EBERHARD KARLS UNIVERSITÄT TÜBINGEN

Institute of Applied Physics

Computational and Theoretical Nanoscience

Superfast anomalous diffusion at interfaces

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Johannes Bleibel
Martin Oettel

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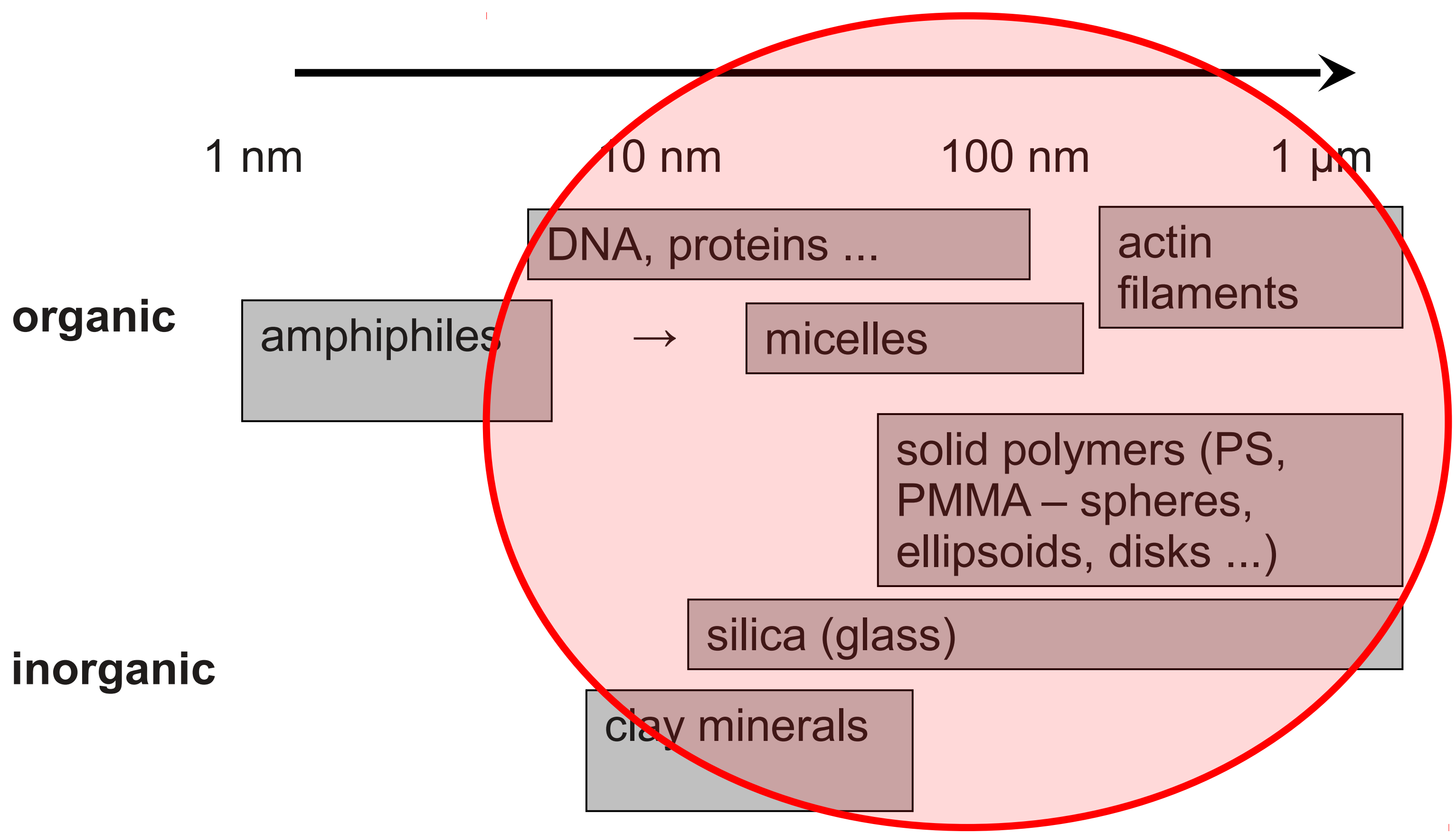
My background

- trained particle theorist (1997-2002)
- switch to liquid state theory, i.e.
  statistical physics of strongly interacting many-body systems
- associated experimental community: Soft Matter, the Colloidal Domain



The Tübingen Nanoscience Project: New paths for an interdisciplinary BSc / MSc

Biology, chemistry and physics are taught on equal footing...

The team

Biology

Klaus Harter
Microbiology of plants: signalling, transcription, bioinformatics

Erik Schäffer
Molecular machines, mechanics of bio-molecules

Chemistry

Reiner Anwander
Organometallic chemistry, nanostruc-tured materials

Andreas Schnepf
Metal-like nano-clusters

Physics

Frank Schreiber
Soft matter, physics of proteins, organic semiconduct.

Martin Oettel
Soft matter: colloids, interfaces

Content

Particles (colloids) at interfaces -a rich field for statistical physics

- Capillary interactions as pseudogravitational interactions
  (pictures, movies, etc. ... something to relax)

- Partial confinement and its impact on hydrodynamic interactions
  Anomalously fast diffusion
  (this is the actual theory part...need some equations to explain the effect!)
  On the way:
  Marangoni effect
  Some basics on hydrodynamic interactions

The Cheerio effect.

The Cheerio effect.

Cheerio effect with superhydrophobic particles.

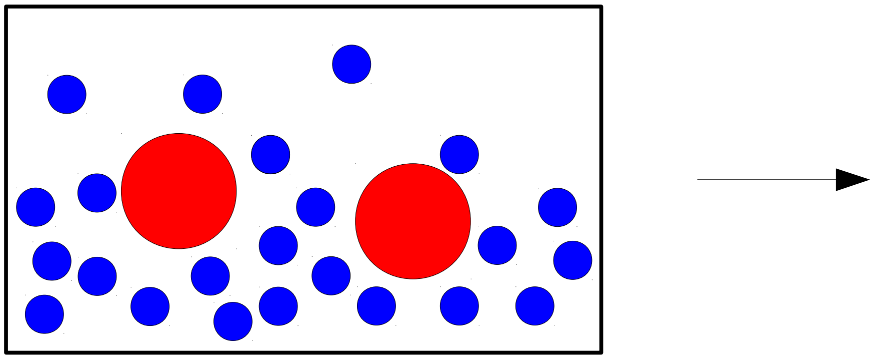
Fluid interfaces: Capillarity

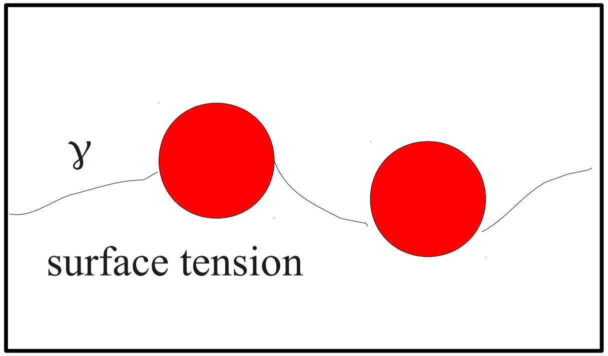
Cheerio effect with superhydrophobic particles.

Comment by a user:
"... *and that, boys and girls, is how planets are created*"

Really?

