Diffusion in Reduced Dimensions

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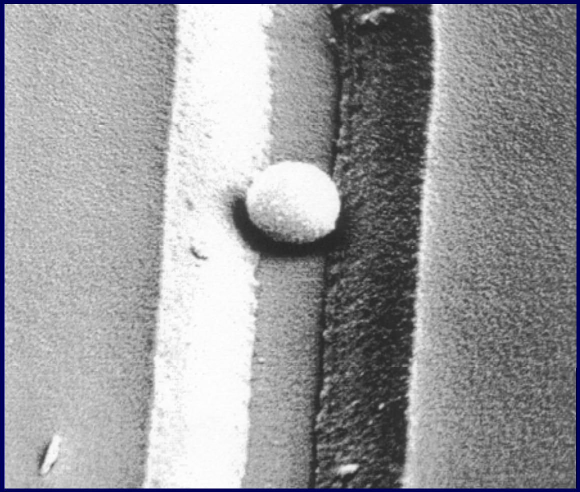
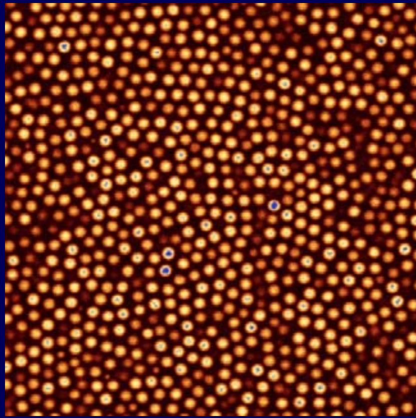


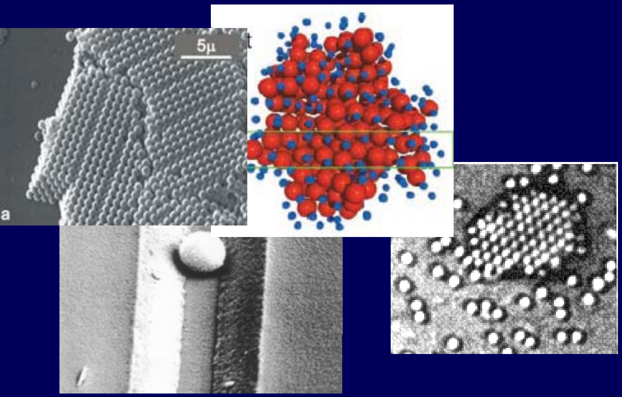
Colloids As Model Systems

Colloids:* = *Solid particles ranging between 10 nm and 10 µm dispersed in liquids

- overdamped motion: → **slow**
- very small elastic constants $\approx \frac{k_B T}{a^3}$ → **soft**
- typical length scales ≈ visible light: → **seeable**



"… the same equations have the same solutions …" (R. Feynman)

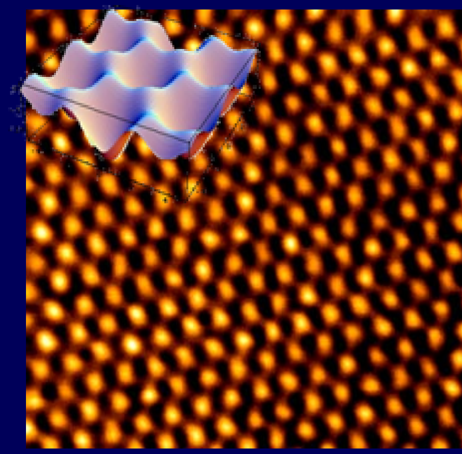


Atoms | ≡ | Colloids
$u(r)_{atom}$ ≡ $u(r)_{colloid}$

- **Phase transitions**
- **Nucleation phenomena**
- **Glass formation**
- **Diffusion through pores and channels**
- **…**

Colloids are „giant" atoms

Epitaxial growth of monolayers

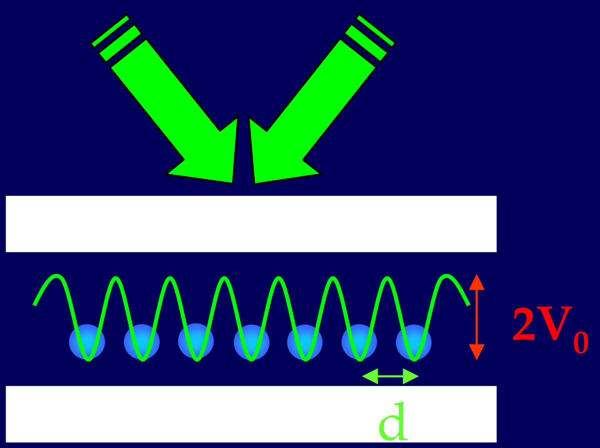


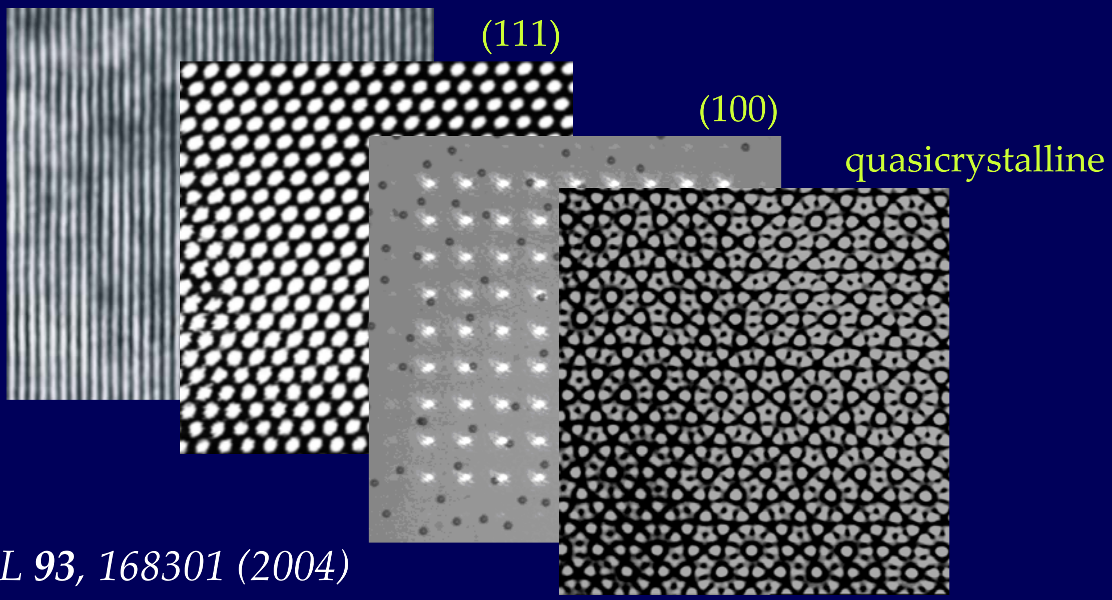
morphology depends on

- lattice mismatch
- substrate strength
- adsorbate-adsorbate interactions

parameters difficult to vary in atomic systems

→ colloids on light-induced substrate potentials





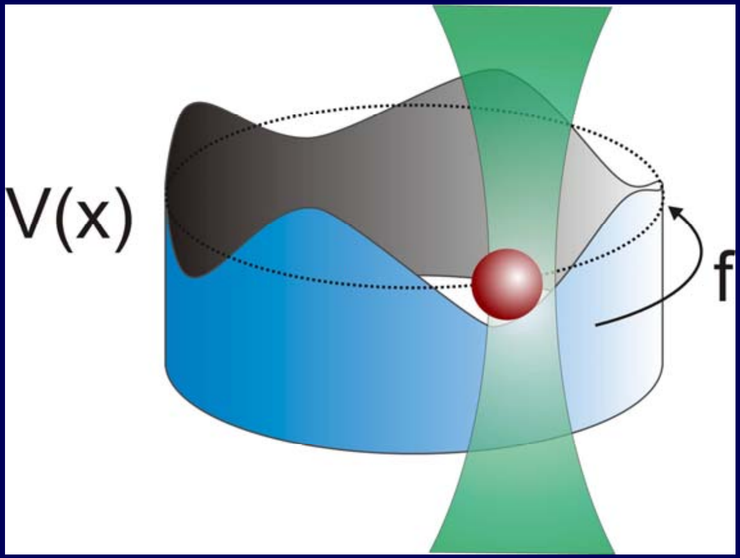
Baumgartl, Brunner, Bechinger, PRL ***93****, 168301 (2004)*
Bechinger, Frey, Soft Matter (Wiley-VCH, 2007)

