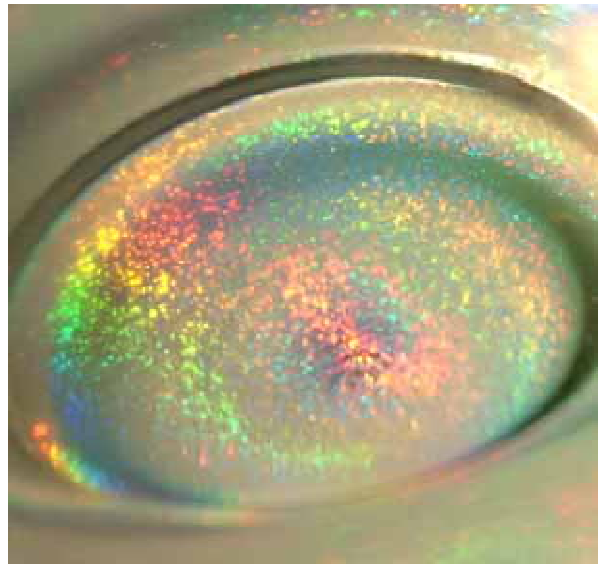
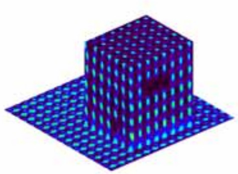
Scattering Techniques in Soft Condensed Matter



Arnout Imhof



Universiteit Utrecht

Soft Condensed Matter, Debye Institute, Utrecht University

Scattering of waves

- Scattering occurs whenever a medium is *inhomogeneous*
- Waves scatter from "obstacles" called *scatterers*:

Water waves (0.1 – 10 m):	ships, ducks
Sound (0.1 – 1000 mm):	sea floor, fish, earth structure, tissue
X-rays (0.1 – 10 nm):	atoms
Neutrons (0.1 – 10 nm):	atomic nuclei
Light (0.1 – 1 μm):	water drops (fog), fat globules (milk), interstellar dust

- Scattering most effective if *obstacle size ~ wavelength*
- All forms of scattering are analogous

Light scattering

Why does *light* (an EM wave) scatter?

- EM waves accelerate charges (electrons) in a medium
- Accelerating charges radiate new EM waves
- Conversion to heat, fluorescence,…

↓ *Scattering*

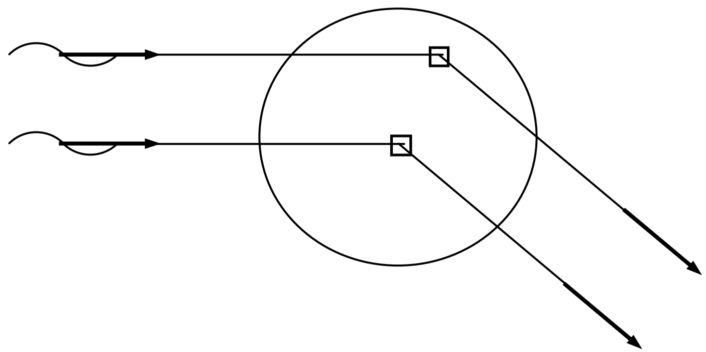
↓ *Absorption*

Absorption + Scattering = Extinction

Interference

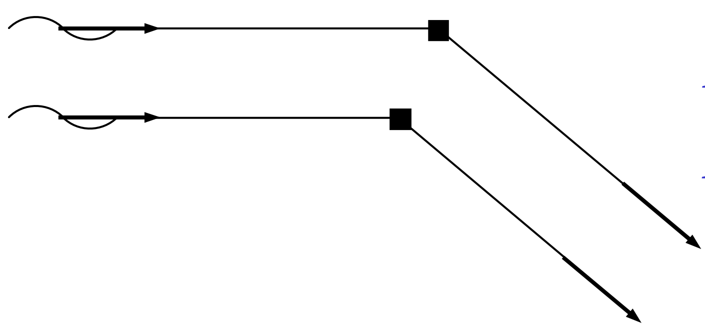
Scattered waves *interfere:*

Intra particle



size, shape

Inter particle



particle ordering (SLS)

particle dynamics (DLS)

Some other scattering terms

Multiple scattering: particle scatters sum of incident and scattered waves

Single scattering: particle scatters only incident wave (weak scattering or particles far apart)

Elastic scattering: frequency of scattered wave equals frequency of incident wave

