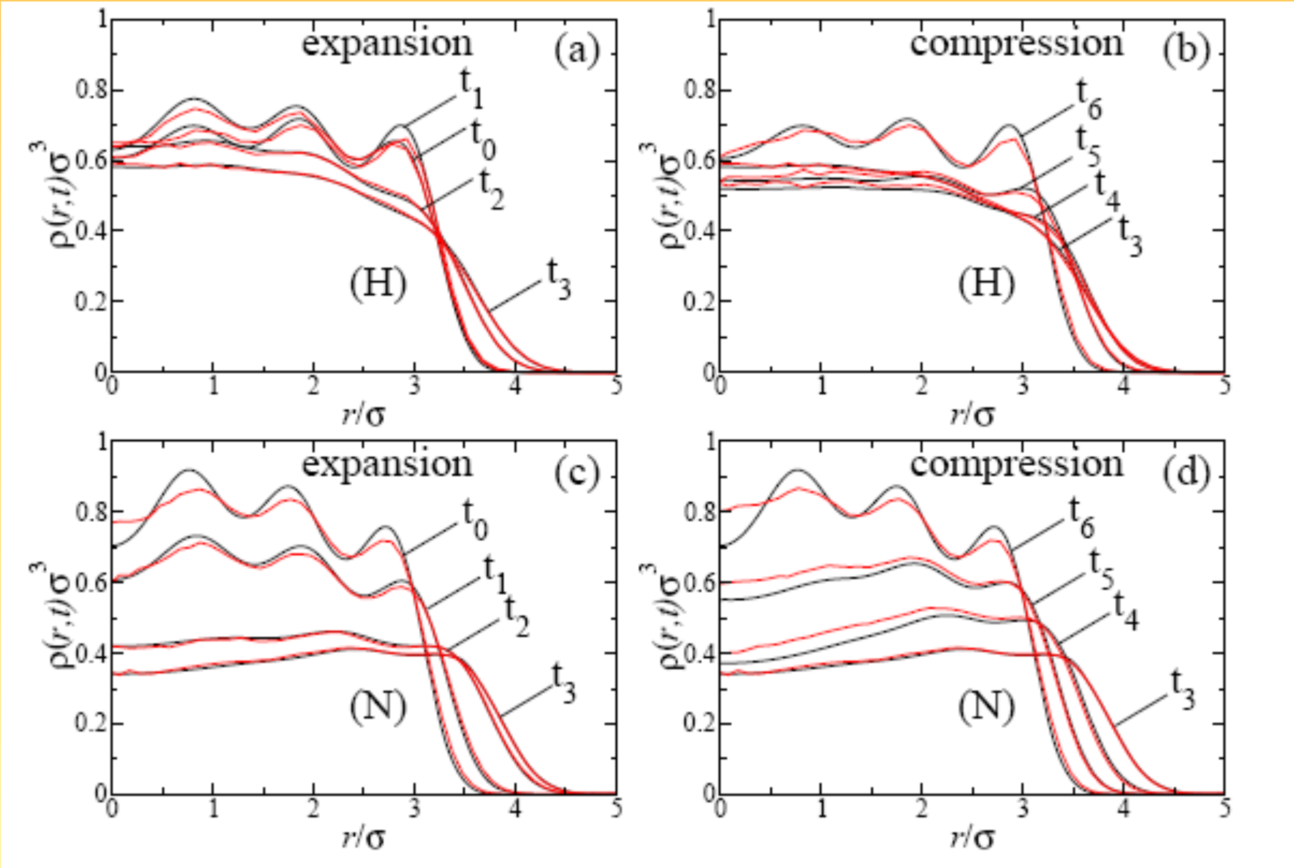


green/red: (N) blue/purple: (H)

stroboscopic view

t_i/t_B = 2.5, 2.6, 2.7, 2.75, 2.85, 2.9, 3.0

i = 0 1 2 3 4 5 6



with HI (H)

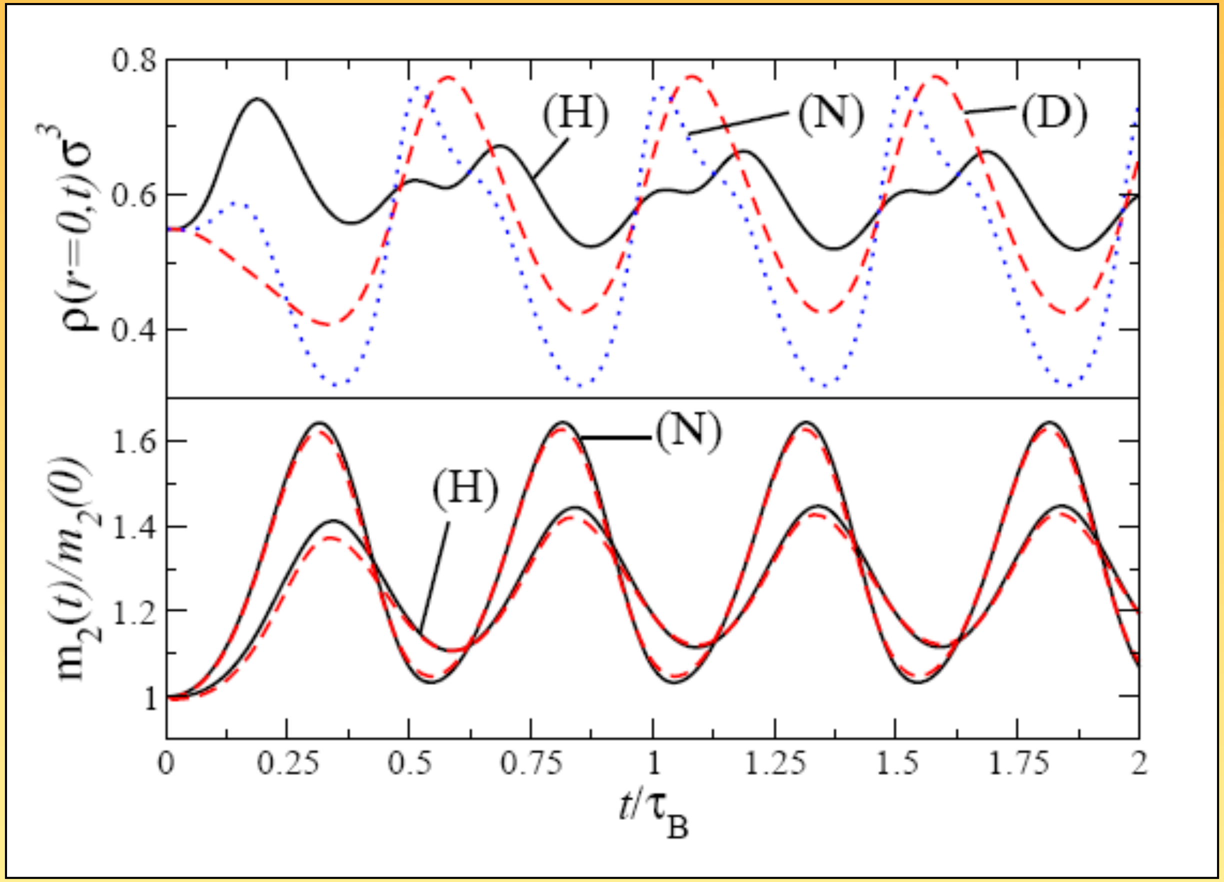
without HI (N)

good agreement between simulation (red) and DDFT (black)

relaxation to the steady state

central density

second moment

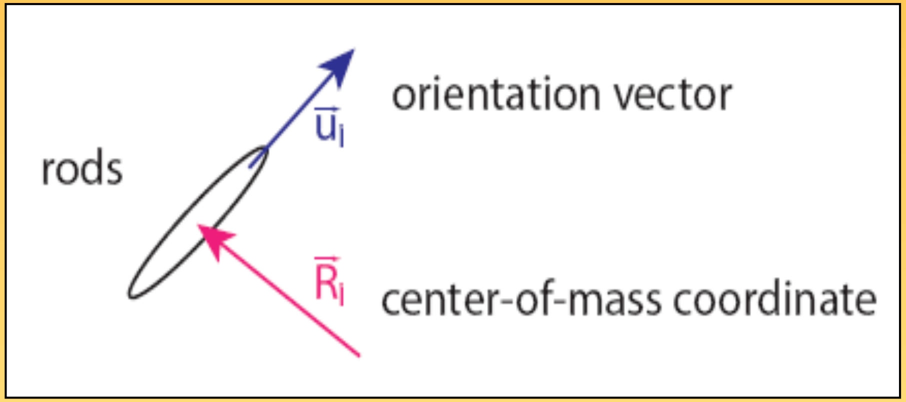


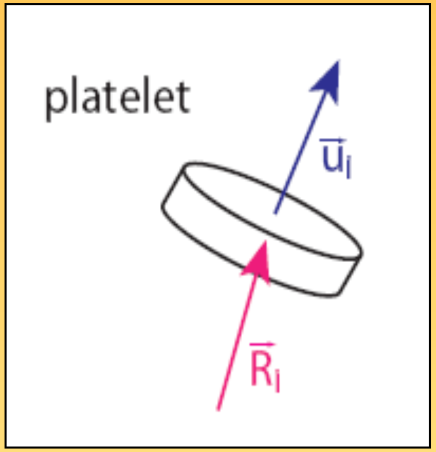
(D) curve $D_o(\phi)$

C. P. Royall et al, PRL **98,** 188304 (2007))

3) Density functional theory for rod-like particles

3.1) Statistical mechanics of rod-like particles





(1) molecular dipolar fluids

(2) rod-like colloids

(3) molecular fluids without dipole moment (apolar), e.g. H_2 molecule

(4) plate-like objects (clays)

now: additional orientational degree of freedom

partition function:

$$Z = \frac{1}{h^{6N} N!} \int_V d^3R_1 \ldots \int_V d^3R_N \int_{\mathbb{R}^3} d^3p_1 \ldots \int_{\mathbb{R}^3} d^3p_N \times$$
$$\times \int_{S_2} d^2u_1 \ldots \int_{S_2} d^2u_N \int_{\mathbb{R}^3} d^3L_1 \ldots \int_{\mathbb{R}^3} d^3L_N \, e^{-\beta\mathcal{H}}$$

with:

$$\mathcal{H} = \underbrace{\sum_{i=1}^{N} \left\{ \frac{\vec{p}_i^2}{2m} + \frac{1}{2}\vec{L}_i (\bar{\bar{\Theta}})^{-1} \vec{L}_i \right\}}_{\text{kinetic energy}} + \underbrace{\frac{1}{2}\sum_{i,j=1}^{N} v(\vec{R}_i - \vec{R}_j, \vec{u}_i, \vec{u}_j)}_{\text{pair interaction energy}} + \underbrace{\sum_{i=1}^{N} V_{\text{ext}}(\vec{R}_i, \vec{u}_i)}_{\text{external energy}}$$

while $\bar{\bar{\Theta}}$ is the inertia tensor and S_2 the unit-sphere in 3d.

central quantity:
one-particle density

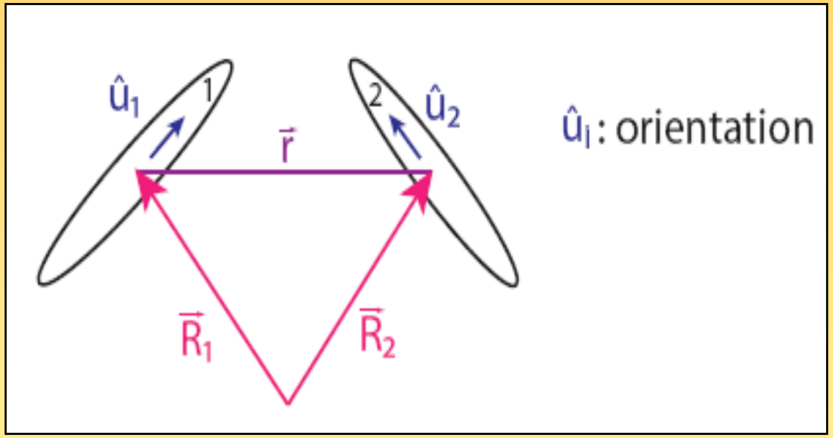
$$\rho_0^{(1)}(\vec{r}, \vec{u}) := \left\langle \sum_{i=1}^{N} \delta(\vec{r} - \vec{R}_i)\delta(\vec{u} - \vec{u}_i) \right\rangle$$

density of center-of-masses:

$$\rho_0(\vec{r}) = \frac{1}{4\pi} \int_{S_2} \mathrm{d}^2 u \;\; \rho_0^{(1)}(\vec{r}, \vec{u})$$

orientational order:

$$f(\vec{u}) = \frac{1}{V} \int_{V} \mathrm{d}^3 r \;\; \rho_0^{(1)}(\vec{r}, \vec{u})$$



$$V(r) \;,\; V_{\mathrm{ext}}(\vec{r}) \;,\; V(\vec{r}, \hat{u}_1, \hat{u}_2) \;,\; V_{\mathrm{ext}}(\vec{r}, \hat{u})$$

$$\rho_0^{(1)}(\vec{r}, \hat{u}) = \langle \sum_{i=1}^{N} \delta(\vec{r} - \vec{R}_i) \delta(\hat{u} - \hat{u}_i) \rangle$$

