Capillary forces on colloids at fluid interfaces

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introduction

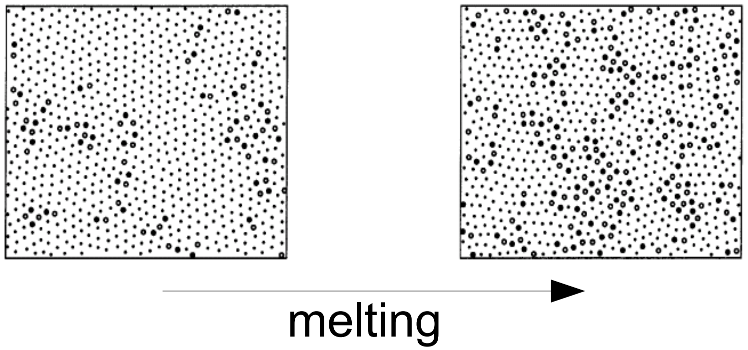
colloids (nm...µm) trapped at fluid interfaces:

two-dimensional structures

• basic research on 2d systems
(e.g., Kosterlitz-Thouless transition)

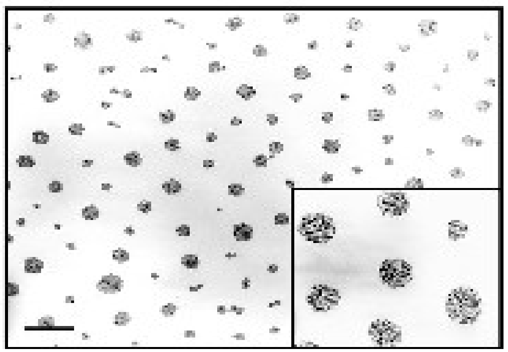
• well-defined cluster shapes, pattern formation
• potential build-up of 3d structures on a solid

$water/air(ca\ 2\mu m)$



Zahn, Lenke and Maret, PRL **82**, 2721 (1999)

$water/air(Ag, -: 0.5\mu m)$



R.P. Sear *et al.*, PRE **59**, R6255 (2004).

colloid assembly controlled by effective interactions

colloids on planar water / air interfaces

Ghezzi and Earnshaw, J.Phys.: Cond.Matt. **9**, L517 (1997)

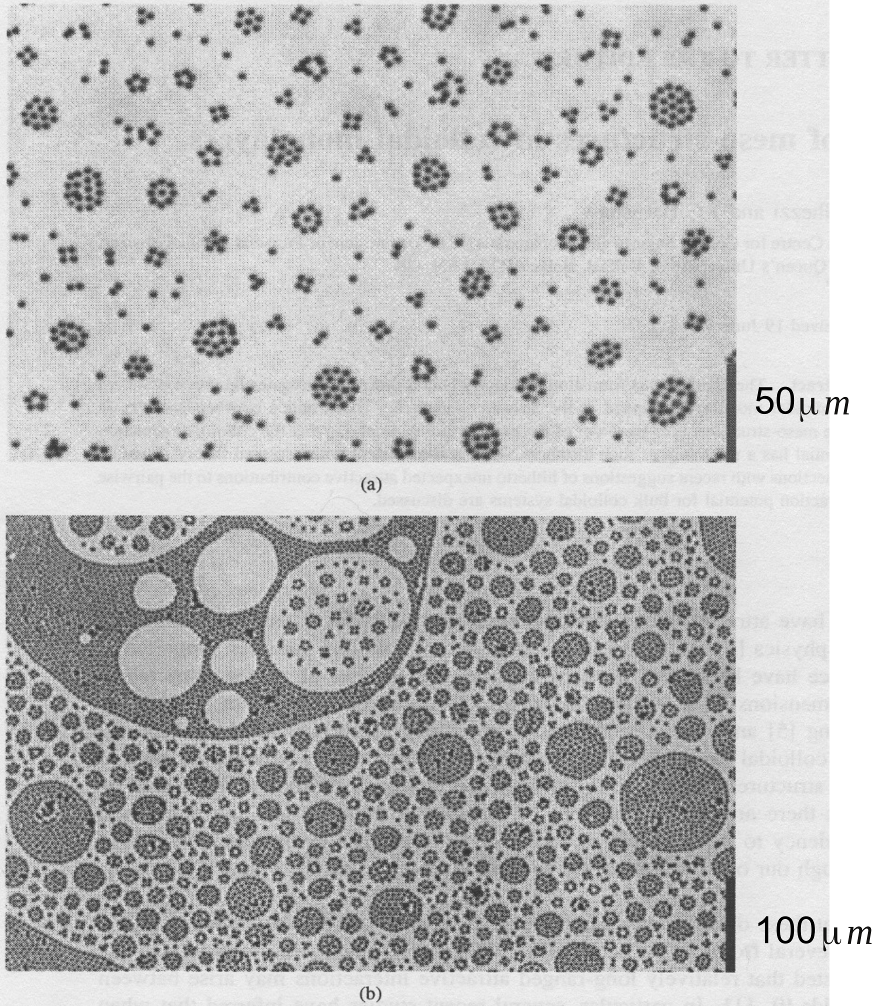


Figure 1. Two video-micrographs of monolayers of 3 μm colloidal particles containing spontaneously generated meso-structures: (a) clusters from dimers to examples containing of order 20 particles; (b) larger and more complex structures. The vertical bars in one corner of each micrograph indicate scale: 50 μm (a); 100 μm (b).

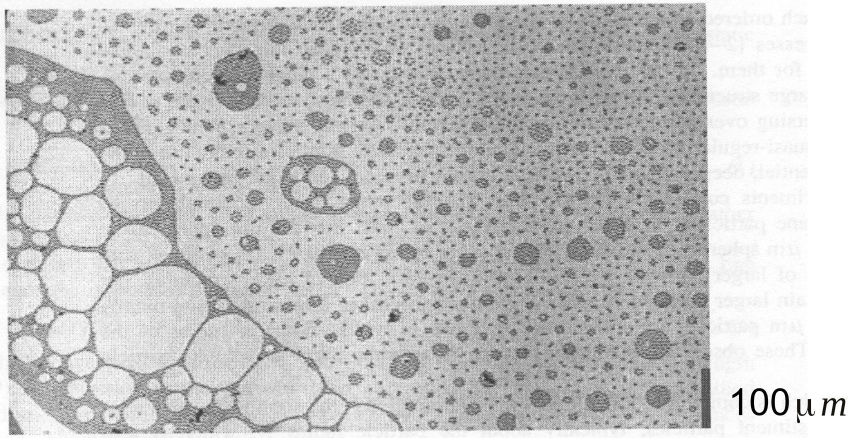


Figure 2. An example of more complex structure in a 3 μm particle monolayer, at lower magnification than in figure 1. The main meso-structure resembles the 'foam' structures previously reported [7]. The vertical bar in one corner of the micrograph indicates 100 μm.

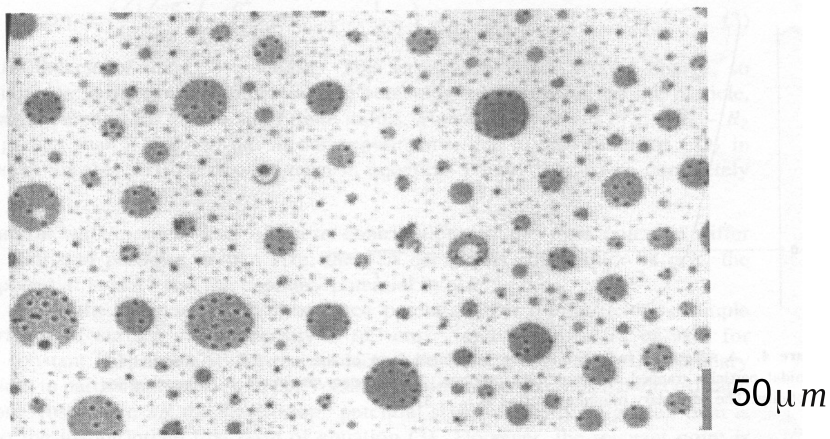
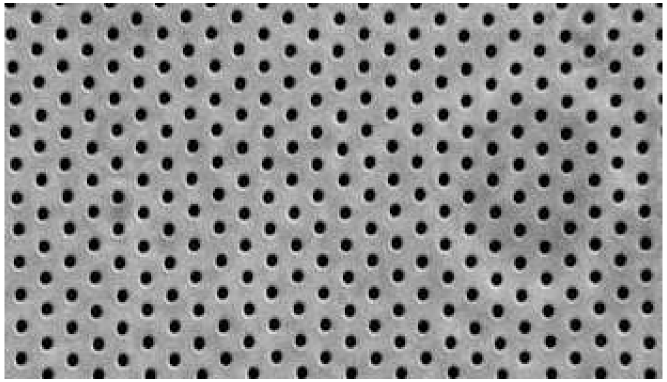


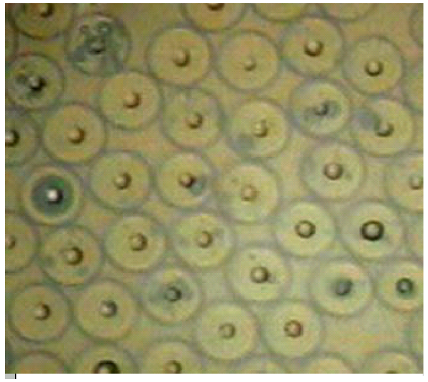
Figure 3. An example of meso-structure formation in a mixed monolayer, comprising 1 μm particles with a smaller number of 3 μm and a very few 5 μm lattices. The grey areas are unresolved meso-structures of 1 μm particles, in which the inter-particle separation is $\sim 3R$. While this separation is not visible here, the depletion zones around the larger particles are readily apparent. The vertical bar in one corner of the micrograph indicates 50 μm.

monolayers at fluid interfaces

spheres
air–water
($R \approx 2\mu m$)



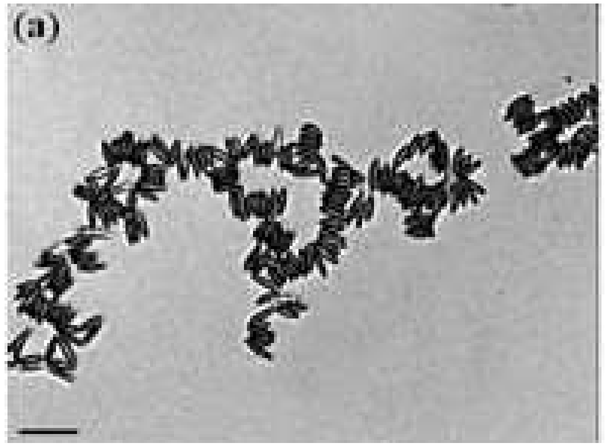
Zahn et al. PRL 90 (2003) 155506



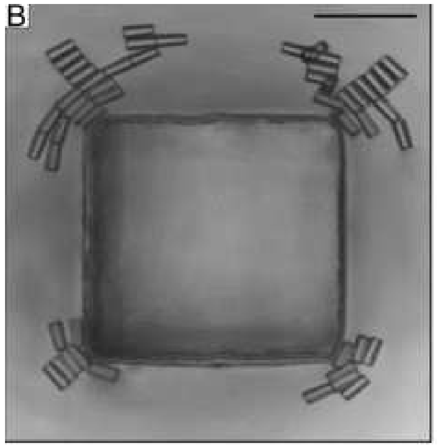
glass
spheres
at air–oil
($R \approx 24\mu m$)

Aubry & Singh, PRE 77 (2008) 056302

ellipsoids
oil–water
(— : $21\mu m$)



Loudet et al. PRL 94 (2005) 018301

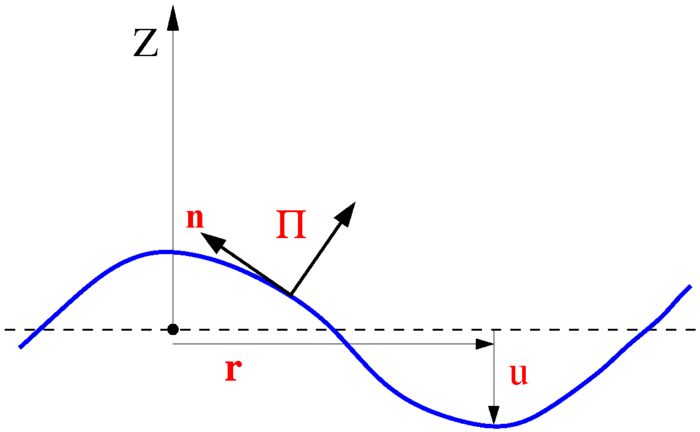


micropost
and rods
oil–water
(— : $100\mu m$)

