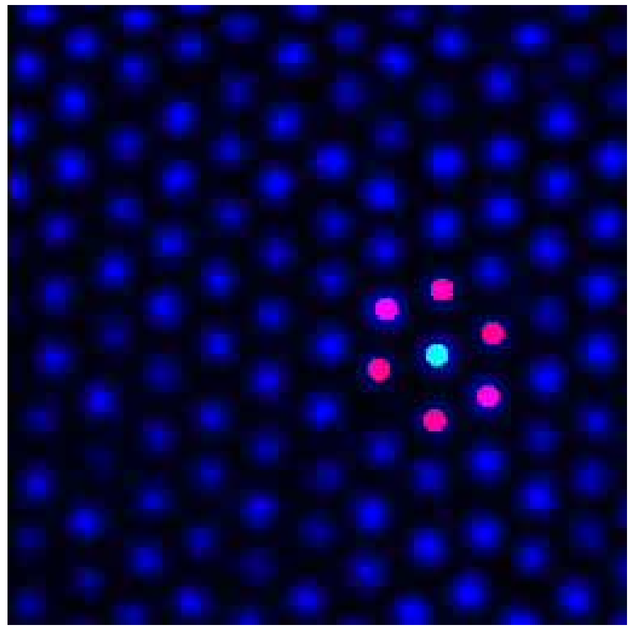
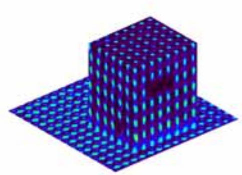
Dynamics of Colloids



Arnout Imhof



Universiteit Utrecht

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Dynamics of Colloids

Dynamics of Soft Matter depends on Brownian motion

- Transport of particles by diffusion
- Rheology (deformation and flow)
- Kinetics of phase separation
- Crystallization kinetics
- …

Outline

- Brownian motion of an individual particle
- Diffusion of interacting particles
- The various diffusion coefficients
- Methods to measure particle diffusion
- Results of experiments

A simple model: The Langevin equation

$$\frac{d\mathbf{p}}{dt} = -\gamma\frac{\mathbf{p}}{m} + \mathbf{f}(t)$$

momentum

friction/mass

random force

$$\langle \mathbf{f}(t) \rangle = \mathbf{0}$$

$$\langle \mathbf{f}(t)\mathbf{f}(t') \rangle = \mathbf{G}\delta(t-t')$$

shorthand for:

$$\begin{pmatrix} f_x f_x & f_x f_y & f_x f_z \\ f_y f_x & f_y f_y & f_y f_z \\ f_z f_x & f_z f_y & f_z f_z \end{pmatrix}$$

matrix to be determined

Integrate:

$$\mathbf{p}(t)=\mathbf{p}(0)\exp(-\gamma t/m)+\int_0^t d\tau\,\mathbf{f}(\tau)\exp(-\gamma(t-\tau)/m)$$

$$\langle \mathbf{p}(\tau)\mathbf{f}(0)\rangle = \langle \mathbf{p}(\tau)\rangle\langle \mathbf{f}(0)\rangle = \mathbf{0}$$

$$\begin{aligned}\langle \mathbf{p}(t)\mathbf{p}(t)\rangle &= \mathbf{p}(0)\mathbf{p}(0)\exp(-2\gamma t/m)\\ &+\int_0^t d\tau\,\cancel{\langle \mathbf{p}(0)\mathbf{f}(\tau)+\mathbf{p}(\tau)\mathbf{f}(0)\rangle}\exp(-\gamma(2t-\tau)/m)\\ &+\int_0^t d\tau_1\int_0^t d\tau_2\,\langle \mathbf{f}(\tau_1)\mathbf{f}(\tau_2)\rangle\exp(-\gamma(2t-\tau_1-\tau_2)/m)\end{aligned}$$

$$\mathbf{G}\delta(\tau_1-\tau_2)$$

$$=\mathbf{p}(0)\mathbf{p}(0)\exp(-\gamma t/m)+\frac{\mathbf{G}m}{2\gamma}\left(1-\exp(-2\gamma t/m)\right)$$

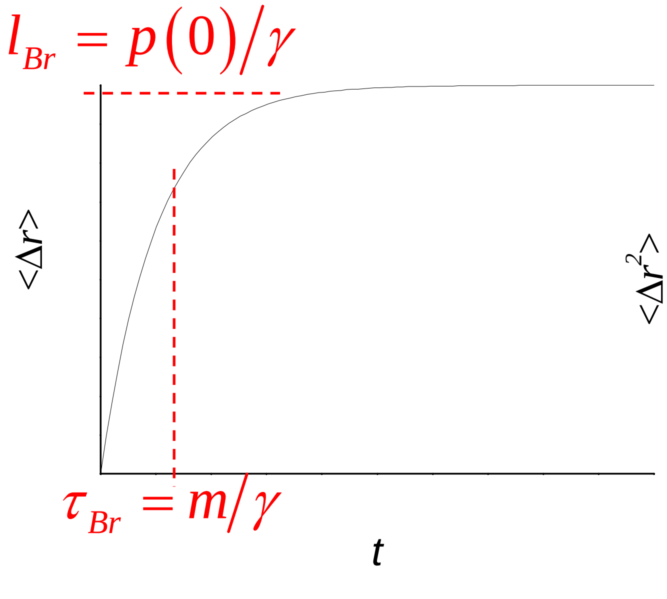
$$\left.\begin{aligned}&\lim_{t\to\infty}\langle \mathbf{pp}\rangle = \frac{\mathbf{G}m}{2\gamma}\\ &\textit{equipartition:}\quad \frac{\langle \mathbf{pp}\rangle}{2m}=\frac{1}{2}kT\,\mathbf{I}\end{aligned}\right\}\quad \boxed{\mathbf{G}=2\gamma kT\,\mathbf{I}}$$

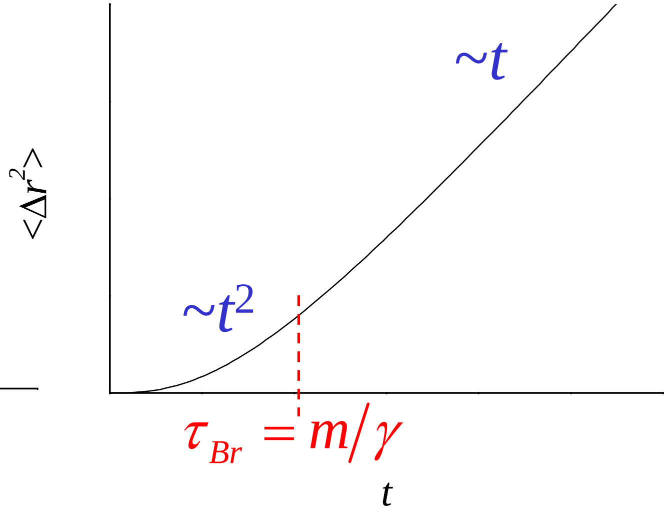
$$\Delta\mathbf{r}(t) \equiv \mathbf{r}(t) - \mathbf{r}(0) = \int_0^t \frac{\mathbf{p}(t)}{m} dt$$

$$= \frac{\mathbf{p}(0)}{\gamma}\left[1 - \exp(-\gamma t/m)\right] + \frac{1}{\gamma}\int_0^t d\tau\, \mathbf{f}(\tau)\left[1 - \exp(-\gamma(t-\tau)/m)\right]$$

$$\langle \Delta\mathbf{r}(t)\Delta\mathbf{r}(t)\rangle = \frac{\mathbf{p}(0)\mathbf{p}(0)}{\gamma^2}\left[1 - \exp(-\gamma t/m)\right]^2$$

$$+ \frac{2mkT}{\gamma^2}\mathbf{I}\left\{\frac{\gamma t}{m} + \frac{1}{2}\left[1 - \exp(-2\gamma t/m)\right] - 2\left[1 - \exp(-\gamma t/m)\right]\right\}$$





The Brownian time scale

Particle motion becomes Brownian (diffusive) after:

$$\tau_{Br} = \frac{m}{\gamma} = \frac{m}{6\pi\eta_0 a} \approx \frac{\rho a^2}{\eta_0} \approx 10^{-8}\ \mathrm{s}$$

$$l_{Br} = \frac{\langle p(0) \rangle}{\gamma} = \frac{\sqrt{3mkT}}{6\pi\eta_0 a} \approx \sqrt{\frac{\rho kT}{\eta_0^2 a}} \approx 10^{-10}\ \mathrm{m}$$

In processes for which $\Delta r >> l_{Br}$ a description on the Brownian time scale is sufficient. Only position coordinates are needed ***(coarse graining)****.*

Diffusion of interacting Brownian particles

Several ways to proceed:

- Liouville equation: $(\mathbf{p}_i, \mathbf{r}_i)$ *and integrate out* $\mathbf{p}_i$
- Langevin equation: *include interaction forces*

$$\left(d\mathbf{p}_i/dt\right) = -\left(\gamma/m\right)\mathbf{p}_i + \sum_j \mathbf{F}_{ij} + \mathbf{f}_i\left(t\right)$$

and integrate out $\mathbf{p}_i$

- Einstein/Batchelor: *immediately start on Brownian time scale*

$$\Downarrow$$

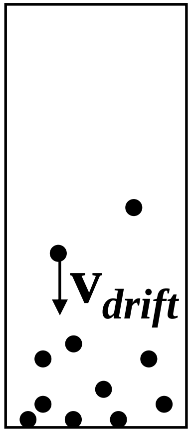
Smoluchowski equation
(generalized diffusion eqn.)