Stochastic Thermodynamics

Driven colloidal systems beyond linear response

Generalized Einstein relation

$$D = k_B T \mu + \int_0^\infty d\tau I(\tau)$$

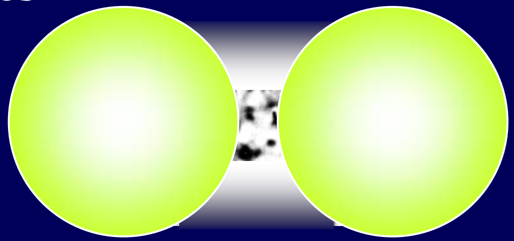


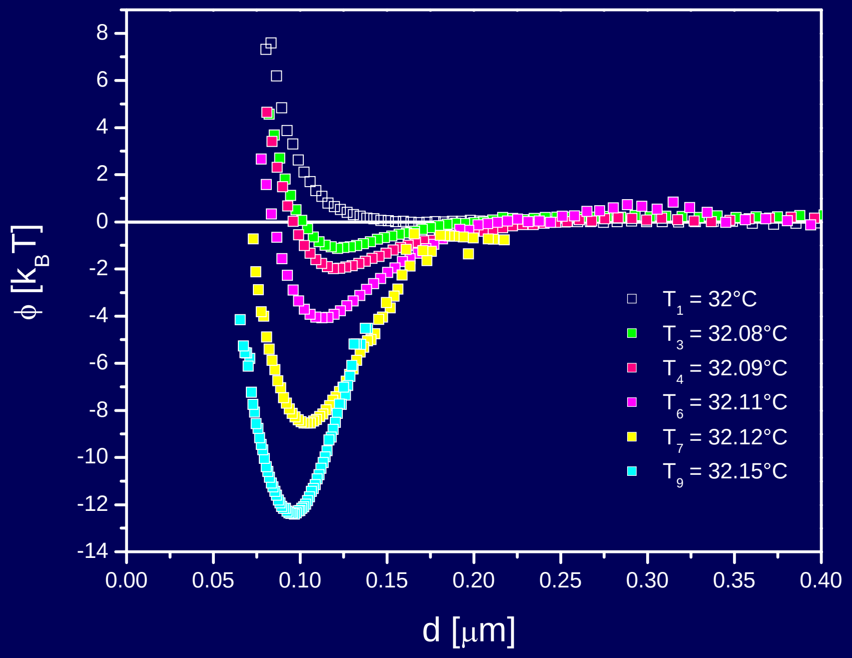
Blickle, Speck, Lutz, Seifert, Bechinger, PRL ***98,*** *210601 (2007)*

Critical Casimir Forces

Confinement of critical fluctuations in binary liquid mixtures near T_c

→ long-ranged forces





water/lutidin

$\eta_C = 29\%$

$T_C = 32\ °C$

Hertlein, Helden, Gambassi, Dietrich, Bechinger, submitted

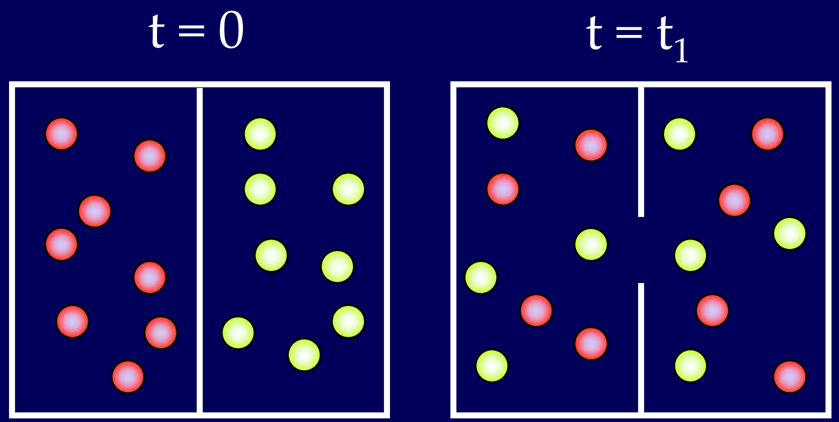
Single-file Diffusion of colloids

Experiments: *Q.-H. Wei, C. Lutz*

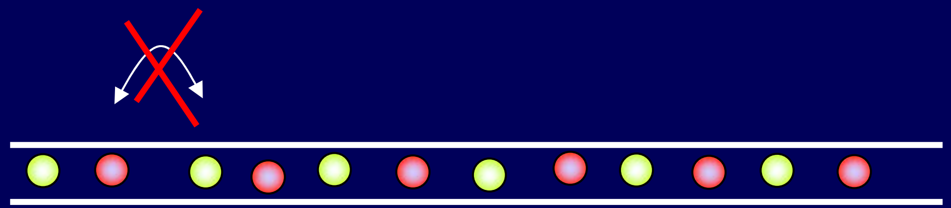
Theorie: *M. Kollmann*

Diffusion in narrow Channels

3D, 2D: mixing



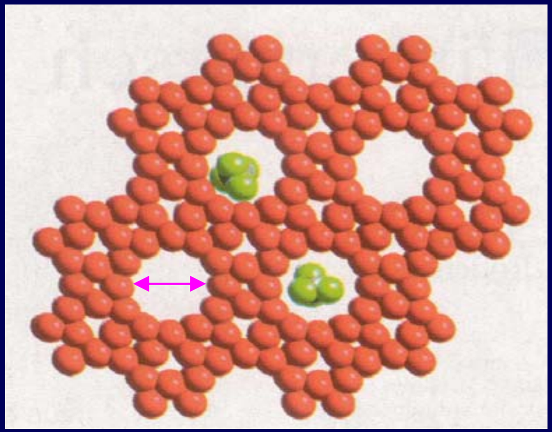
1D: sequence unchanged



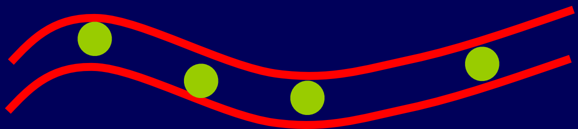
1D diffusion entirely different

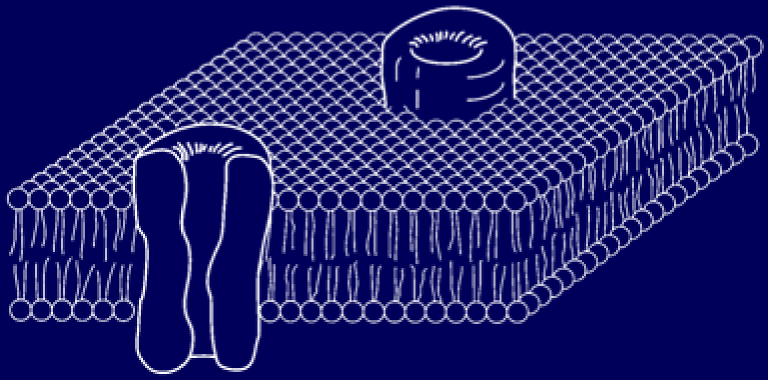
Realization of SF conditions

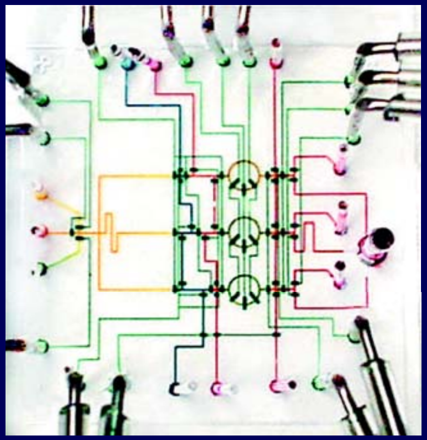
- molecular sieves (zeolites)
- carbon nanotubes
- ionic transport through membranes
- reptation in polymer melts
- microfluid devices
- ...



0.73nm



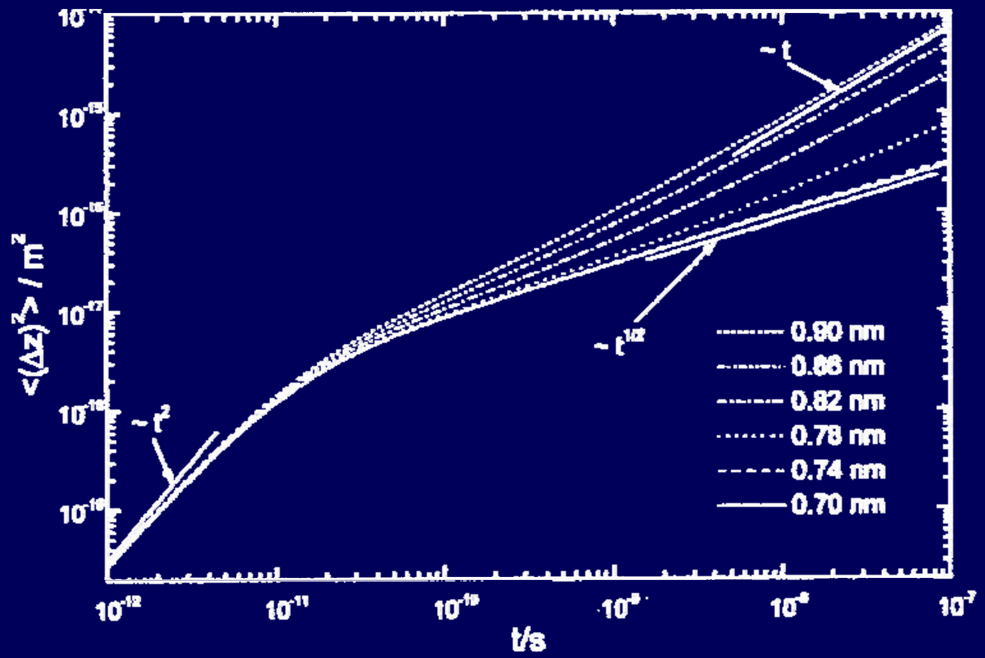




Single-File Diffusion

$$\lim_{t\to\infty}\left\langle \Delta x(t)^2 \right\rangle = 2F\sqrt{t}$$

*Levitt, Phys. Rev. A **8**, 3050 (1973)*
*Fedders, Phys. Rev. B **17**, 40 (1978)*
*van Beijeren, Kehr, Kutner, Phys. Rev. **B**, 28, 5711 (1983)*
*Kärger, J. Phys. Rev. A **45**, 4173 (1992)*