Cavallaro et al. PNAS 27 (2011) 20923

capillary forces

- deformation of interface relative to reference plane $u(\mathbf{r})$
  given pressure normal to the interface $\Pi(\mathbf{r})$
- interface in mechanical equilibrium for given $\Pi(\mathbf{r})$
- approximation: small deviations from flat interface: $|\nabla u| \ll 1$
  (very good for realistic conditions)



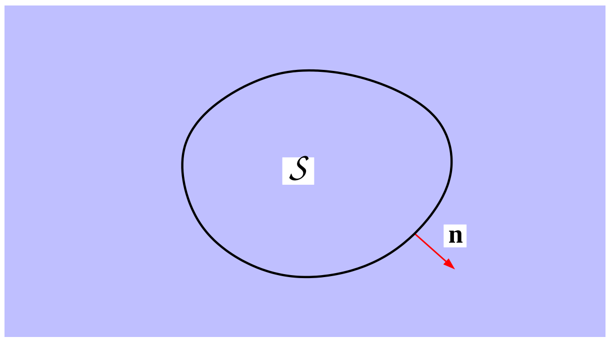
local vertical mechanical balance:

$$\nabla^2 u = \frac{1}{\gamma}(-\Pi) + \frac{u}{\lambda^2}$$

Young-Laplace equation

λ = capillary length ($\sim$ mm)

γ = surface tension



in–plane mechanical balance:

$$\mathbf{F}_{||}^{\mathcal{S}} = \left[\oint_{\partial\mathcal{S}} d\ell\, \mathbf{n}\, \gamma\right]_{||} = -\int_{\mathcal{S}} dA\, (-\Pi)\, \nabla_{||} u$$

capillary force on region $\mathcal{S}$

$\mathbf{n}$: normal to $\mathbf{e}_z - \nabla_{||} u(x,y)$ and normal to tangent of $\partial\mathcal{S}$

Müller, Deserno, Guven, EPL 69 (2005)

Domínguez, Oettel, S.D., JCP 128 (2008)

capillary forces on single particle

$$\nabla^2 u = \frac{1}{\gamma}(-\Pi) + \frac{u}{\lambda^2} \qquad \mathbf{F}_{||}^{\mathcal{S}} = -\int_{\mathcal{S}} dA\,(-\Pi)\,\nabla_{||} u$$

gravitational or electrostatic analogy

interfacial deformation u	$\leftrightarrow$	gravitational potential
capillary length $\lambda = \sqrt{\gamma/(\Delta\varrho g)}$	$\leftrightarrow$	"screening" length
density of vertical force Π	$\leftrightarrow$	$-$ mass density
vertical force f (capillary monopole)	$\leftrightarrow$	$-$ mass
particle–interface contact line	$\leftrightarrow$	generation of multipolar moments

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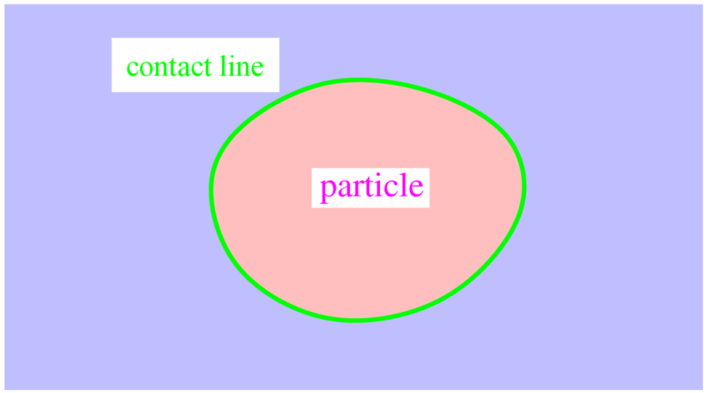
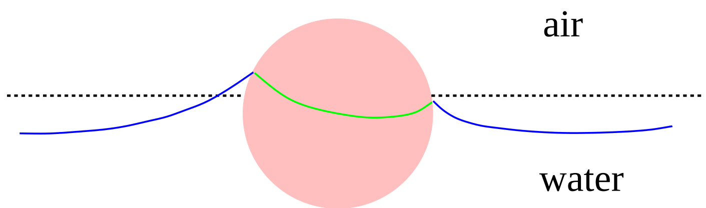
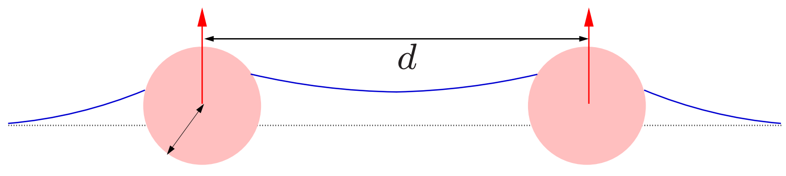




effective capillary interaction $\Rightarrow$ screened 2D gravity

two colloids: capillary monopoles

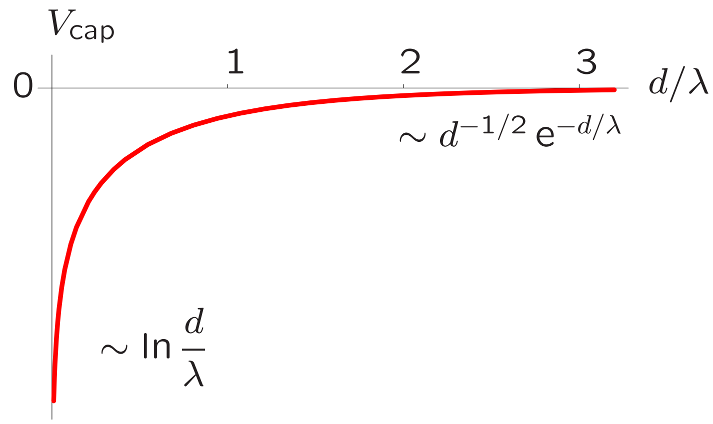


capillary monopole: f = vertical force

capillary force: $F = -V'_{\text{cap}}(d)$

effective potential:

$$V_{\text{cap}}(d) = -\frac{f^2}{2\pi\gamma} K_0\left(\frac{d}{\lambda}\right)$$



mean interparticle separation $\ell \sim 10 - 100\ \mu$m

capillary length $\lambda \approx 1$ mm

$\Rightarrow$ plasma parameter (number of interacting neighbors) $(\lambda/\ell)^2 \sim 10^2 - 10^4 \gg 1$

$\Rightarrow$ long–ranged

λ, f, γ, R, ℓ easily tunable in experiments

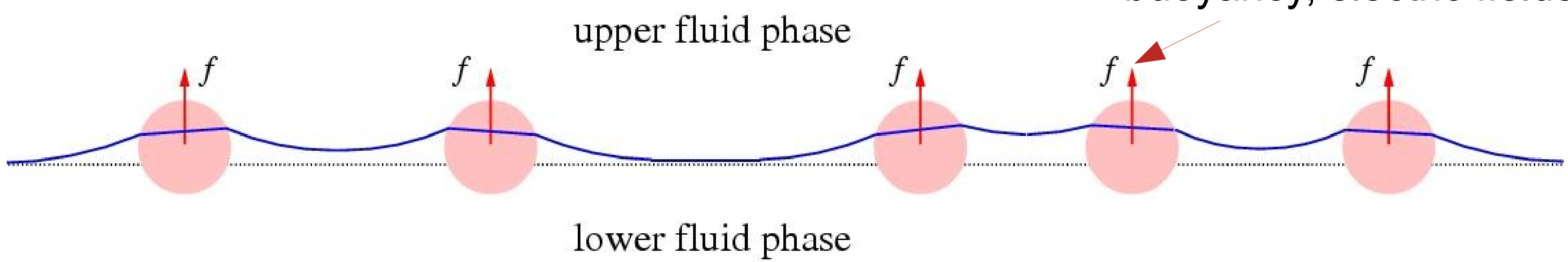
Kralchevsky & Nagayama, Adv. Colloid Interface Sci. (2000)   Oettel & S.D., Langmuir (2008)

several colloids

$$\Pi = f\,\delta(\boldsymbol{r}) \;\rightarrow\; u = \frac{f}{2\pi\gamma} K_0\left(\frac{r}{\lambda}\right) \approx \frac{f}{2\pi\gamma} \ln\left(\frac{r}{\lambda}\right)$$

single particle = capillary monopole
= mass in a 2d world

buoyancy, electric fields ...



$$V(d) \approx -f\,u(d) \approx \frac{-f^2}{2\pi\gamma} \ln\left(\frac{d}{\lambda}\right)$$

"gravitational" potential between two colloids
cut off at capillary length λ

gravity: $f \sim R^3 \;\rightarrow\; V \sim R^6$

colloids at water-air interfaces

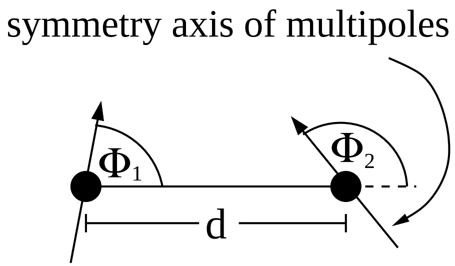
$R = 10\,\mu m \;\rightarrow\; V \sim 1\,k_B T$

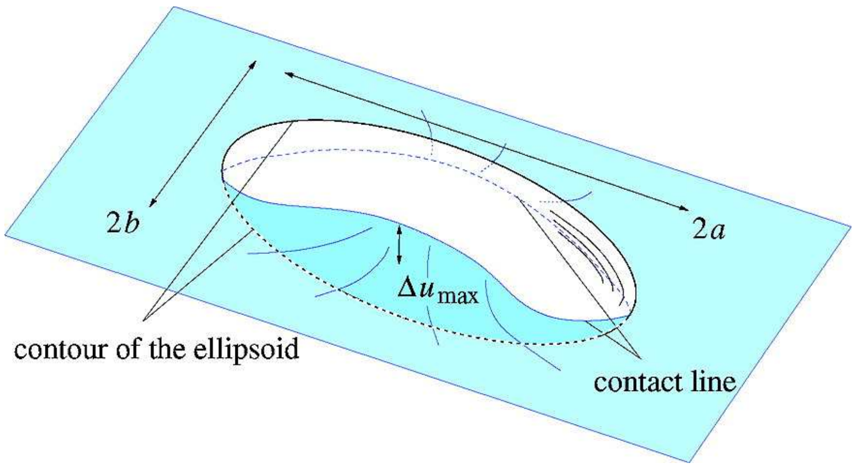
$R = 1\,\mu m \;\rightarrow\; V \sim 10^{-6}\,k_B T$

capillary multipoles

- two arbitrary capillary "charge distributions"
  $\Longrightarrow$ multipoles $q_l^{(1)}$ and $q_k^{(2)}$ at distance d
- capillary potential:

$$U_{\text{cap}} = \gamma \sum_{l,k \in Z \setminus 0} c_{lk}\, q_l^{(1)} q_k^{(2)} \frac{\exp(il\Phi_1 + ik\Phi_2)}{d^{|l|+|k|}}$$