Brownian motion

Einstein's argument:

Equilibrium in the presence of an external force:

$$\mathbf{K} = -\nabla\Phi$$



1) In equilibrium Boltzmann says:

$$P(\mathbf{r}) = P_0 \exp(-\Phi / kT)$$

Probability density function (~ concentration)

2) On the other hand: *drift flux + diffusive flux = 0*

$$P\mathbf{v}_{drift}$$

$$P\,\mathbf{K}/\gamma$$

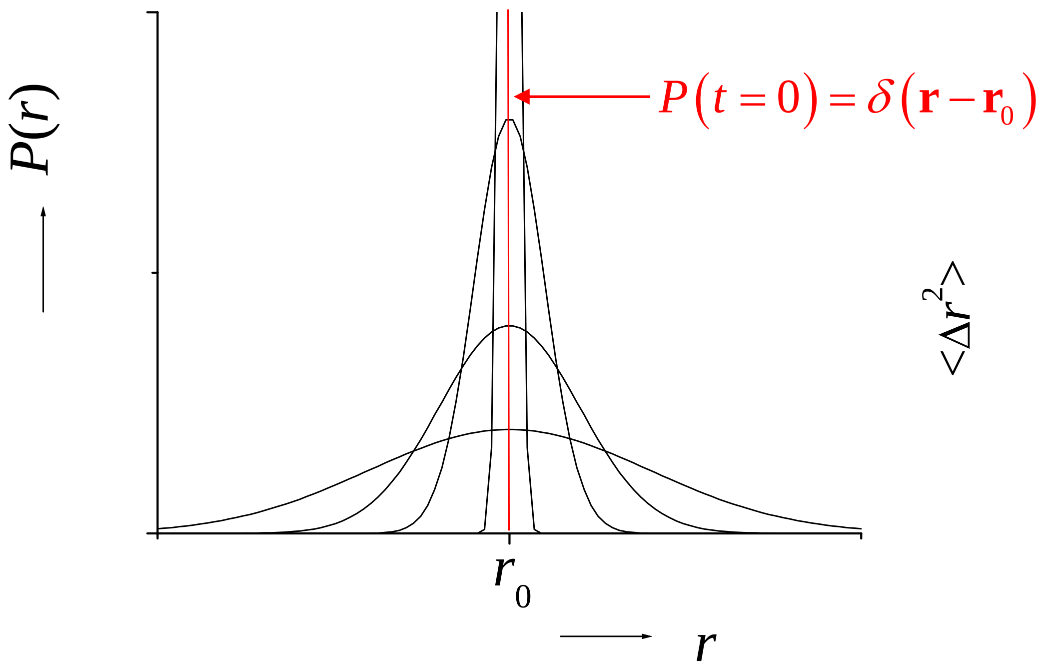
$$\mathbf{J} = -(P/\gamma)\nabla\Phi \quad -D_0\nabla P \quad = \quad 0 \qquad \Rightarrow \boxed{D_0 = \frac{kT}{\gamma}}$$

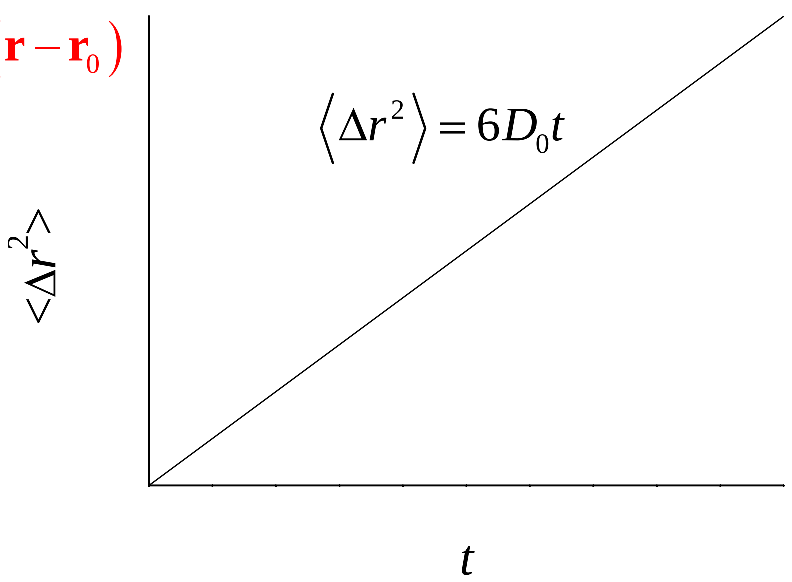
Now <u>remove</u> the external force:

System will return to equilibrium with flux: $\mathbf{J} = -D_0 \nabla P$

Continuity equation (conservation of particles): $\dfrac{\partial P}{\partial t} = -\nabla \cdot \mathbf{J}$

$$\boxed{\frac{\partial P}{\partial t} = D_0 \nabla^2 P}$$





Diffusion of interacting particles

Particle interaction potential: $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$

Imagine that we turn on an extra interaction: $\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$

1) Boltzmann :

$$P_N(\mathbf{r}_1, \ldots, \mathbf{r}_N) = P_N^0 \exp\left(-\frac{U + \Phi}{kT}\right)$$

probability density of finding
particle 1 *at* $\mathbf{r}_1$
<u>and</u> 2 *at* $\mathbf{r}_2$
<u>and</u> …

2) Total flux = 0:

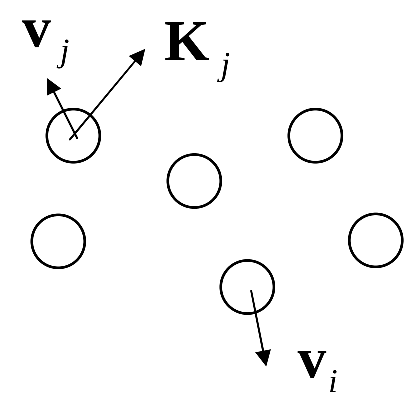
$$\mathbf{J}^{\text{interaction}} + \mathbf{J}^{\text{diff}} = \mathbf{0}$$

$$\mathbf{J}_i^{\text{diff}} = -\sum_j \mathbf{D}_{ij} \cdot \nabla_j P_N$$

diffusion matrices

$$\mathbf{J}_i^{\text{interaction}} = P_N \mathbf{v}_i$$
$$= P_N \sum_j \mathbf{M}_{ij}\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\right)\cdot\mathbf{K}_j$$

microscopic mobility matrices



"Hydrodynamic interactions"

$$\sum_j \left\{ P_N \mathbf{M}_{ij}\cdot\nabla_j\left(U+\Phi\right) + \mathbf{D}_{ij}\cdot\nabla_j P_N \right\} = 0$$

$$\sum_j \left\{ \mathbf{M}_{ij} - \frac{\mathbf{D}_{ij}}{kT} \right\}\cdot\nabla_j\left(U+\Phi\right) = 0$$ for any choice of Φ

$\boxed{\mathbf{D}_{ij} = kT\mathbf{M}_{ij}}$ = generalization of the Einstein relation

*depend on **all** particle positions*

Now <u>turn off</u> the extra potential Φ.

equilibrium is restored by:

the diffusive flux $$\mathbf{J}_i^{\text{diff}} = -\sum_j \mathbf{D}_{ij} \cdot \nabla_j P_N$$

and interaction flux $$\mathbf{J}_i^{\text{int}} = -P_N \sum_j \mathbf{M}_{ij} \cdot \nabla_j U$$

Continuity equation (conservation of particles):

$$\frac{\partial P_N}{\partial t} = -\sum_i \nabla_i \cdot \left(\mathbf{J}_i^{\text{diff}} + \mathbf{J}_i^{\text{int}} \right)$$

$$\boxed{\frac{\partial P_N\left(\mathbf{r}_1, \ldots, \mathbf{r}_N, t\right)}{\partial t} = \sum_{i,j} \nabla_i \cdot \mathbf{D}_{ij} \cdot \left\{ \nabla_j P_N + P_N \nabla_j \left(U/kT \right) \right\}}$$

Smoluchowski equation

$$\boxed{\frac{\partial P_N\left(\mathbf{r}_1,\ldots,\mathbf{r}_N,t\right)}{\partial t}=\sum_{i,j}\underbrace{\nabla_i\cdot\mathbf{D}_{ij}}_{\substack{\text{hydrodynamic}\\\text{interactions}}}\cdot\left\{\nabla_j P_N+P_N\nabla_j\underbrace{\left(U/kT\right)}_{\substack{\text{direct}\\\text{interactions}}}\right\}}$$

Assuming *absence of H.I.* <u>and</u> *absence of D.I.* ,

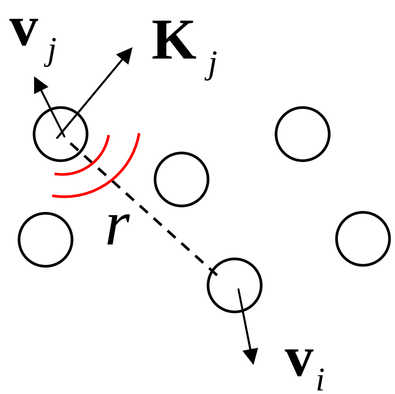
$$\mathbf{D}_{ii}=D_0\mathbf{I} \qquad U\equiv 0$$

$$\mathbf{D}_{ij}=\mathbf{0}$$

we recover the diffusion equation:

$$\boxed{\frac{\partial P}{\partial t}=D_0\nabla^2 P}$$

Hydrodynamic interactions



1) H.I. are *many-body:*

$$\mathbf{v}_i = \sum_j \mathbf{M}_{ij}\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\right)\cdot\mathbf{K}_j$$

2) H.I. are *fast*:

$$\tau_H \approx \frac{\rho_0}{\eta_0} r^2 \approx \frac{\rho_0}{\eta_0} a^2 \approx \tau_{Br}$$

3) H.I. are *long range:*

$$M_{ij} \approx O\left(\frac{1}{r}\right)$$

Hydrodynamic interactions

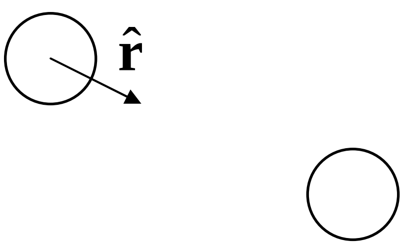
For **two** spheres the solution is relatively easy:

$$\mathbf{v}_i = \sum_{j=1}^{2} \mathbf{M}_{ij} \cdot \mathbf{K}_j \qquad (\, i = 1, 2 \,)$$

$$\mathbf{M}_{ij} = \frac{1}{3\pi\left(a_i + a_j\right)} \left\{ A_{ij}\hat{\mathbf{r}}\hat{\mathbf{r}} + B_{ij}\left(\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}}\right) \right\}$$

along line of centers

perp. to line of centers



$$A_{11} = 1 - \frac{60\lambda^3}{(1+\lambda)^4 \rho^4} + O\left(\rho^{-6}\right)$$