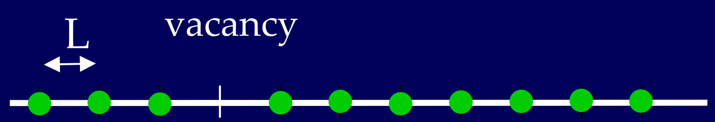
σ_P= 0.383nm (≅ CF_4)

*Hahn, Kärger, J. Phys. Chem. B, **102**, 5766 (1998)*

Kärger´s Derivation of $t^{1/2}$ - Law

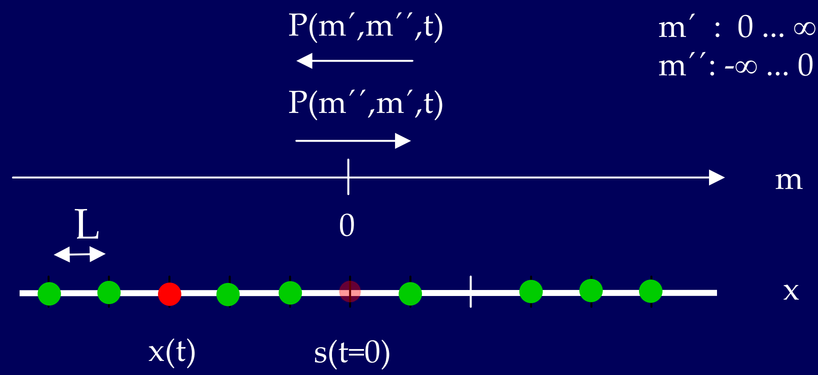
J. Kärger, Phys. Rev. ***A*** *45, 4173 (1992)*

1D exclusion model



$\Theta \approx 1$: motion of particles and vacancies highly correlated

→ consider vacancy motion



$$\left\langle x^2(t)\right\rangle = L^2(1-\Theta)\int_{m'=0}^{\infty}\int_{m''=-\infty}^{0}\left[P(m',m'',t)+P(m'',m',t)\right]dm'dm''$$

normal diffusion of vacancies

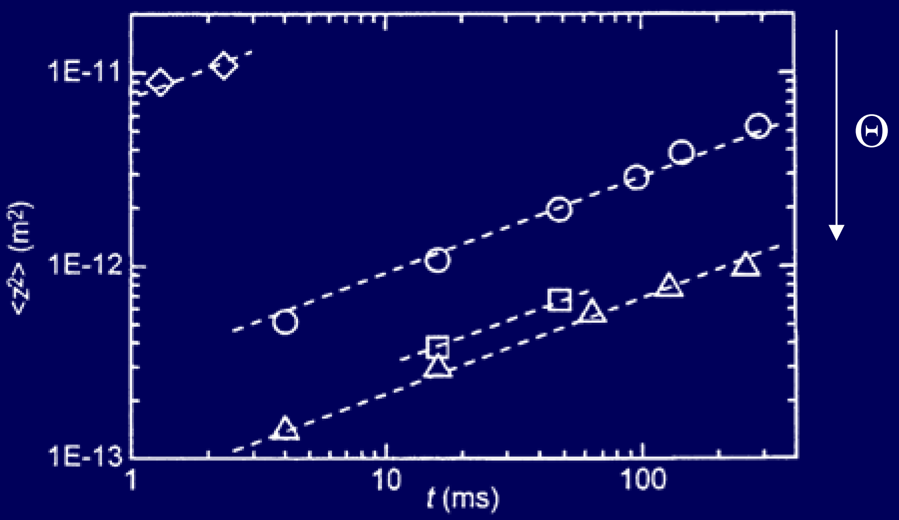
$$P(m',m'',t) = \left[\frac{L^2}{4\pi D_v t}\right]^{1/2} \exp\left[-(Lm'-Lm'')^2/(4D_v t)\right]$$

$$\left\langle x^2(t)\right\rangle = \left[\frac{2}{\pi}\right]^{1/2} L^2 \frac{1-\Theta}{\Theta}\left[\frac{t}{\tau}\right]^{1/2}$$

✓

SFD in Zeolites

CF_4 / $AlPO_4$-5



SFD ✓

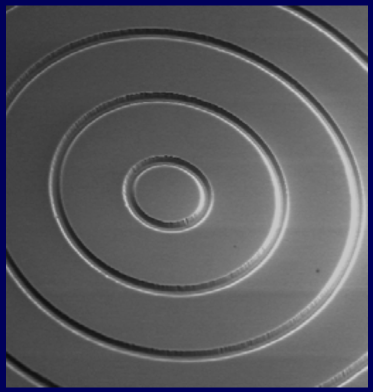
Hahn, Kärger, Kukla, Phys. Rev. Lett. ***76****, 2762 (1996)*

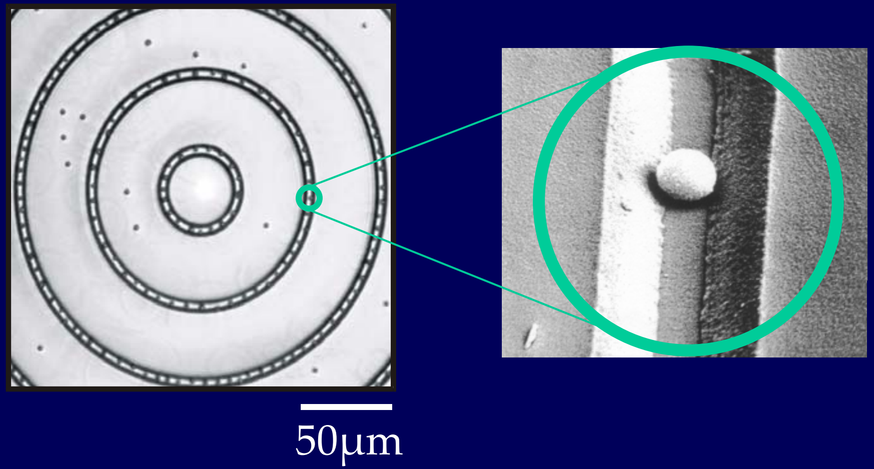
However: controversial results for CH_4 / $AlPO_4$-5: SFD and ND

➡ no ideal pore structure?
interaction across adjacent pores ?

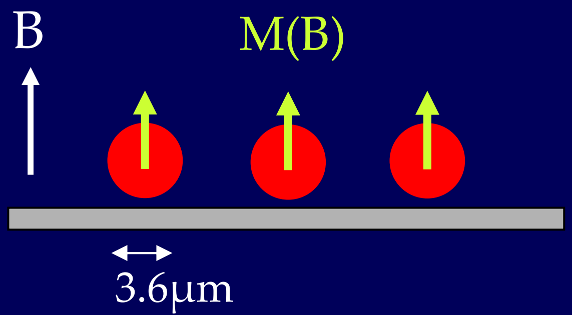
SFD in colloidal systems

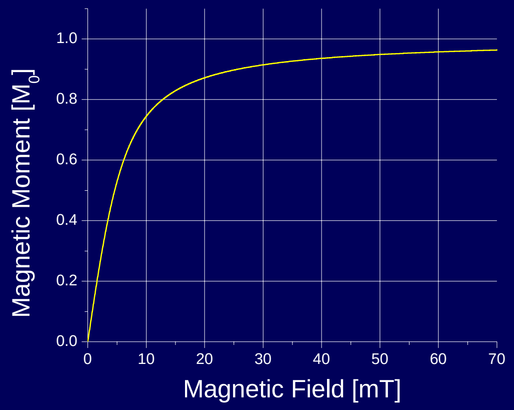
channel structures:





particles:





$$M = M_0 \cdot \left(\coth(\alpha B) - \frac{1}{\alpha B} \right)$$

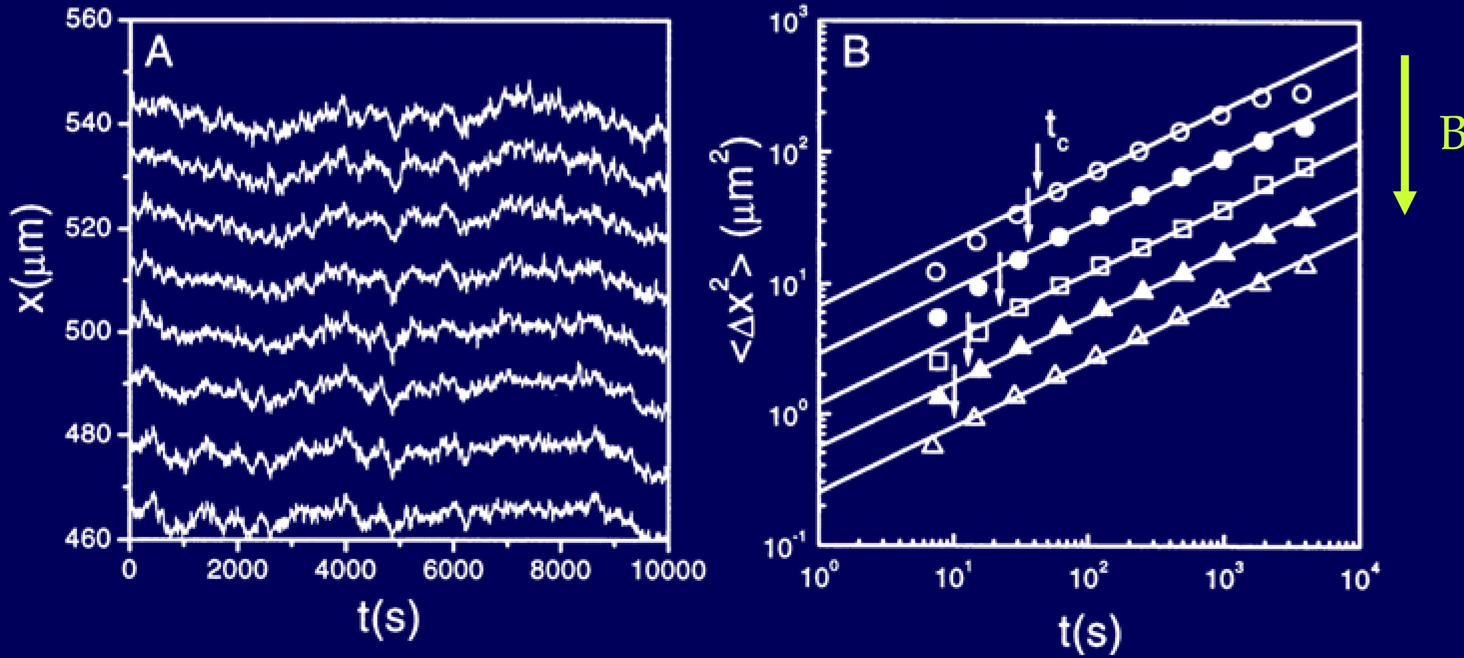
$$M_0 = 6 \times 10^{-13}\,Am^2$$

$$\alpha = \frac{\mu}{k_B T}$$

Direct Observation of SFD

single particle trajectories

MSD

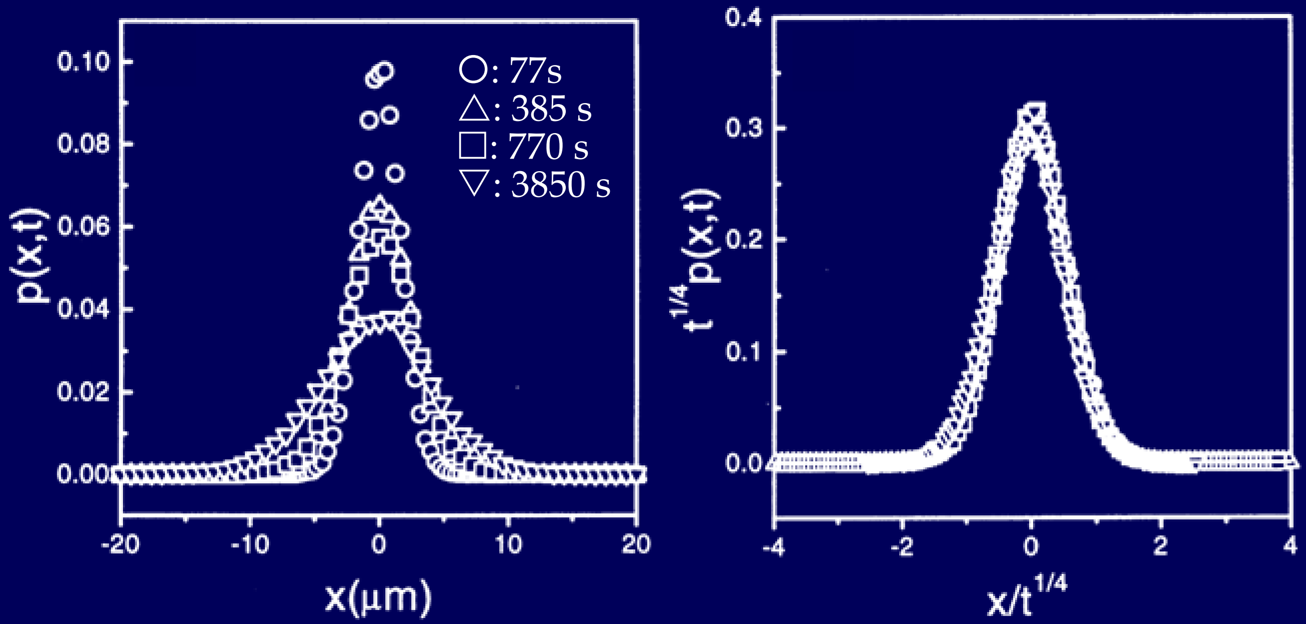


$$\left\langle \Delta x^2 \right\rangle = 2F\sqrt{t}$$

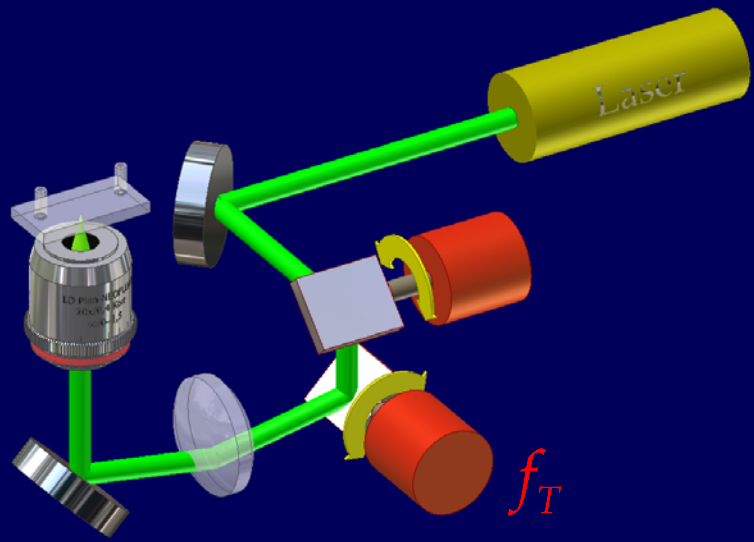
Wei, Bechinger, Leiderer, Science ***287****, 625 (2000)*

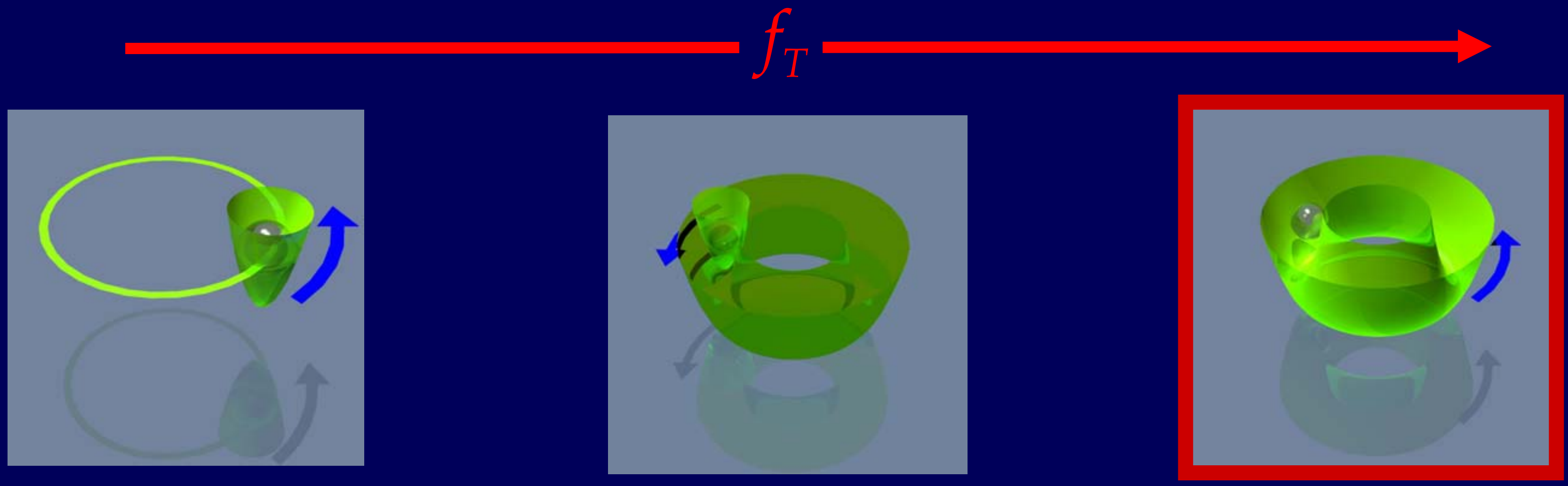
Propagator

$$p(x,t)_{x=0,t=0} = \frac{1}{\sqrt{4\pi F t^{1/4}}} \exp\left(-x^2/4Ft^{1/2}\right) \qquad \text{(hard rods)}$$