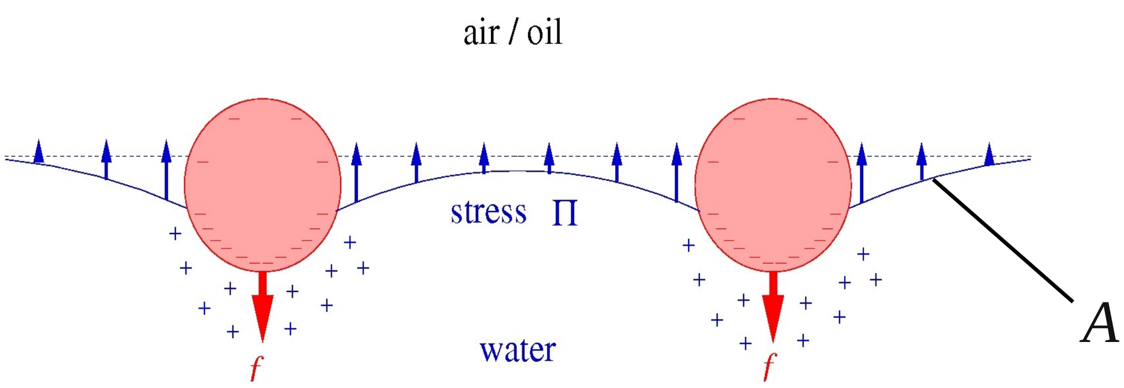
two freely floating ellipsoids: permanent capillary quadrupoles

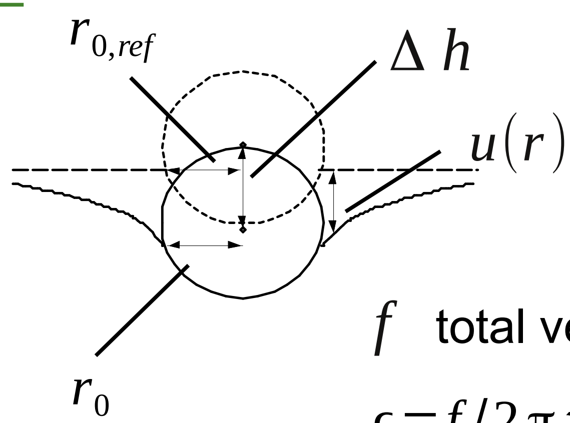
theory: $U_{\text{cap}} \sim \Delta u_{\text{max}}^2\, d^{-4}$

exp: confirmed for tip-tip
side–side: $\sim d^{-3.1}$

Loudet, PRL 97 (2006)

small charged colloids – induced multipoles





f total vertical force

$\epsilon = f / 2\pi\gamma r_{0,ref}$

$$\mathcal{F} = \gamma/2 \int_A d^2 r [(\nabla_r u)^2 + u^2/\lambda^2]$$

change of surface area and restoring force

$$-\int_A d^2 r\, \Pi(\mathbf{r})\, u(\mathbf{r}) - f\,\Delta h$$

„pulling“ the meniscus and „pushing“ the colloid

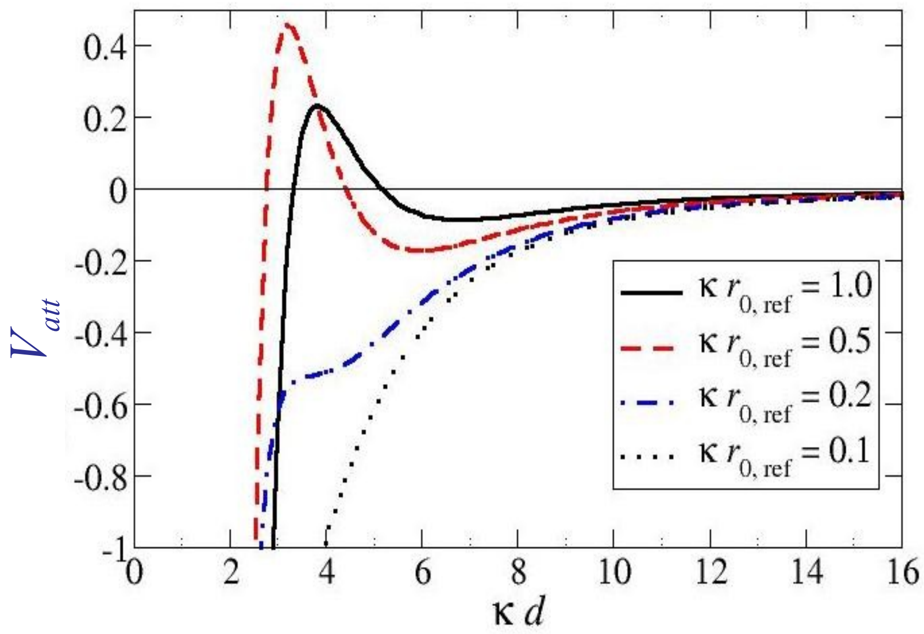
$$+\gamma/(2\mathrm{r}_0) \int_{\partial A} dl\, (u - \Delta h)^2 + O(\epsilon^3)$$

change in colloid surface energy

- need model for $\Pi(\mathbf{r})$ form renormalized electrostatics
- minimize with respect to $u(\mathbf{r})$ and h
- $V_{att} = \mathcal{F}(d) - \mathcal{F}(d\to\infty)$, V_{rep} : *direct interaction of the particles*

Dominguez, Oettel, S.D., PRE (2005), J. Chem. Phys. (2007)

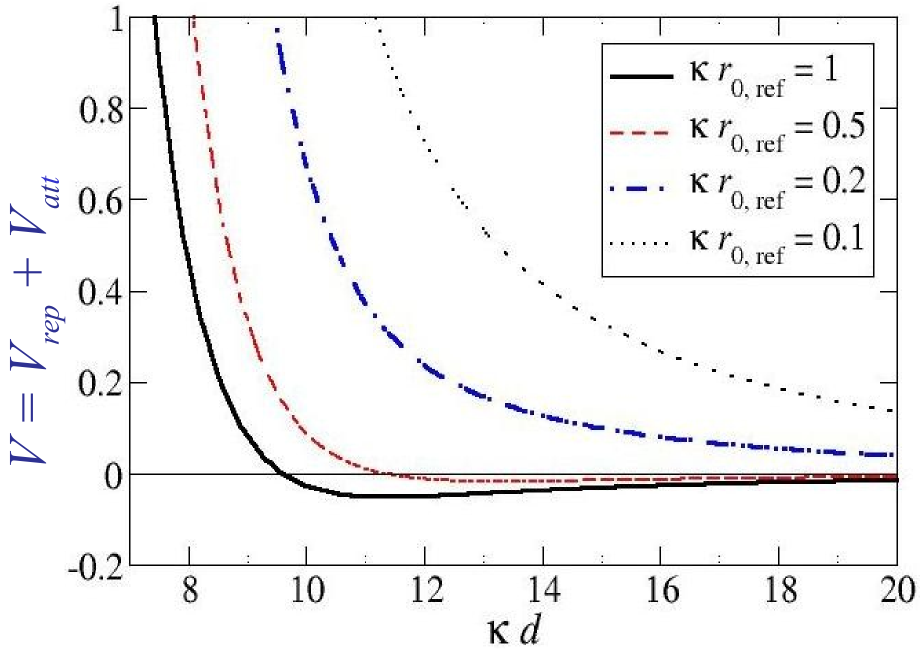
capillary potential



$\kappa^{-1} r_{0,ref} \leq 1:$

κ^{-1} additional length scale (Debye-Hueckel screening length)

total effective potential



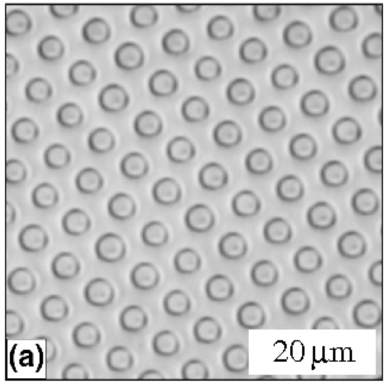
position of minimum: $\kappa d > 10$

conditions for appearance of minimum:

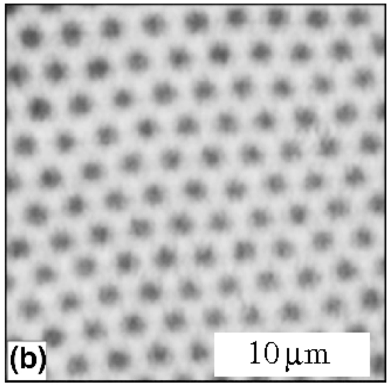
- $\kappa R \sim 1$
- $\epsilon = f / (2\pi\gamma r_0) \geq 0.5 \quad \rightarrow$
  colloidal charge density > $1 .... 5\ e / nm^2$
  (rather large)

Oettel, Dominguez, S.D., JPCM 17 (2005)

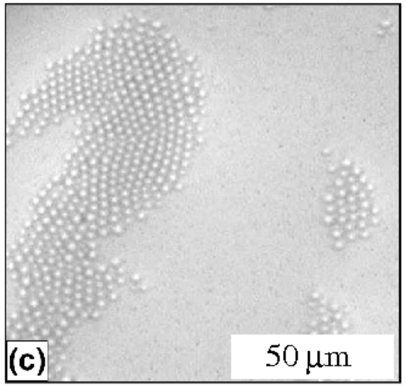
effective interactions of colloids on nematic films



$2R \approx 7\,\mu m \qquad h \approx 60\,\mu m$

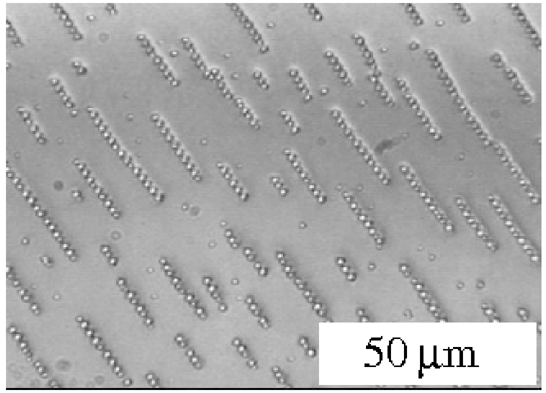


$2R \approx 1\,\mu m \qquad h \approx 60\,\mu m$



with surfactant added

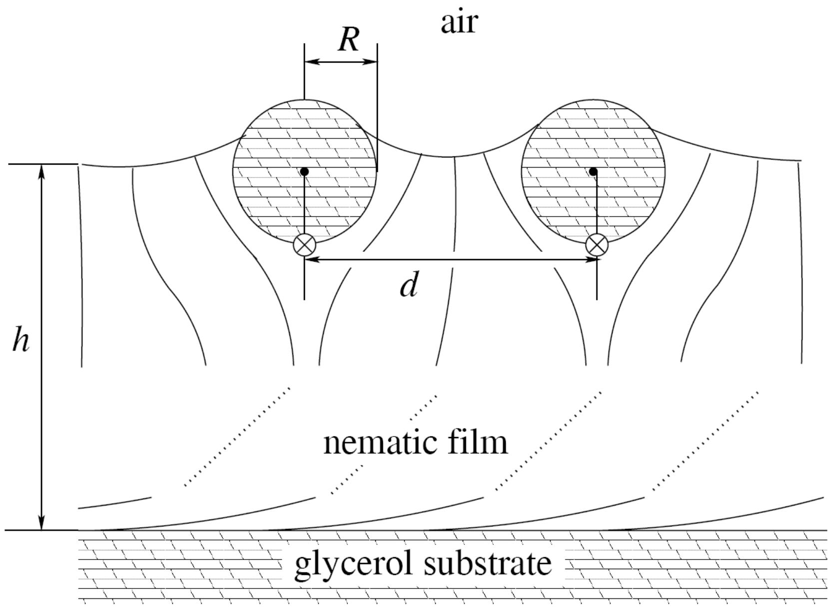
$2R \approx 1\,\mu m \qquad h \approx 60\,\mu m$



$2R \approx 7\,\mu m \qquad h \approx (7-10)\,\mu m$

cluster formation: capillary attraction vs. elastic repulsion

I. I. Smalyukh et al., Phys. Rev. Lett. ***93,*** *117801 (2004)*



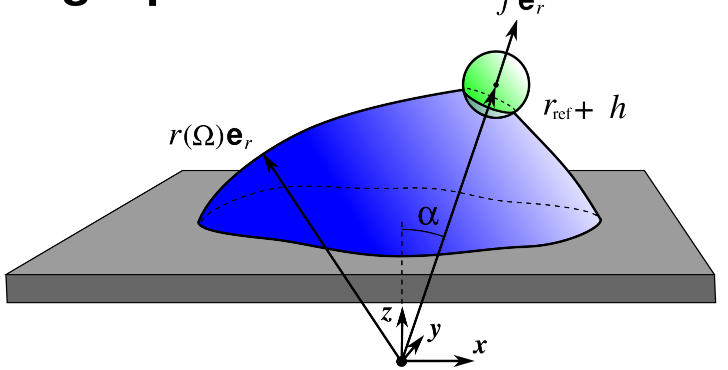
$$V_{el}(d \gg R, h \to \infty) \propto \left(\frac{R}{d}\right)^5,$$ quadrupolar repulsion