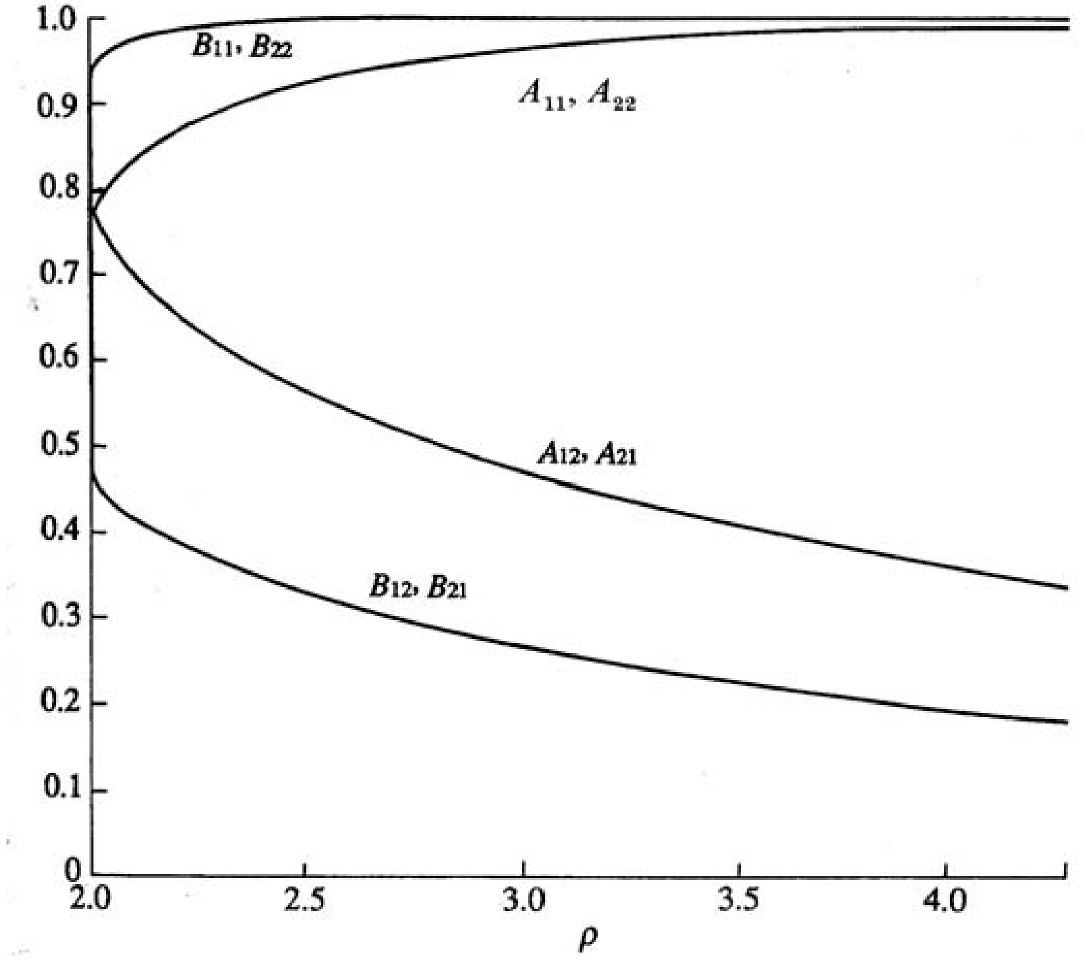
$$A_{12} = \frac{3}{2\rho} - \frac{2\left(1+\lambda^2\right)}{(1+\lambda)^2 \rho^3} + O\left(\rho^{-7}\right)$$

$$B_{11} = 1 + O\left(\rho^{-7}\right)$$

$$B_{12} = \frac{3}{4\rho} - \frac{1+\lambda^2}{(1+\lambda)^2 \rho^3} + O\left(\rho^{-7}\right)$$

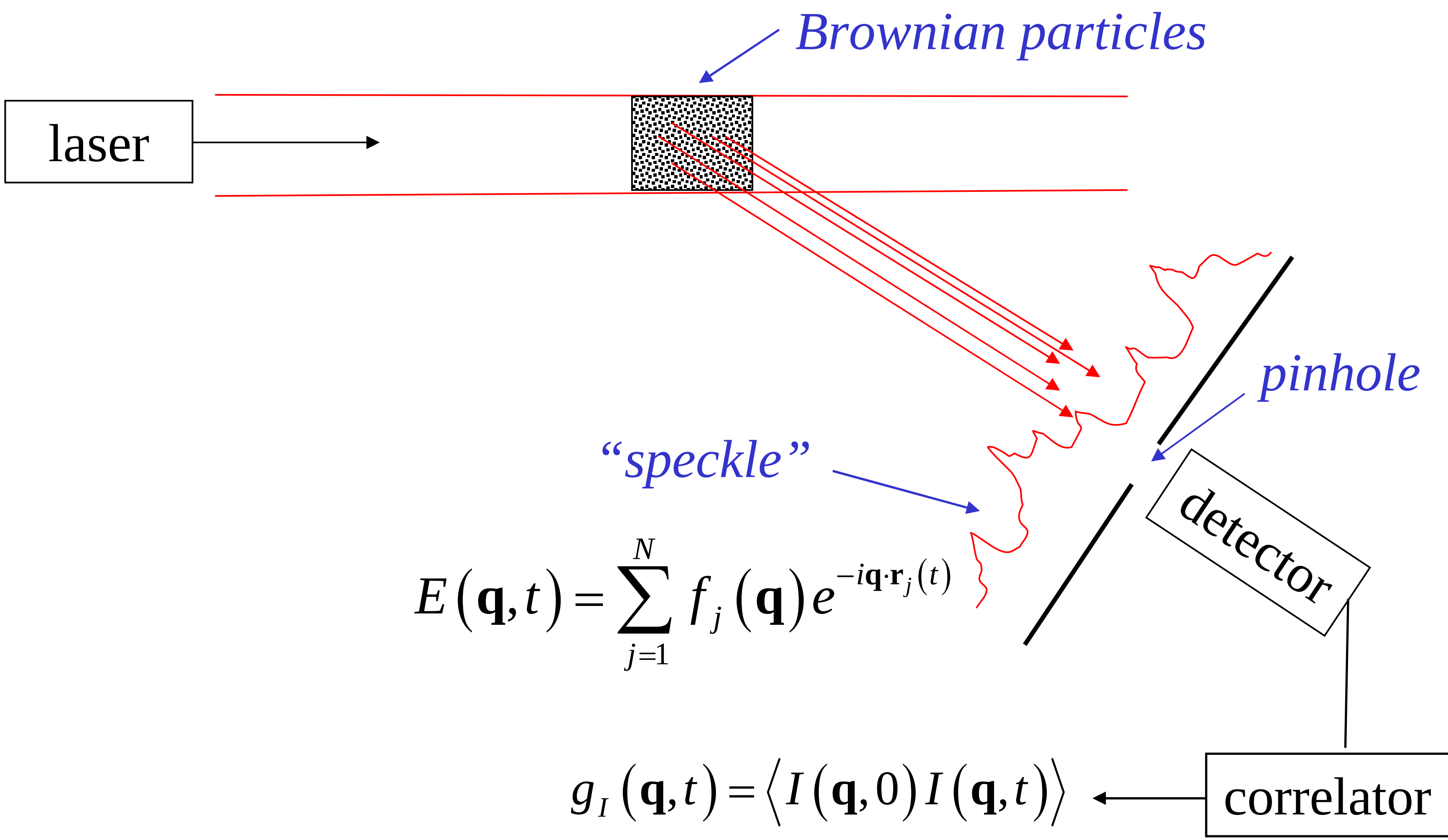
$$\rho = 2r/\left(a_1 + a_2\right)$$

$$\lambda = a_2/a_1$$



G.K. Batchelor, *J. Fluid Mech.* **74**, 1 (1976)

Dynamic light scattering



$$E(\mathbf{q},t)=\sum_{j=1}^{N} f_j(\mathbf{q})\, e^{-i\mathbf{q}\cdot\mathbf{r}_j(t)}$$

$$g_I(\mathbf{q},t)=\langle I(\mathbf{q},0)\, I(\mathbf{q},t)\rangle$$

Dynamic Light Scattering

What is measured is the "intensity autocorrelation function":

$$g_I(\mathbf{q},t) = \langle I(\mathbf{q},0)\, I(\mathbf{q},t)\rangle$$

$$= \langle I\rangle^2 + \left|\langle E(\mathbf{q},0)\, E^*(\mathbf{q},t)\rangle\right|^2$$

Siegert relation

(If scattering volume >> "correlation volume".)

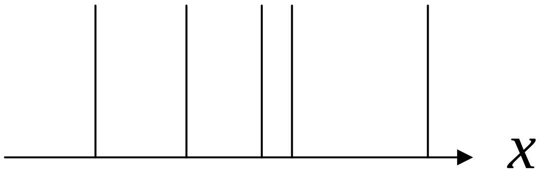
$$S_c(\mathbf{q},t) = \frac{\langle E(\mathbf{q},0)\, E^*(\mathbf{q},t)\rangle}{\langle I\rangle}$$

$$= \left\langle \frac{1}{N}\sum_{j,k=1}^{N} \exp\left(i\mathbf{q}\cdot\left[\mathbf{r}_j(0) - \mathbf{r}_k(t)\right]\right)\right\rangle$$

"dynamic structure factor"

Dynamic structure factor is related to the *microscopic density*:

$$\rho(\mathbf{r},t)=\sum_{j=1}^{N}\delta\left(\mathbf{r}-\mathbf{r}_j(t)\right)$$



Its Fourier transform is:

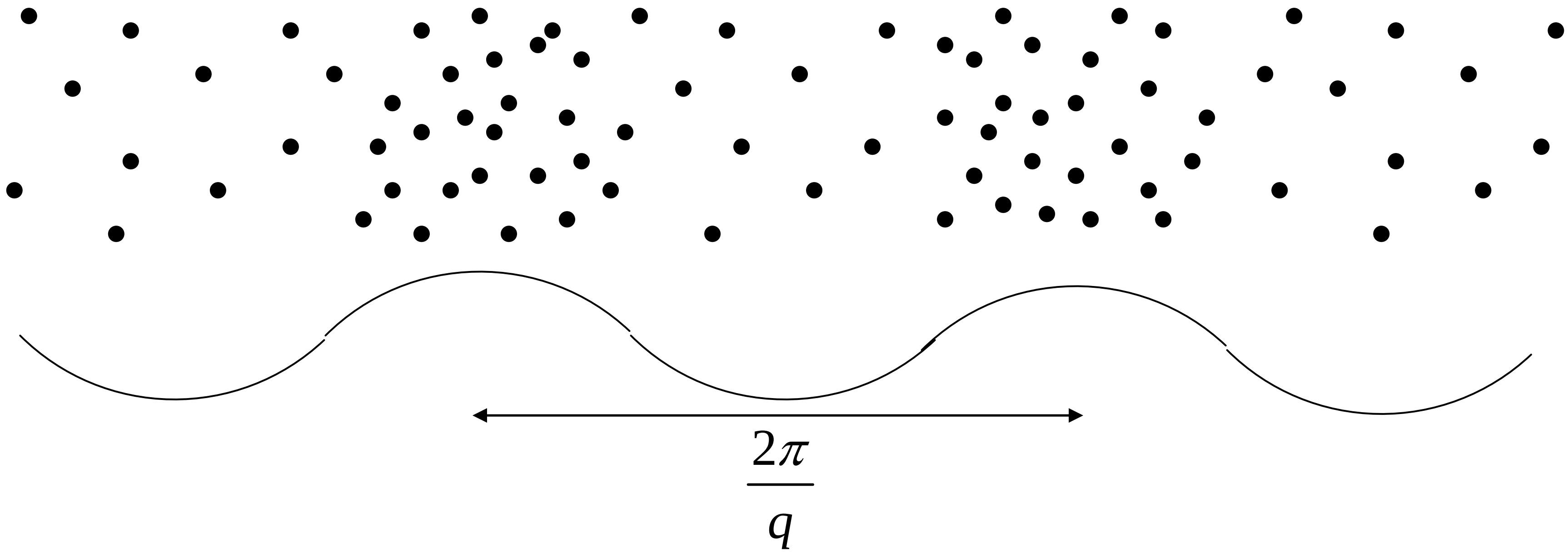
$$\rho(\mathbf{q},t)=\int d\mathbf{r}\,\rho(\mathbf{r},t)\exp(-i\mathbf{q}\cdot\mathbf{r})=\sum_{j=1}^{N}\exp\left(-i\mathbf{q}\cdot\mathbf{r}_j(t)\right)$$

of which the time-autocorrelation function is precisely $S_c(\mathbf{q},t)$:

$$\boxed{\frac{1}{N}\left\langle\rho(\mathbf{q},t)\,\rho(\mathbf{q},t=0)\right\rangle=\left\langle\frac{1}{N}\sum_{j,k}\exp\left(i\mathbf{q}\cdot\left[\mathbf{r}_j(0)-\mathbf{r}_k(t)\right]\right)\right\rangle=S_c(\mathbf{q},t)}$$

Collective diffusion

<u>Interpretation</u>: *decay of fluctuations in the microscopic density*



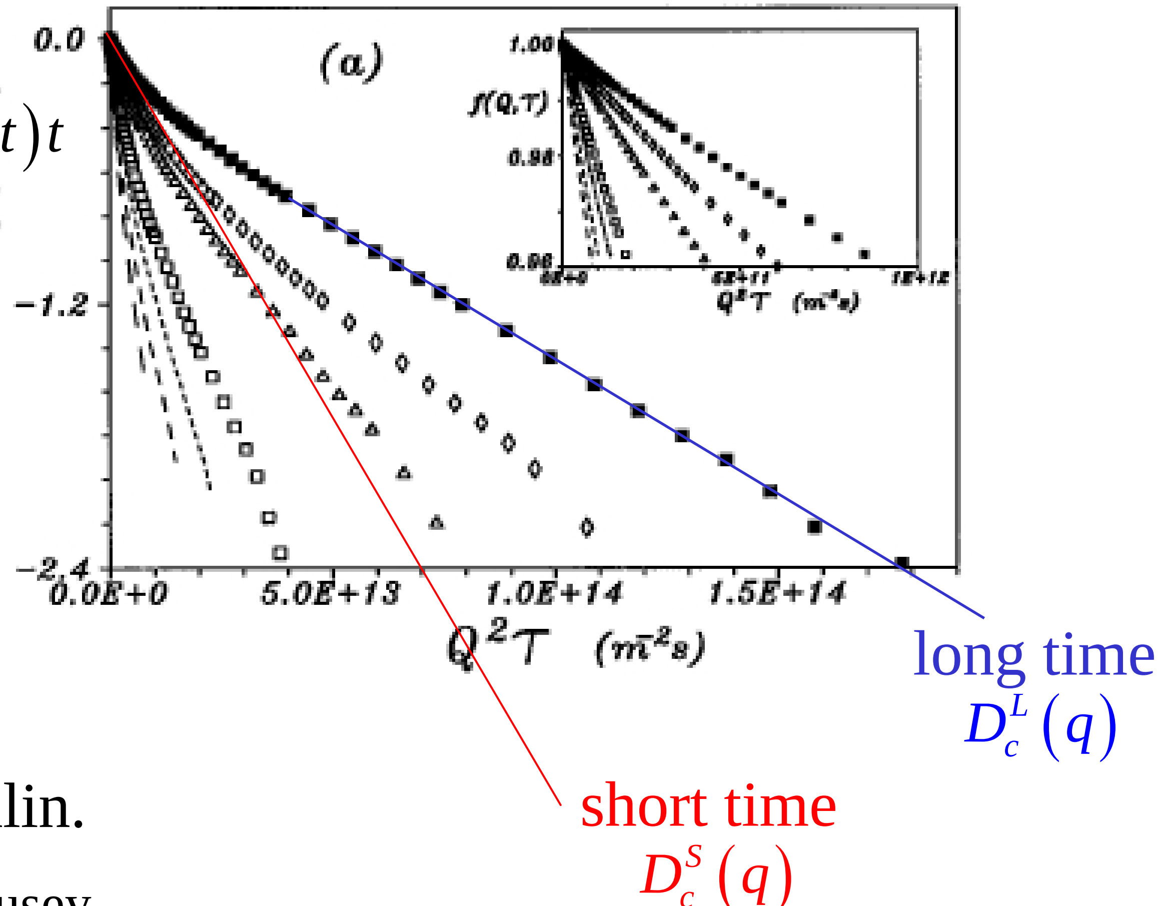
For interacting particles: $$S_c(q,t) = S(q)\exp\left(-q^2 D_c(q,t)\,t\right)$$

<u>Definition</u> of $D_c(\mathbf{q},t)$

("collective diffusion coefficient")

Collective diffusion

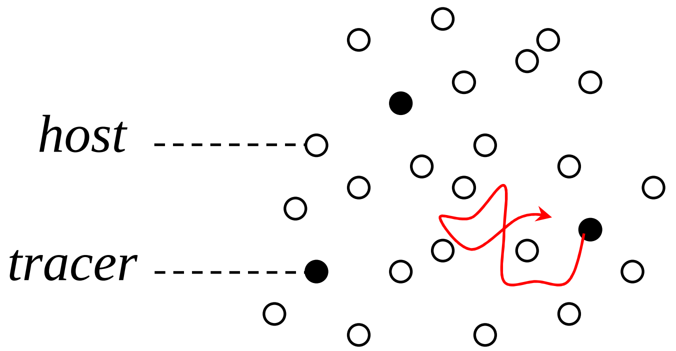
$$\ln S_c(\mathbf{q},t) = -q^2 D_c(\mathbf{q},t)\,t$$



Hard sphere pmma particles in *cis*-decalin.

P. N. Segrè and P. N. Pusey, *Phys. Rev. Lett.* **77**, 771 (1996)

Self-diffusion



Make most particles invisible except "*tracer particles*"

$$S_c(\mathbf{q},t) = \left\langle \frac{1}{N} \sum_{j,k=1}^{N} \exp\left(i\mathbf{q}\cdot\left[\mathbf{r}_j(0) - \mathbf{r}_k(t)\right]\right) \right\rangle$$

$$S_s(\mathbf{q},t) = \left\langle \frac{1}{N} \sum_{j=1}^{N} \exp\left(i\mathbf{q}\cdot\left[\mathbf{r}_j(0) - \mathbf{r}_j(t)\right]\right) \right\rangle$$

Tracers are independent and identical

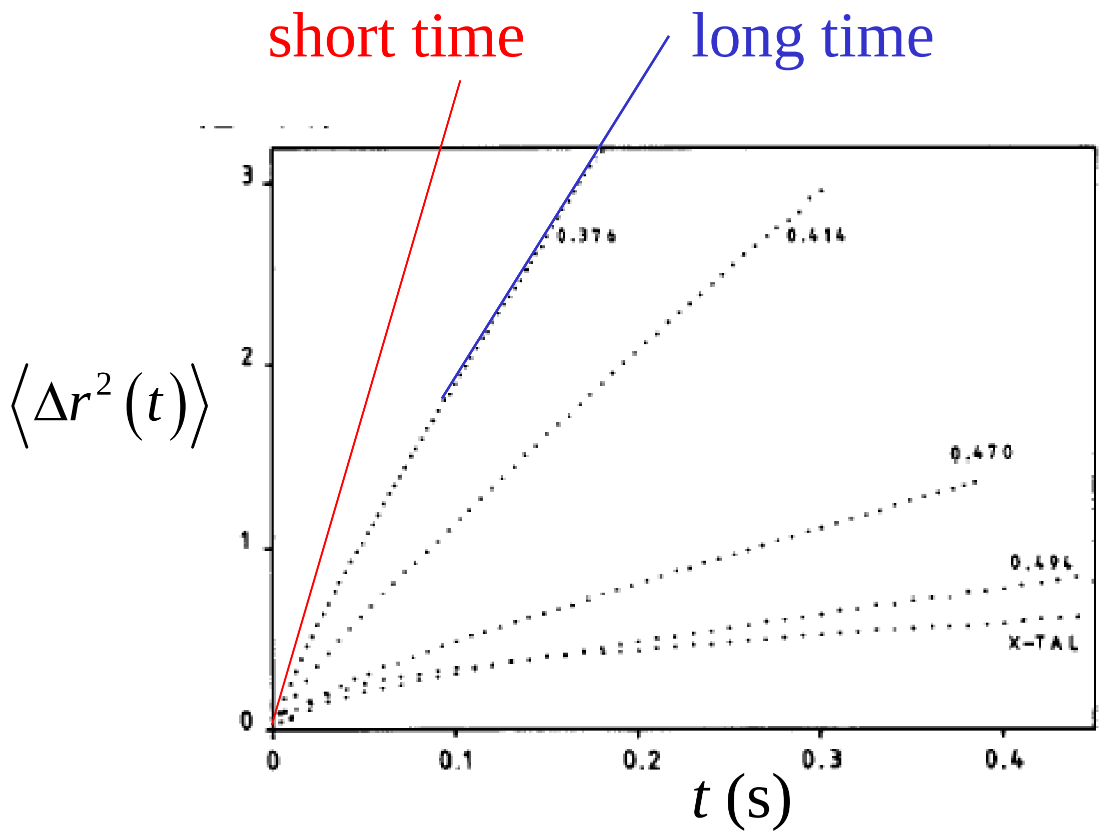
$$= \left\langle \exp\left(i\mathbf{q}\cdot\left[\mathbf{r}_1(0) - \mathbf{r}_1(t)\right]\right) \right\rangle$$

$$= \exp\left(-q^2 D_s(t)\, t\right)$$

Definition of $D_s(t)$

("self-diffusion coefficient")