A single drawing pin floating on water illustrating the balance between surface tension and the weight of the floating object. This picture was described as the `phenomenal anti-intuitively floating-upside-down thumbtack' by the blog of the Annals of Improbable Research. (*Dominic Vella's page)*



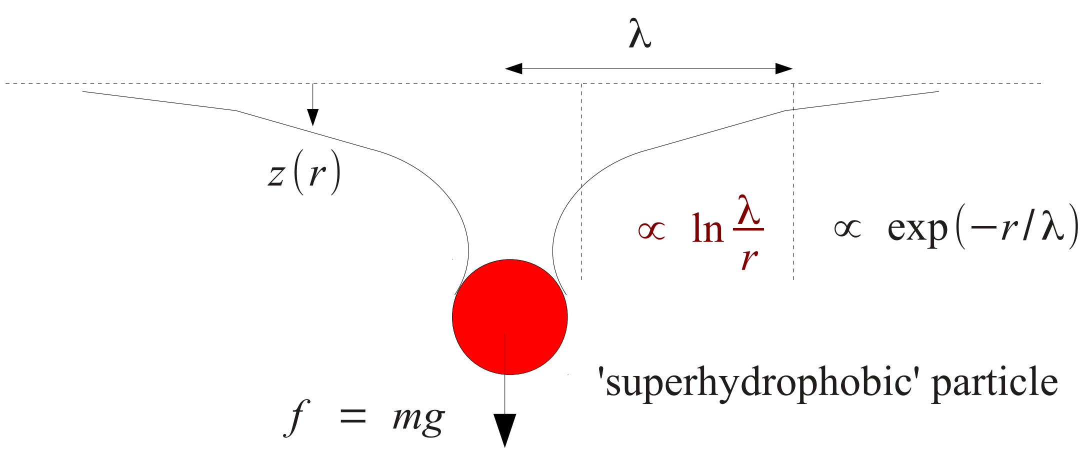


Free energy = surface energy + gravity + particle boundary energy

$$F \approx \frac{\gamma}{2} \int dx\, dy \left([\nabla z(x,y)]^2 + \frac{z(x,y)^2}{\lambda^2} \right) + \text{ boundary energy}$$

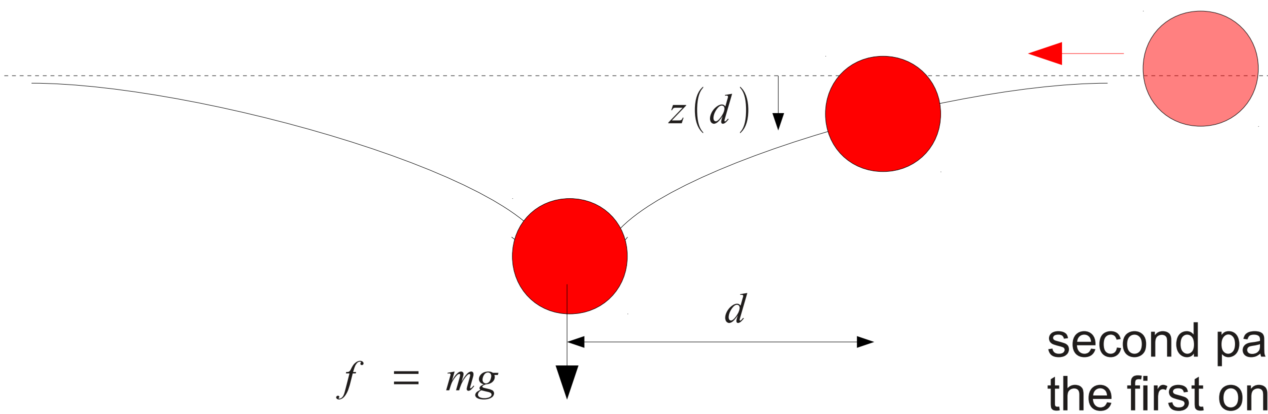
$$\lambda = \sqrt{\frac{\gamma}{g(\rho_1 - \rho_2)}} \text{ capillary length } \approx 3 \text{ mm}$$

Minimization



"long-ranged" deformation ...
up to λ

Interaction between two particles:



second particle “falls” into dimple of the first one:

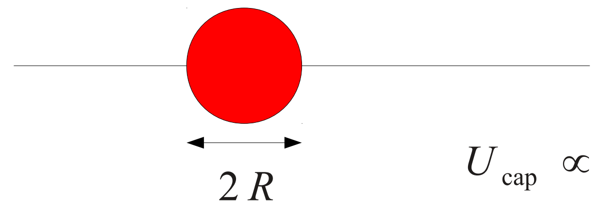
$$U_{\mathrm{cap}} = f \; z(d) \propto \frac{f^2}{\gamma} \ln\frac{d}{\lambda} \quad (d < \lambda)$$

Well, that is indeed gravitational attraction ...

- but in 2 dimensions
- with a cutoff $\lambda \sim \mathrm{mm}$
- with an extra dimension around where solvent can flow

Fluid interfaces: Capillarity as pseudogravity

Now we have to go to microscales:



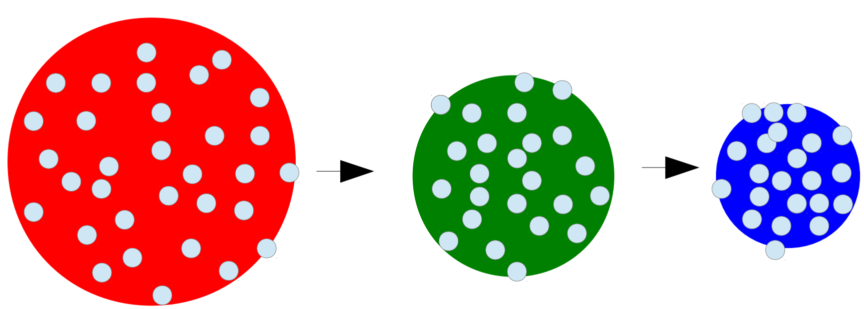
$$R \sim \mu\mathrm{m} \;\rightarrow\; \frac{f^2}{\gamma} \sim kT \qquad\qquad U_{\mathrm{cap}} \propto \frac{f^2}{\gamma} \ln\frac{d}{\lambda} \quad (d < \lambda)$$

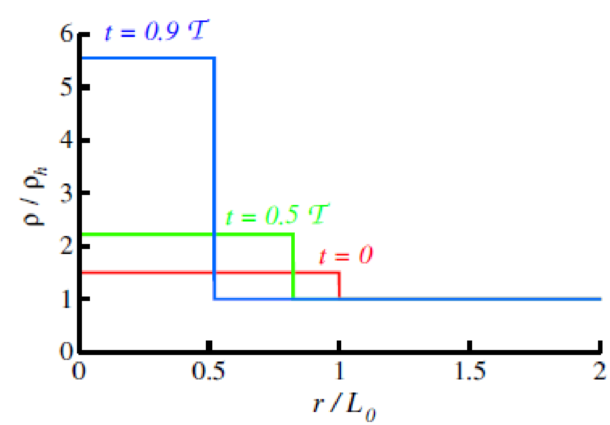
A system with Brownian motion acting against pseudogravitational attraction

If $\dfrac{f^2}{\gamma} \gg kT$ and $\lambda \rightarrow \infty$:

Cold collapse (reference model for cosmologists):

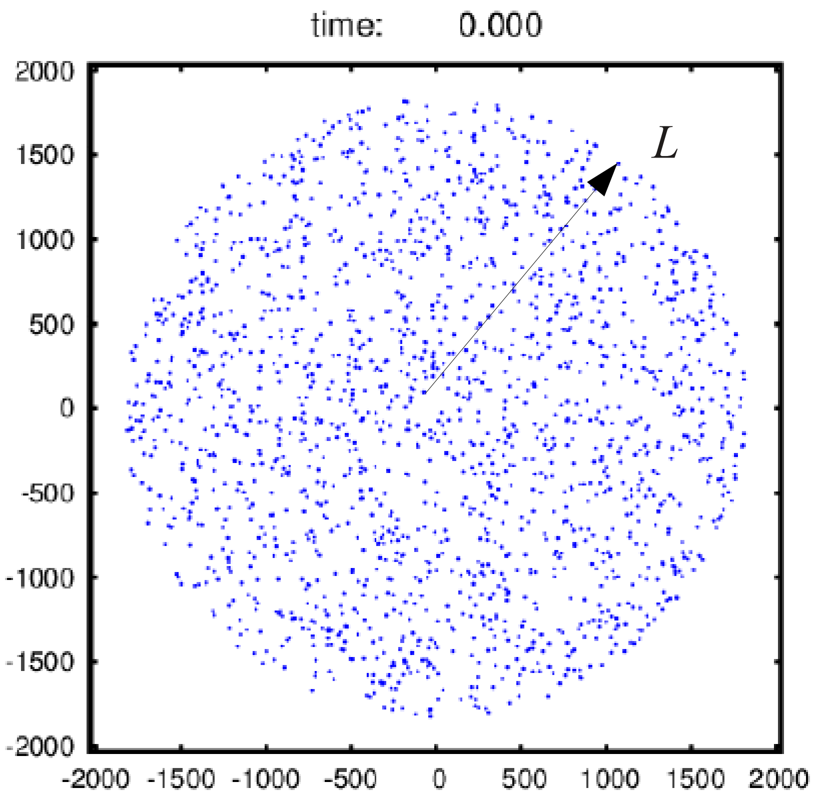
"A spherical patch of dust collapses uniformly to a point with infinite mass density."