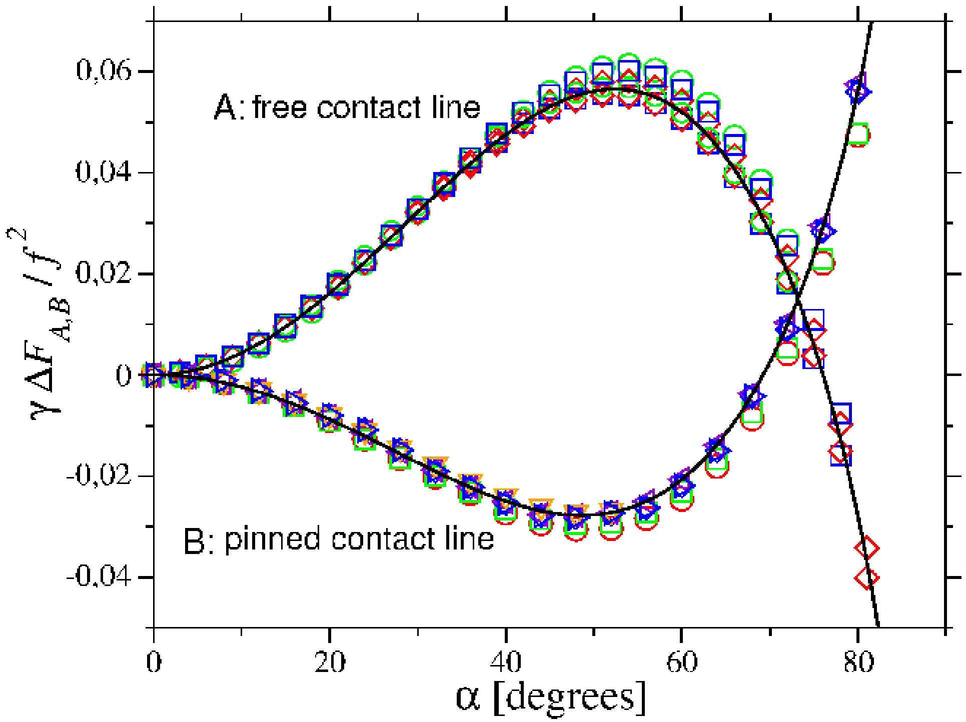
$$V_{men}(d,h) \propto \left(\frac{R}{h}\right)^6 \log\left(\frac{d}{R}\right) + |const| \left(\frac{R}{d}\right)^5,$$

M. Oettel, A. Dominguez, M. Tasinkevych and S. Dietrich, Eur. Phys. J. E (2009)

capillary interactions on sessile droplets

single particle

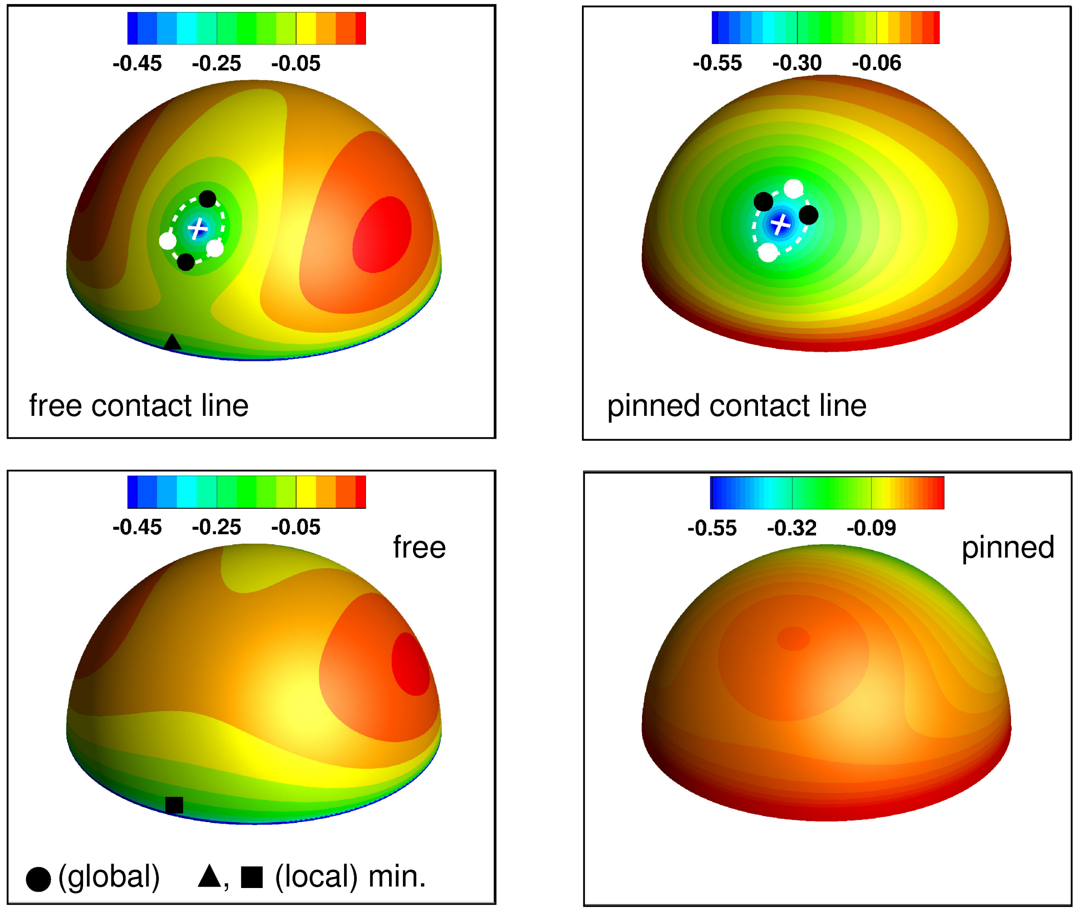




——— pointlike particle, linear analytic theory

symbols: numerical for different sizes,
contact angles, and f

fixed (+) and probe particles

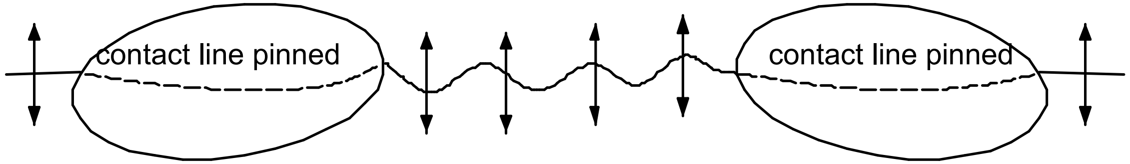


free pair sticks together and seeks global minimum

Guzowski, Tasinkevych, Dietrich, Eur. Phys. J. E (2010); Soft Matter (2011)

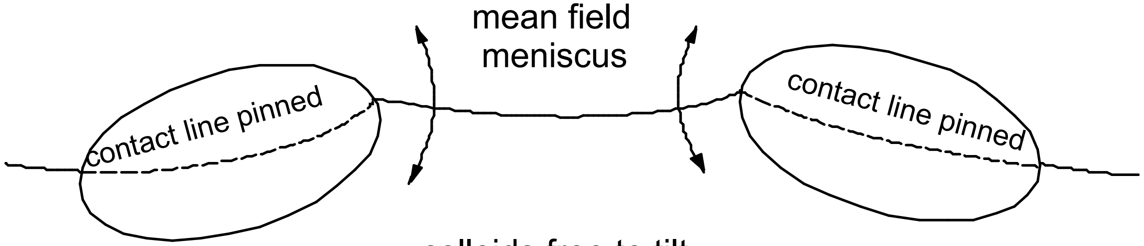
interface and colloid fluctuations

interface fluctuation (colloid and contact line fixed)



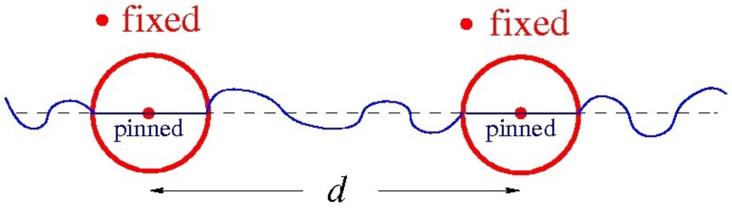
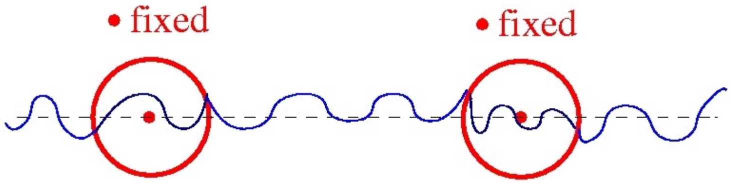
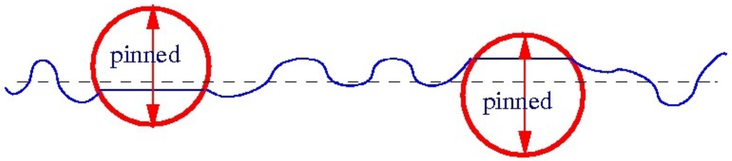
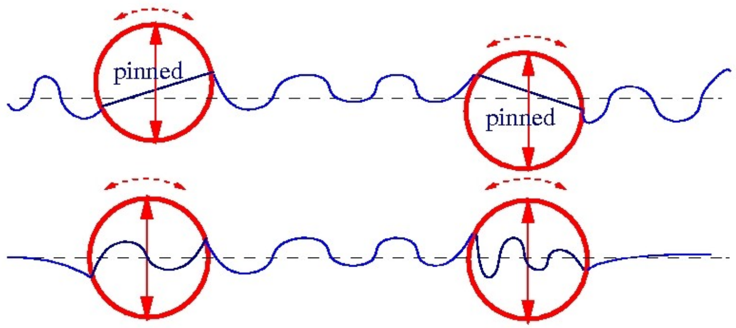
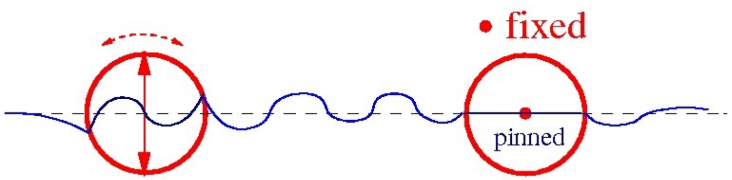
colloids are fixed

colloid fluctuations: vertical position
orientation
contact line position



colloids free to tilt

Lehle, Oettel, PRE 75 (2007)

configuration	asymptotics of fluctuation–induced potential
	$\ln \ln d$ (attractive)
	$\ln \ln(\text{const} + d)$ (attractive)
	$\frac{1}{d^4}$ (attractive)
	$\frac{1}{d^8}$ (attractive)
	$\frac{1}{d^6}$ (repulsive)

fluid of capillary monopoles

long range, screened

$$\nabla^2 U - \frac{U}{\lambda^2} = -\frac{f}{\gamma}\varrho$$

particle conservation

$$\frac{\partial \varrho}{\partial t} = -\nabla \cdot (\varrho \mathbf{v})$$

overdamped (Stokesian) dynamics

$$\varrho \frac{\mathbf{v}}{\Gamma} = -\nabla p + f \varrho \nabla U$$

self–gravitating fluid

long range

$$\nabla^2 \Phi = 4\pi G m \varrho$$

particle conservation

$$\frac{\partial \varrho}{\partial t} = -\nabla \cdot (\varrho \mathbf{v})$$

inertial (Newtonian) dynamics

$$\varrho \left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{v}\right] = -\nabla p - m\varrho\nabla\Phi$$

f: capillary monopole
ϱ: colloid number density
p: pressure
λ: capillary length
Γ: mobility
∇ $= \nabla_{||}$