Channels Made by Optical Tweezers

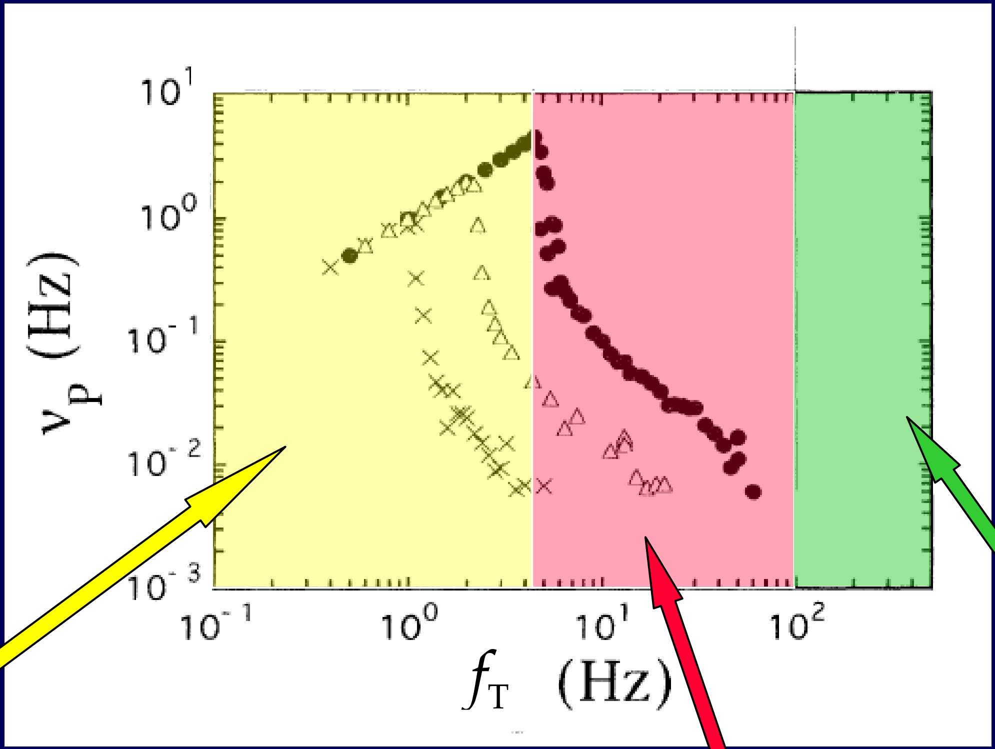




Single moving trap | **intermediate regime** | **quasi-static toroidal trap**

*Lutz, Reichert, Stark, Bechinger, EPL **74,** 719 (2006)*

Scanning Optical Fields



phase-locked

$$\nu_P = f_T$$

diffusive

phase-slip

$$\nu_P = \frac{2}{(2\pi R)^2 f_T} \frac{1}{w_0} \left[\frac{V_{foc}}{6\pi\eta a} \right]^2$$

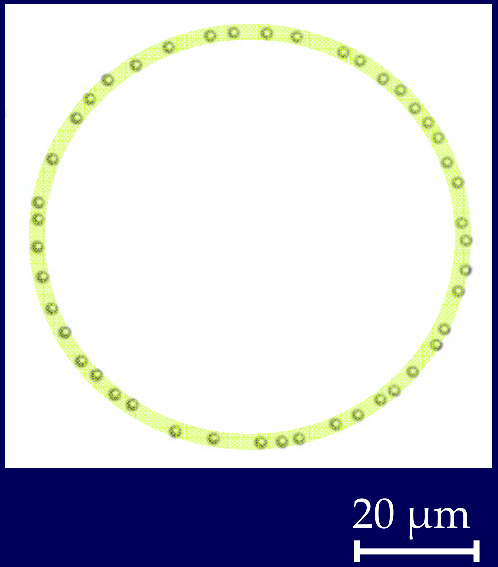
Faucheux, Stolovitzky, Libchaber, Phys. Rev. E ***51,*** *5239 (1995)*

Channels Made by Optical Tweezers

$f_T \approx 300$ Hz

2.9 μm PS particles

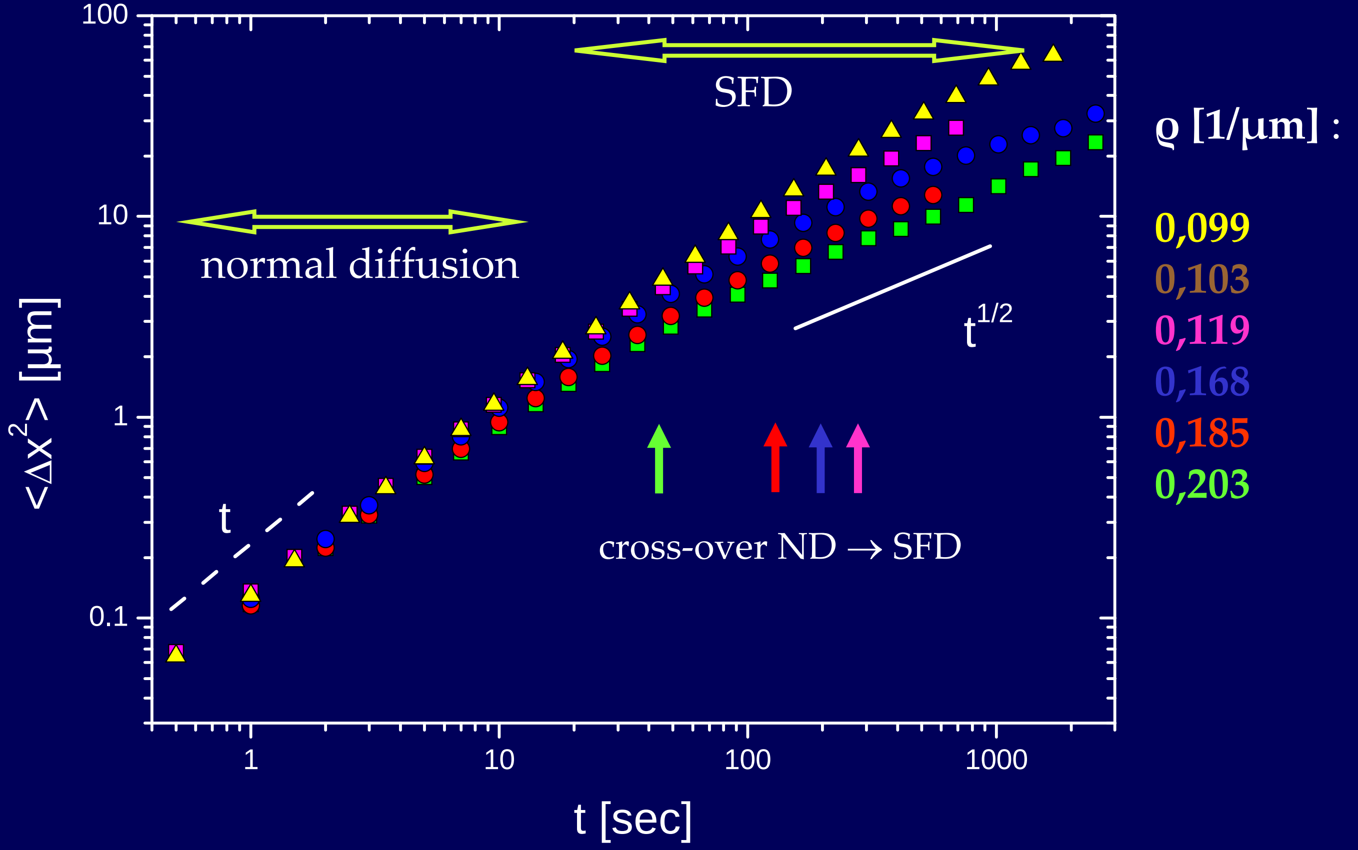
$$\beta u(r) = (Z^*)^2 \lambda_B \left(\frac{\exp(\kappa\sigma)}{1+\kappa\sigma} \right)^2 \frac{\exp(-\kappa r)}{r}$$



Advantages

- In situ control of channel geometry and particle number density
- Higher particle mobility due to absence of sticking boundary conditions @ walls