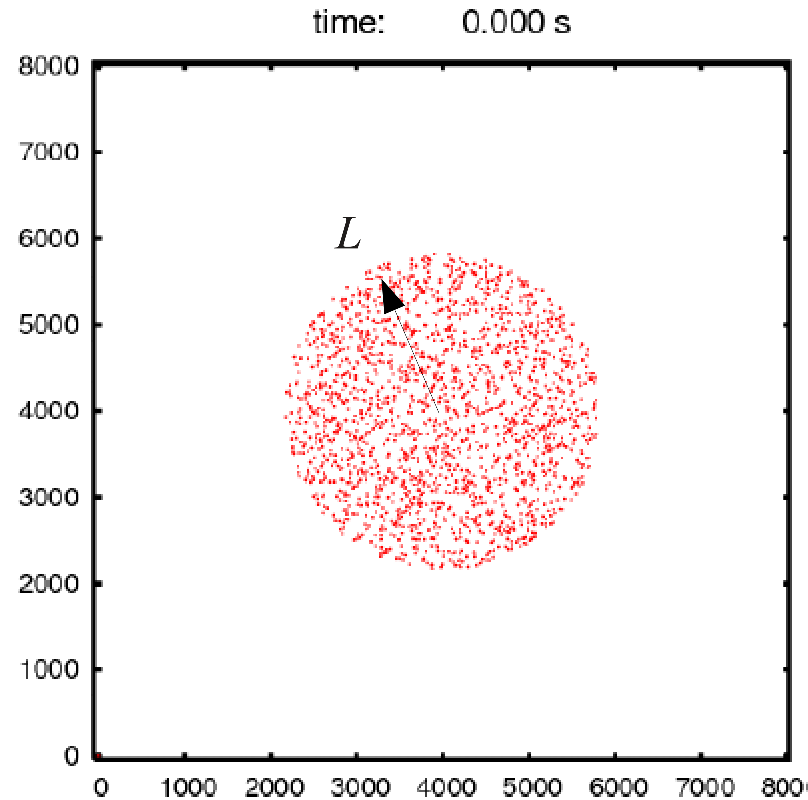




Fluid interfaces: Capillarity as pseudogravity

Brownian dynamics simulations with μm particles, room temperature





large λ : like cold collapse

$$\frac{\lambda}{L} = 1.5$$

medium λ : shock waves at rim

$$\frac{\lambda}{L} = 0.25$$

'realistic' parameters:

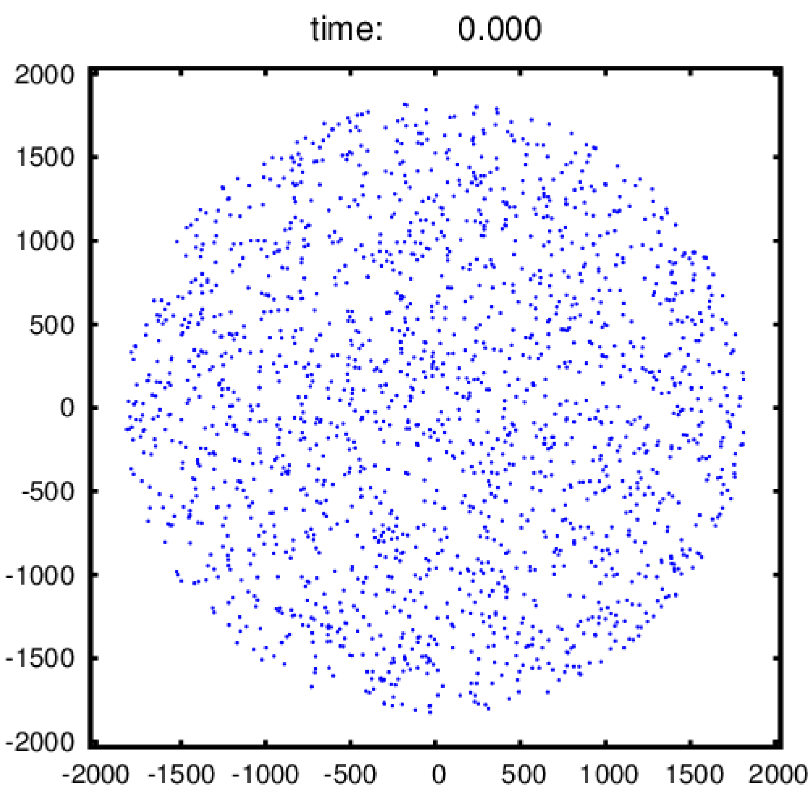
particle radius: $R = 10\,\mu\mathrm{m}$, water-air surface tension

→ maximum capillary pair attraction energy : $\sim 1\, k_B T$

patch size : $L = 1.8\,\mathrm{mm}$

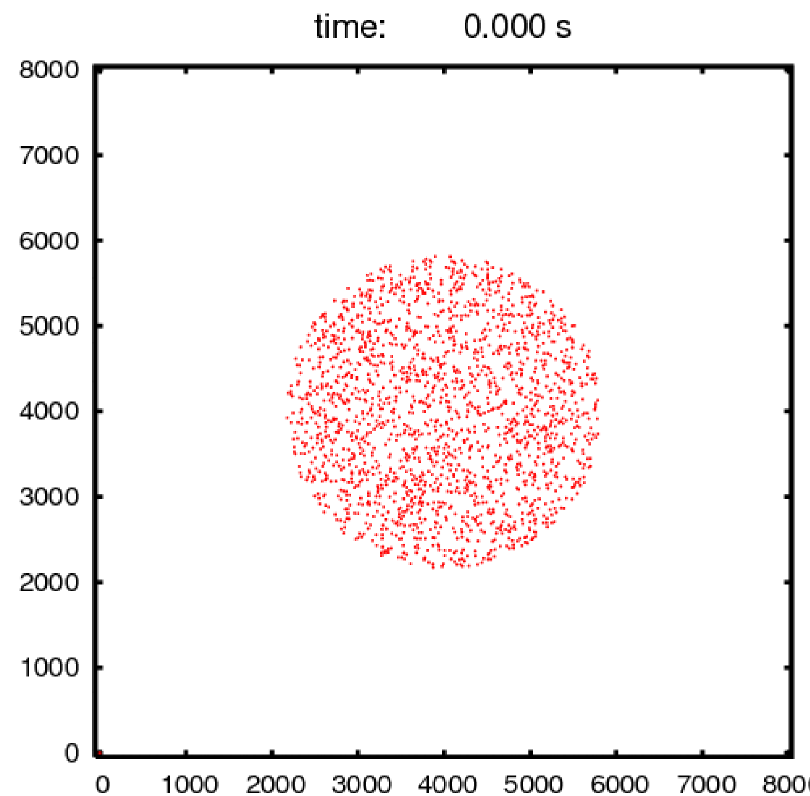
(Simulations J. Bleibel)

Brownian dynamics simulations with µm particles, room temperature



large λ : like cold collapse

$$\frac{\lambda}{L} = 1.5$$



medium λ : shock waves at rim

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→ maximum capillary pair attraction energy : $\sim 1\, k_B T$