ϱ: particle number density
p: pressure

mean-field diffusion equation (ensemble averaged)

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) = \Gamma \nabla [\rho \nabla \frac{\delta \mathcal{F}}{\delta \rho(\boldsymbol{r})}] \quad \text{(DDFT)}$$

$\rho_0(\boldsymbol{r})$

$$= \Gamma \nabla \cdot [\nabla p(\rho) - f \rho \nabla U]$$

"expanding" flow:
repulsive 2d pressure

"collapsing" flow:
attractive capillarity

coarse-grained (averaged) interface deformation:

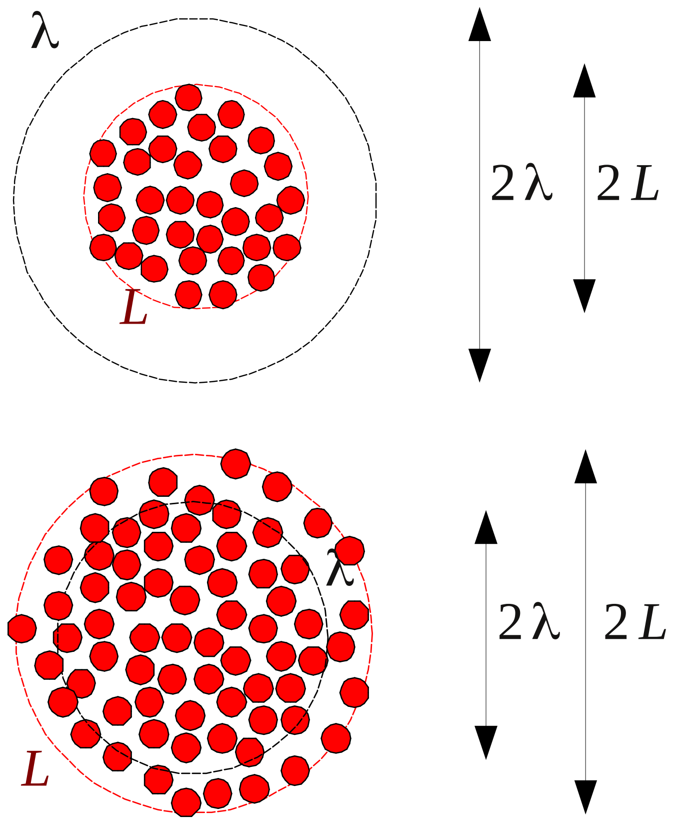
$$\nabla^2 U(\boldsymbol{r}) - \frac{1}{\lambda^2} U(\boldsymbol{r}) = -\frac{f}{\gamma} \rho(\boldsymbol{r}) \longrightarrow U[\rho(\boldsymbol{r}), f, \lambda]$$

screened Poisson equation

attractive energy of a colloidal cluster

capillary energy per particle

$$e_{cap} = \frac{1}{N} \sum_{i<j} V(r_{ij}) \approx -\rho L^2 \frac{f^2}{8\gamma} \times \begin{cases} \left(1 + 2 \ln \frac{\lambda}{L}\right) \\ \frac{\lambda^2}{L^2} \end{cases}$$



energy per particles from repulsions: e_{short}

due to thermal motion ($\longrightarrow p[\rho(\boldsymbol{r})]$), colloidal hard cores, charges, ...

Dominguez, Oettel, S.D., PRE 82, 011402 (2010)
Pergamenshchik, PRE 85, 021403 (2012)

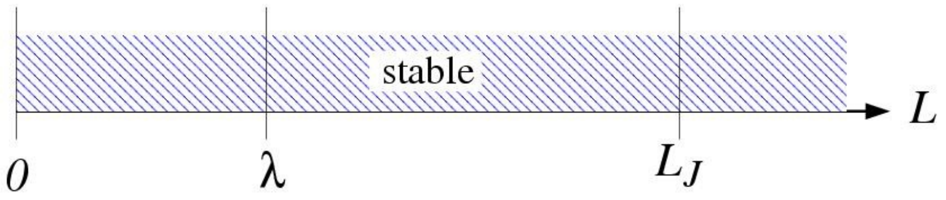
cluster stability

critical system size = Jeans' length

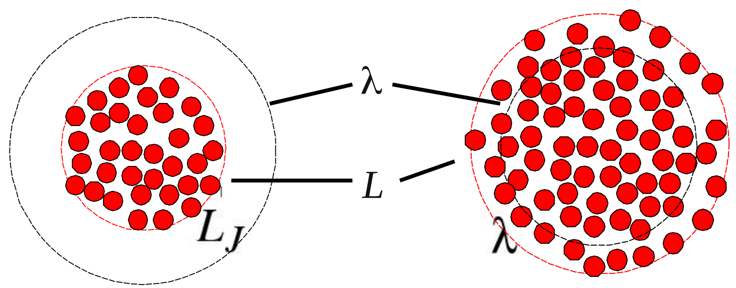
$$e_{cap} = e_{short} \rightarrow L_J \simeq \frac{1}{f}\sqrt{8\frac{\gamma}{\rho}e_{short}}$$

For $e_{short} \sim k_B T$, a classic result is recovered:
J. H. Jeans,
“The Stability of a Spherical Nebula", Philosophical Transactions of the Royal Society of London A 199,1 (1902)

homogeneous distribution stable for any size L

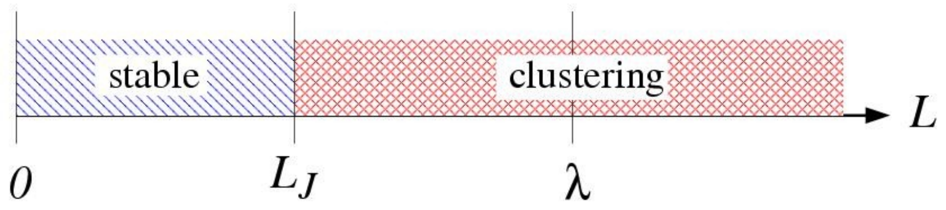


$e_{cap} \sim L^2$



$e_{cap} \sim \lambda^2$

homogeneous distribution stable for $L < L_J$



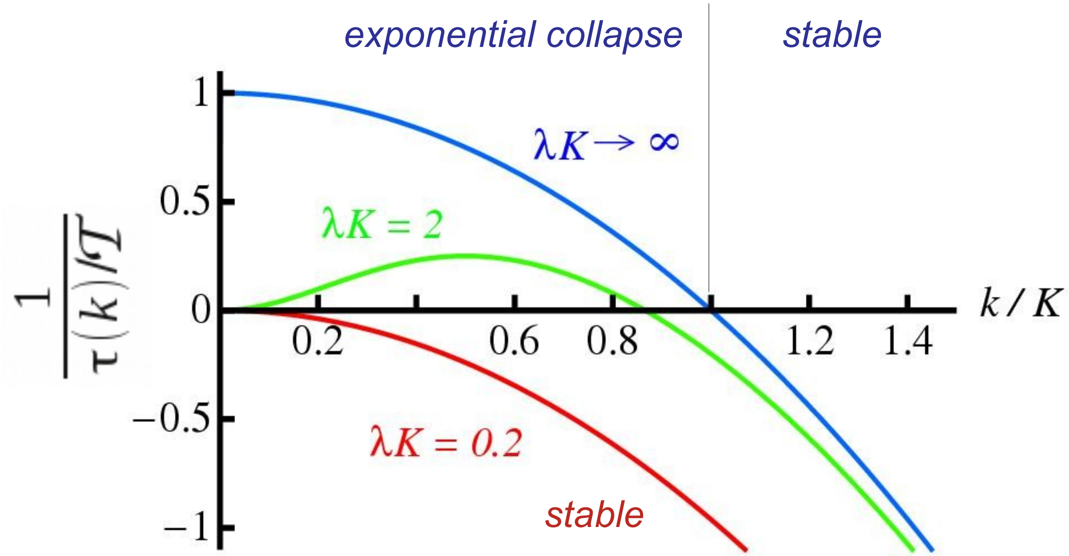
system collapses until new equilibrium is reached

linear stability analysis

mean field diffusion equation:

$$\rho(\boldsymbol{r},t)=\rho_0+\delta\rho(\boldsymbol{r},t)$$
$$U(\boldsymbol{r},t)=U_0+\delta U(\boldsymbol{r},t)$$

Fourier transform and linear stability analysis: $\delta\tilde{\rho}(k,t)\sim e^{t/\tau(k)}$



$\lambda K \leq 1$: all modes stable

characteristic scales:

Jeans' length

$$\frac{1}{K}=\frac{1}{f}\sqrt{\frac{\gamma\, p'(\rho_0)}{\rho_0}}$$

Jeans' time

$$\mathcal{T}=\frac{\gamma}{\Gamma f^2\rho_0}$$

experimental realization of collapse

conditions:

$$\frac{1}{\sqrt{\rho_0}} \ll \lambda, \quad R < \frac{1}{K} < \lambda$$

initial density

with reduced mean interparticle separation $q = \frac{1}{\sqrt{\rho_0}} / R$

particle radius

example: charged colloids at air-water interface

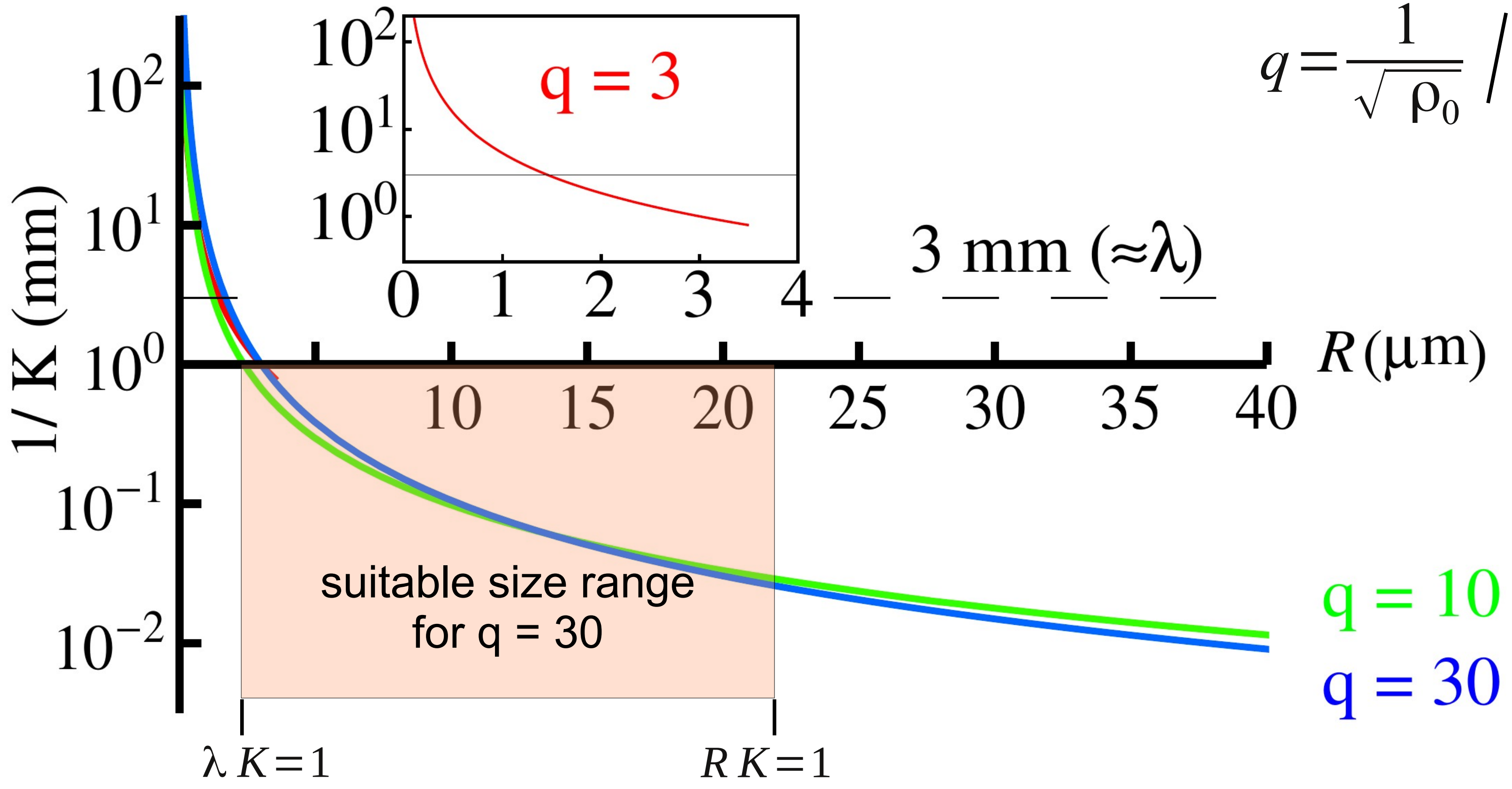
Jeans' length

$$\frac{1}{K} = \frac{1}{f}\sqrt{\frac{\gamma\, p'(\rho_0)}{\rho_0}} = \frac{1}{K(R,q)}$$