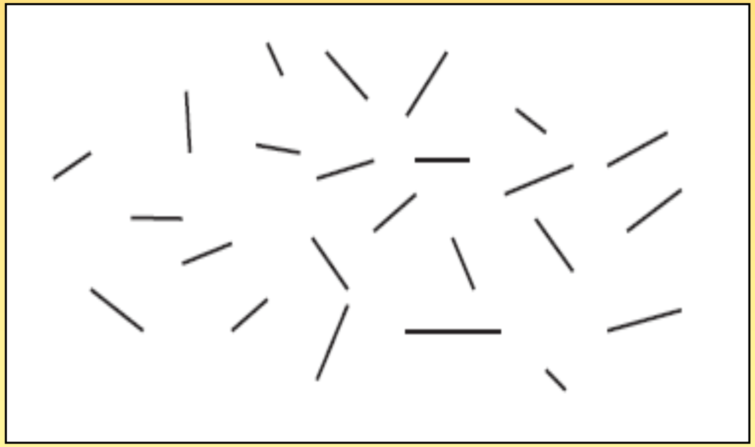
pair correlation function:

$$g(\vec{R}_1 - \vec{R}_2, \hat{u}_1, \hat{u}_2) := \frac{\left\langle \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \delta(\vec{R}_1 - \vec{R}_i)\delta(\vec{R}_2 - \vec{R}_j)\delta(\hat{u}_1 - \hat{u}_j)\delta(\hat{u}_2 - \hat{u}_j) \right\rangle}{\rho_0^{(1)}(\vec{R}_1, \hat{u}_1)\rho_0^{(1)}(\vec{R}_2, \hat{u}_2)}$$

Different phases are conceivable:

(1) **fluid** (disordered) phase, isotropic phase

center-of-mass-positions and orientations are disordered



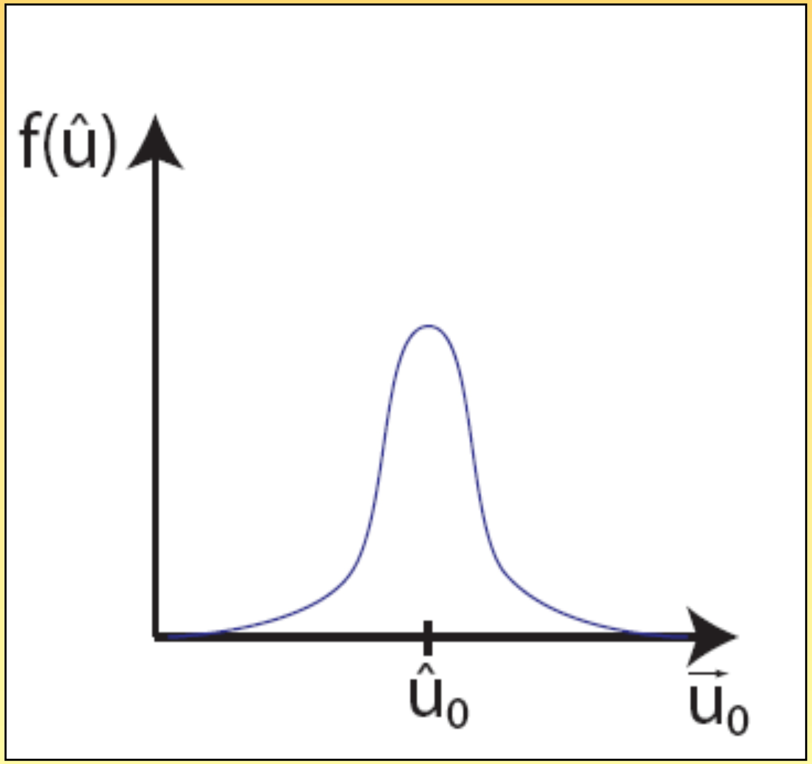
$$\rho_0^{(1)}(\vec{r}, \hat{u}) = \rho_0 = \text{const}$$

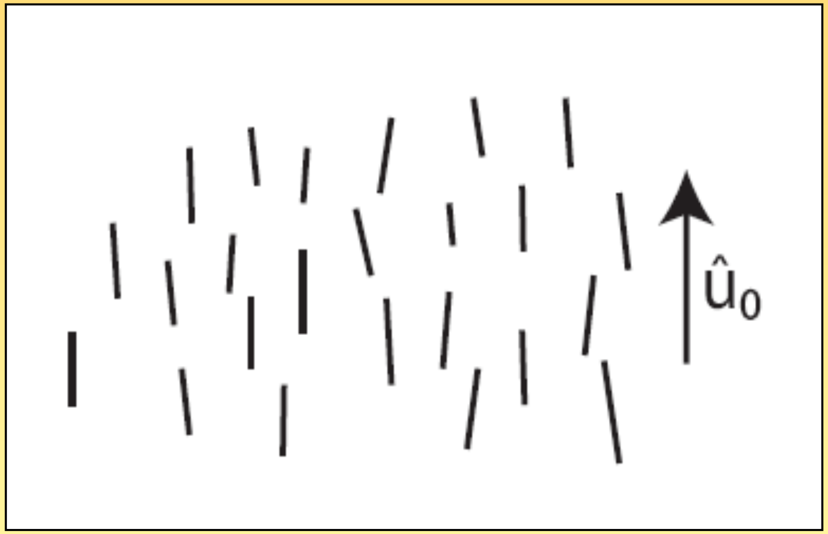
(2) **nematic** phase

positions are disordered and orientations are ordered

$$\rho_0^{(1)}(\vec{r}, \hat{u}) = \rho f(\hat{u})$$

$\hat{u}_0$: nematic director





nematic order parameter

$\rightsquigarrow$ 3x3 tensor:

$$\bar{\bar{Q}} = \langle \frac{1}{N} \sum_{i=1}^{N} \left(\frac{3}{2} \hat{u}_i \otimes \hat{u}_i - \frac{1}{2} \mathbb{1} \right) \rangle$$

with:

$$\hat{u}_i \otimes \hat{u}_i = \begin{pmatrix} u_{ix}u_{ix} & u_{ix}u_{iy} & u_{ix}u_{iz} \\ u_{iy}u_{ix} & u_{iy}u_{iy} & u_{iy}u_{iz} \\ u_{iz}u_{ix} & u_{iz}u_{iy} & u_{iz}u_{iz} \end{pmatrix}$$

$$\begin{aligned} \mathrm{Tr}\bar{\bar{Q}} &= \frac{1}{2} \langle \mathrm{Tr}(3\hat{u}_i \otimes \hat{u}_i - \mathbb{1}) \rangle \\ &= \frac{1}{2} \langle 3 \cdot 1 - 3 \rangle = 0 \quad \rightsquigarrow \bar{\bar{Q}} \text{ traceless} \end{aligned}$$

$$\bar{\bar{Q}} \text{ symmetric } \Rightarrow \bar{\bar{Q}} \text{ diagonalizable}$$

three eigenvalues $\lambda_1 \geq \lambda_2 \geq \lambda_3,$ with $\lambda_1 + \lambda_2 + \lambda_3 = 0$

largest eigenvalue: $\lambda_1 \equiv S$

$\rightsquigarrow$ nematic director: corresponding eigenvector

perfect orientation: $\hat{u}_i \equiv \hat{u}_0$ for all $i;\ S = 1,\ \hat{u}_0$ nematic director

→ if the two lower eigenvalues are identical, $\lambda_2 = \lambda_3$: **uniaxial** nematics

→ if $\lambda_2 \neq \lambda_3$: **biaxial** nematics

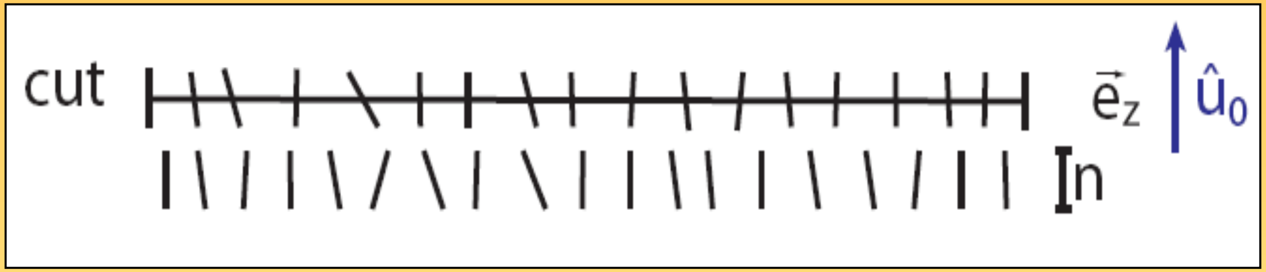
→ in isotropic phase: $\bar{\bar{Q}},\ S = 0$

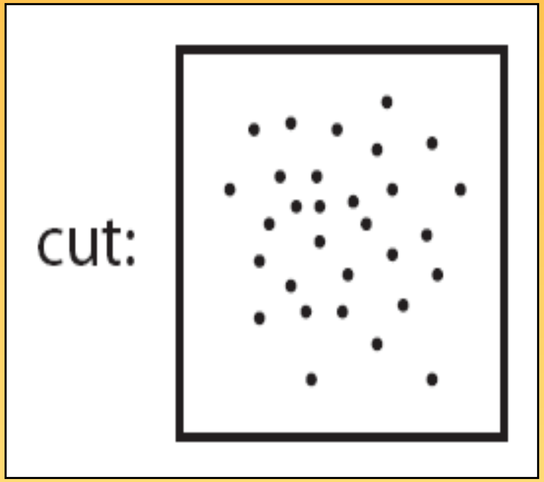
experimental effect: **birefringence**

(3) smectic A phase

position ordered along $\hat{u}_0,$ orientation ordered

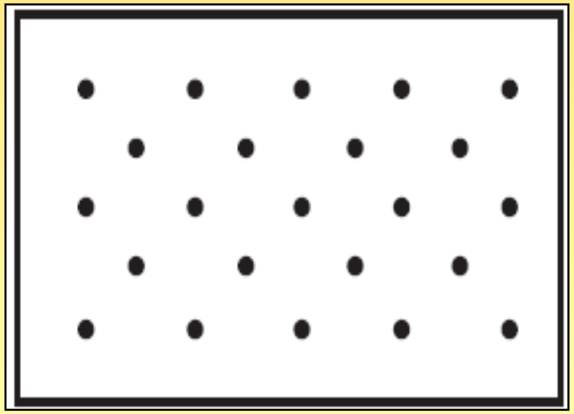
$\rho_0^{(1)}(\vec{r},\hat{u}) = \rho(z,\vec{u})$ z-periodic





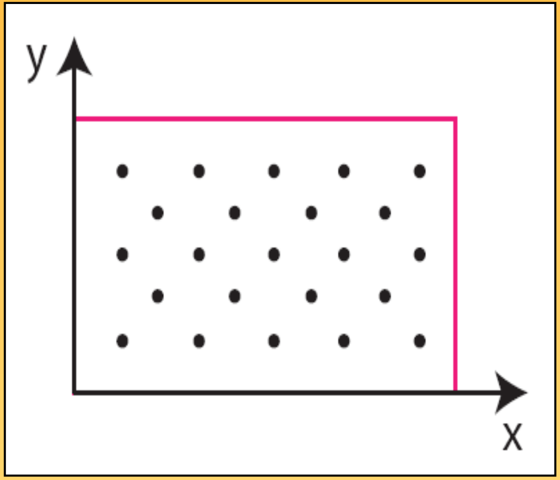
(4) smectic B phase

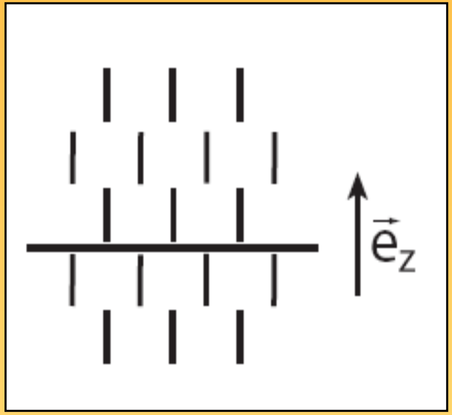
as smectic A phase but in plane triangular lattice



(5) columnar phase:

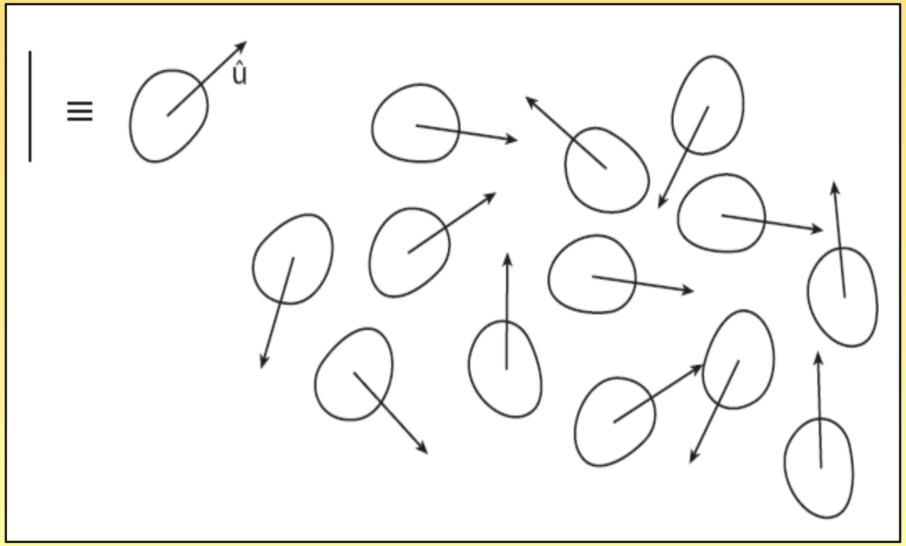
$$\rho_0^{(1)}(\vec{r}, \hat{u}) = \rho(x, y, \hat{u})$$