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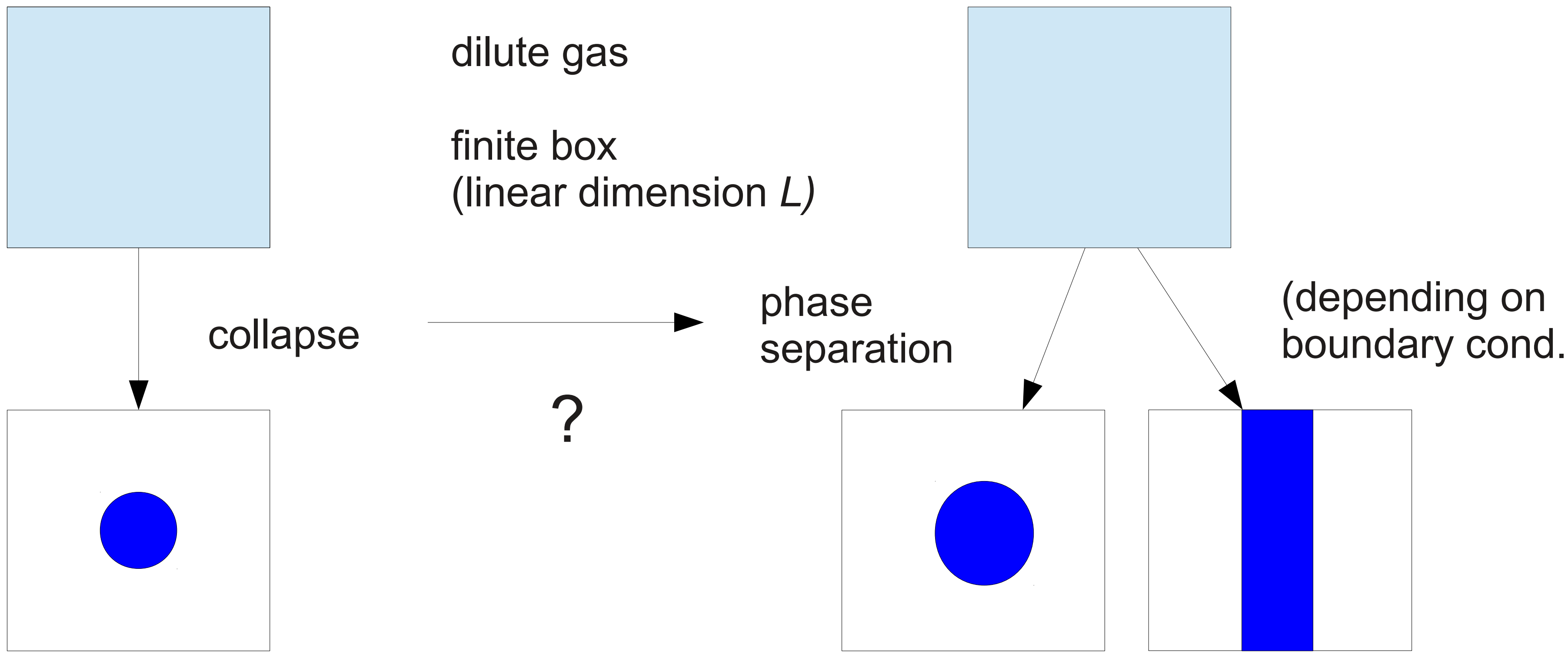
(Simulations J. Bleibel)

Fluid interfaces: Capillarity as pseudogravity

$\lambda \rightarrow \infty$: gravitation

$\lambda \rightarrow 0$: short range attraction



- all densities
- (almost) all temperatures

- densities in coexistence region
- $T < T_c$

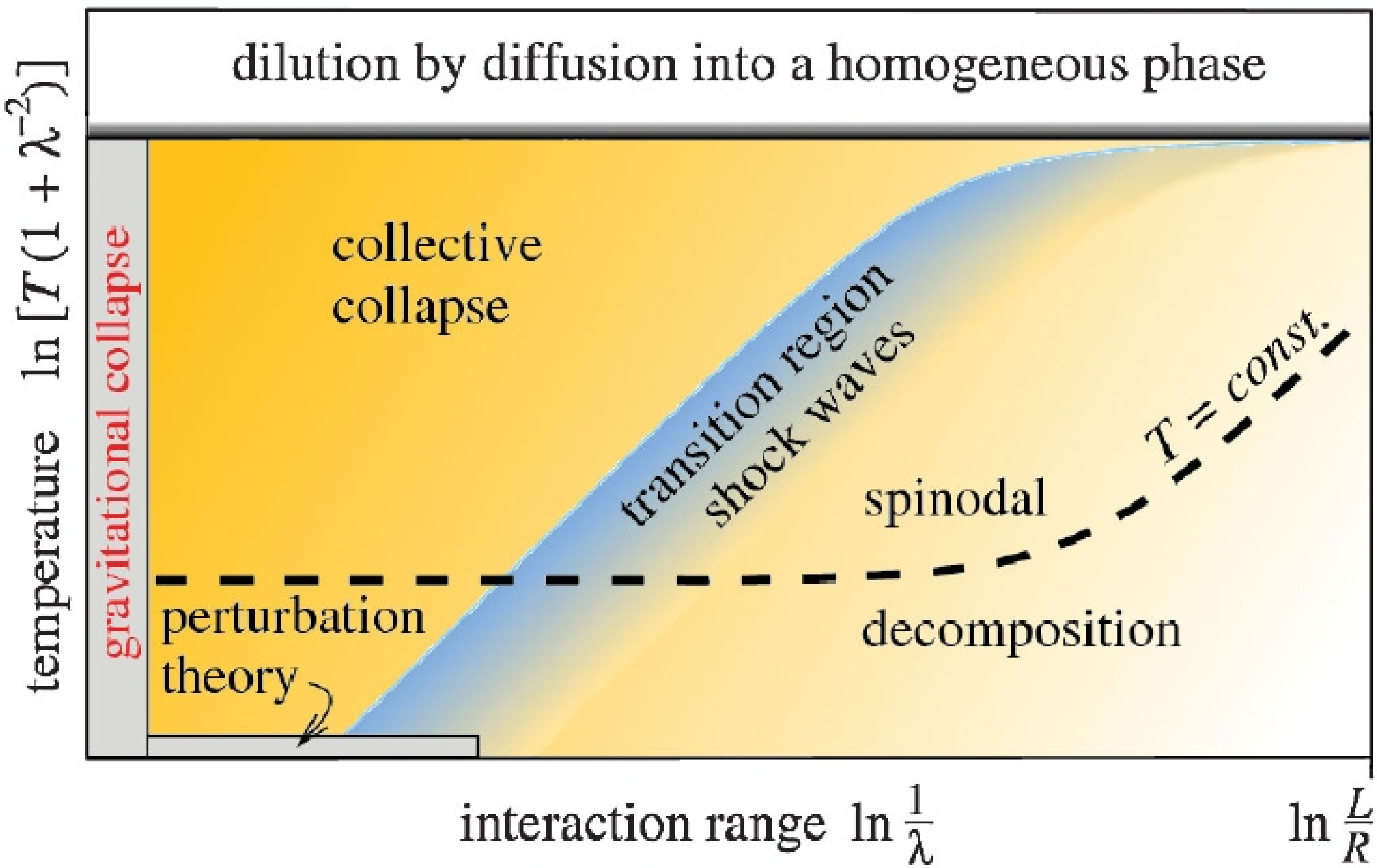
Fluid interfaces: Capillarity as pseudogravity

Dynamical phase diagram: interpolating between 'normal' fluids and 'gravitational' fluids

„effective“ *T*:

$$\frac{k_B T}{u_{att}}$$

per particle



J. Bleibel, S. Dietrich, A. Dominguez, and M. Oettel,
Shock waves in capillary collapse of colloids: a model system for two--dimensional screened gravity,
Phys. Rev. Lett. 107, 128302 (2011).

J. Bleibel, A. Dominguez , M. Oettel and S. Dietrich,
Capillary attraction induced collapse of colloidal monolayers at fluid interfaces,
Soft Matter 10, 4091 (2014).

Summary of this part

Gravitational attraction ...