exp.: f due to external *electric* field ⟶ induced dipoles ⟶

dipole-dipole int. ⟶ $p(\rho_0)$ from MC

$$q = \frac{1}{\sqrt{\rho_0}} \Big/ R$$



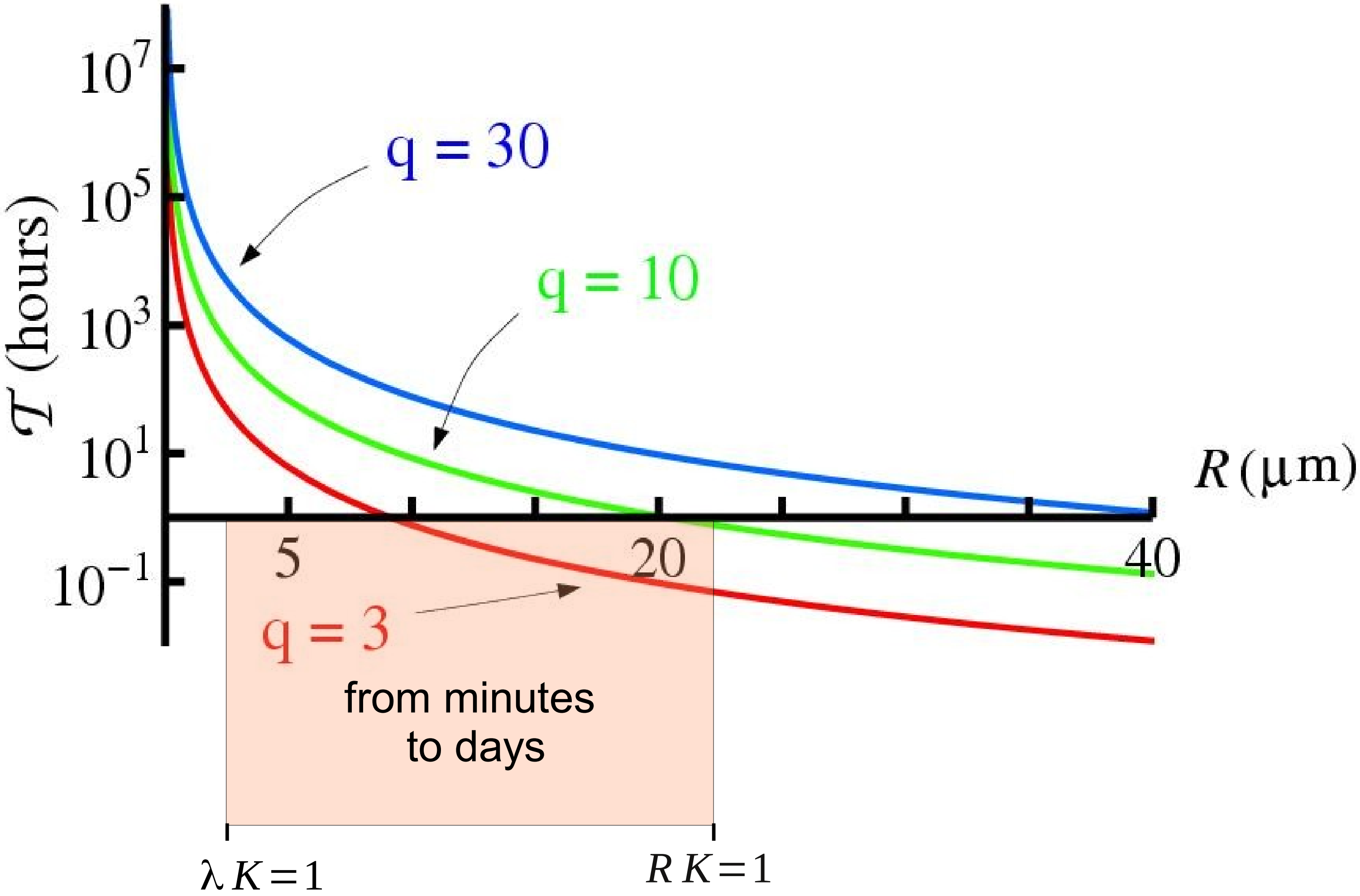
Aubry, Singh, Janjua, Nudurupati, PNAS 105, 3711 (2008)
Dominguez, Oettel, S.D., PRE 82, 011402 (2010)

Jeans' time

$$\mathcal{T} = \frac{\gamma}{\Gamma f^2 \rho_0}$$

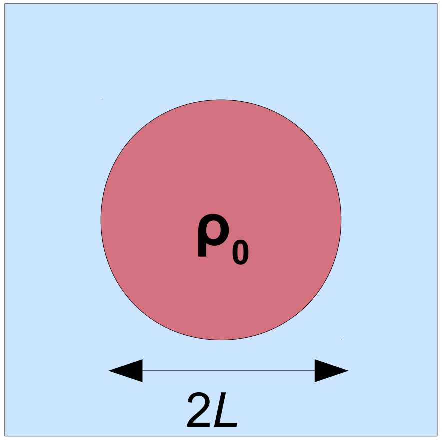
gravity: $f(R) \sim R^3$

$$\Gamma(\text{water}) = \frac{1}{3\pi\eta R}$$



R range as for 1/K, for q =10

collapse dynamics



- Brownian dynamics simulation with realistic parameters

- solution of diffusion equation

$$\frac{\partial\hat{\rho}}{\partial\hat{t}} = -\hat{\nabla}\cdot\left[-\hat{\rho}\hat{\nabla}\hat{U}(\hat{\lambda}) - T_{eff}\hat{\nabla}\hat{p}(\hat{\rho})\right] \qquad T_{eff} = \frac{\gamma k_B T}{f^2 \rho_0 L^2}$$

- perturbation theory around
  cold collapse solution of diffusion eq.
  for $T_{eff} = 0$, $1/\lambda = 0$

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

$$\hat{L}(\hat{t}) = \sqrt{1-\hat{t}}$$

uniform collapse, singularity at $t = \mathcal{T}$

$$\hat{r} = \frac{r}{L},\ \hat{t} = \frac{t}{\mathcal{T}},\ \hat{\lambda} = \frac{\lambda}{L},\ \hat{U} = \frac{U}{L},\ \hat{\rho} = \frac{\rho}{\rho_0},\ \hat{p} = \frac{p}{k_B T \rho_0}$$

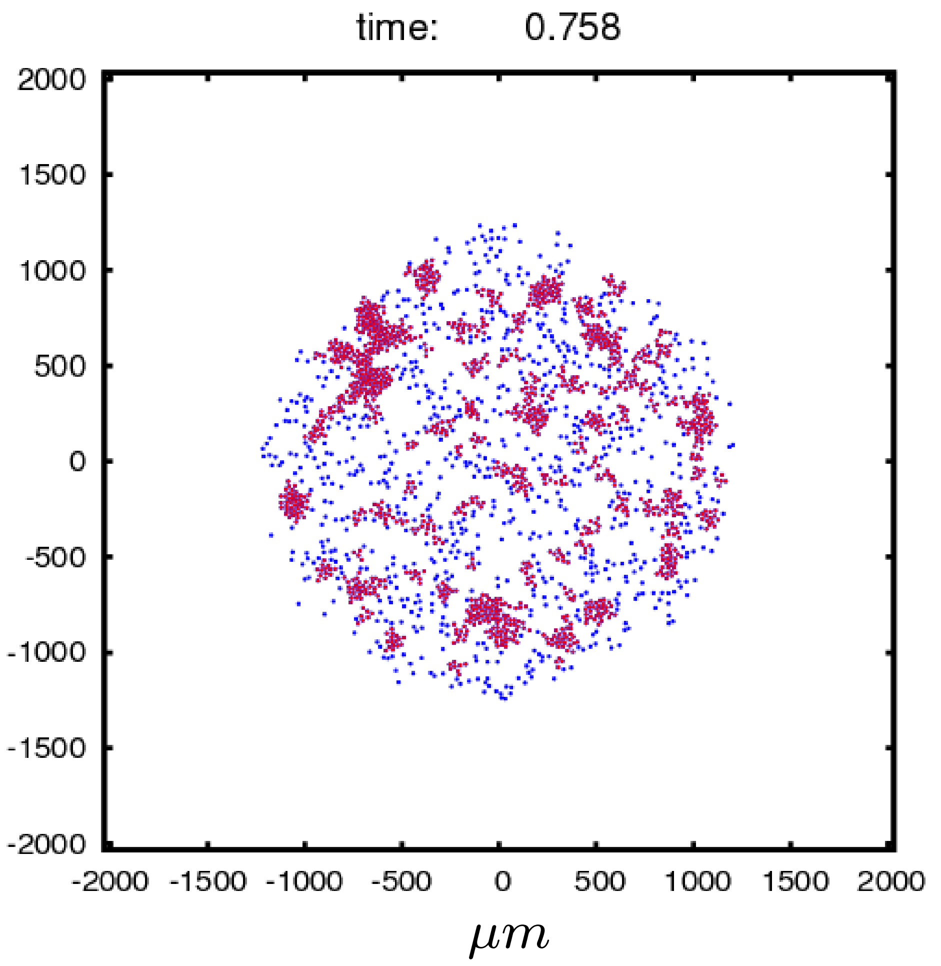
Brownian dynamics simulation

$T_{\text{eff}} = 3.1 \times 10^{-4}$

$\lambda/L = \hat{\lambda} = 1.50$

$\lambda = 80.0 L_J$

red particles:
parts of a cluster
($\geq$ 3 neighbors within $3.25R$)