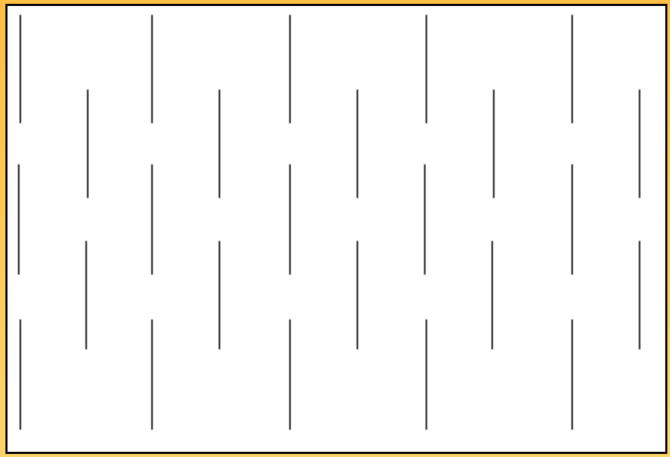
(6) plastic crystal:

$$\rho_0^{(1)}(\vec{r}, \hat{u}) = \hat{f}(\vec{r})$$



positions ordered,
orientations disordered

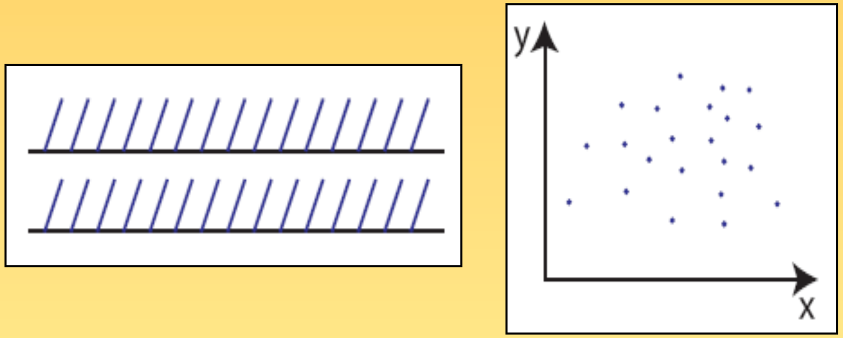
(7) full crystalline phases



positions and orientations ordered

further more „exotic“ phases:

smectic C



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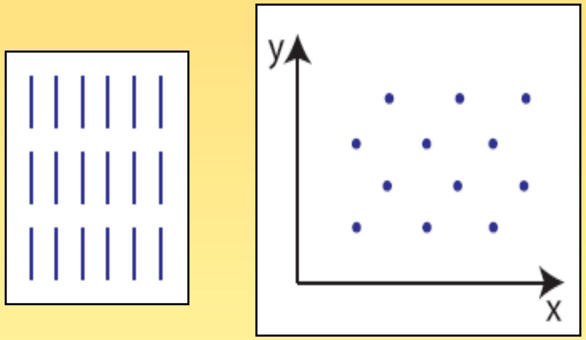
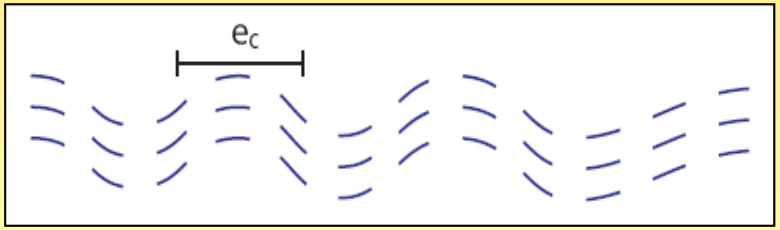
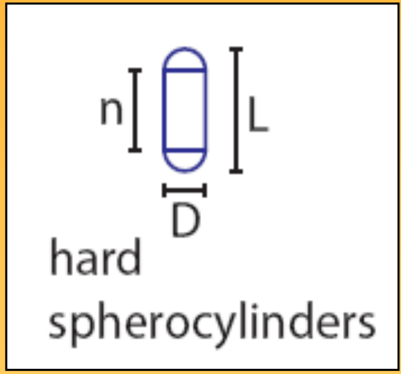


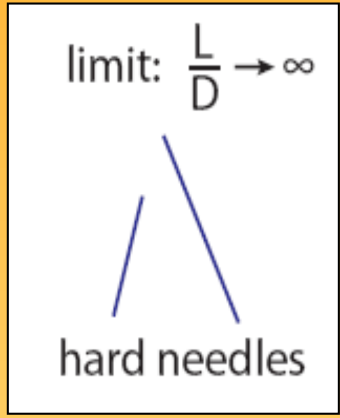
cholesteric



3.2) Simple models

hard objects





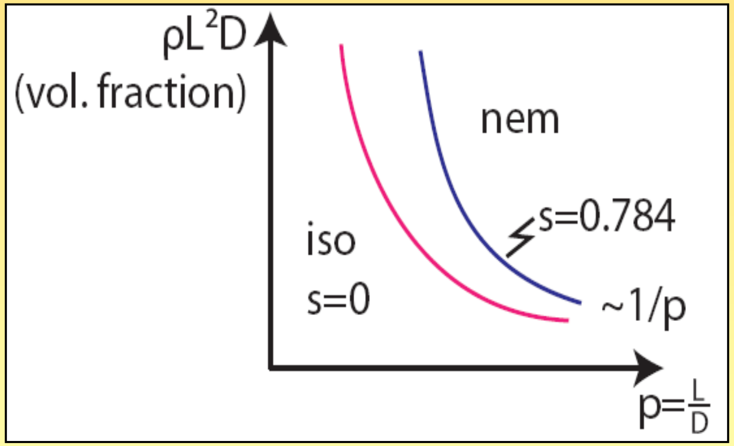
A) Analytical results by Onsager, 1948

consider limit $p = \frac{L}{D} \to \infty$ virial expansion up to 2 order gets exact result:

there is an **isotrop-nematic transition**, first order (with density jump)

$$\rho_{\text{iso}} \to \rho_{\text{nem}}$$
$$\rho_{\text{iso}} L^2 D = 4.189\ldots$$
$$\rho_{\text{nem}} L^2 D = 5.376\ldots$$

at coexistence $S = 0.784$

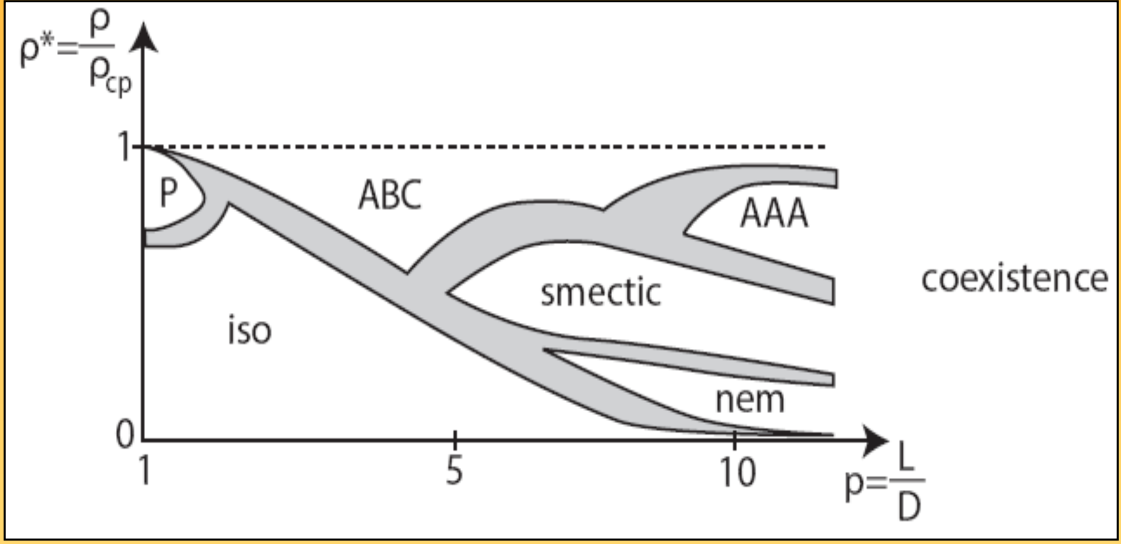


correlations to finite p

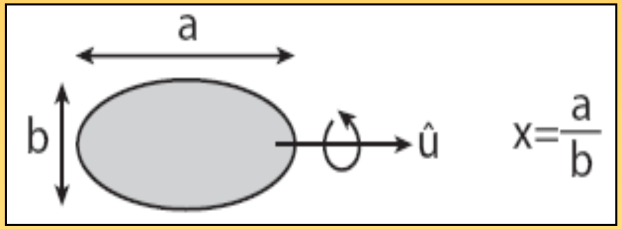
irrelevant only for $p \gtrsim 200$

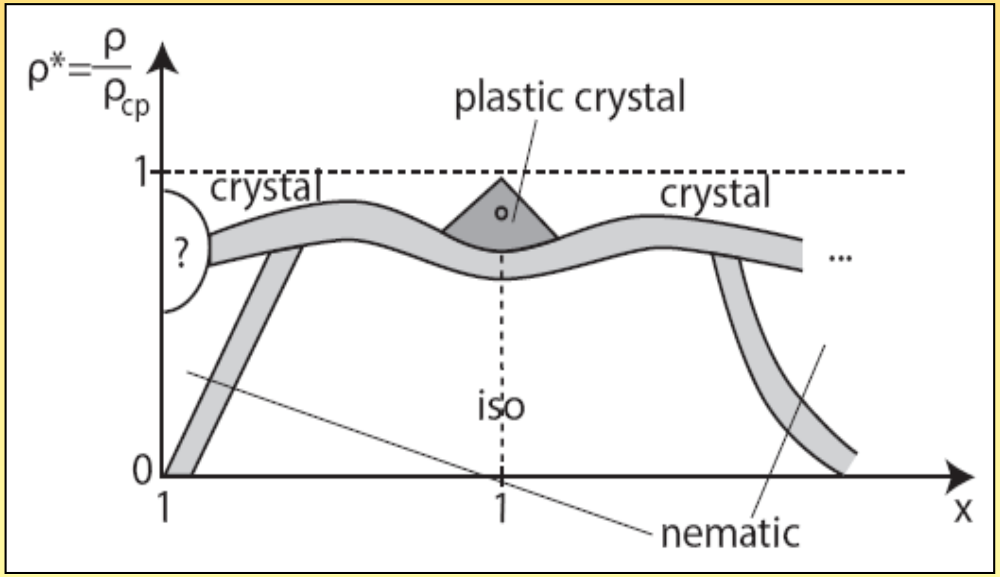
B) Computer simulations

phase diagram of hard spherocylinders



hard ellipsoids





x < 1 : coins

x > 1 : rods

symm $x \to \frac{1}{x}$ for the topology

C) Density functional theory

There exists a **unique grandcanonical free energy functional** $\Omega(T,\mu,[\rho^{(1)}])$

(functional of the one-particle density) which becomes minimal for the equilibrium

density $\rho_0^{(1)}(\vec{r},\hat{u})$ and **equals** then **the real grand canonical free energy**

$$\left.\frac{\delta\Omega(T,\mu,[\rho^{(1)}])}{\delta\rho^{(1)}(\vec{r},\hat{u})}\right|_{\rho^{(1)}=\rho_0^{(1)}(\vec{r},\hat{u})} = 0$$

$$\Omega(T,\mu,[\rho^{(1)}]) = \underbrace{k_BT\int \mathrm{d}^3r\int \mathrm{d}^2u\ \rho^{(1)}(\vec{r},\hat{u})[\ln(\Lambda^3\rho^{(1)}(\vec{r},\hat{u}))-1]}_{\mathcal{F}_{\mathrm{id}}[\rho^{(1)}]}$$

$$+\int \mathrm{d}^3r\mathrm{d}^2u\ (V_{\mathrm{ext}}(\vec{r},\hat{u})-\mu)\rho^{(1)}(\vec{r},\hat{u}) + \underbrace{\mathcal{F}_{\mathrm{exc}}(T,[\rho^{(1)}])}_{\text{approximations needed}}$$

$\mathcal{F}_{\text{exc}}(T, [\rho^{(1)}])$ **for spherocylinders:**

1) **SMA** (smoothed density approximations) R. Holyst et al, 1988

→ yields several stable liquid crystalline phases

(isotropic, nematic, smectic A, crystalline)

2) **MWDA** (H. Graf, 1999)

→ improved results with plastic, AAA phase

3) **extension of Rosenfeld theory** (K.Mecke and H.Hansen-Goos)

other interaction (beyond hard body)

perturbation theory within mean-field approach

3.3) Brownian dynamics of rod-like particles

start from Smoluchowski picture

$$\hat{u} \equiv \hat{\omega}$$

full probability density distribution

$$P(\underbrace{\vec{r}_1,\ldots,\vec{r}_N}_{\vec{r}^{\,N}};\underbrace{\hat{\omega}_1,\ldots,\hat{\omega}_N}_{\hat{\omega}^{N}},t)$$

Smoluchowski equation:

(Textbook J.K.G. Dhont)

$$\frac{\partial}{\partial t}P = \hat{L}_S P$$

Smoluchowski operator

total potential energy

$$\hat{L}_s = \sum_{i=1}^{N}\left\{\vec{\nabla}_{\vec{r}_i}\bullet\overleftrightarrow{D}(\hat{\omega}_i)\bullet\left[\vec{\nabla}_{\vec{r}_i}+\frac{1}{k_BT}\vec{\nabla}_{\vec{r}_i}U(\vec{r}^{\,N},\hat{\omega}^{N},t)\right]\right.$$

$$\left.+D_r\hat{R}_i\bullet\left[\hat{R}_i+\frac{1}{k_BT}\hat{R}_iU(\vec{r}^{\,N},\hat{\omega}^{N},t)\right]\right\}$$

$$\hat{R}_i = \hat{\omega}_i\times\vec{\nabla}_{\hat{\omega}_i}$$

$$\overleftrightarrow{D}(\hat{\omega}_i) = D^{\parallel}\hat{\omega}_i\otimes\hat{\omega}_i + D^{\perp}(\overleftrightarrow{1}-\hat{\omega}_i\otimes\hat{\omega}_i)$$

idea of Archer and Evans JCP 121, 4246 (2004)

integrate Smoluchowski equation $N\int dr_2 \ldots \int dr_N \int d\hat{\omega}_2 \ldots \int d\hat{\omega}_N$

$$\frac{\partial \rho(\vec{r},\hat{\omega},t)}{\partial t} = \vec{\nabla}_{\vec{r}} \bullet \vec{D}(\hat{\omega}) \bullet \left[\vec{\nabla}_{\vec{r}} \rho(\vec{r},\hat{\omega},t) + \frac{1}{k_B T} \rho(\vec{r},\hat{\omega},t) \vec{\nabla}_{\vec{r}} V_{ext}(\vec{r},\hat{\omega},t) - \frac{\vec{F}(\vec{r},\hat{\omega},t)}{k_B T} \right]$$

$$+ D_r \hat{R} \bullet \left[\hat{R}\rho(\vec{r},\omega,t) + \frac{1}{k_B T} \rho(\vec{r},\hat{\omega},t) \nabla_{\vec{r}} V_{ext}(\vec{r},\hat{\omega},t) - \frac{1}{k_B T} \vec{T}(\vec{r},\hat{\omega},t) \right]$$

with average force and torque

$$\vec{F}(\vec{r},\hat{\omega},t) = -\int d^3 r' \int d^2 \omega' \rho^{(2)}(\vec{r},\vec{r}',\hat{\omega},\hat{\omega}',t) \vec{\nabla}_{\vec{r}} V_2(\vec{r},\vec{r}',\vec{\omega},\vec{\omega}',t) = \rho_0(\vec{r},\hat{\omega}) \vec{\nabla}_{\vec{r}} \frac{\delta F_{exc}[\rho]}{\delta \rho_0(\vec{r},\hat{\omega})}$$

$$\vec{T}(\vec{r},\hat{\omega},t) = -\int d^3 r' \int d^2 \omega' \rho^{(2)}(\vec{r},\vec{r}',\hat{\omega},\hat{\omega}',t) \hat{R}_{\vec{r}} V_2(\vec{r},\vec{r}',\vec{\omega},\vec{\omega}',t) = \rho_0(\vec{r},\hat{\omega}) \hat{R} \frac{\delta F_{exc}[\rho]}{\delta \rho_0(\vec{r},\hat{\omega})}$$

in general unknown

in equilibrium (Gubbins CPL 76, 329 (1980)) “adiabatic“ approximation: assume the pair correlations in nonequilibrium are the same as those for an equilibrium system with the same one-body density profile (established by a suitable $V_{ext}(\vec{r},\hat{\omega},t)$)

$$\frac{\partial\rho(\vec{r},\hat{\omega},t)}{\partial t} = \vec{\nabla}_{\vec{r}} \bullet \vec{\vec{D}}(\hat{\omega}) \bullet \left[\rho(\vec{r},\hat{\omega},t)\vec{\nabla}_{\vec{r}} \frac{\delta F[\rho(\vec{r},\hat{\omega},t)]}{\delta\rho(\vec{r},\hat{\omega},t)}\right] + D_r \hat{R}\left[\rho(\vec{r},\hat{\omega},t)\hat{R}\frac{\delta F[\rho(\vec{r},\hat{\omega},t)]}{\delta\rho(\vec{r},\hat{\omega},t)}\right]$$

DDFT

with the equilibrium Helmholtz free energy density functional

$$F[\rho] = k_B T \int d^3r \int d\hat{\omega}\rho(\vec{r},\hat{\omega})\left[\ln\left(\Lambda^3\rho(\vec{r},\hat{\omega})\right) - 1\right] + F_{ext}[\rho] + \int d^3r \int d\hat{\omega}\rho(\vec{r},\hat{\omega})V_{ext}(\vec{r},\hat{\omega},t)$$

(M. Rex, H.H. Wensink, H.L., PRE 76, 021403 (2007)) approximation for the density functional

mean-field

$$F_{exc}[\rho] = \frac{1}{2}\int d^3r \int d^3r' \int d\hat{\omega} \int d\omega' \rho(\vec{r}, \hat{\omega}') v_2(\vec{r}, \vec{r}', \hat{\omega}, \hat{\omega}')$$

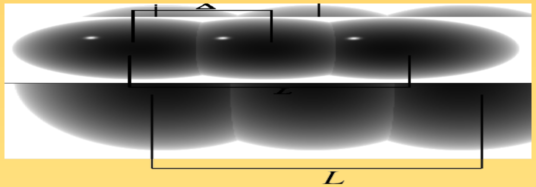
time independent

(caveat: brings ideal rotational dynamics)

Model

Gaussian segment-segment interaction

$$v_2(\vec{r}_i, \vec{r}_i, \hat{\omega}_i, \hat{\omega}_i) = \varepsilon \sum_{\alpha=-K}^{K} \sum_{\beta=-K}^{K} \exp(-\frac{\left| r_{\alpha\beta} \right|^2}{\sigma^2})$$



$$N_s = 3L = \sigma$$

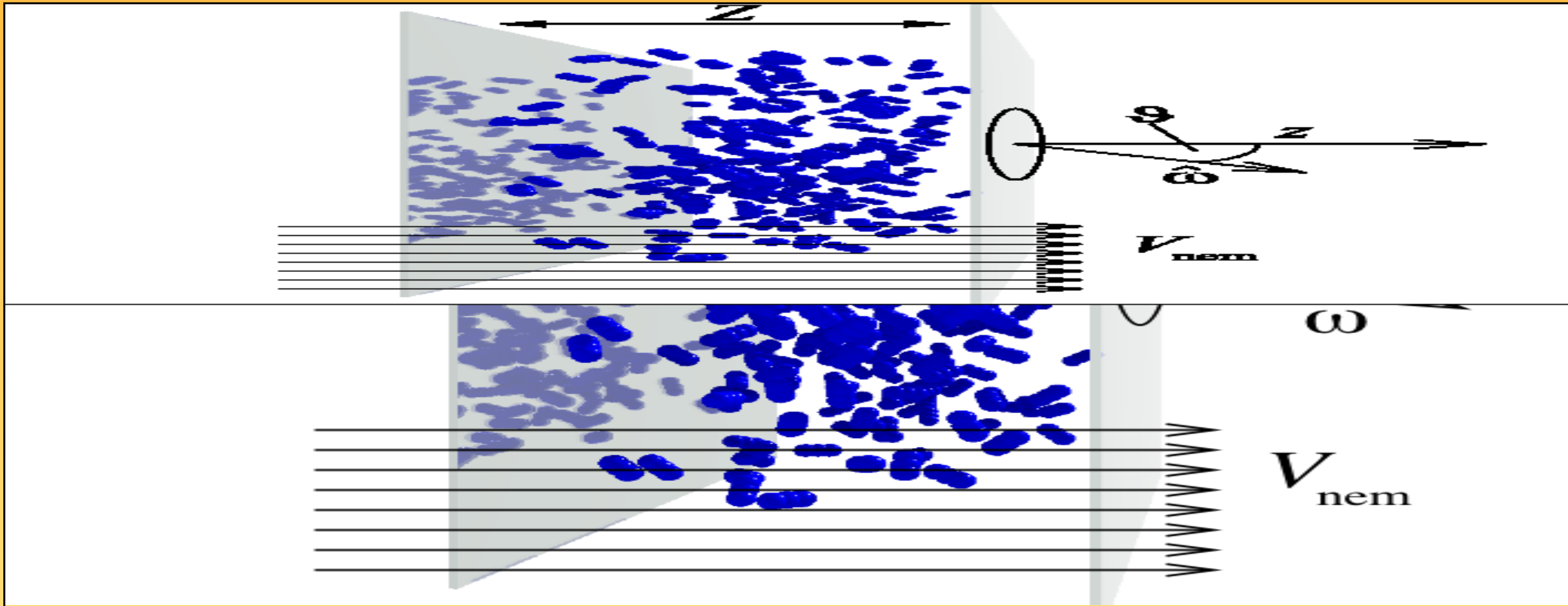
$$\Delta = \frac{L}{N_s - 1}$$

$$V_{ext}(\vec{r}, \hat{\omega}, t) =$$

$$V_0 (\frac{Z}{Z(t)})^{10}$$ confining slit

$$V_0 (\frac{Z}{Z(t)})^{10} - \Phi_0 \cos^2 \vartheta$$ aligning field

$$V_0 = 10 k_B T = \Phi_0$$


Z
ϑ
z
ω̂
V_{nem}
ω
V_{nem}

	Set-ups	$V_{\mathrm{ext}}(\mathbf{r},\omega,t)$
A	slow compression	$V_0\left(\frac{z}{Z(t)}\right)^{10},\ Z(t)=\begin{cases}2\sigma & \text{if } t<0\\ 2\sigma-ct & \text{if } 0\le t\le\tau_{\mathrm{B}}\\ \sigma & \text{if } t>\tau_{\mathrm{B}}\end{cases}$
B	slow expansion	$V_0\left(\frac{z}{Z(t)}\right)^{10},\ Z(t)=\begin{cases}\sigma & \text{if } t<0\\ \sigma+ct & \text{if } 0\le t\le\tau_{\mathrm{B}}\\ 2\sigma & \text{if } t>\tau_{\mathrm{B}}\end{cases}$
C	instantaneous expansion	$V_0\left(\frac{z}{Z(t)}\right)^{10},\ Z(t)=\begin{cases}\sigma & \text{if } t<0\\ 2\sigma & \text{if } t\ge 0\end{cases}$

Results

full density

$$\rho(z,\vartheta,t)$$

orientationally averaged density

$$\rho(z,t) = \int_0^{\pi/2} d\vartheta \sin\vartheta \rho(z,\vartheta,t)$$

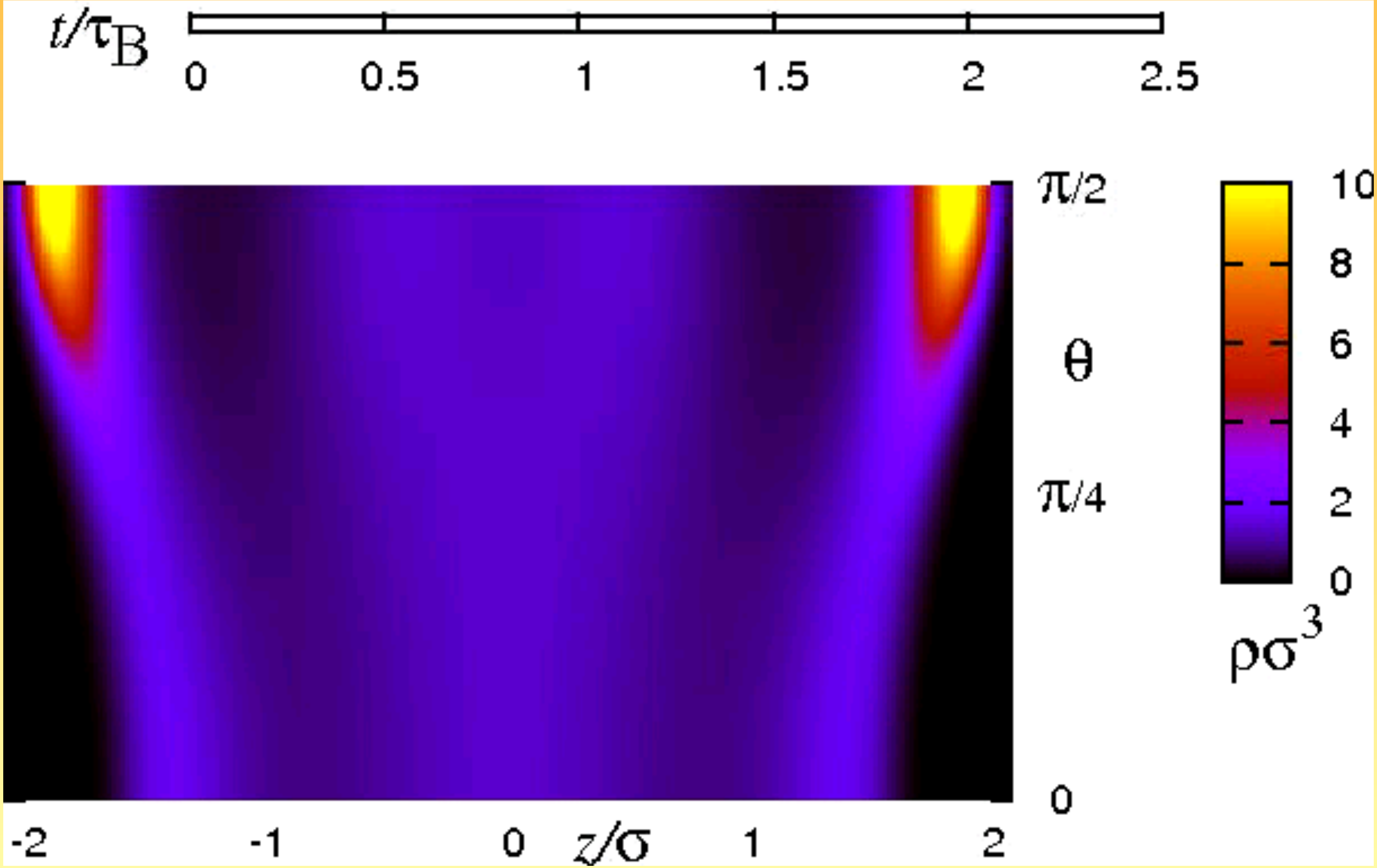
orientational ordering

$$S(z,t) = \frac{1}{\rho(z,t)} \int_0^{\pi/2} d\vartheta \sin\vartheta \left[\frac{3}{2}\cos^2\vartheta - \frac{1}{2}\right] \rho(z,\vartheta,t)$$