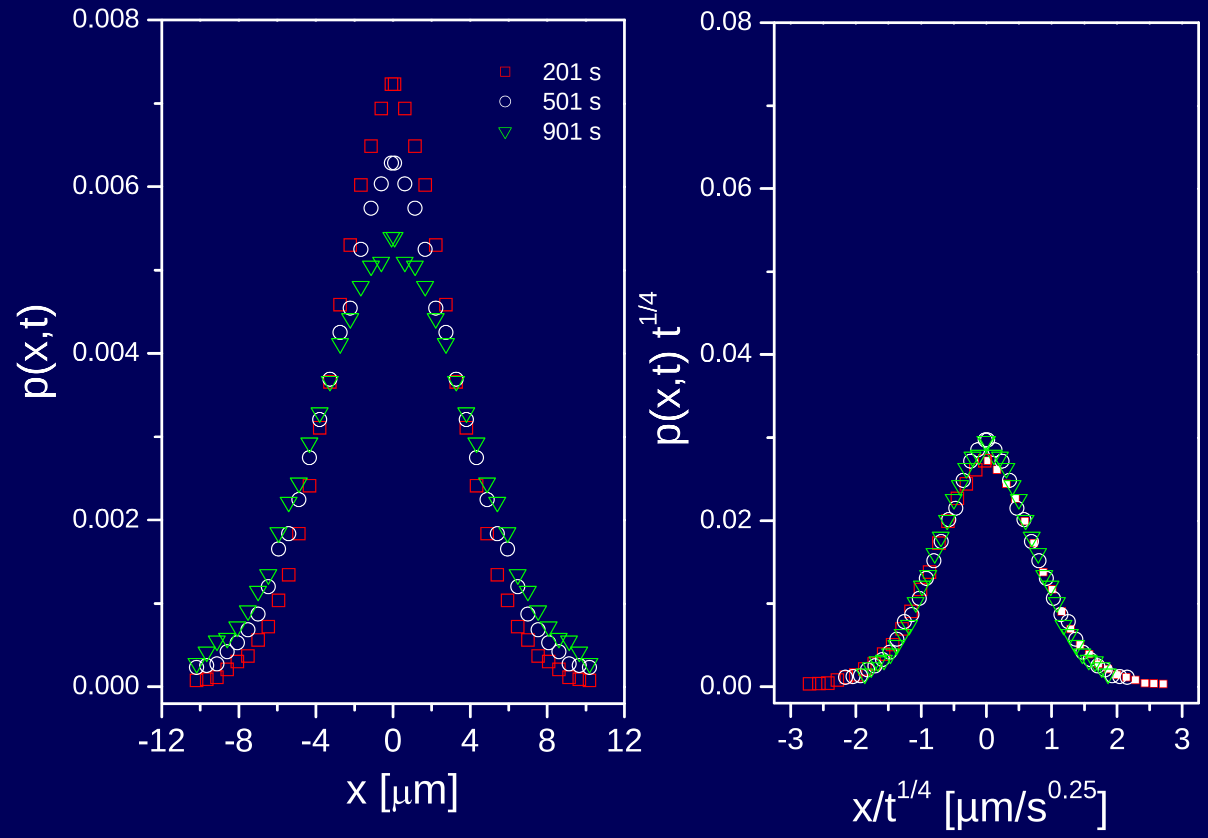
Crossover: Normal Diffusion to SFD



Lutz, Kollmann, Bechinger, PRL ***93****, 026001 (2004)*

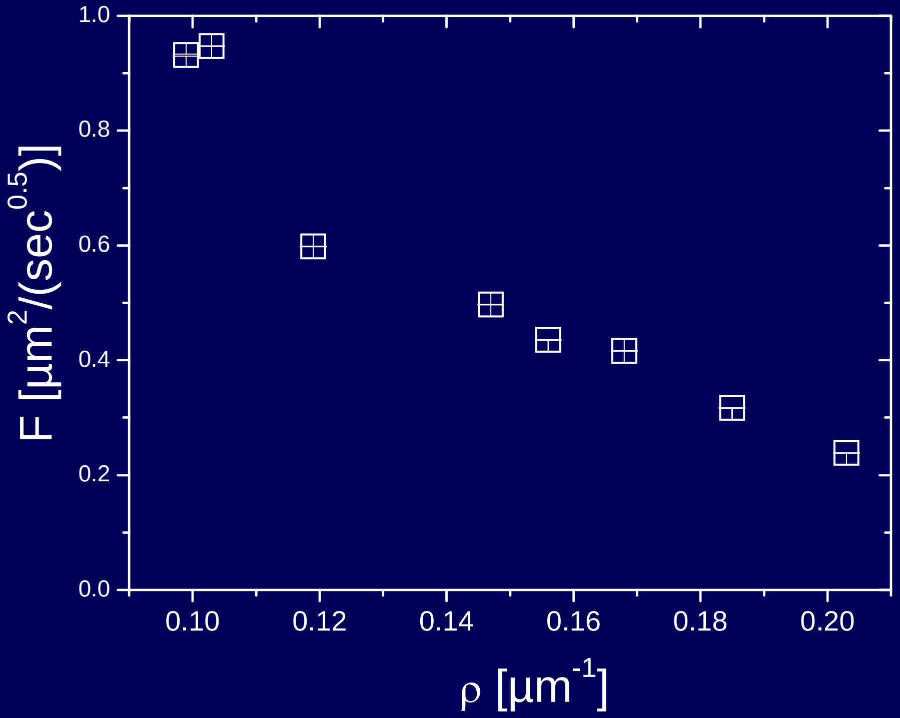
Propagator

$$p(x,t)_{x=0,t=0} = \frac{1}{\sqrt{4\pi F t^{1/4}}} \exp\left(-x^2/4Ft^{1/2}\right)$$



Lutz, Kollmann, C. Bechinger, J. Phys. Cond. Mat. ***16,*** *S4075 (2004)*

SF Mobility



*Lutz, Kollmann, Bechinger, PRL **93**, 026001 (2004)*

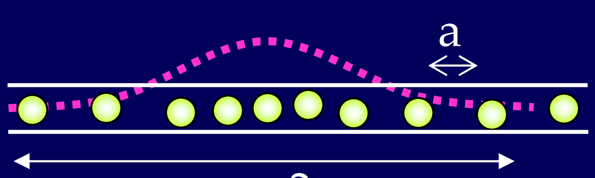
F from Intrinsic System Properties

$$\lim_{t\to\infty}\left\langle \Delta x^2(t)\right\rangle = \underbrace{\frac{2S(q,t=0)}{\varrho}\sqrt{\frac{D^{eff}(q)}{\pi}}}_{2F}\sqrt{t}$$

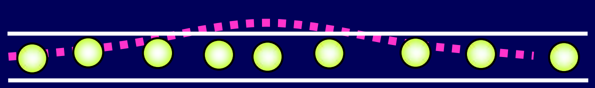
Kollmann PRL ***90****, 180602 (2003)*

Valid for any pair interaction
HI treated pairwise additive
infinite system
long-wavelength limit $(q \ll a^{-1})$

Why MSD is related to collective diffusion coefficient $D^{eff}(q)$?



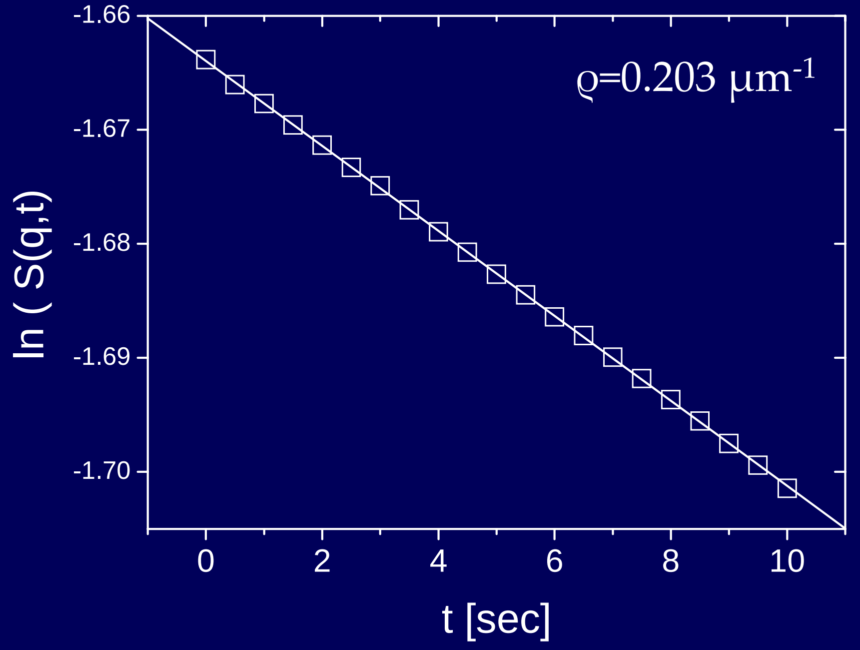
$$\lambda = \frac{2\pi}{q}$$



1D: Decay of density mode ⟺ trajectory of every single particle

Dynamic Structure Factor

$$S(q,t) = \frac{1}{N}\left\langle \sum_{i,j} \exp\left(-iq[x_j(t+\tau) - x_i(\tau)]\right) \right\rangle_\tau$$