gravitational collapse

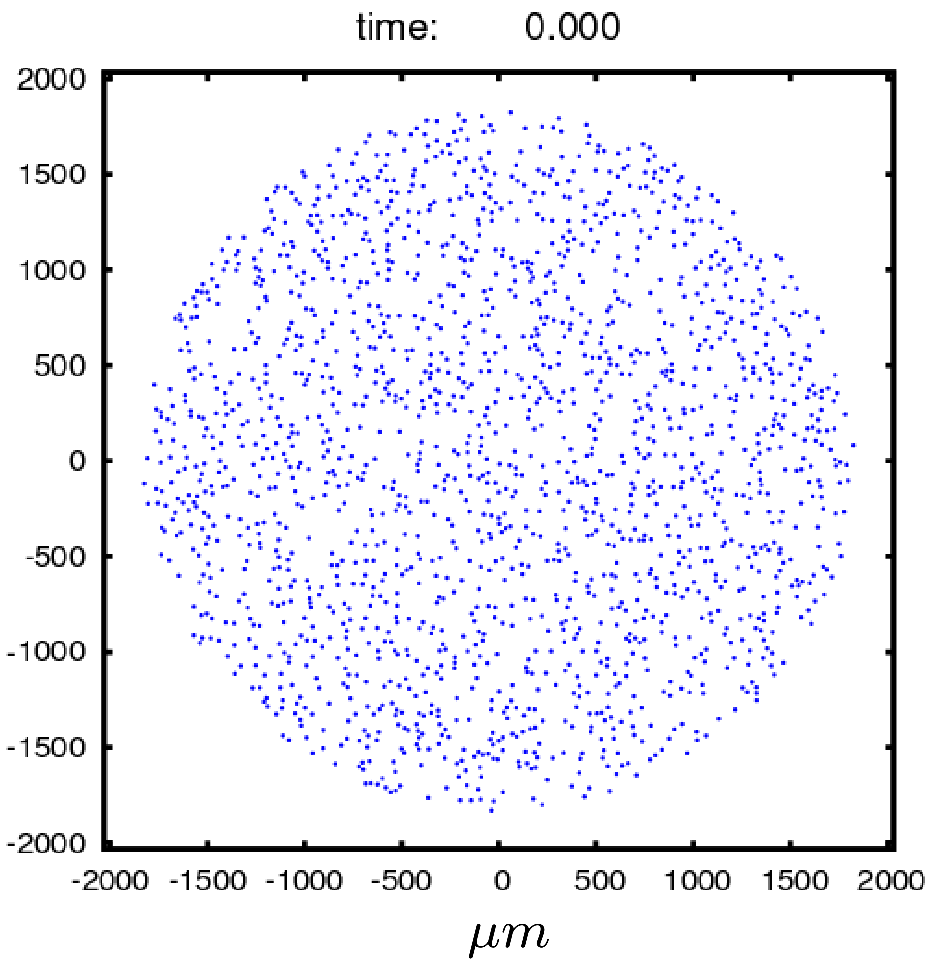
Brownian dynamics simulation

$T_{\text{eff}} = 3.1 \times 10^{-4}$

$\lambda/L = \hat{\lambda} = 0.25$

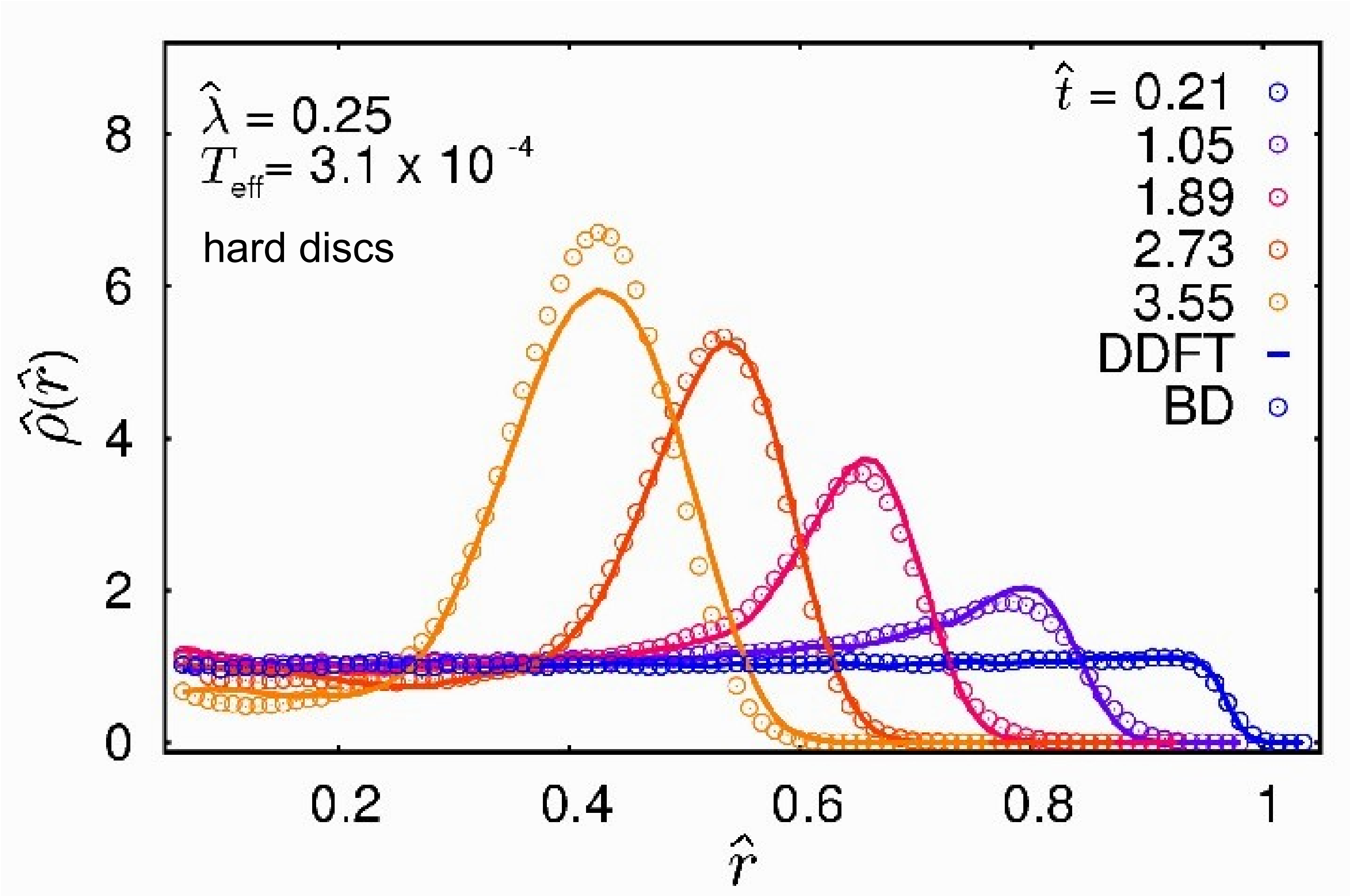
$\lambda = 13.3 L_J$

red particles:
parts of a cluster
($\geq$ 3 neighbors within $3.25R$)



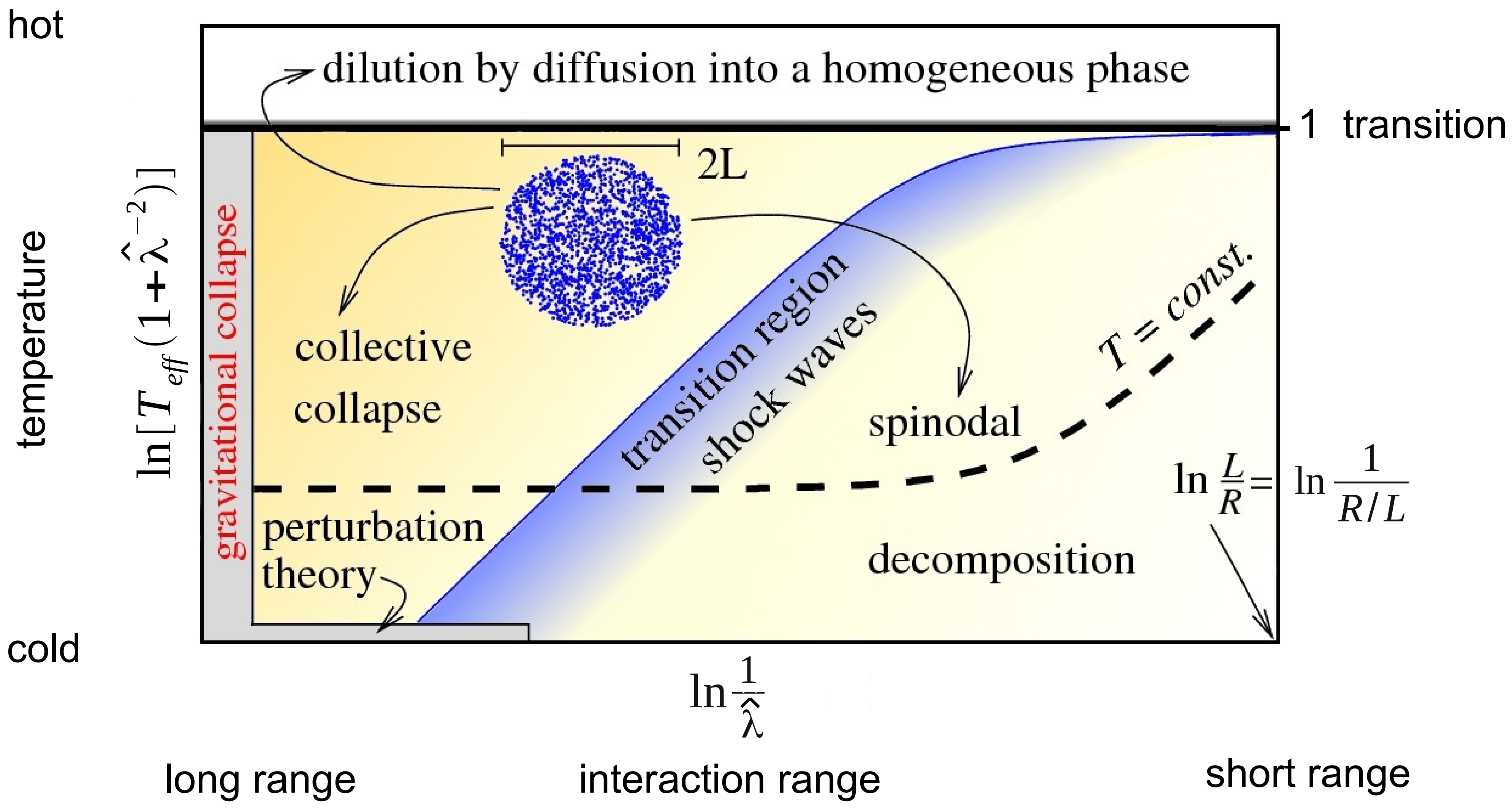
shockwave formation

appearance of a travelling shock wave



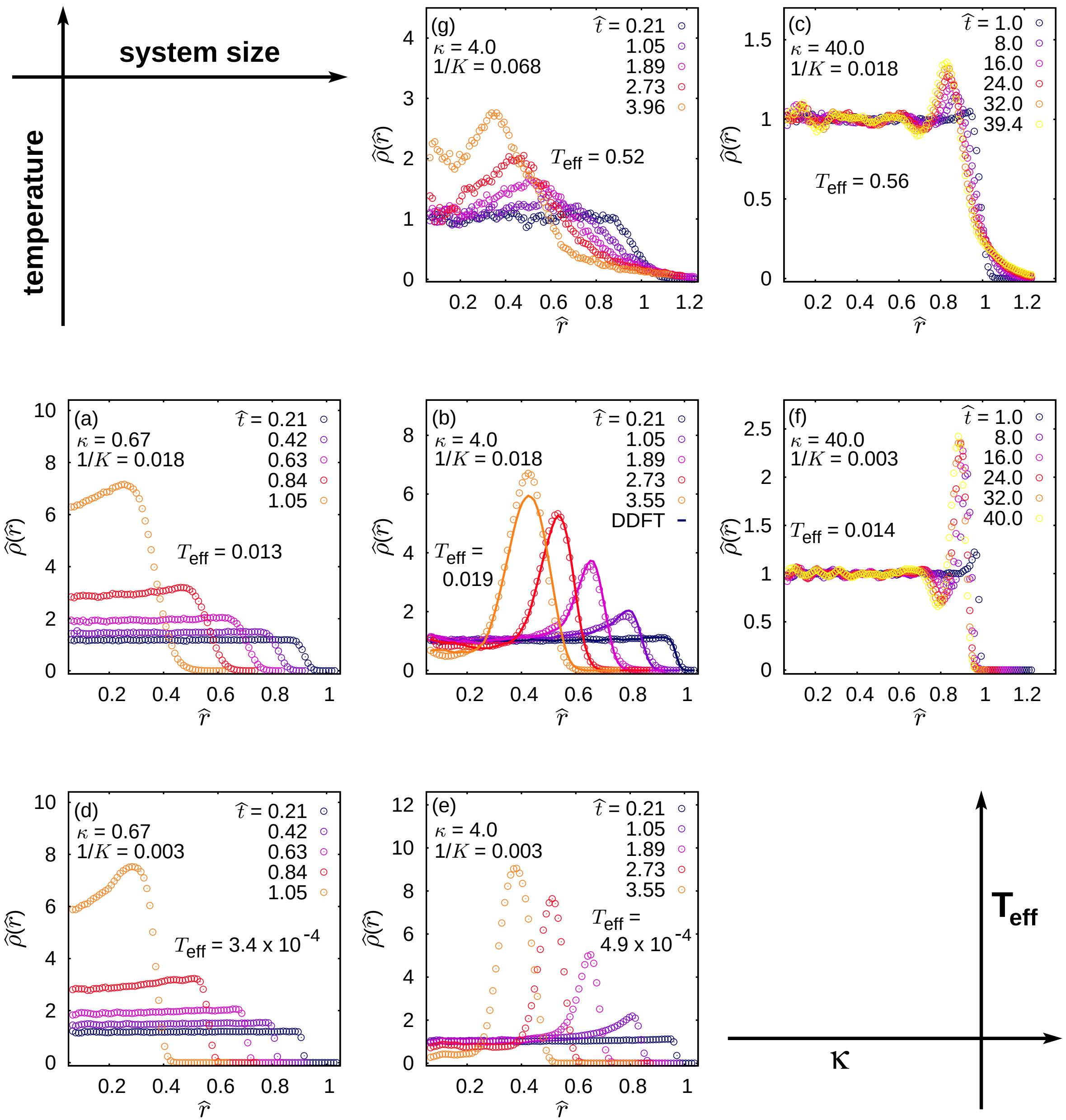
$\rho_0(\hat{r}, L)$: discrete initial distribution (see BD)

tentative dynamic "phase diagram"