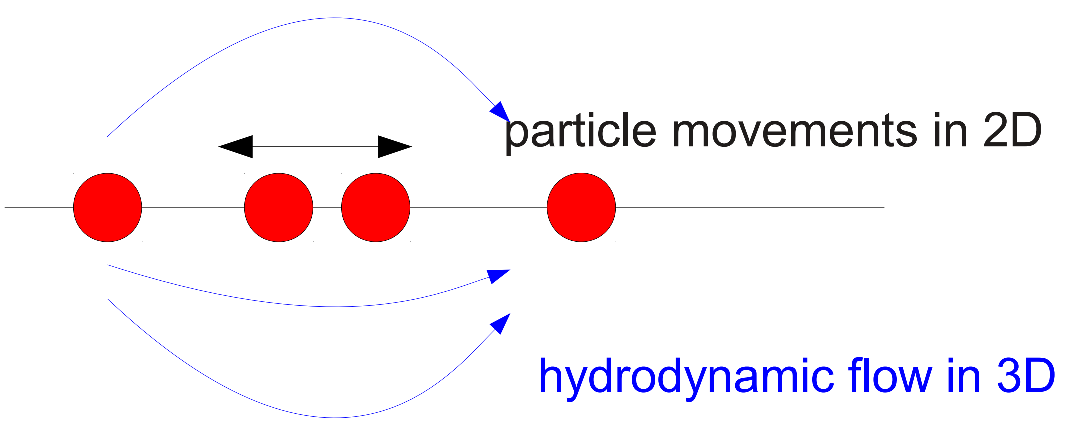
- but in 2 dimensions
- with a cutoff $\lambda \sim \mathrm{mm}$

tunable → interesting, interpolating fluid

but ...

- with an extra dimension around where solvent can flow

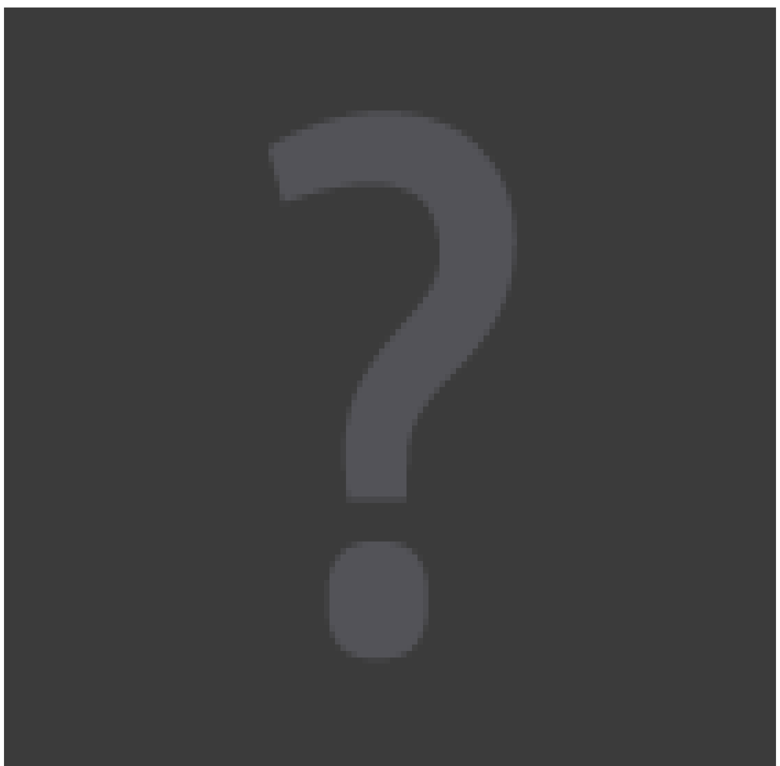
anomalously fast diffusion due to extra dimension



Partial confinement: Anomalous diffusion

Appetizer: Again the capillary (pseudogravitational) system

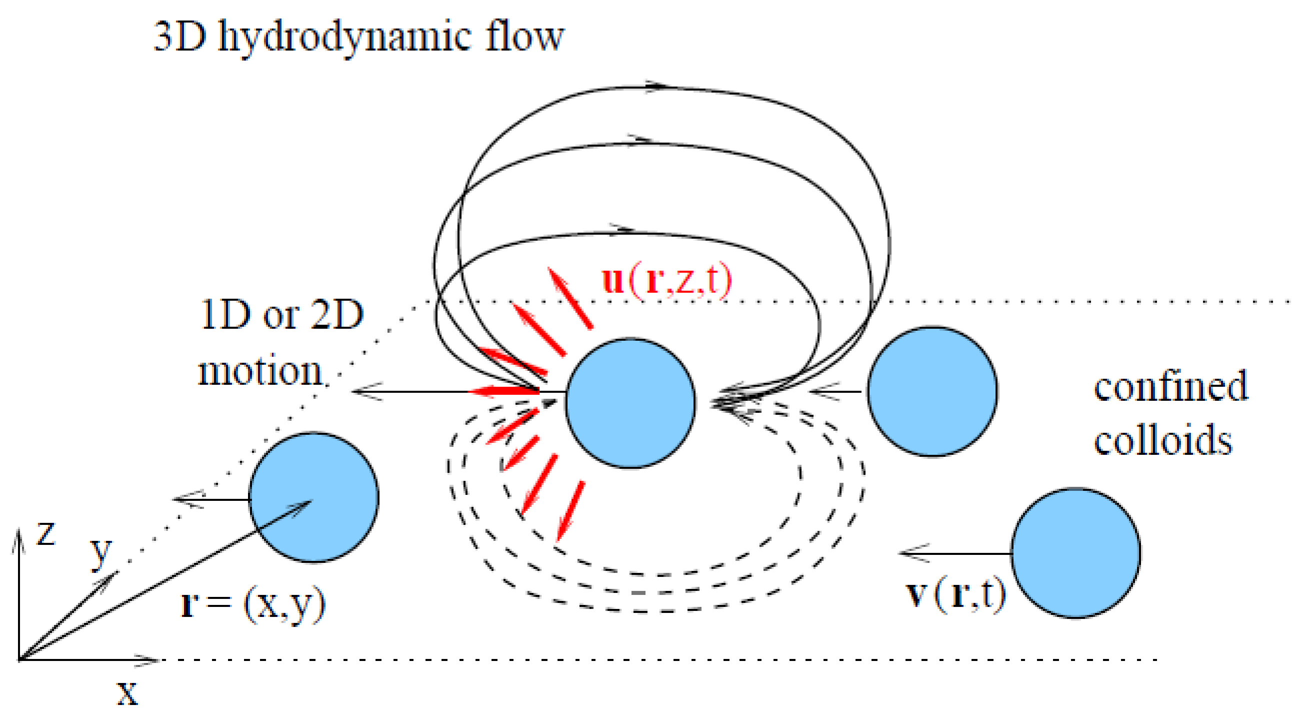
Brownian dynamics



with hydrodynamics:
Stokesian dynamics (2-particle interactions)

Partially confined motion

generic setup:

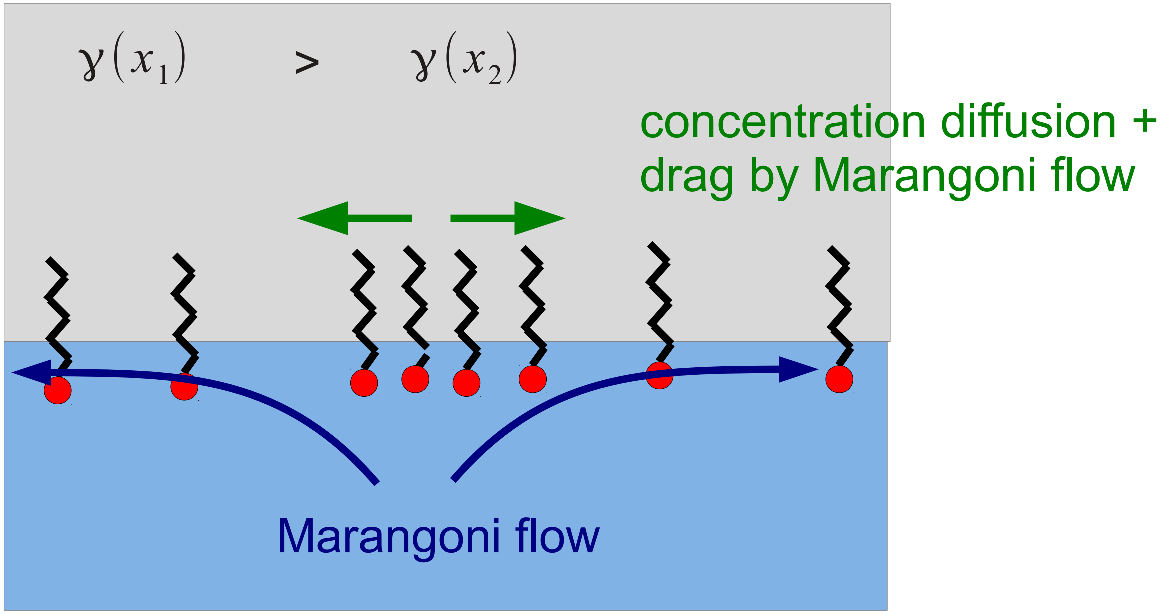


primary example: colloids trapped at a fluid interface
but also ... soap at water interface