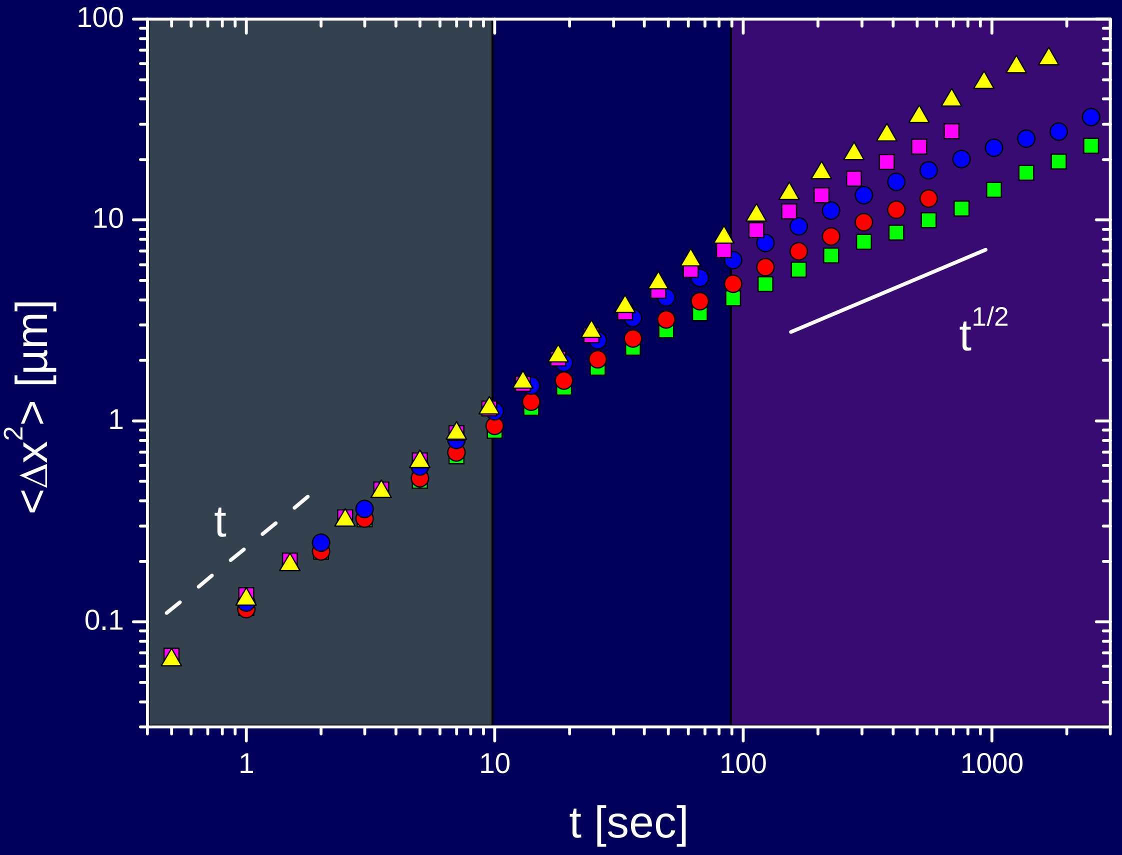
$$q = 4q_{min}$$

$$\left(q_{min} = \frac{2\pi}{\lambda_{max}} = \frac{1}{R}\right)$$

$q \ll a^{-1}$: $S(q,t) = S(q,0)\exp\left(-q^2 D^{eff}(q)t\right)$ Nägele, *Phys. Rep.* **272**, 215 (1996)

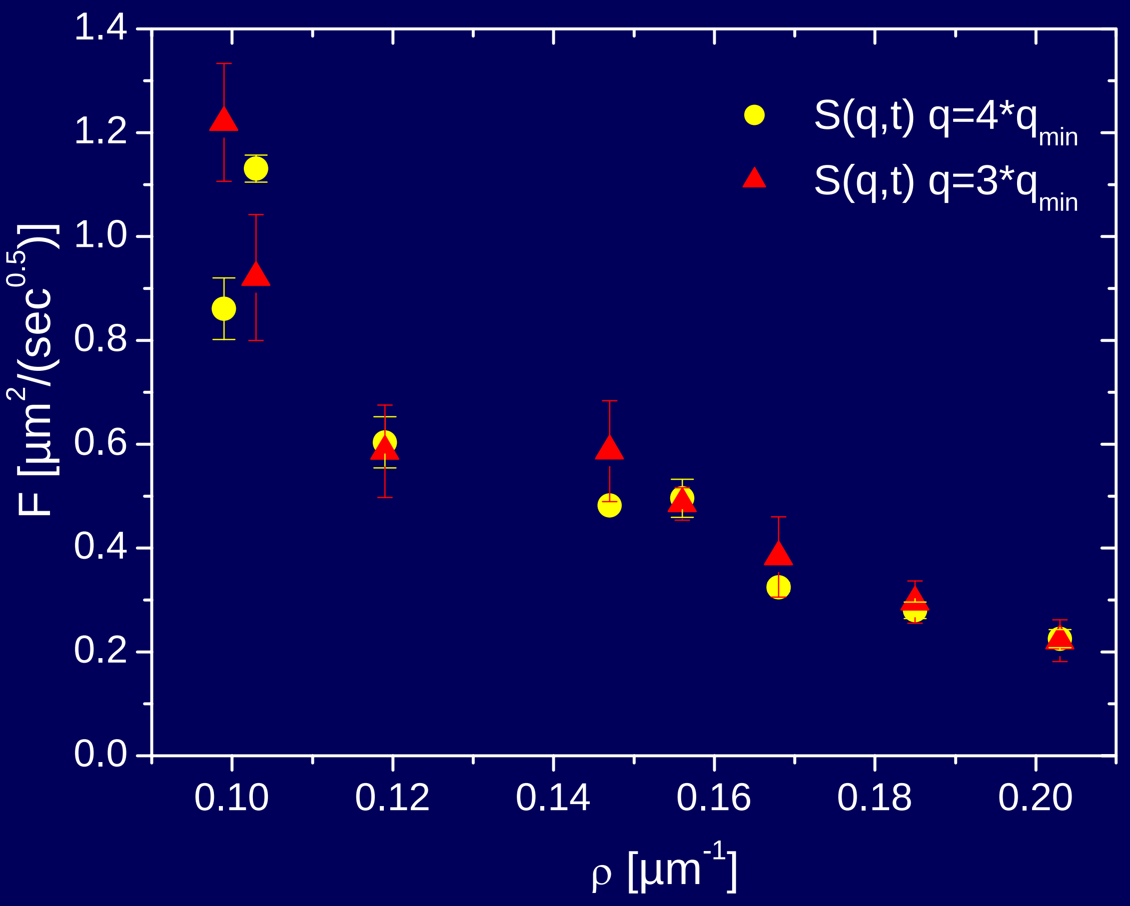
F can be obtained at short times ($t < t_c$) !!

F from Short-Time Behavior



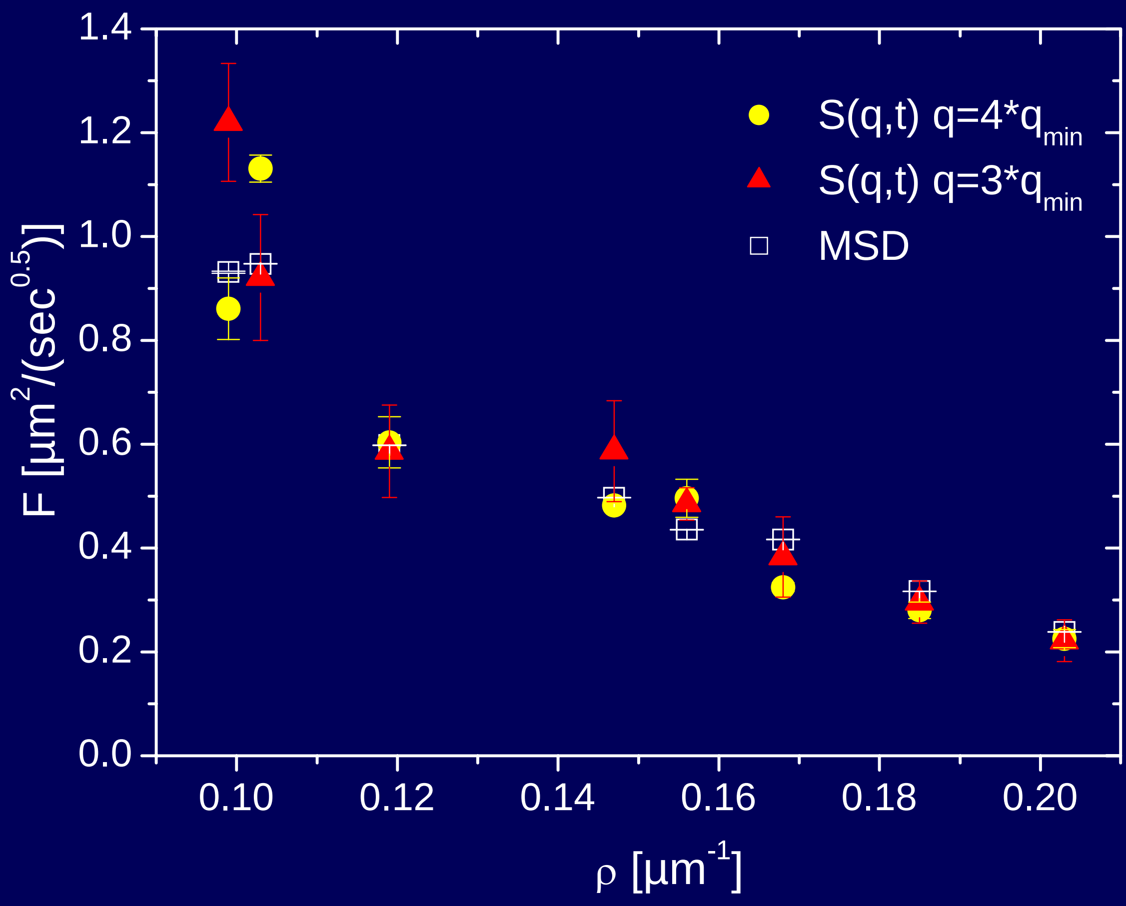
$$F = \frac{S(q,0)}{\varrho}\sqrt{\frac{D^{eff}(q)}{\pi}} \Longrightarrow \left\langle \Delta x^2 \right\rangle = 2F\sqrt{t}$$