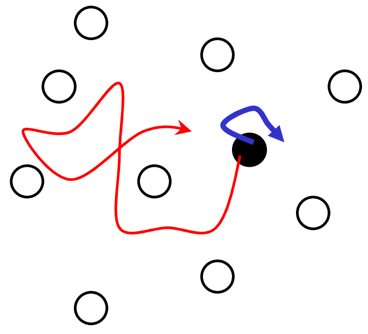
Self-diffusion



W. van Megen and S. M. Underwood,
J. Chem. Phys. **91**, 552 (1989)

Host particles:
pmma spheres index matched in decalin/CS_2

Tracer particles:
silica spheres



Experimental aspects: Suppression of multiple scattering

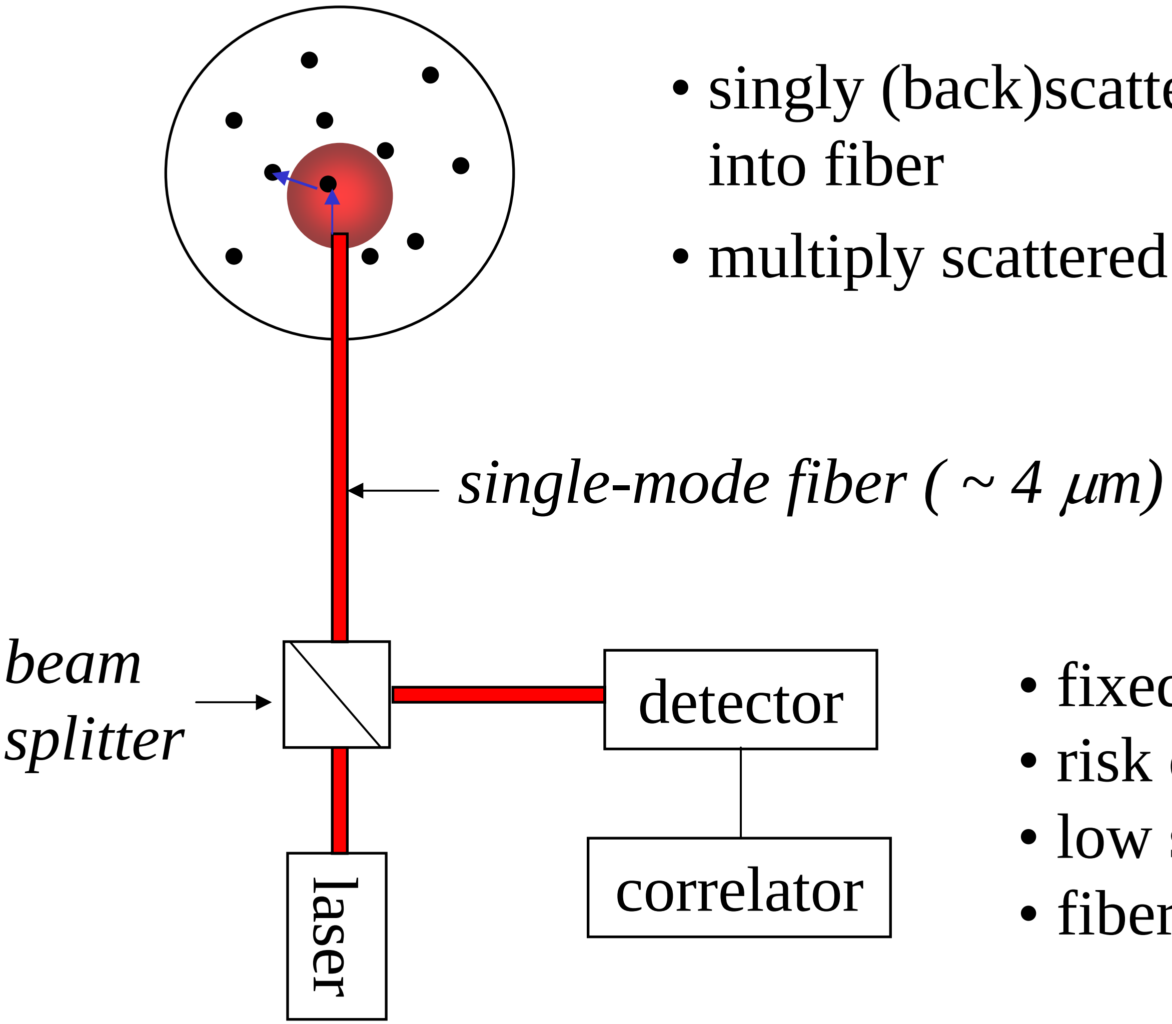
High concentrations: multiple scattering contributes to the IACF (even in nearly index matched suspensions).

Solutions:

- Use weakly scattering radiation (X-rays, neutrons)
- Use extremely small sample volume (FOQELS)
- Cross-correlate light scattered at different angles, but same **q**, since scattering at different **q**'s is uncorrelated. (TCDLS, 3DDLS)
- Use (fluorescent) labeling techniques (FRAP, FRS)

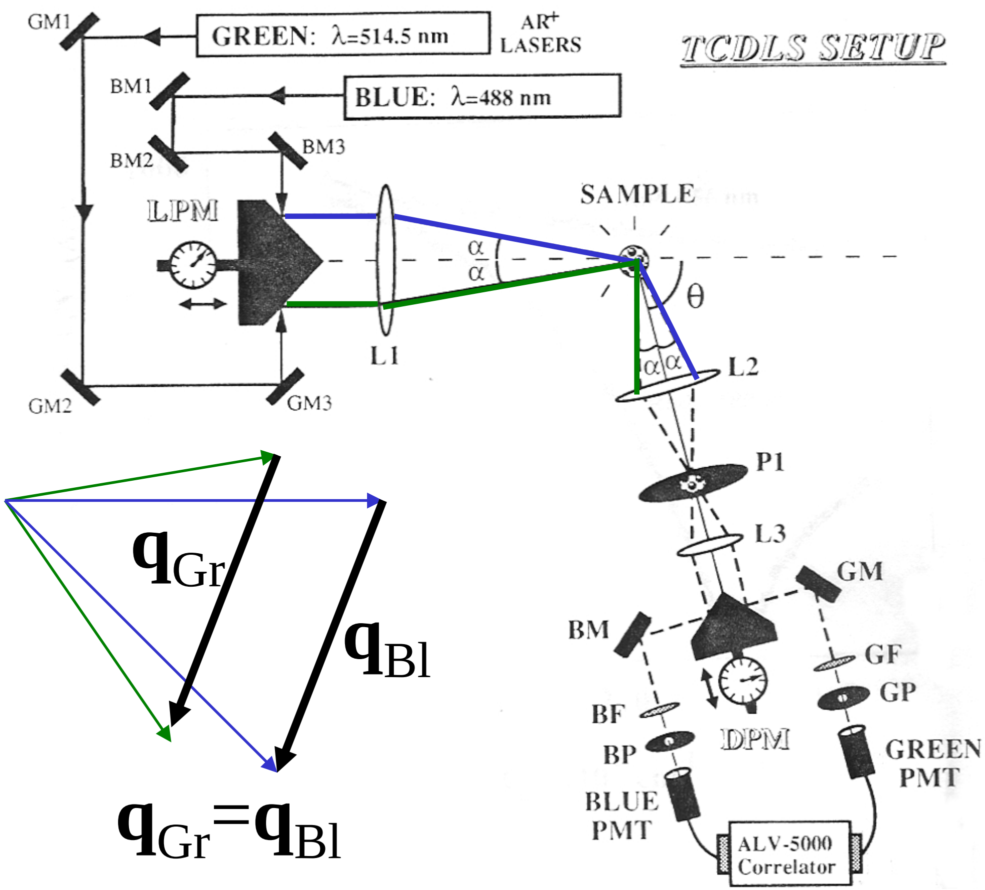
Fiber Optic QELS

- singly (back)scattered light returns into fiber
- multiply scattered light escapes



- fixed $q = 4\pi n/\lambda$
- risk of fiber-tip reflection
- low signal
- fiber may influence particles

Two-color DLS

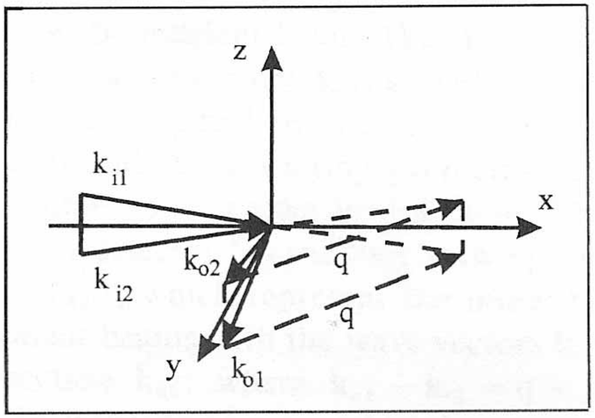


- variable *q*
- limited to reasonably transparant samples
- difficult to align

$$\mathbf{q}_{Gr}=\mathbf{q}_{Bl}$$

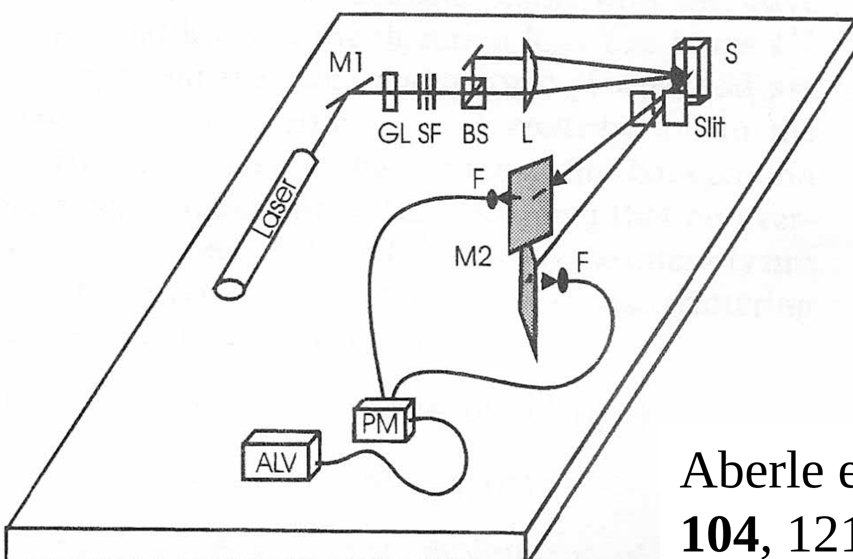
Segre et al., J. Mod. Opt. **42**, 1929 (1995)