Partial confinement: Anomalous diffusion

The Marangoni effect is partially confined motion

The Marangoni effect: Gradients of surface tension set fluid in motion



- $\nabla\gamma$ is an aerial force density (N/m^2) which pulls on the fluid elements
- fluid flow (Marangoni flow) drags along the soap molecules and enhances their concentration diffusion
- analogy to colloidal system: thermal motion and mutual capillary force pulls on fluid elements

Partially confined motion

- Overdamped dynamics – appropriate for microparticles
- Include hydrodynamic interactions perturbatively on the two-particle level

On the individual particle level:

particle velocity = mobility x force + random kicks

$$\boldsymbol{v}_i = \boldsymbol{\Gamma}_{ij} \boldsymbol{F}_j^{ext} + \text{noise}$$

General diffusion tensor

$$\Gamma_{ij}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \approx \Gamma_0 \boldsymbol{I} \delta_{ij} + \Gamma^{(2)}(\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j)$$

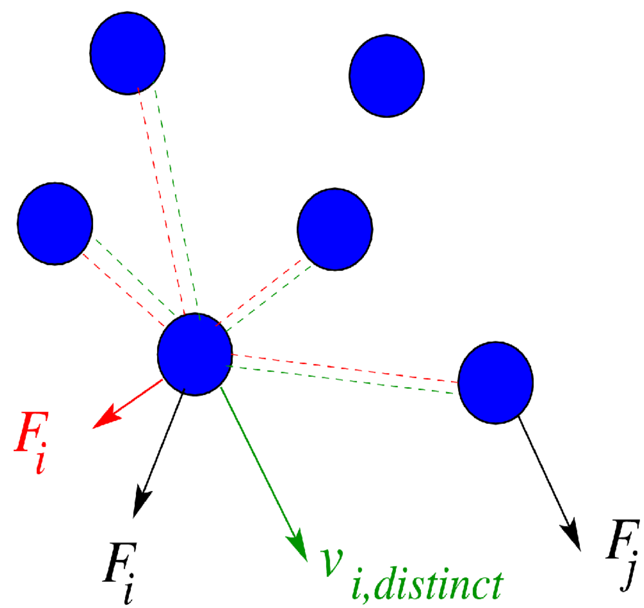
Include only pair terms

$$\Gamma^{(2)}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = \Gamma_0 \left[\delta_{ij} \sum_{l \neq i} \boldsymbol{\omega}_{11}(\boldsymbol{r}_{il}) + (1 - \delta_{ij}) \boldsymbol{\omega}_{12}(\boldsymbol{r}_{ij}) \right]$$

Self interaction term
Distinct interaction term

Partially confined motion

Velocity of particle *i* instantaneously reacts to forces on particle *j*



$$v_{i,self} = \Gamma_0 \sum_{j \neq i} \omega_{11}(r_{ij})\, F_i$$

$$v_{i,distinct} = \Gamma_0 \sum_{j \neq i} \omega_{12}(r_{ij})\, F_j$$

Full diffusion tensor: solution of Stokes equation for velocity field $\boldsymbol{u}(\boldsymbol{r})$

$$\eta \nabla^2 \boldsymbol{u} - \nabla p = 0$$

$$\boldsymbol{u}_{\partial B_i} = \boldsymbol{v}_i$$ Boundary condition

$$\boldsymbol{F}_{i,hydro} = \int_{\partial B_i} \Pi \, d\boldsymbol{A}$$ Force on particle *i* by integration of stress tensor

Systematic 1/*r* expansion for two particles

$$\boldsymbol{\omega}_{11}(\boldsymbol{r}) = O(r^{-4}) \approx 0$$

(bulk)

$$\boldsymbol{\omega}_{12}(\boldsymbol{r}) = \underbrace{\frac{3\sigma_H}{8} \underbrace{\frac{1}{r}(\boldsymbol{I} + \hat{\boldsymbol{r}}\hat{\boldsymbol{r}})}_{\text{Oseen tensor}} + \frac{1}{16}\frac{\sigma_H^3}{r^3}(\boldsymbol{I} - 3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}})}_{\text{Rotne-Prager tensor}}$$

long-ranged!

Partially confined motion: A diffusion equation

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \boldsymbol{j} = -\nabla \cdot (\rho \boldsymbol{v})$$

continuity equation

particle velocity field

$$\boldsymbol{j}(\boldsymbol{r},t) = -D_0 \nabla \rho(\boldsymbol{r},t) - D_0 \rho(\boldsymbol{r},t) \underbrace{\int d\boldsymbol{r}' \boldsymbol{\omega}_{12}(\boldsymbol{r}-\boldsymbol{r}') \nabla' \rho(\boldsymbol{r}',t)}$$

Fick's law

Marangoni flow field: drags along the particles

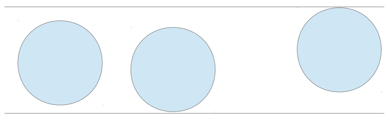
This equation is nonlinear. Linearize for small density fluctuations $\rho(\boldsymbol{r},t)=\rho_0+\delta\rho(\boldsymbol{r},t)$ and take Fourier transform

$$\frac{\partial \delta\tilde{\rho}(\boldsymbol{k},t)}{\partial t} = -D_0 k^2 \left(1 + \rho_0 \hat{\boldsymbol{k}} \cdot \tilde{\boldsymbol{\omega}}_{12}(\boldsymbol{k}) \cdot \hat{\boldsymbol{k}}\right) \delta\tilde{\rho}(\boldsymbol{k},t)$$

$$D(k) = D_0 \left(1+\rho_0 \hat{\boldsymbol{k}} \cdot \tilde{\boldsymbol{\omega}}_{12}(\boldsymbol{k}) \cdot \hat{\boldsymbol{k}}\right)$$

wavelength-dependent diffusion coefficient

The "hidden" dimension:

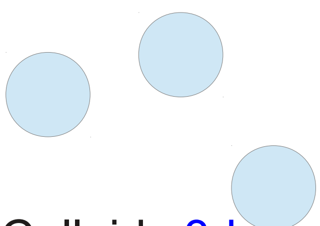


Colloids quasi-2d
Solvent quasi-2d

FT in 2d

$$\omega_{12}(\boldsymbol{r}) \propto \left(\boldsymbol{I} \log \frac{L}{r} + \hat{\boldsymbol{r}}\hat{\boldsymbol{r}} \right) \rightarrow$$

$$\hat{\boldsymbol{k}} \cdot \tilde{\omega}_{12} \cdot \hat{\boldsymbol{k}} = 0$$

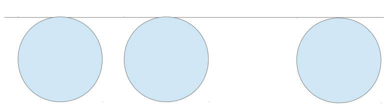


Colloids 3d
Solvent 3d

FT in 3d

$$\omega_{12}(\boldsymbol{r}) = \frac{1}{r}\left(\boldsymbol{I} + \hat{\boldsymbol{r}}\hat{\boldsymbol{r}} \right) \rightarrow$$

$$\hat{\boldsymbol{k}} \cdot \tilde{\omega}_{12} \cdot \hat{\boldsymbol{k}} = 0$$



Colloids quasi-2d
Solvent 3d

FT in 2d

$$\omega_{12}(\boldsymbol{r}) \propto \frac{1}{r}\left(\boldsymbol{I} + \hat{\boldsymbol{r}}\hat{\boldsymbol{r}} \right) + O\left(r^{-3}\right) \rightarrow$$

$$\hat{\boldsymbol{k}} \cdot \tilde{\omega}_{12} \cdot \hat{\boldsymbol{k}} \propto \frac{1}{k} + O\left(k^{0}\right) + \ldots$$

Interpretation: The solvent flow is not incompressible on the colloidal plane!