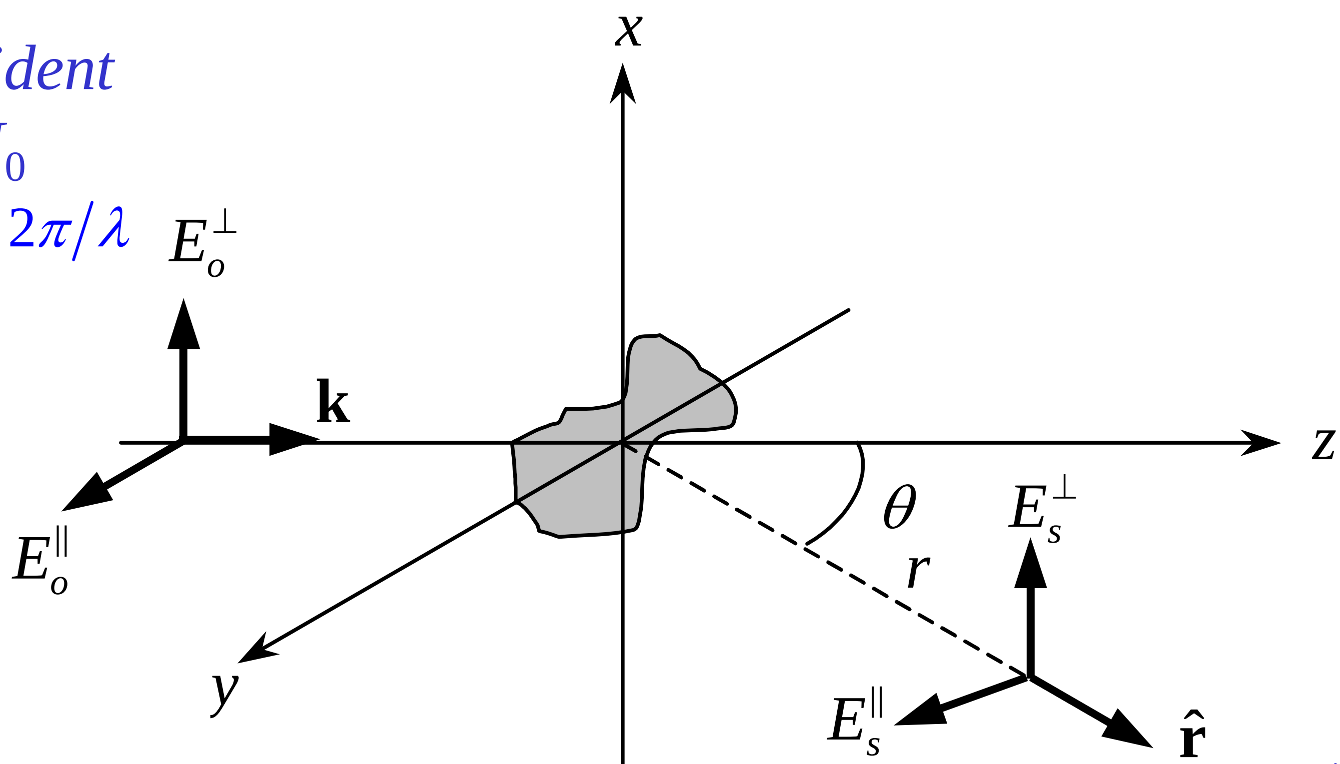
Inelastic scattering: frequencies differ

The scattering geometry

incident

I_0

$|\mathbf{k}| = 2\pi/\lambda$



scattered

$$I_s(\theta,\varphi) = \frac{I_0 F(\theta,\varphi)}{k^2 r^2}$$

Measuring scattered light

As a function of angle: $$I_s(\theta,\varphi)=\frac{I_0 F(\theta,\varphi)}{k^2 r^2}$$ [J.m^{-2}.s^{-1}]