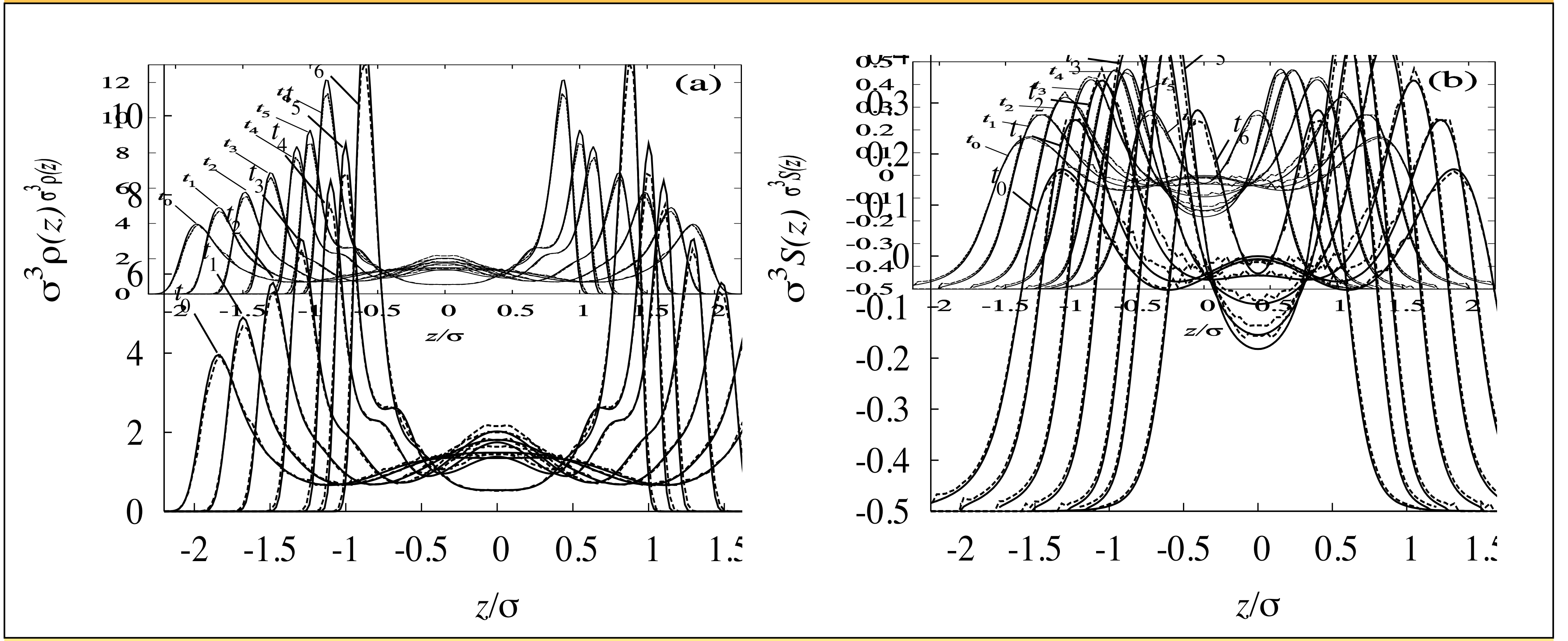
second moment

$$m_2(t) = \sum_{-\infty}^{\infty} dz z^2 (\rho(z,t) - \rho(z,t=\infty))$$

slow compression (set-up A) full density $\rho(z, \vartheta, t)$

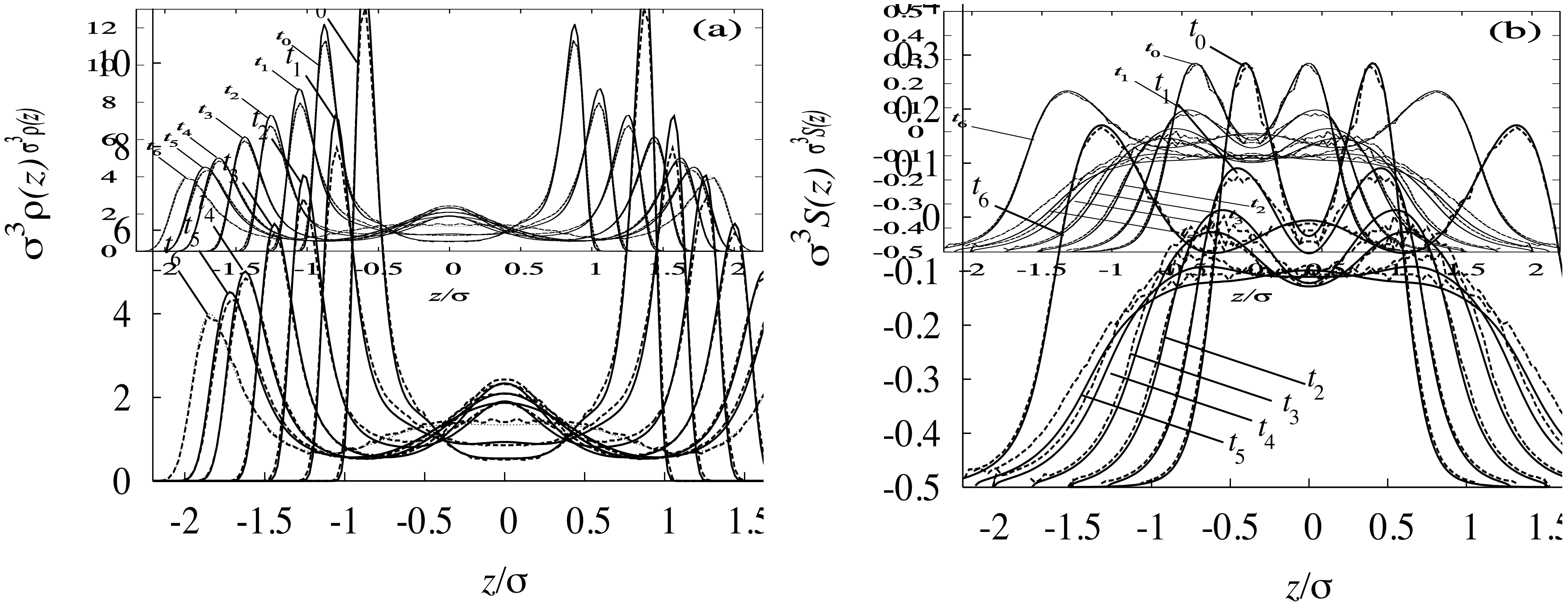


set-up A DDFT (solid curves) and BD (dashed curves)

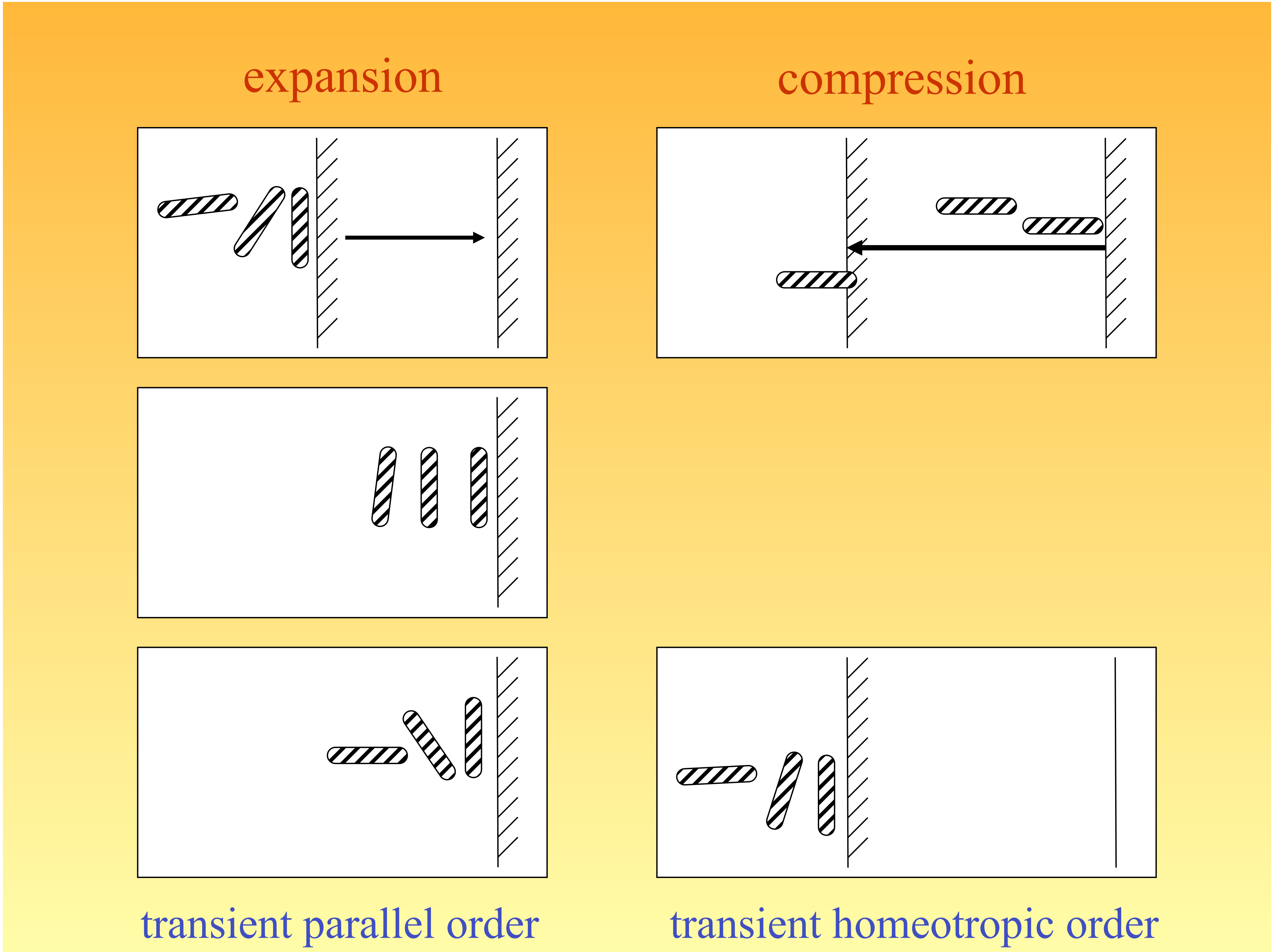


$t_0 = 0.0 \quad t_1 = 0.2\tau_B, \quad t_2 = 0.4\tau_B, \quad t_3 = 0.6\tau_B, \quad t_4 = 0.8\tau_B, \quad t_5 = 0.9\tau_B, \quad t_6 = 15.0\tau_B$

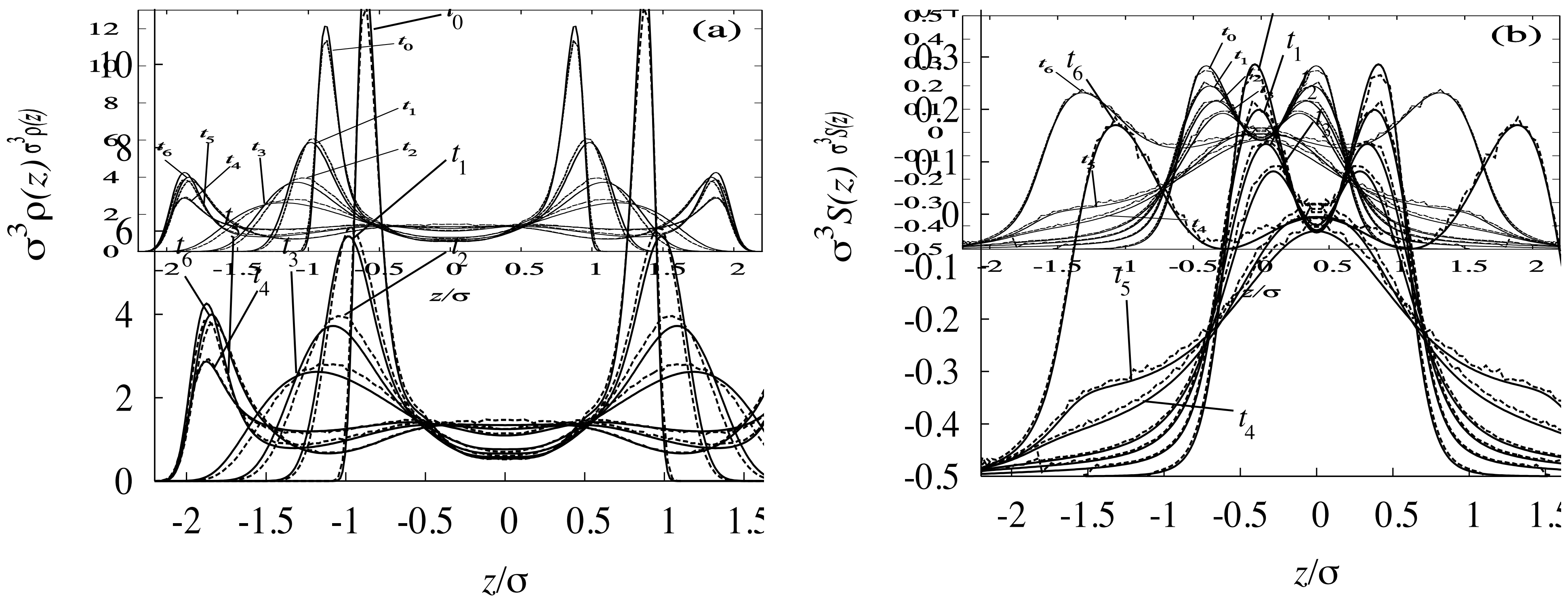
set-up B DDFT (solid curves) and BD (dashed curves)