3D DLS



Two beams of same color, but a few degrees out-of-plane.

$$\mathbf{q}_1 = \mathbf{q}_2$$

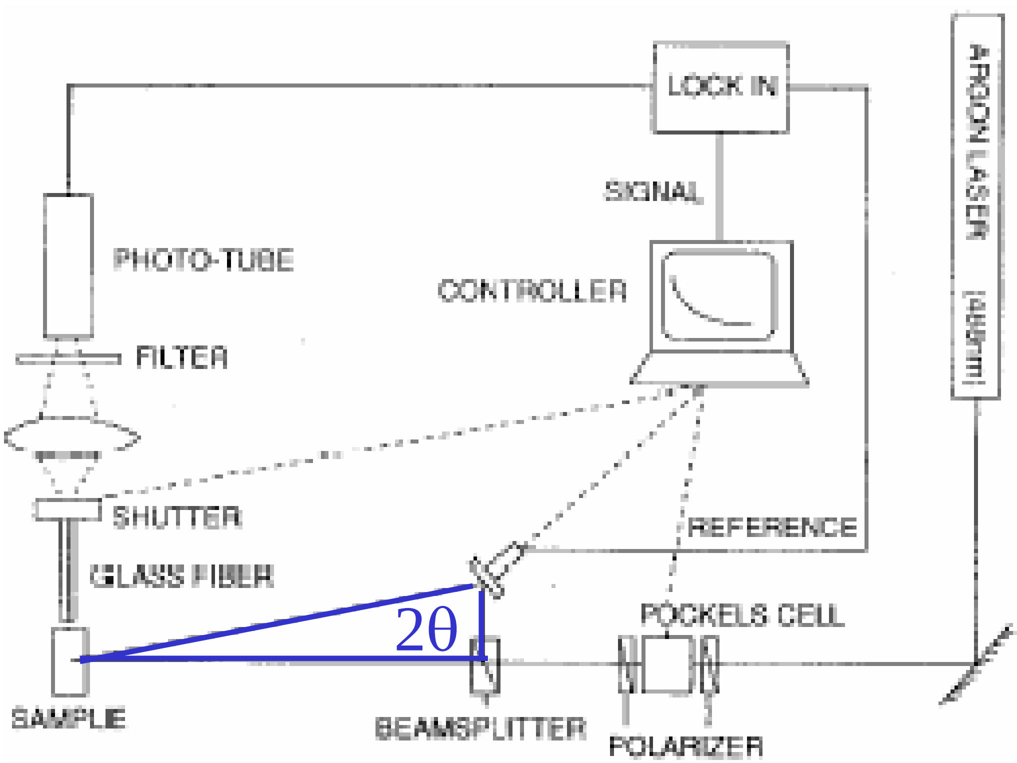


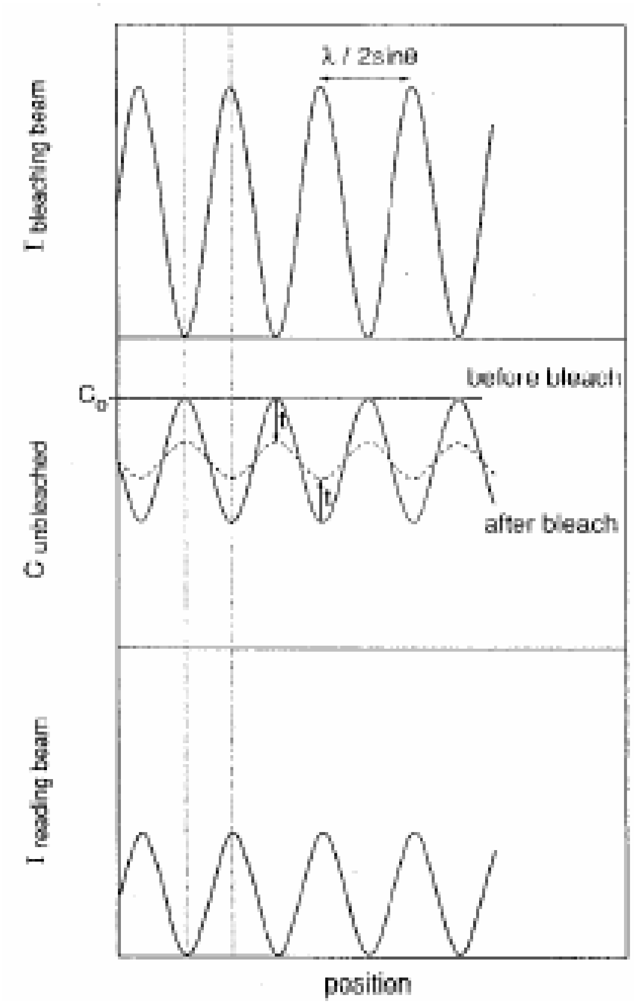
- variable *q*
- limited to reasonably transparant samples
- easier to align

Aberle et al., Prog. Colloid Polym. Sci. **104**, 121 (1997)

Fluorescence Recovery After Photobleaching

Interference pattern made by crossing two laser beams bleaches fluorescent particles: $q = 4\pi \sin\theta / \lambda$



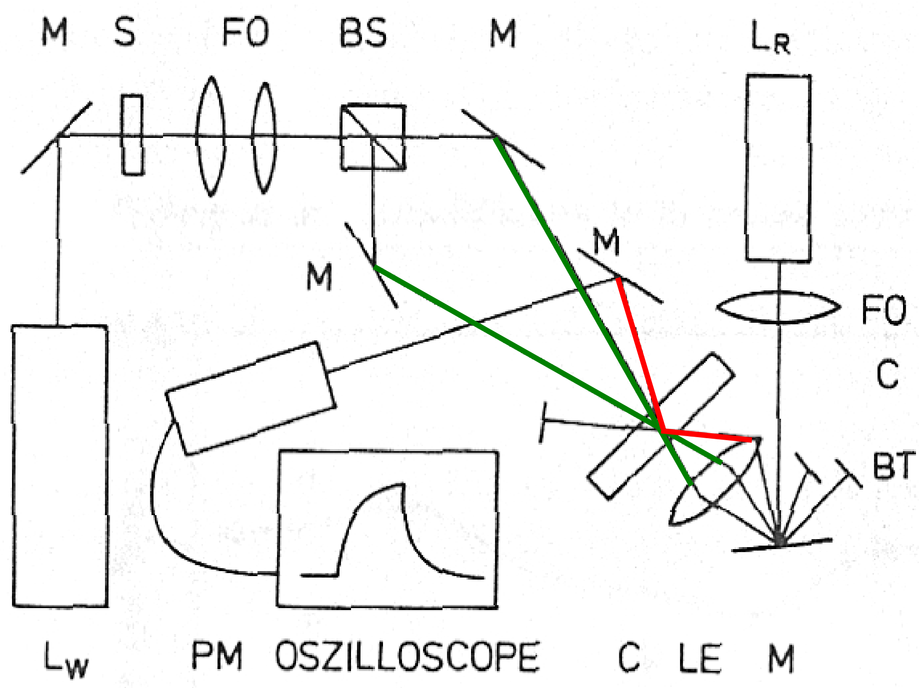


• multiple scattering no problem

• only long time self-diffusion

Forced Rayleigh scattering

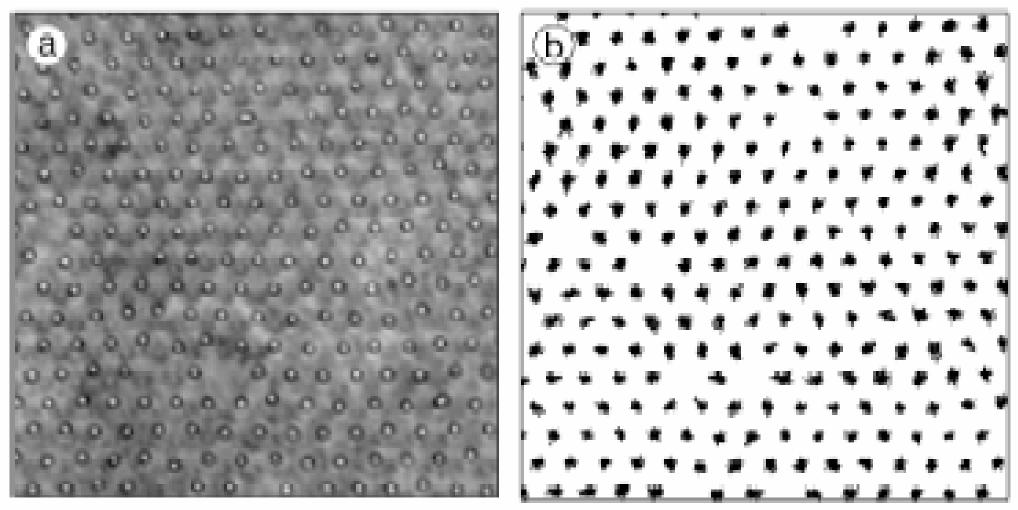
Interference pattern made by crossing two laser beams changes refractive index of dyed particles.



Palberg et al., Prog. Colloid Polym. Sci. **84**, 397 (1991)

- multiple scattering no problem
- only long time self-diffusion
- alignment of two lasers

Microscopy



Weiss et al., J. Chem. Phys. **109**, 8659 (1998).