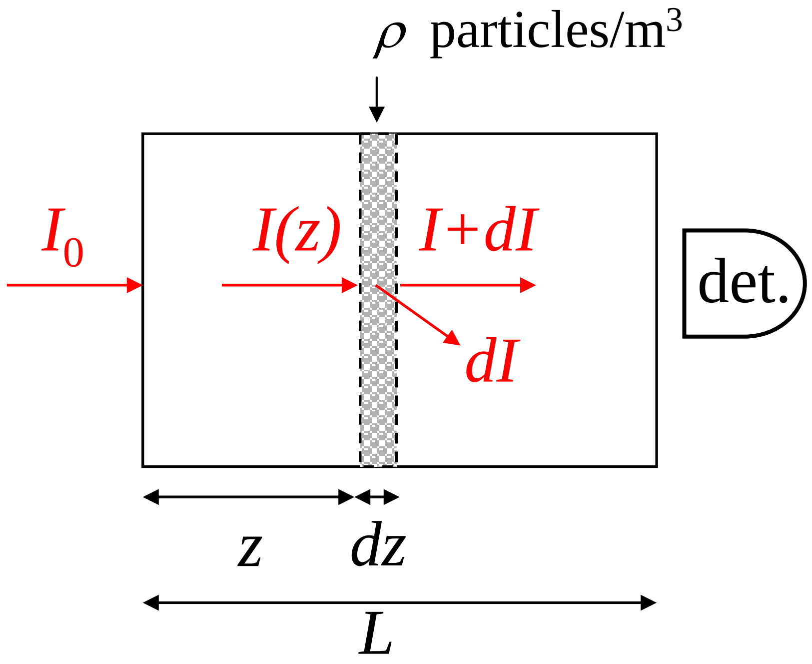
Scatt. cross section: $$C_{sca}=\frac{P_s}{I_0}=\frac{1}{k^2}\int_{4\pi} F(\theta,\varphi)\sin\theta d\theta d\varphi$$ [m^2]

↑ *total scattered power*
(per unit incident intensity)

$$C_{abs}=\frac{P_{abs}}{I_0}$$

$$C_{ext}=C_{sca}+C_{abs}$$

Cross sections are obtained from transmission measurements:



$$dI = -\rho C_{ext} I(z) dz$$

$$I_t = I_0 \exp\left(-\rho C_{ext} L\right)$$

Scattering – our approach

- Point particle
- Large particle
- Ensembles of (large) particles
- Moving particle
- Ensemble of (large) moving particles

Scattering by one small particle

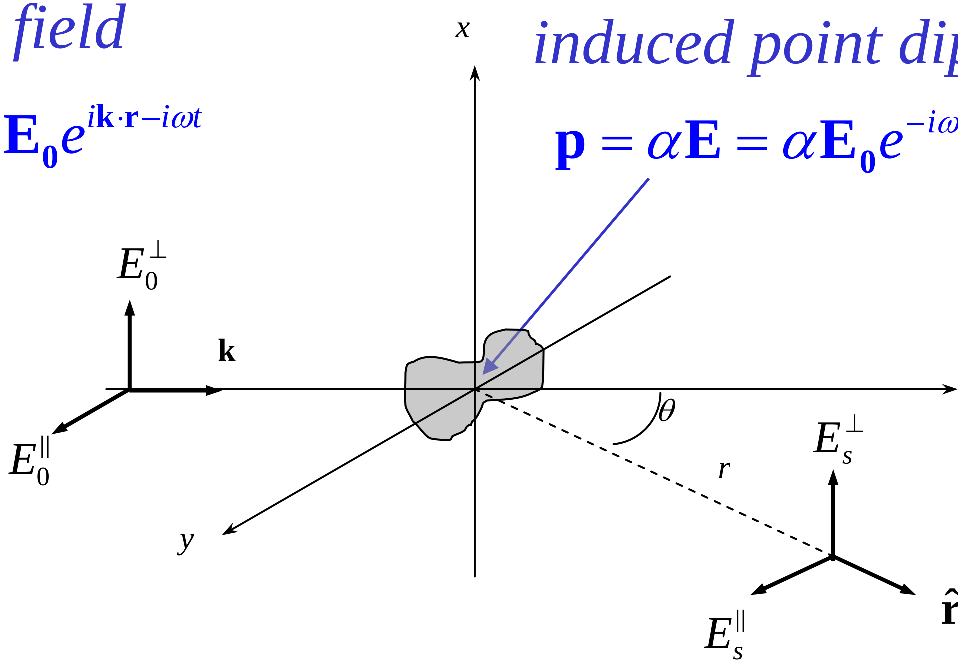
Size << λ *(Rayleigh scattering)*

incident field

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E_0} e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t}$$

induced point dipole

$$\mathbf{p} = \alpha \mathbf{E} = \alpha \mathbf{E_0} e^{-i\omega t}$$



radiated field

$$\mathbf{E}_s = \frac{1}{4\pi\varepsilon_m v^2 r}\left[\hat{\mathbf{r}} \times \left(\hat{\mathbf{r}} \times \ddot{\mathbf{p}}(t - r/v)\right)\right]$$

$$\begin{pmatrix} E_s^{\parallel} \\ E_s^{\perp} \end{pmatrix} = \alpha \frac{k^2}{4\pi\varepsilon_m r} e^{ikr - i\omega t} \begin{pmatrix} E_0^{\parallel} \cos\theta \\ E_0^{\perp} \end{pmatrix}$$