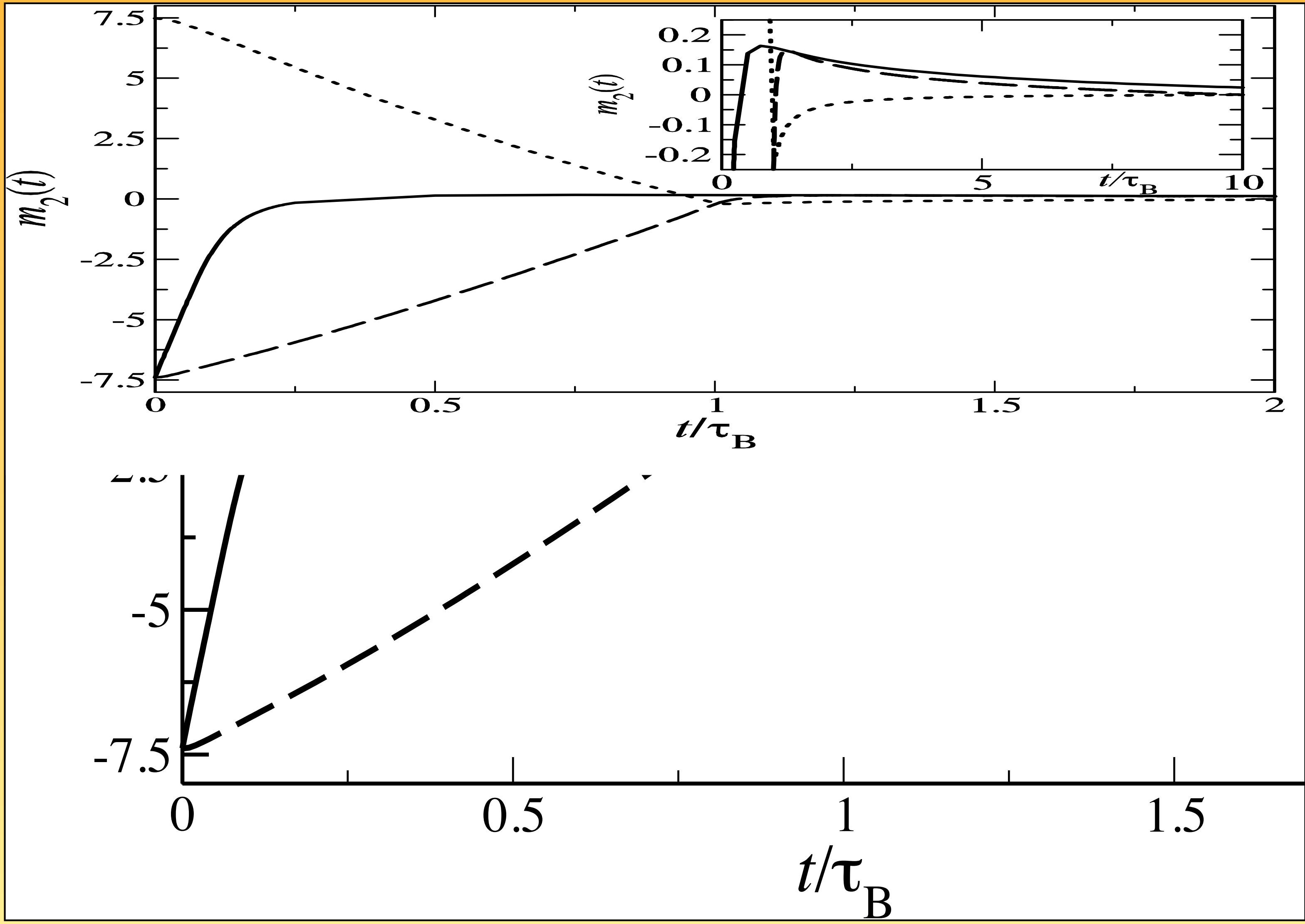
$t_0 = 0.0 \quad t_1 = 0.2\tau_B, \quad t_2 = 0.4\tau_B, \quad t_3 = 0.6\tau_B, \quad t_4 = 0.8\tau_B, \quad t_5 = 0.9\tau_B, \quad t_6 = 15.0\tau_B$


expansion
compression
transient parallel order
transient homeotropic order

set-up C DDFT (solid curves) and BD (dashed curves)



$t_0 = 0.0 \quad t_1 = 0.02\tau_B, \quad t_2 = 0.04\tau_B, \quad t_3 = 0.06\tau_B, \quad t_4 = 0.08\tau_B, \quad t_5 = 0.25\tau_B, \quad t_6 = 15.0\tau_B$



short-dashed: slow compression (set-up A)
long-dashed: slow expansion (set-up B)
full curve: instantaneous expansion (set-up C)

Conclusions

- generalization of DDFT towards anisotropic colloidal particles
- good agreement with BD simulation for nontrivial relaxation problems

future:

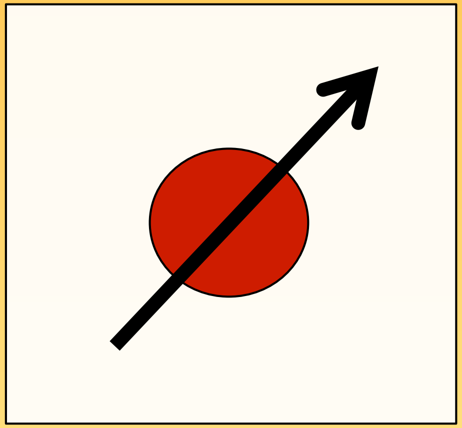
- more realistic density functionals (FMT) as proposed by

  Mecke and Hansen-Goos.

see A. Härtel, R. Blaak, HL,Phys. Rev. E 81, 051703 (2010)

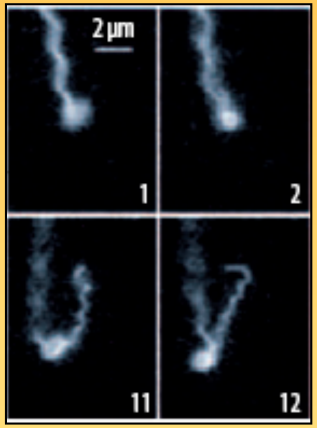
From „passive“ to „active“ particles

inert particle
in an external field

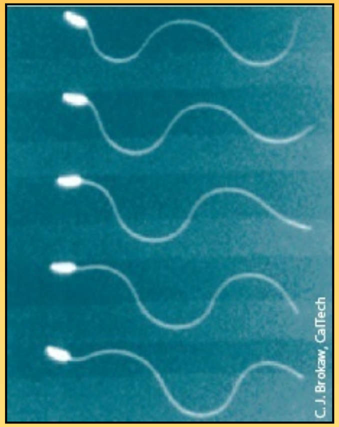


Self-propelled particles with an external motor

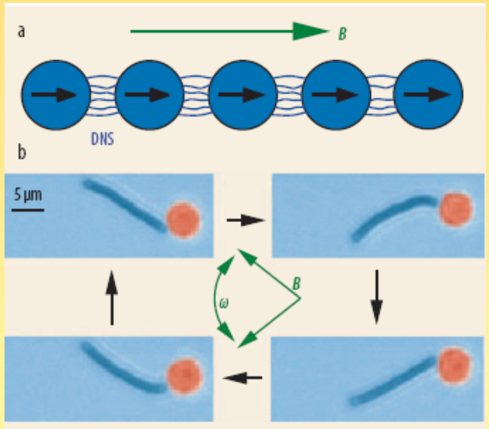
- bacteria (E. coli)



- sperm



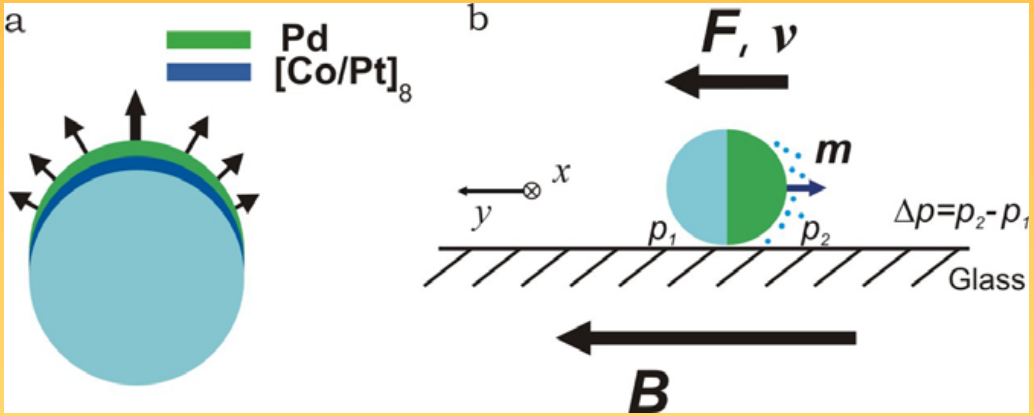
- colloidal microswimmers („micromotors“)



GENUINE NONEQUILIBRIUM

COLLOIDAL MICROSWIMMERS

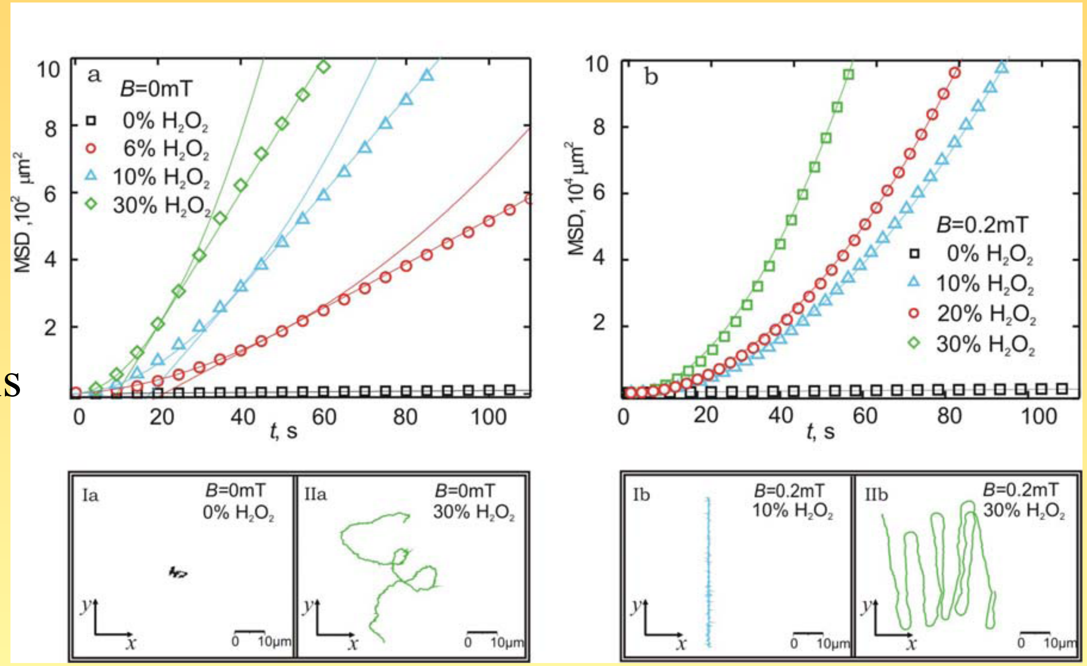
anisotropic (capped) colloidal particles suspended in water
+
H_2O_2