SFD -Mobility



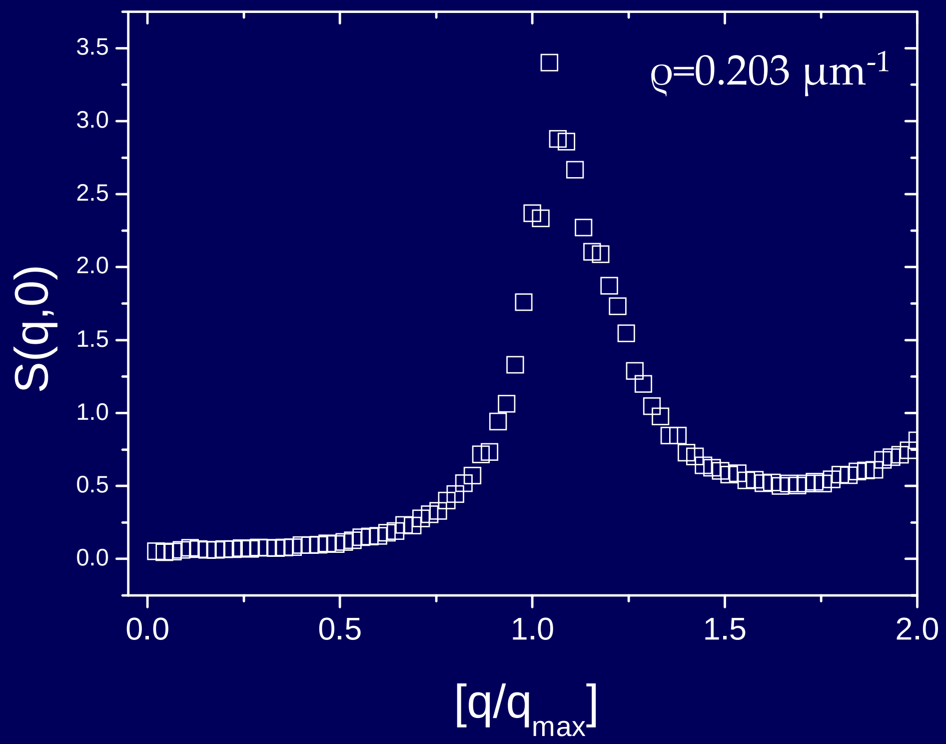
*Lutz, Kollmann, Bechinger, PRL **93**, 026001 (2004)*

SFD -Mobility



*Lutz, Kollmann, Bechinger, PRL **93**, 026001 (2004)*

Finite Size Effects ?



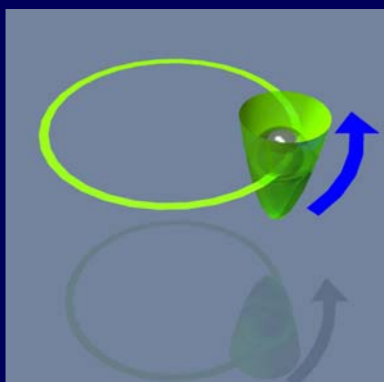
$$q_{max} = \frac{2\pi}{a}$$

$$\lim_{q\to 0} \frac{\partial S(q,0)}{\partial q} \approx 0$$

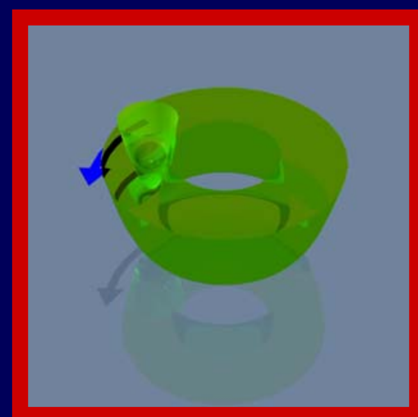
From Diffusive to Driven Motion

f_T

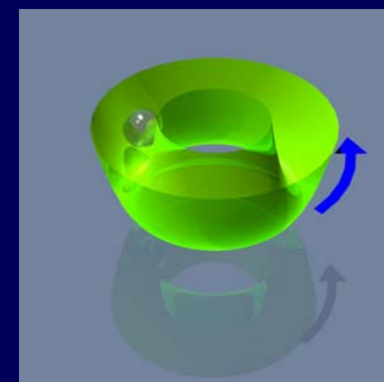
f_T →



Single moving trap



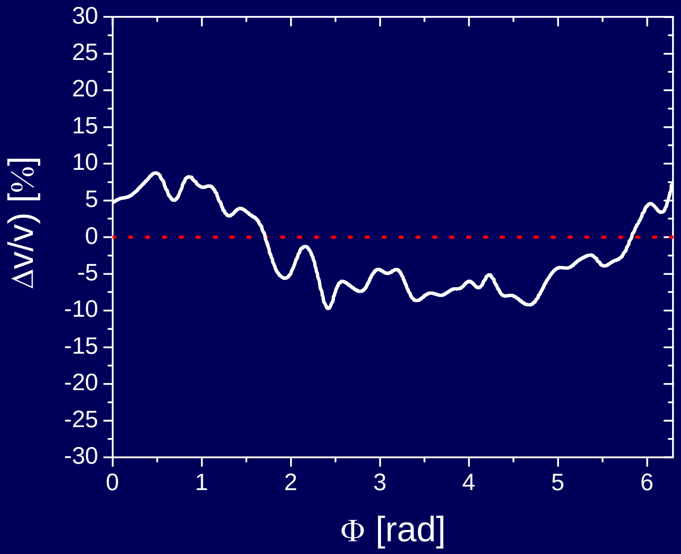
intermediate regime



quasi-static toroidal trap

*Lutz, Reichert, Stark, Bechinger, EPL **74,** 719 (2006)*

Phase-Slipe Regime



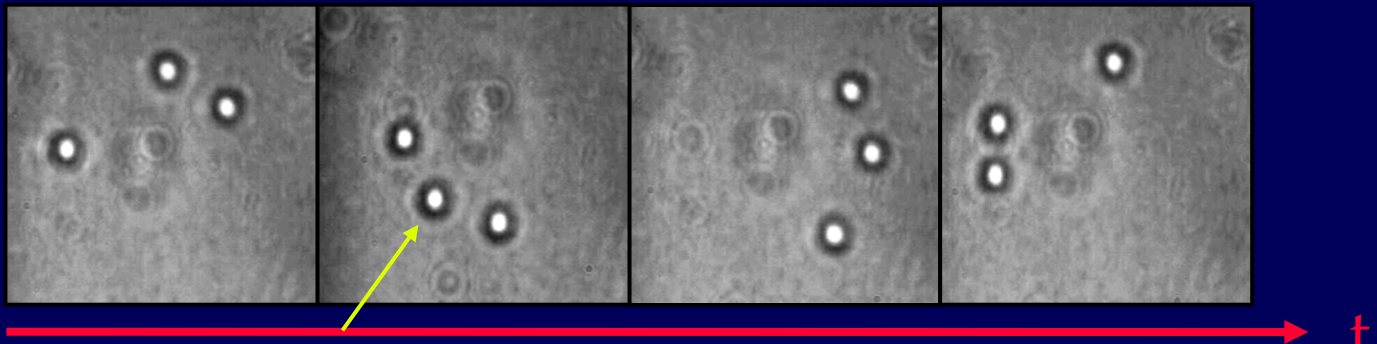
- silica particles, σ = 3μm
- ethanol (3D tweezing)
- $f_T = 76 Hz$

constant, non-conservative force

Circling Particles in Toroidal Trap

- silica particles, $\sigma = 3\mu m$
- electrostatic interaction , $\kappa^{-1} \approx 300nm$
- ethanol (3D tweezing)
- $f_T = 76Hz$

mechanism:



particle pair catches up with isolated sphere

max. screening from fluid flow

→ highest mobility

escape of the two front particles

particle pair catches up with isolated sphere

Lutz, Reichert, Stark, Bechinger, Europhys. Lett., ***74****, 719 (2006)*

Summary

Colloids are versatile model systems for statistical physics

„Colloids are the computer simulator´s dream" (Daan Frenkel)

- realization of SF-conditions in colloidal systems

  topographic structures, optical tweezers

- transition from normal diffusion to SFD

  dependence of crossover from particle interaction and density

- F obtained from collective system behavior

  asymptotic single-particle properties derived from short-time collective behavior