The (2d-3d) diffusion equation becomes:

$$\frac{\partial \delta \tilde{\rho}(\boldsymbol{k},t)}{\partial t} = -D_0 k^2 \left(1 + \frac{1}{k L_{\text{hydro}}}\right) \delta \tilde{\rho}(\boldsymbol{k},t)$$

$L_{\text{hydro}} = \frac{4}{3\pi \rho_0 \sigma_H}$	new characteristic length, above which there should be deviations from normal diffusive behavior
$t_{\text{hydro}} = \frac{L_{\text{hydro}}^2}{D_0}$	associated time scale over which the „normally diffusing" system reaches L_{hydro}

Green's function for this diffusion equation

$$\tilde{G}_{\text{2d-3d}}(\boldsymbol{k},t) = \exp\left(-k^2 \; D(k) t\right), \qquad D(k) = D_0 \left(1 + \frac{1}{k L_{\text{hydro}}}\right)$$

singularity in the diffusion coefficient!

Fourier back transform not easy! For long times $t \gg t_{\text{hydro}}$ we obtain

$$G_{\text{2d-3d}}(\boldsymbol{r},t) = \frac{t_{\text{hydro}}}{2\pi D_0 t^2} \left[1 + \left(\frac{r}{L_{\text{hydro}}}\right)^2 \left(\frac{t_{\text{hydro}}}{t}\right)^2\right]^{-\frac{3}{2}} \propto \frac{1}{r^3} \text{ for any fixed } t$$

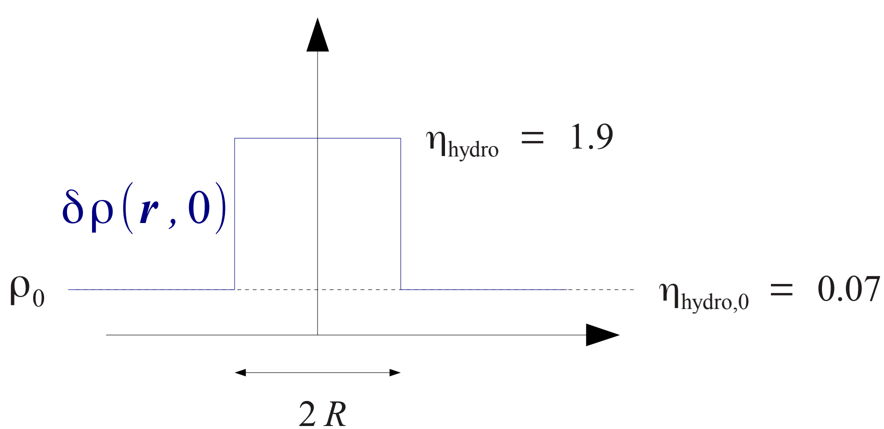
Partial confinement: Anomalous diffusion

Simulations (Johannes Bleibel)

- quasi-2D truncated Stokesian dynamics simulations
  (Brownian dynamics + 2-particle HI up to $1/r^3$)
- allow for random kicks out of plane → confine particles to plane
  with a (strong) potential
- difficult because of statistics, therefore:
  „polymeric“ particles with hydrodynamic radius but no direct interactions

initial profile - top-hat

hydrodynamic packing fraction $\eta_{\mathrm{hydro}} = \pi a_{\mathrm{hydro}}^2 \rho$

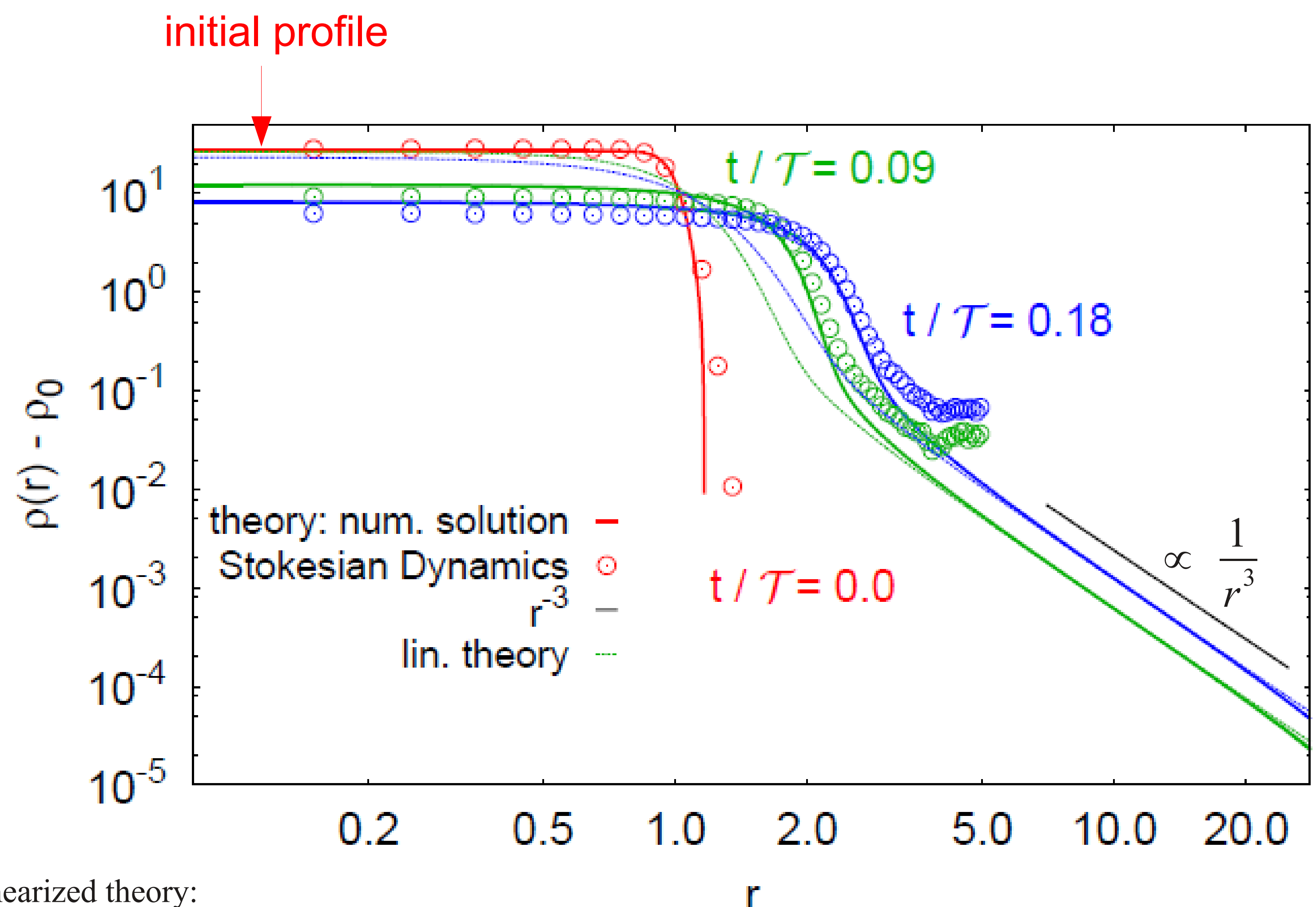


physical model parameters:

$$a_{\mathrm{hydro}} = 10 \ \mu\mathrm{m}$$
$$R = 100 \ \mu\mathrm{m}$$
$$L_{\mathrm{box}} = 1\,000 \ \mu\mathrm{m}$$
$$N_0 = 212 \quad \text{(background particles)}$$
$$\delta N = 188 \quad \text{(additional particles)}$$

periodic boundary conditions

Simulations (Johannes Bleibel) - Results for the decay of a top-hat profile



linearized theory:

$$\delta\rho(r,t) = \delta\rho(r,0) * G_{2d\text{-}3d}(r,t)$$

All features of $G_{2d\text{-}3d}$ **are present !**

Partial confinement: Anomalous diffusion

Solution for the capillary (pseudogravitational) system

Brownian dynamics

with hydrodynamics:
Stokesian dynamics (2-particle interactions)

J. Bleibel, A. Dominguez, F. Günther, J. Harting and M. Oettel
Hydrodynamic interactions induce anomalous diffusion under partial confinement
Soft Matter 10, 2945 (2014).