catalytic chemical reaction at the surface
⇒ **drive**

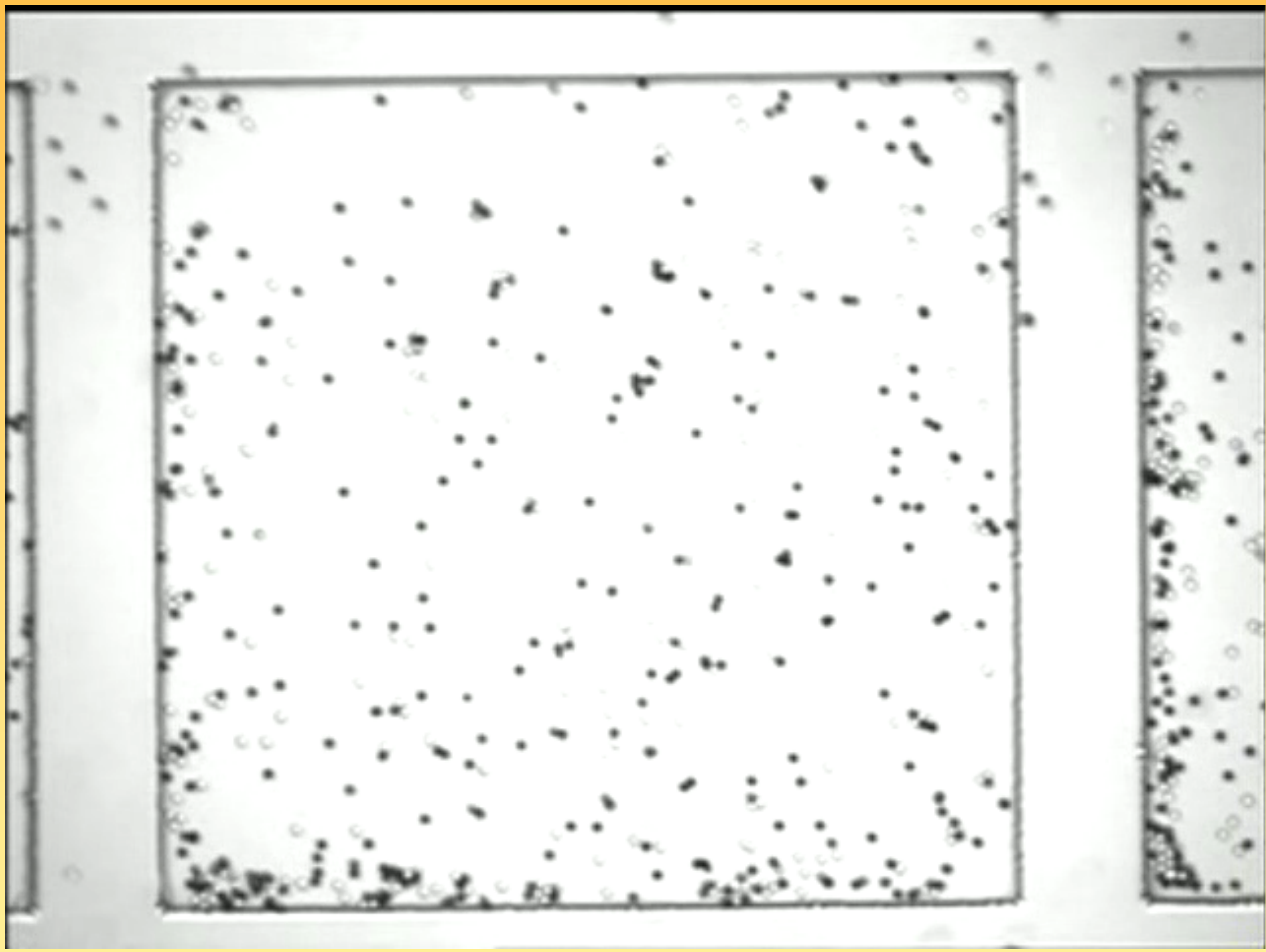
plus external magnetic field

trajectories
Brownian motion is relevant



arXiv: 0807.1619, L. Baraban, P. Leiderer, A. Erbe et al

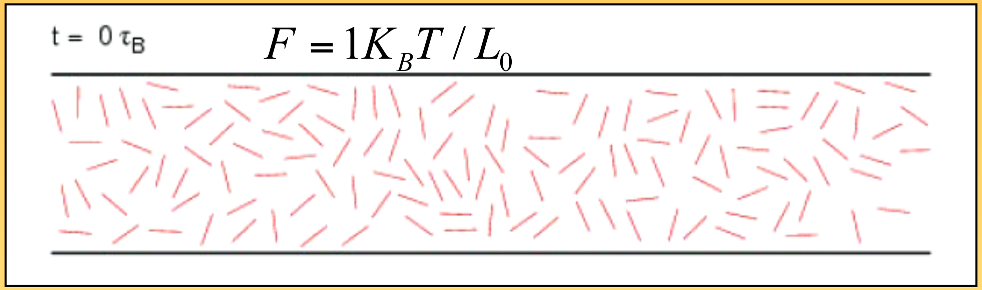
L. Baraban, private communication

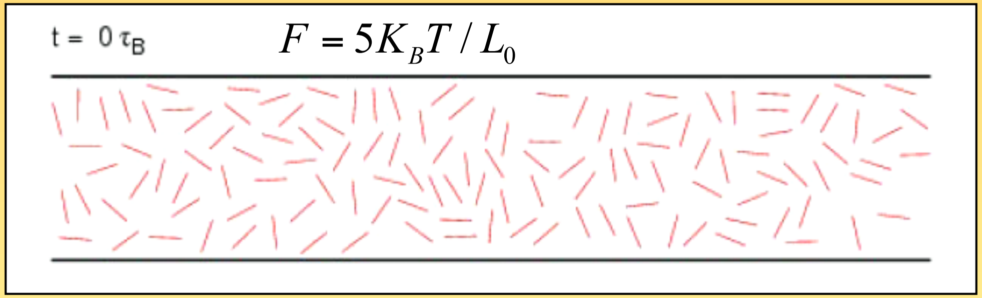


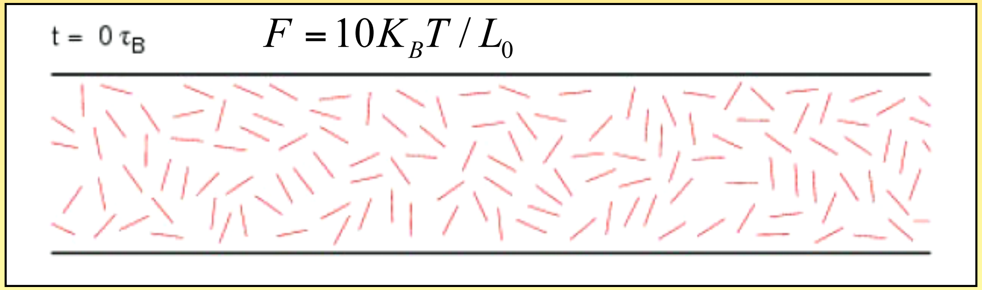
mixture of „**active**“ and „**passive**“ particles in confining geometry
wall aggregation?

b) Collective behaviour (no torque)

Self-propelled Brownian rods in a confining channel







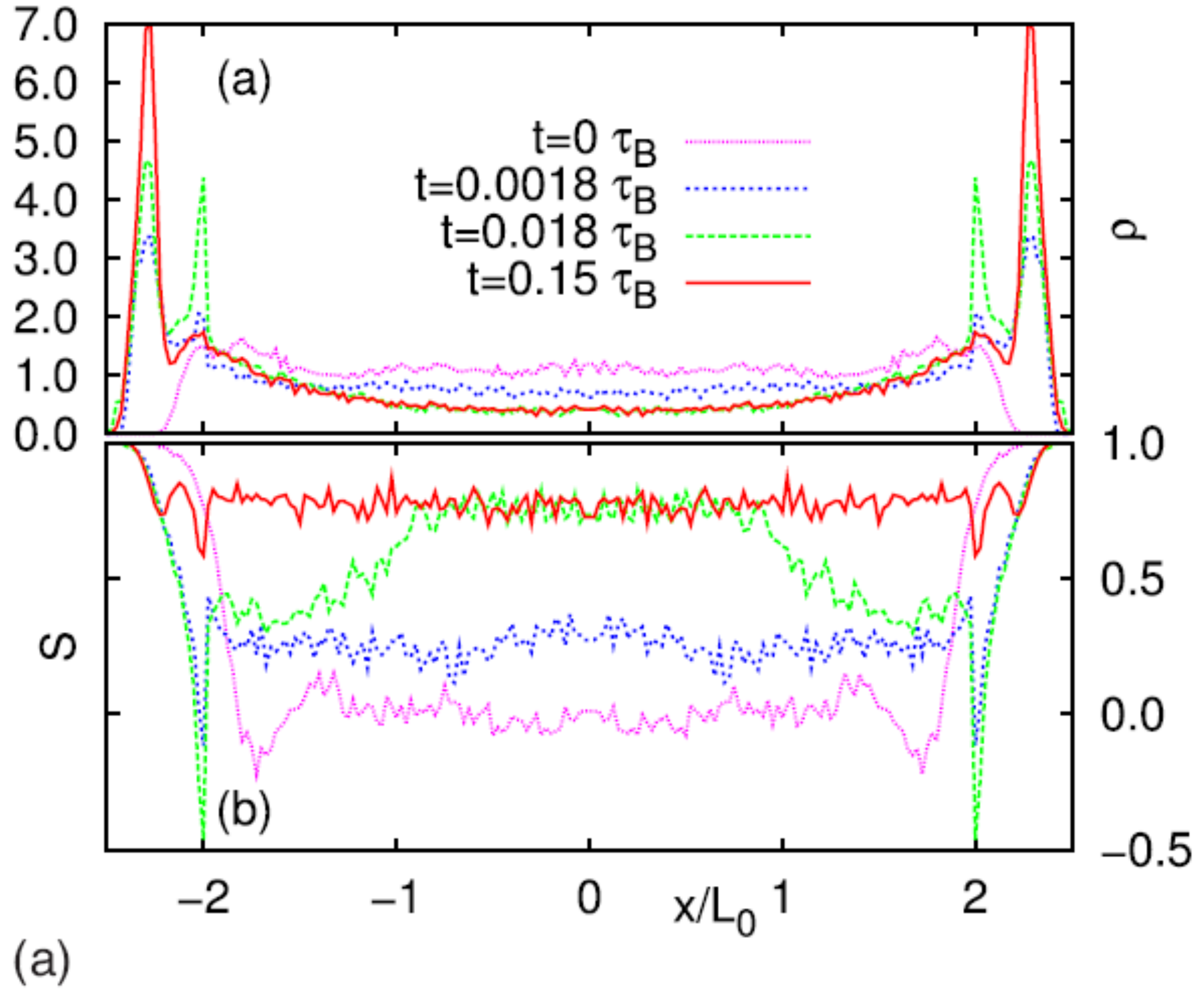
- aggregation near system walls
- transient hedgehog clusters
- in line with a microscopic dynamical density functional theory

H. H. Wensink, HL, Phys. Rev. E. 78, 031409 (2008)

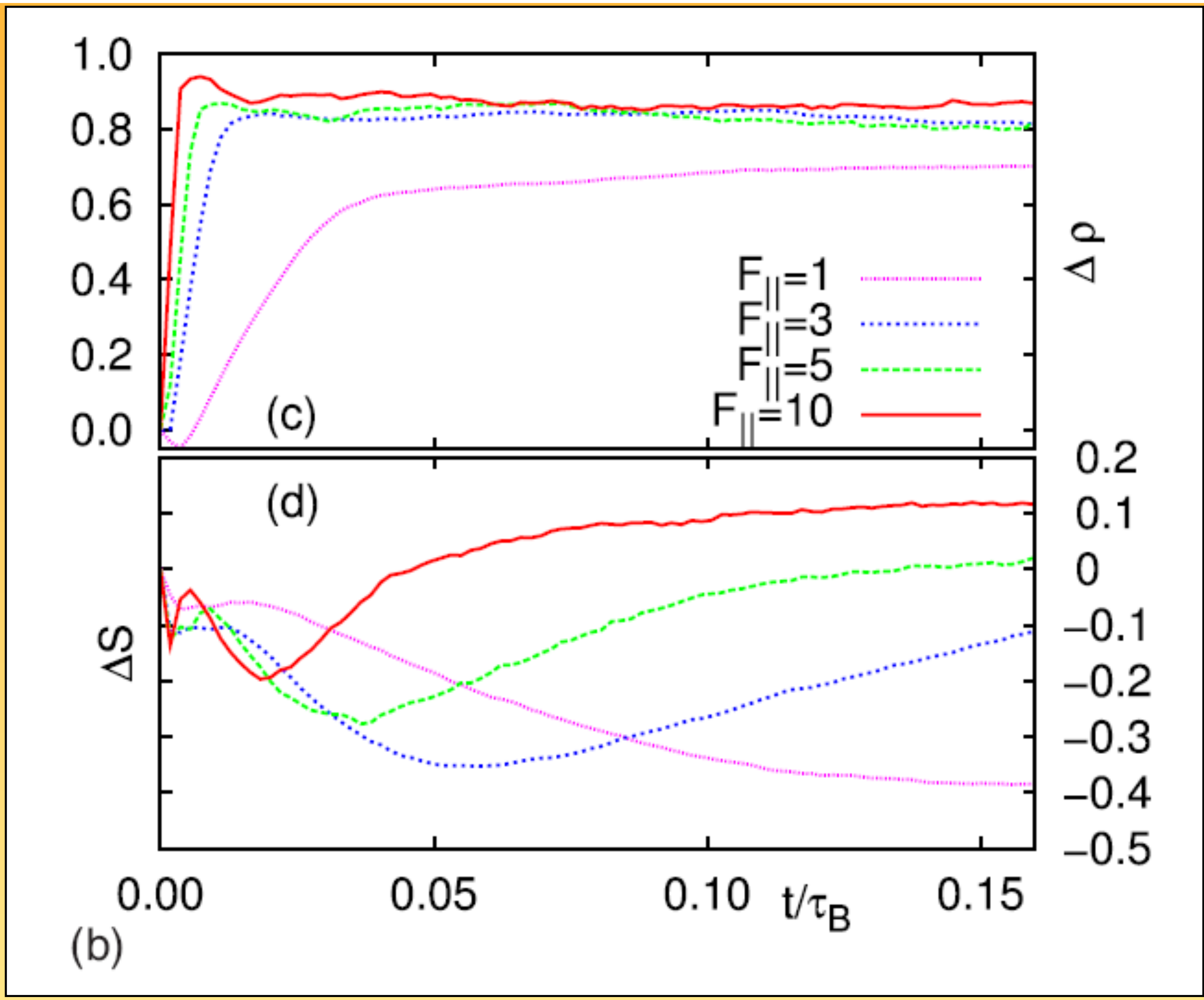
$$\partial_t \rho = \boldsymbol{\nabla} \cdot \mathbf{D}_T \cdot [\boldsymbol{\nabla} \rho + \rho \boldsymbol{\nabla} (\beta U_{\mathrm{int}} + \beta U_{\mathrm{wall}}) - \beta F_{\parallel} \rho \hat{\mathbf{u}}]$$
$$+ D_R [\partial_\varphi^2 \rho + \partial_\varphi \rho \partial_\varphi (\beta U_{\mathrm{int}} + \beta U_{\mathrm{wall}})],$$

$$\beta U_{\mathrm{int}}(\mathbf{r}, \hat{\mathbf{u}}) = - \int d\mathbf{r}' d\hat{\mathbf{u}}' (\exp[-\beta U_{\mathrm{rod}}] - 1) \rho(\mathbf{r}', \hat{\mathbf{u}}'),$$