- direct visual info
- spatially resolved
- transparant (or thin) samples needed
- limited to large or well-separated particles
- only long time data

Calculation and Measurement of diffusion coefficients

All techniques measure (in one way or another) the dynamic structure factors:

$$S_c(\mathbf{q},t) = \frac{1}{N}\sum_{i,j}^{N}\left\langle \exp\left\{ i\mathbf{q}\cdot\left(\mathbf{r}_j(0)-\mathbf{r}_k(t)\right)\right\}\right\rangle$$

$$= \left\langle \exp\left\{ i\mathbf{q}\cdot\left(\mathbf{r}_1(0)-\mathbf{r}_1(t)\right)\right\}\right\rangle + (N-1)\left\langle \exp\left\{ i\mathbf{q}\cdot\left(\mathbf{r}_2(0)-\mathbf{r}_1(t)\right)\right\}\right\rangle$$

What <…> means is:

equilibrium PDF

$$\left\langle f(\Gamma_0)\, g(\Gamma)\right\rangle = \int d\Gamma_0 \int d\Gamma\; f(\Gamma_0)\, g(\Gamma)\, P_N^{eq}(\Gamma_0) P_N(\Gamma_0,\Gamma,t)$$

$$\Gamma_0 = \left(\mathbf{r}_1(0),\ldots,\mathbf{r}_N(0)\right)$$

$$\Gamma = \left(\mathbf{r}_1(t),\ldots,\mathbf{r}_N(t)\right)$$

conditional PDF

(on initial condition Γ_0)

The conditional PDF is the solution of the Smoluchowski equation:

$$\begin{cases} \dfrac{\partial P_N}{\partial t} = \hat{\Omega}_S P_N \\ P_N\left(t=0\right) = \delta\left(\Gamma - \Gamma_0\right) \end{cases}$$

$$\begin{aligned} \hat{\Omega}_S\left(\ldots\right) &= \sum_{i,j}^{N} \nabla_i \cdot \mathbf{D}_{ij} \cdot \left(\nabla_j\left(\ldots\right) + \left(\ldots\right)\nabla_j\left(U/kT\right)\right) \\ &= \nabla \cdot \mathbf{D} \cdot \left(\nabla\left(\ldots\right) + \left(\ldots\right)\nabla\left(U/kT\right)\right) \end{aligned}$$

Its formal solution is:

$$P_N\left(\Gamma_0, \Gamma, t\right) = \exp\left\{\hat{\Omega}_S t\right\} P_N\left(t=0\right) \qquad \exp\left\{\hat{\Omega}_S t\right\} = \sum_{n=0}^{\infty} \frac{t^n}{n!} \hat{\Omega}_S^n$$

So we can write:

$$\begin{aligned} \left\langle f\left(\Gamma_0\right) g\left(\Gamma\right)\right\rangle &= \int d\Gamma_0 \int d\Gamma\, f\left(\Gamma_0\right) g\left(\Gamma\right) P_N^{eq}\left(\Gamma_0\right) P_N\left(\Gamma_0, \Gamma, t\right) \\ &= \int d\Gamma\, g\left(\Gamma\right) \exp\left\{\hat{\Omega}_S t\right\} \int d\Gamma_0\, f\left(\Gamma_0\right) P_N^{eq}\left(\Gamma_0\right) \delta\left(\Gamma - \Gamma_0\right) \\ &= \int d\Gamma\, g\left(\Gamma\right) \exp\left\{\hat{\Omega}_S t\right\} \left[f\left(\Gamma\right) P_N^{eq}\left(\Gamma\right)\right] \end{aligned}$$

Short time self-diffusion

Choose:
$$f(\Gamma) = \exp\{i\mathbf{q}\cdot\mathbf{r}_1\}$$
$$g(\Gamma) = \exp\{-i\mathbf{q}\cdot\mathbf{r}_1\}$$

$$\exp\{-q^2 D_s(t)t\} = \int d\Gamma \exp\{-i\mathbf{q}\cdot\mathbf{r}_1(t)\}\exp\{\hat{\Omega}_S t\}\left[\exp\{i\mathbf{q}\cdot\mathbf{r}_1(t)\}P_N^{eq}(\Gamma)\right]$$

Take the short time expansion:

$$-q^2 D_s^S = \int d\Gamma \exp\{-i\mathbf{q}\cdot\mathbf{r}_1(t)\}\hat{\Omega}_S\left[\exp\{i\mathbf{q}\cdot\mathbf{r}_1(t)\}P_N^{eq}(\Gamma)\right]$$

$$\hat{\Omega}_S(\ldots) = \nabla\cdot\mathbf{D}\cdot\left(\nabla(\ldots)+(\ldots)\nabla(U/kT)\right)$$

$+$ *partial integration*

$$\boxed{D_s^S = \left\langle \hat{\mathbf{q}}\cdot\mathbf{D}_{11}(\Gamma)\cdot\hat{\mathbf{q}}\right\rangle_{eq}}$$

general formula for short time self diffusion

Up to *pair interactions* we get:

$$\frac{D_s^S}{D_0} = 1 + (N-1)\int d\Gamma\, P_N^{eq}\hat{\mathbf{q}}\cdot\left\{(A_{11}-1)\hat{\mathbf{r}}_{12}\hat{\mathbf{r}}_{12} + (B_{11}-1)(\mathbf{I}-\hat{\mathbf{r}}_{12}\hat{\mathbf{r}}_{12})\right\}\cdot\hat{\mathbf{q}}$$

$$= 1 + \frac{(N-1)}{V^2}\int d\mathbf{r}_1 \int d\mathbf{r}_2\; g\left(|\mathbf{r}_1-\mathbf{r}_2|\right)\hat{\mathbf{q}}\cdot\left\{(A_{11}-1)\hat{\mathbf{r}}_{12}\hat{\mathbf{r}}_{12} + (B_{11}-1)(\mathbf{I}-\hat{\mathbf{r}}_{12}\hat{\mathbf{r}}_{12})\right\}\cdot\hat{\mathbf{q}}$$

$$= 1 + \frac{4\pi(N-1)}{3V}\int_0^\infty dr\, r^2 \left(A_{11}+2B_{11}-3\right) g(r)$$

Up to *pair interactions* for *hard spheres*:

$$g(r) = \exp\{-V(r)/kT\}$$

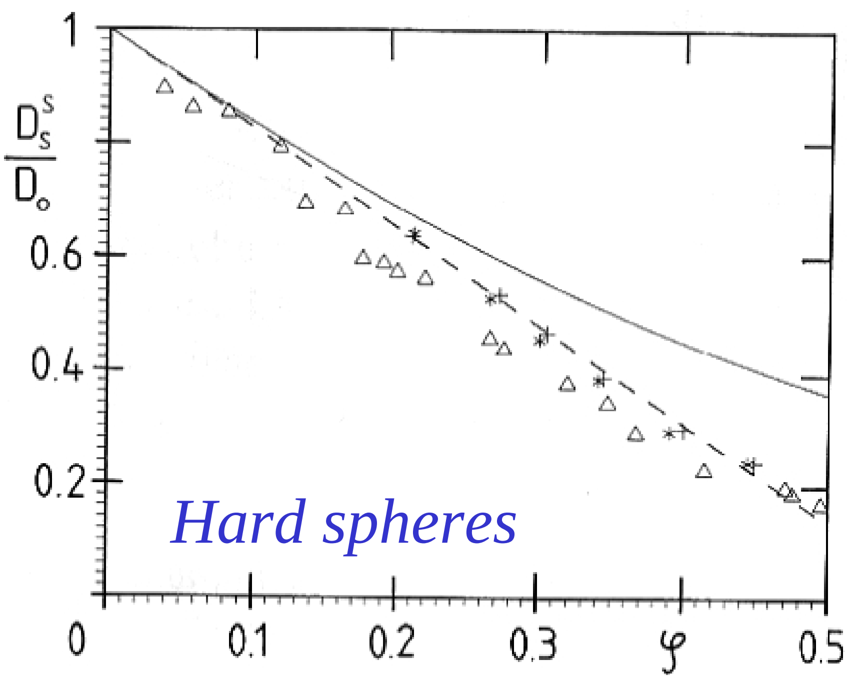
$$= \begin{cases} 1 & \text{for } r \geq 2a \\ 0 & \text{for } r < 2a \end{cases}$$

$$\boxed{\frac{D_s^S}{D_0} = 1 - \frac{15}{8}\phi}$$

Short time self-diffusion

$$D_s^S = \left\langle \hat{\mathbf{q}} \cdot \mathbf{D}_{11}\left(\Gamma\right) \cdot \hat{\mathbf{q}} \right\rangle_{eq}$$
$$= D_0\left(1 - 1.83\phi + 0.91\phi^2\right)$$

- Depends on *hydrodynamic interactions* with all particles
- Not on *direct interactions* (but indirectly through equilibrium PDF !)



+ quadratic term

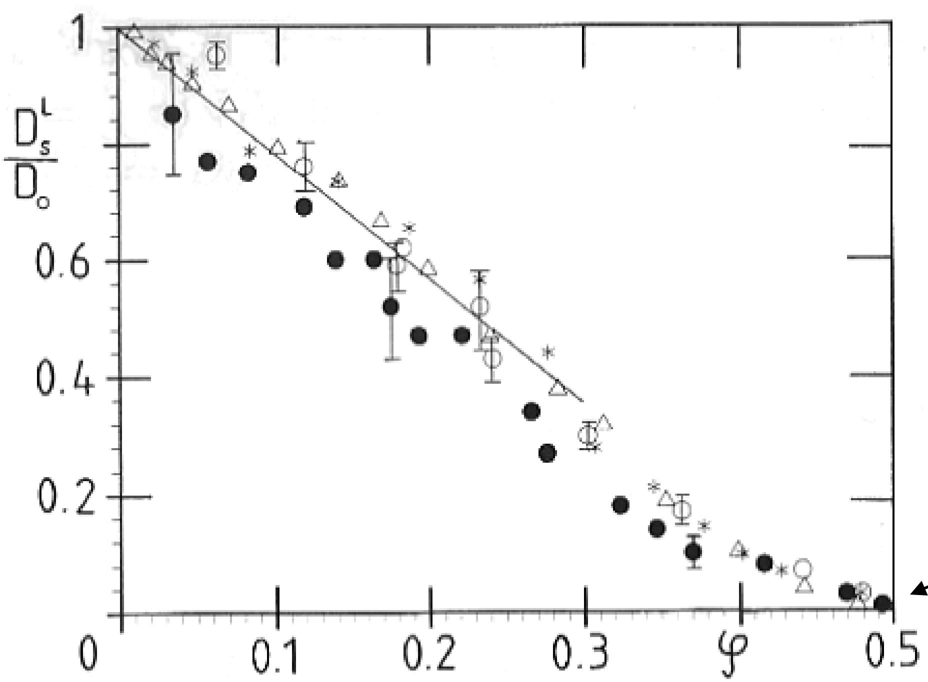
first order ϕ

Long time self-diffusion

Hard spheres:

$$\frac{D_s^L}{D_0} = 1 - 2.10\phi + \ldots$$

- Depends on *hydrodynamic interactions* and *direct interactions*.



vanishes at freezing

Short time collective diffusion

$$D_c^S(q) = D_0 \frac{H(q)}{S(q)}$$

q-dependent !