Bleibel, S.D., Dominguez, Oettel, PRL 107, 128302 (2011)
Bleibel, Dominguez, Oettel, S.D., EPJ E 34, 125 (2011)

dynamic phase diagram ↔ Brownian dynamics simulations



$$\kappa = 1/\widehat{\lambda}$$

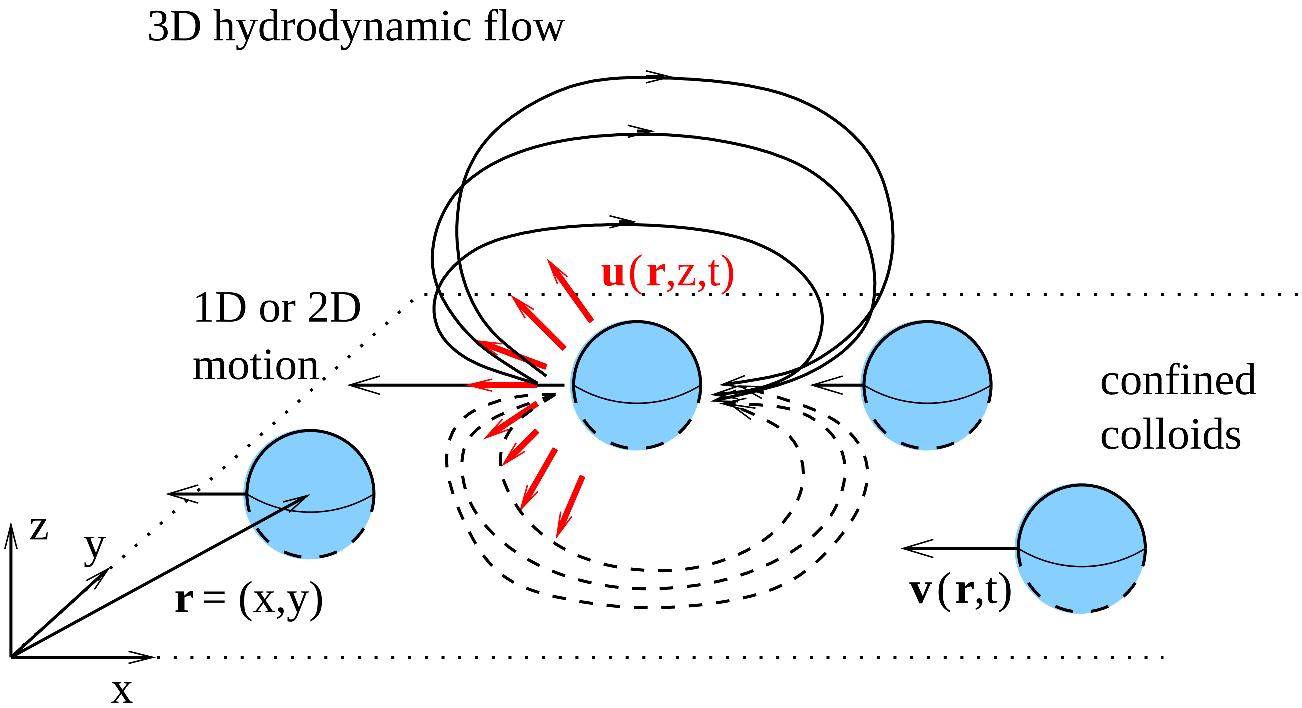
Bleibel, SD, Domínguez,

Oettel, Soft Matter (2014)

Supplementary Informations

Confined colloids: Hydrodynamic interactions

- Colloids trapped at a fluid interface: partially confined motion



Bleibel, Domínguez, Günther, Harting,Oettel, Soft Matter Comm. (2014)

Bleibel, Domínguez, Oettel, JPCM (2015)

Hydrodynamic interactions

- Overdamped dynamics appropriate for microparticles

- include hydrodynamic interactions perturbatively on the two–particle level

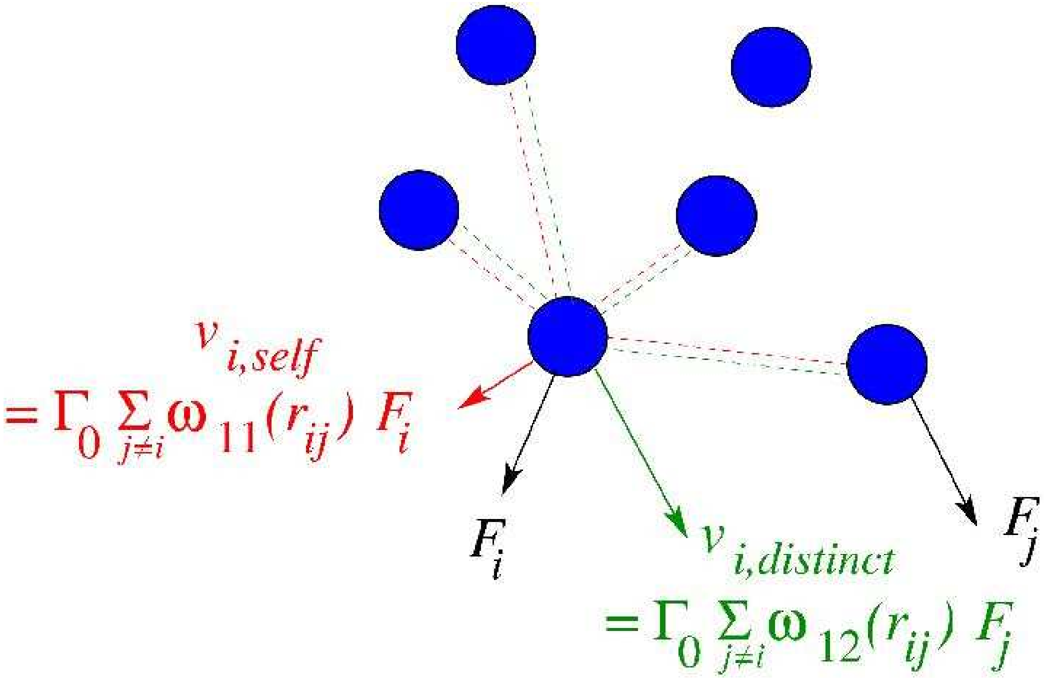
On the individual particle level (pair-terms only):

$$\begin{aligned} \vec{v}_i &= \boldsymbol{D}_{ij} \vec{F}_j^{ext} + noise \\ \boldsymbol{D}_{ij} &= \Gamma_0 \mathbb{1} \delta_{ij} + \boldsymbol{D}^{(2)}(\vec{r}_i - \vec{r}_j), \quad \Gamma_0 = \frac{1}{6\pi\eta a} \end{aligned}$$

Self and distinct interaction terms:

$$\boldsymbol{D}^{(2)}(\vec{r}_{ij}) = \Gamma_0 \left[\delta_{ij} \sum_{i \neq l} \boldsymbol{\omega}_{1\leftrightarrow 1}(\vec{r}_{il}) + (1 - \delta_{ij}) \boldsymbol{\omega}_{1\leftrightarrow 2}(\vec{r}_{ij}) \right]$$

Hydrodynamic interactions



- neglect self term ($\boldsymbol{\omega}_{1\leftrightarrow 1}(\vec{r}) \propto r^4$)
- use bulk Rotne Prager Tensor for distinct part:

$$\boldsymbol{\omega}_{1\leftrightarrow 2}(\vec{r}) = \frac{3}{4}\frac{a}{r}(\mathbb{1} + \hat{\vec{r}}\hat{\vec{r}}) + \frac{1}{2}\frac{a^3}{r^3}(\mathbb{1} - 3\hat{\vec{r}}\hat{\vec{r}})$$

Stokesian Dynamics:

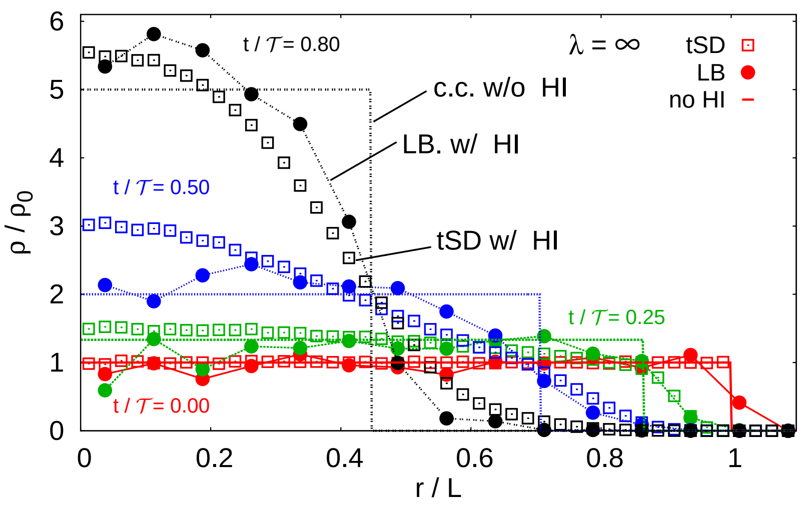
- flow field $\vec{u}$ of the 3D fluid due to point force at position $\vec{r}$

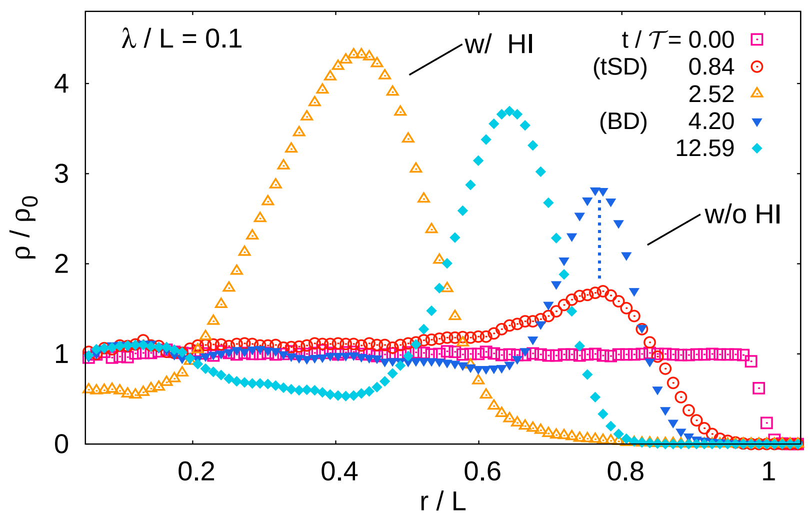
$$\eta \nabla^2 \vec{u} - \nabla p = -\delta(\vec{r})\vec{F}, \quad \nabla \cdot \vec{u} = 0$$

Stokesian dynamics simulations

- cold collapse
- infinite interaction range
- compare SD, LB3D and analytical result

- speedup of capillarity– driven collapse
- $\lambda/L = 0.1$
- compare BD and SD





Bleibel, Domínguez, Günther, Harting,Oettel, Soft Matter Comm. (2014)