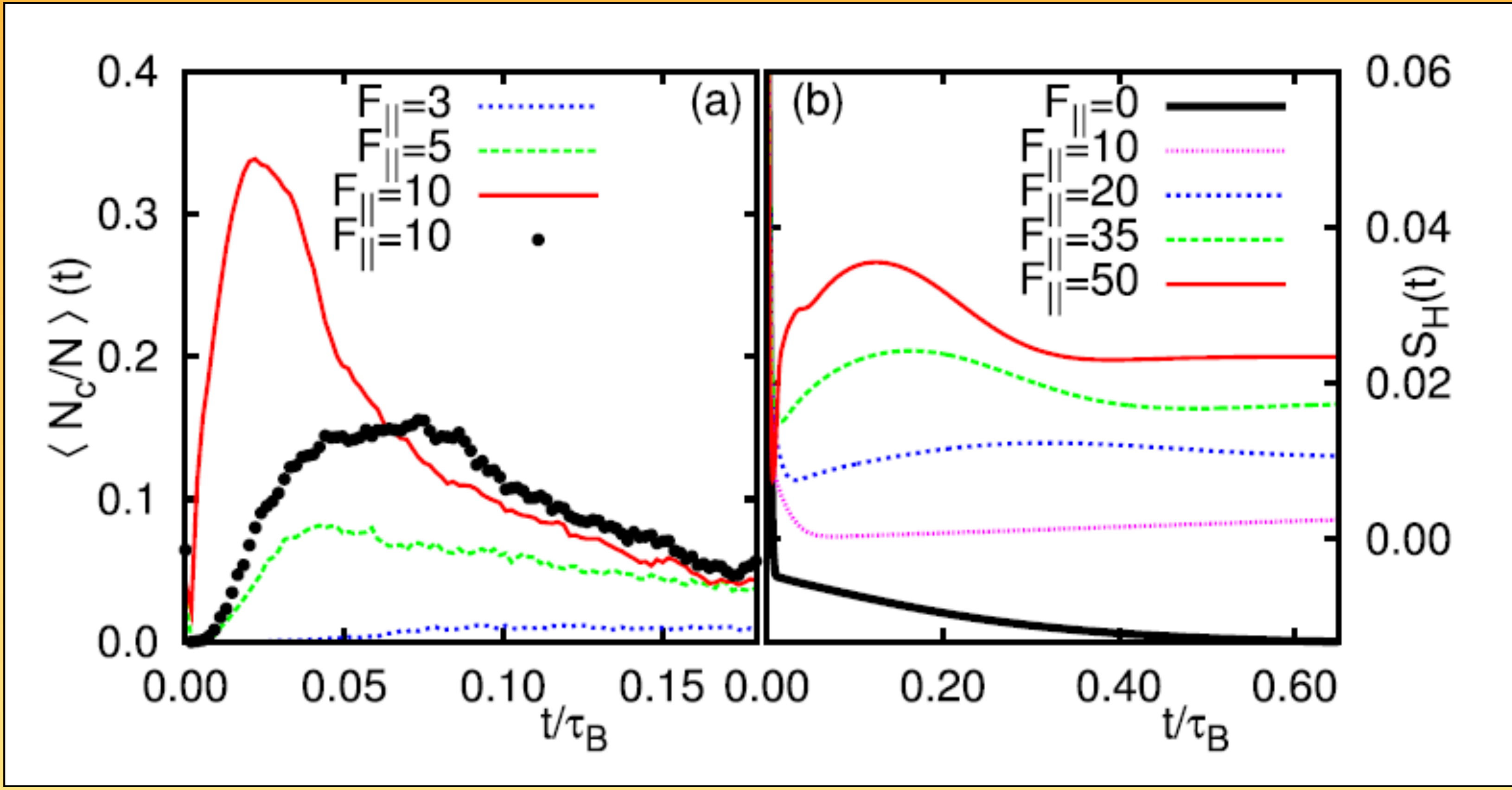
$$\beta U_{\mathrm{int}} = \delta \beta F_{\mathrm{exc}}[\rho] / \delta \rho$$



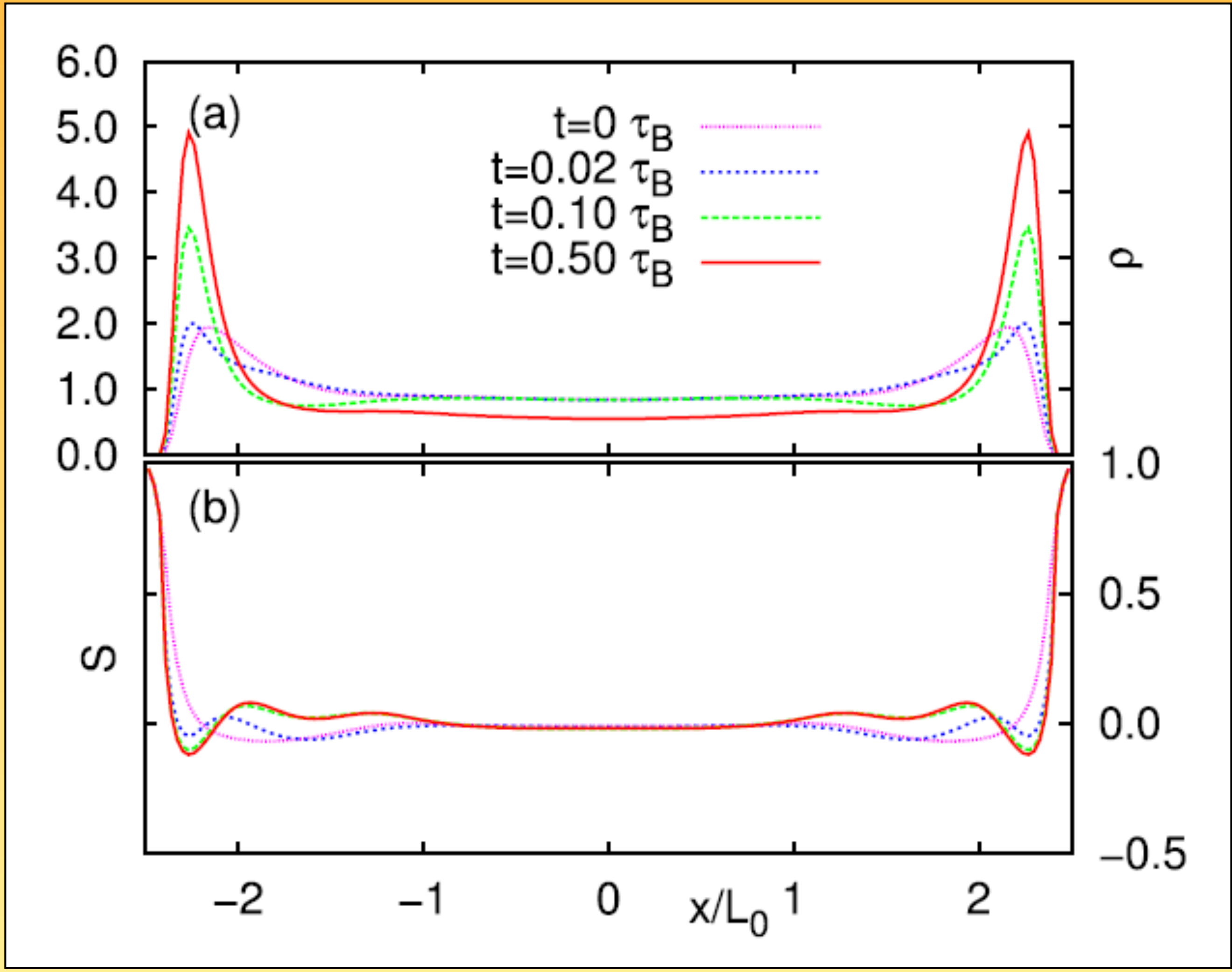
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(a)
t=0 τB
t=0.0018 τB
t=0.018 τB
t=0.15 τB
ρ
1.0
0.5
0.0
−0.5
S
(b)
−2
−1
0
x/L0
1
2
(a)



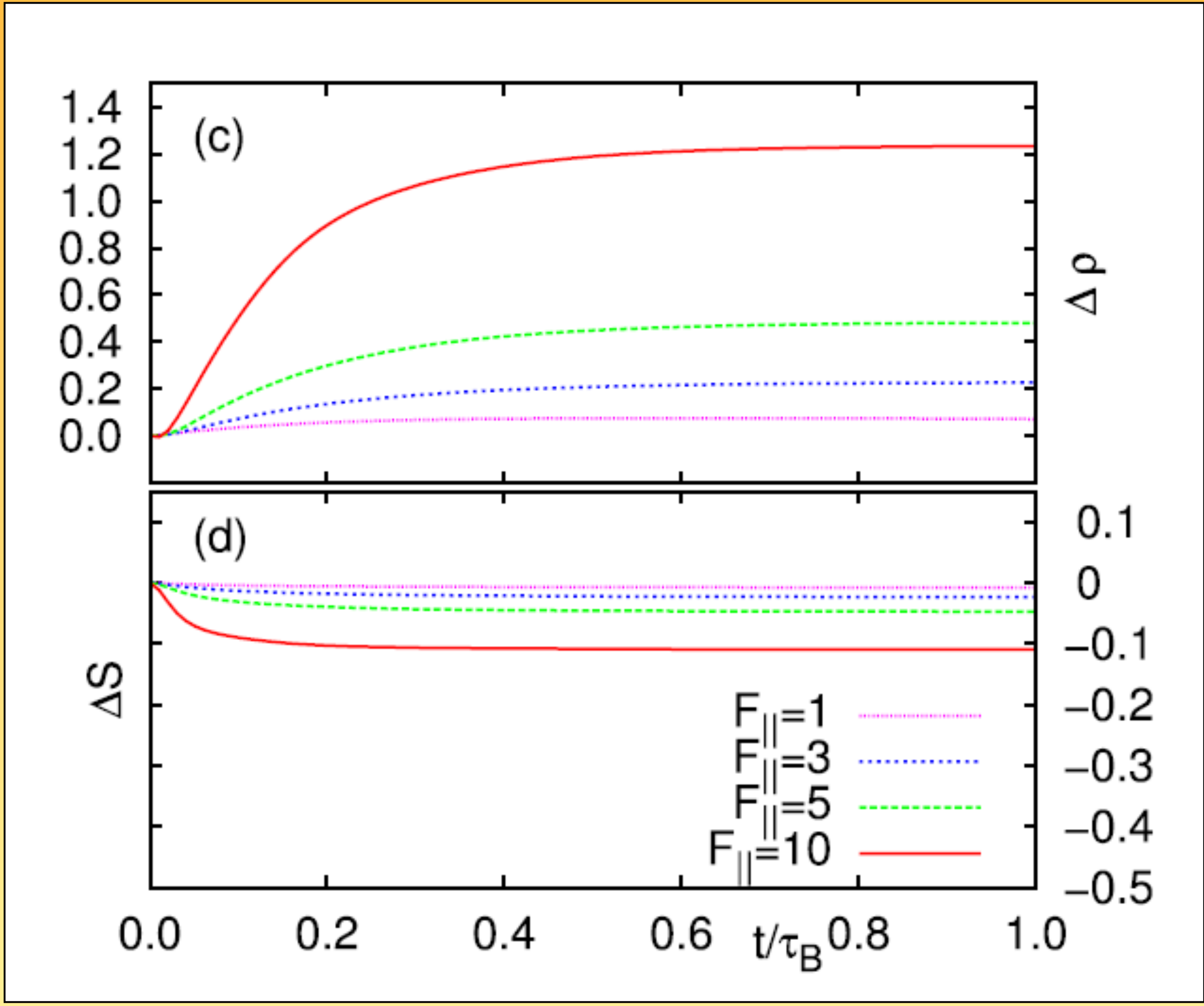
(Color online) Time-dependent profiles for the number density $\rho(x)$ (a) and nematic order parameter $S(x)$ (b) for $F_{\parallel} = 10k_BT/L_0$ and $\kappa L_0 = 10$ obtained from simulations. (c) Adsorption $\Delta\rho = \int_0^{L_0}[\rho(x,t) - \rho(x,0)]dx$ and (d) excess orientation $\Delta S = \int_0^{L_0}\rho(x)[S(x,t) - S(x,0)]dx / \int_0^{L_0}dx\,\rho(x)$ showing the evolution of the rod structure with respect to the equilibrium initial state near the channel walls.



(Color online) (a) Average number fraction of clustered rods (N_c/N) versus time. The solid curve corresponds to an initial state of freely rotating rods, the points to an aligned state where $\hat{\mathbf{u}}_i \perp \hat{\mathbf{n}}$ for each particle i. (b) Time evolution of the hedgehog strength $S_H(t)$ of a hedgehog nucleus [see Eq. (2)] from dynamical density functional theory.



(a)
(b)
t=0 τB
t=0.02 τB
t=0.10 τB
t=0.50 τB
ρ
S
x/L0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.0
0.5
0.0
−0.5
−2
−1
0
1
2


(c)
(d)
Δρ
ΔS
t/τB
F||=1
F||=3
F||=5
F||=10
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.1
0
−0.1
−0.2
−0.3
−0.4
−0.5
0.0
0.2
0.4
0.6
0.8
1.0