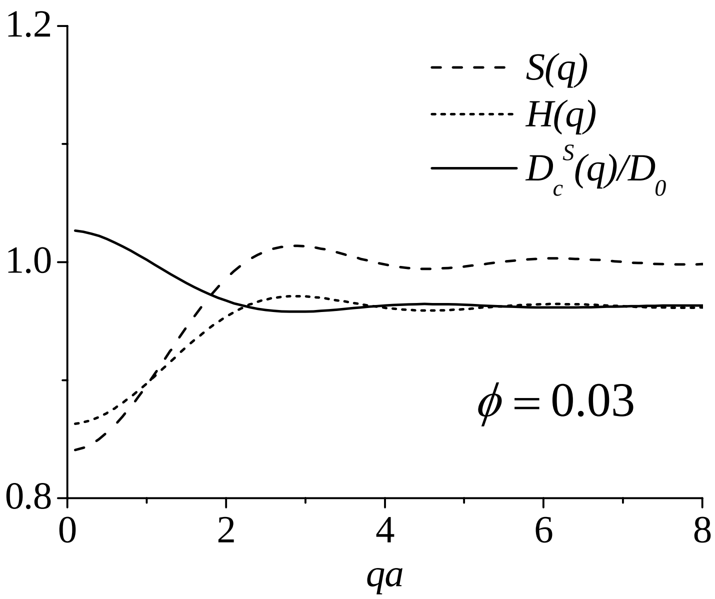
$$H(q) = \frac{1}{N}\sum_{i,j=1}^{N}\left\langle \left(\hat{\mathbf{q}} \cdot \frac{\mathbf{D}_{ij}(\Gamma)}{D_0} \cdot \hat{\mathbf{q}}\right) \exp\left\{ i\mathbf{q} \cdot \left(\mathbf{r}_i - \mathbf{r}_j\right)\right\}\right\rangle_{eq}$$

contains only the hydrodynamics
(but averaged over the structure !)

For hard spheres up to first order in ϕ (approx. H.I.):

$$S(q) = 1 - 24\phi \frac{\sin(2qa) - (2qa)\cos(2qa)}{(2qa)^3}$$

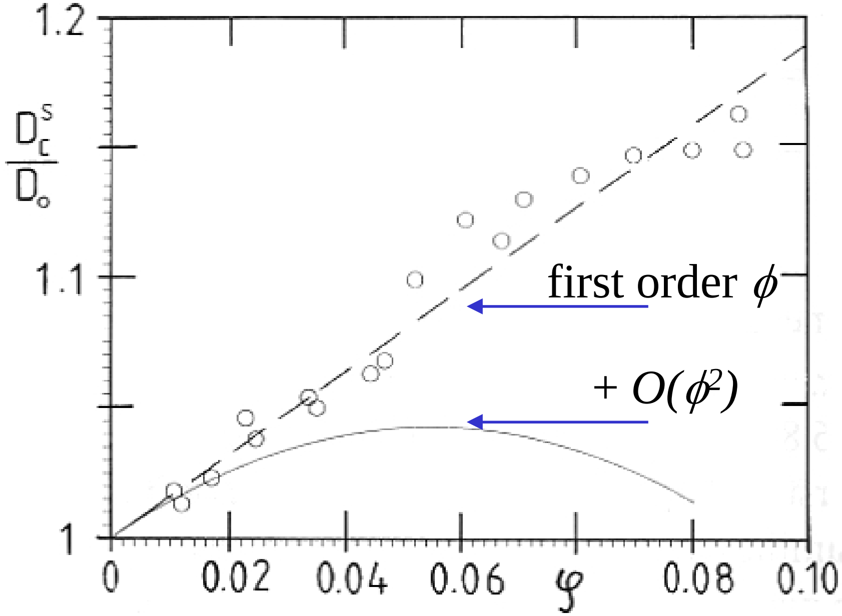
$$H(q) = 1 - \frac{15}{8}\phi - 15\phi \frac{\sin(2qa) - (2qa)\cos(2qa)}{(2qa)^3}$$



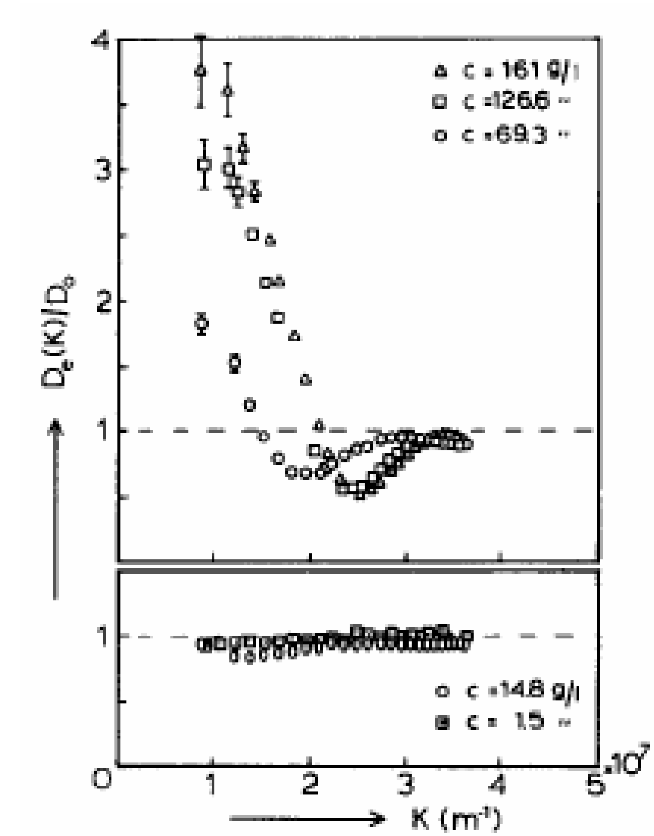
Short time collective diffusion

Hard spheres

$$\frac{D_c^S(q=0)}{D_0} = 1 + 1.45\phi + O\left(\phi^2\right)$$



Charged spheres

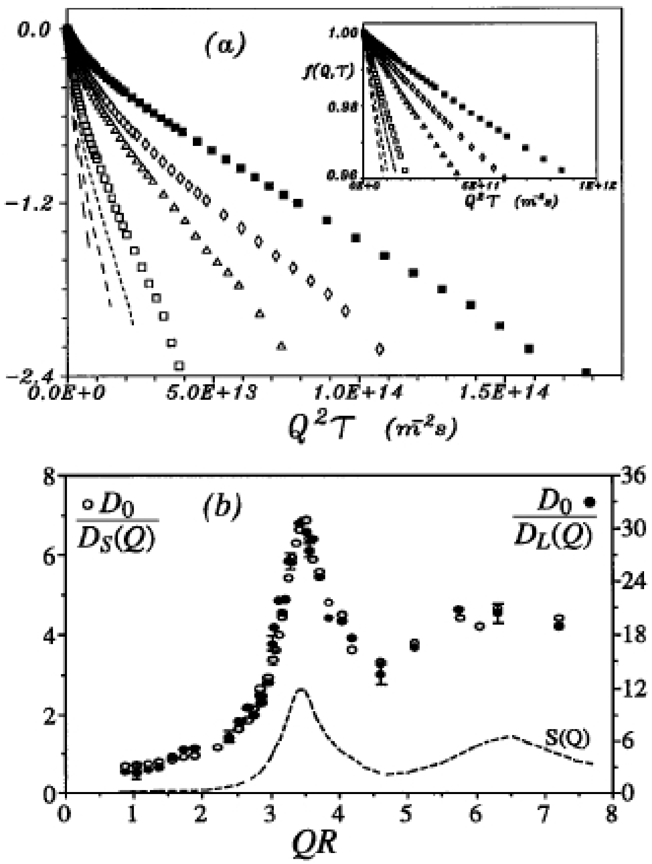


Philipse & Vrij, J. Chem. Phys. **88**, 6459 (1988)

Long time collective diffusion

$$\ln S_c(\mathbf{q},t) = -q^2 D_c(\mathbf{q},t)\,t$$

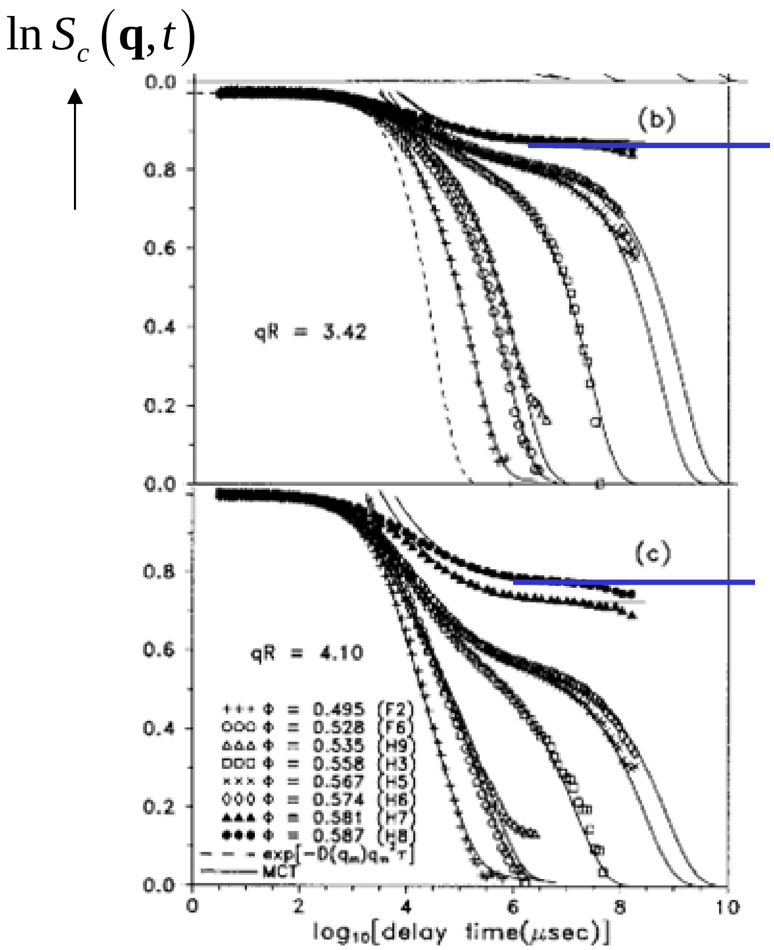
Hard spheres
(ϕ=0.465)



Short and long time collective diffusion differ by constant factor: *no explanation yet.*

P. N. Segrè and P. N. Pusey,
Phys. Rev. Lett. **77**, 771 (1996).

Colloidal glasses



$$D_c^L(q) = 0$$

Long time decay stops at ϕ~0.58:

Particles can only move inside "neighbor cages", but cages remain intact indefinitely.

W. van Megen and S. M. Underwood, *Phys. Rev. Lett.* **70**, 2766 (1993)