J. Bleibel, A. Dominguez and M. Oettel
3D hydrodynamic interactions lead to divergences in 2D diffusion
Proceedings of Liquids 2014 (JPCM 2015)

Long-ranged diffusion fields $\propto r^{-3}$
"suck" in the particles toward the center

Experiment? An old one needs to be reinterpreted...(Lin,Rice, Weitz 1995)

PHYSICAL REVIEW E VOLUME 51, NUMBER 1 JANUARY 1995

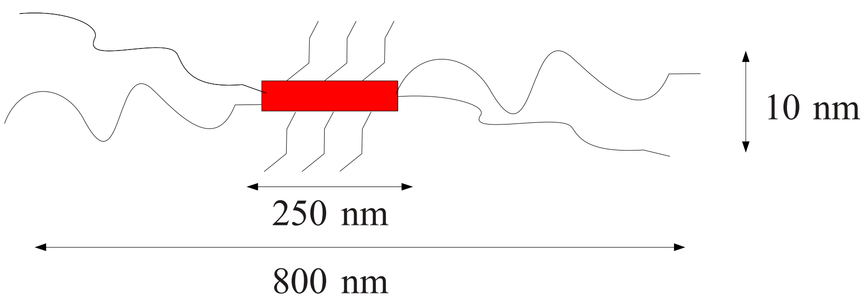
Experimental evidence for the divergence of a transport coefficient in a quasi-two-dimensional fluid

We report experimental evidence for the divergence of the collective diffusion coefficient in a quasi-two-dimensional fluid. The system studied is a monolayer of nearly monodisperse self-assembled disks of the diblock copolymer polystyrene-*b*-polymethylmethacrylate, supported in the air/water interface, and the method used to measure the collective diffusion coefficient is dynamic evanescent wave light scattering. In all cases studied, in a system of interacting particles the collective diffusion coefficient, which depends on the sum of the time integrals of the velocity autocorrelation and crosscorrelation functions for all pairs of particles, is proportional to the self-diffusion coefficient. It has been predicted that the self-diffusion coefficient of a two-dimensional fluid does not exist, i.e., that the apparent self-diffusion coefficient defined by the time integral of the velocity autocorrelation function diverges as $t \to \infty$, implying that so, also, will the collective diffusion coefficient of a two-dimensional fluid. Our experimental data are consistent with this qualitative expectation and they also agree with the asymptotic dependence on time ($t \to \infty$), wave vector ($Q \to 0$), and surface density of the self-diffusion coefficient of a two-dimensional fluid predicted by Yuan and Oppenheim [H.H.-H. Yuan and I. Oppenheim, Physica **90A**, 1 (1978); **90A**, 21 (1978); **90A**, 561 (1978)].

So, it is a perfect 2d-3d setup but the analysis was done for 2d...

Partial confinement: Anomalous diffusion

Experiment? An old one needs to be reinterpreted...(Lin,Rice, Weitz 1995)



These are „soft disks“ with hopefully large hydrodynamic radius !

Measurement:

Static Light Scattering: structure factor (SLS) $S(k)$

Dynamic Light Scattering: collective diffusion coefficient (DLS) $D(k)$

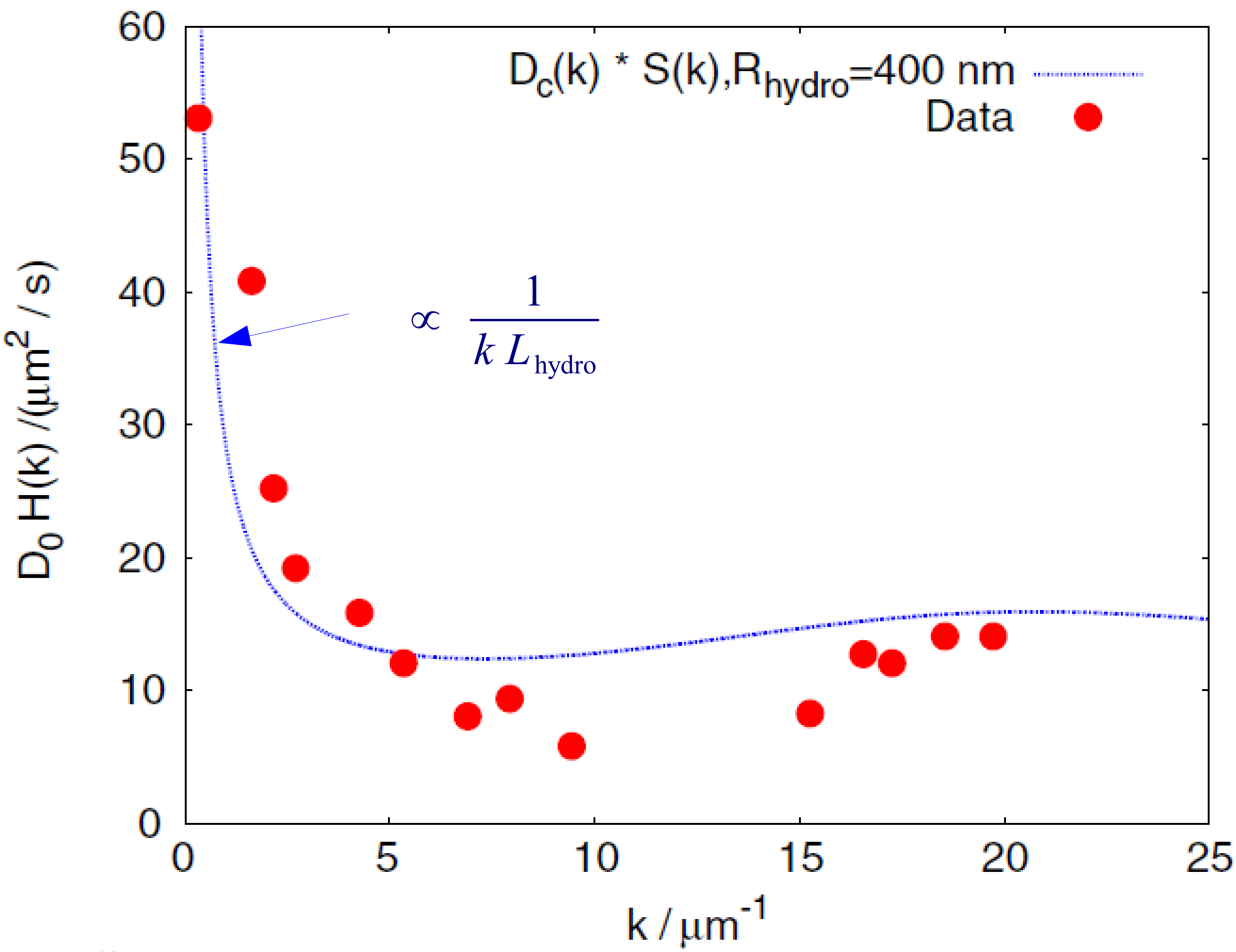
interpretation $$D(k) = D_0 \frac{H(k)}{S(k)}$$

with „hydrodynamic function“ $H(k)$

In our 2d-3d system: $$H(k) = 1 + \frac{1}{k L_{\text{hydro}}}$$

Partial confinement: Anomalous diffusion

Experiment? Lin,Rice, Weitz 1995 and reanalysis 2013



corresponding lengthscale → 1260 630 315

$\frac{2\pi}{k}$ [nm]

Summary of this part

- „normal“ fluids: power series of $D(k) = D_0(1+\beta_2 k^2+\dots)$

  → exponential decay of Green's function
  → „normal“ diffusion $\langle r^2 \rangle \propto t$

- partially confined systems: singularity in $D(k) = D_0\left(1+\frac{1}{k\,L_{\text{hydro}}}\right)$

  → power-law decay of Green's function
  → anomalously fast diffusion $\langle r^2 \rangle$ infinite

- corroboration by simulation (tSD)
  reinterpretation of an older experiment

- generic effect:
  particle confinement (1d,2d) + solvent flow (3d)

  ↓

  anomalous diffusion

THANK YOU!