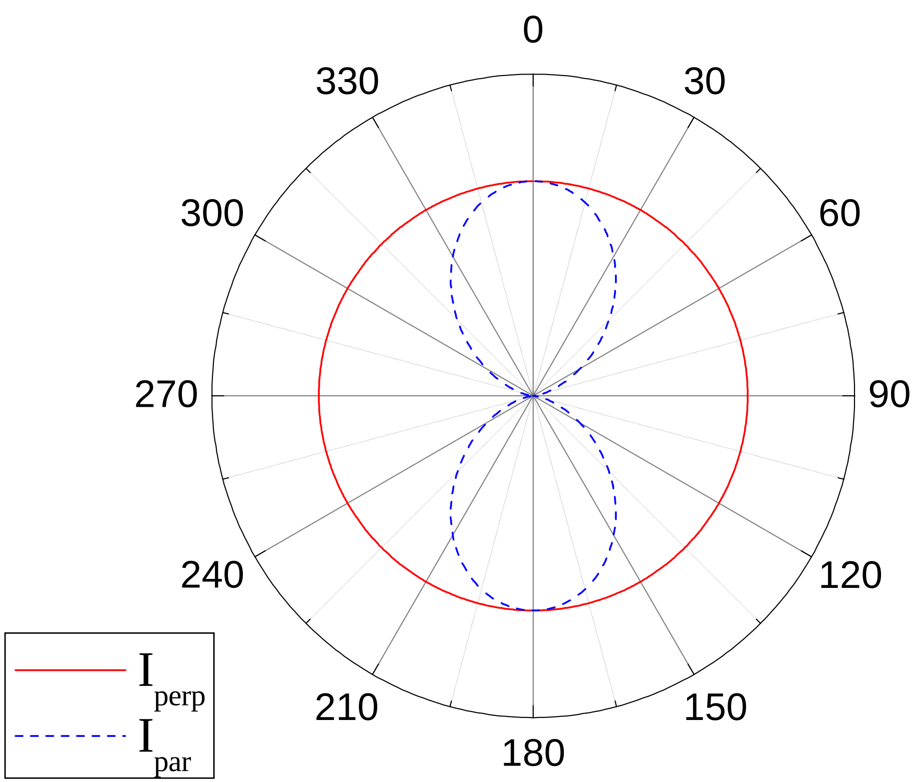
$$I_s(\theta) = I_0 \frac{k^4}{32\pi^2\varepsilon_m^2 r^2} |\alpha|^2 \left(1+\cos^2\theta\right)$$

$$\alpha = 3\varepsilon_m \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} V_p$$

$$= 3\varepsilon_m \frac{m^2 - 1}{m^2 + 2} V_p \qquad \left(m = \frac{n_p}{n_m} \right)$$

$$= I_0 \frac{9\pi^2}{2\lambda^4 r^2} \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 V_p^2 \left(1+\cos^2\theta\right)$$

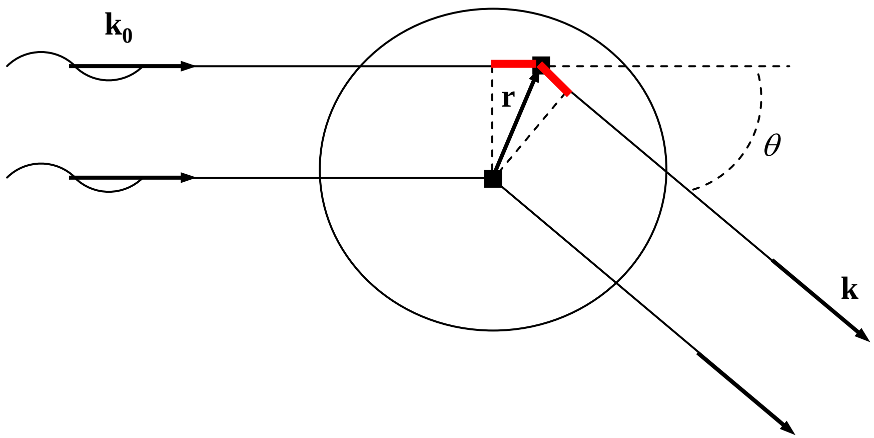
(Rayleigh)



Scattering by a large particle

Rayleigh-Gans-Debye approximation:

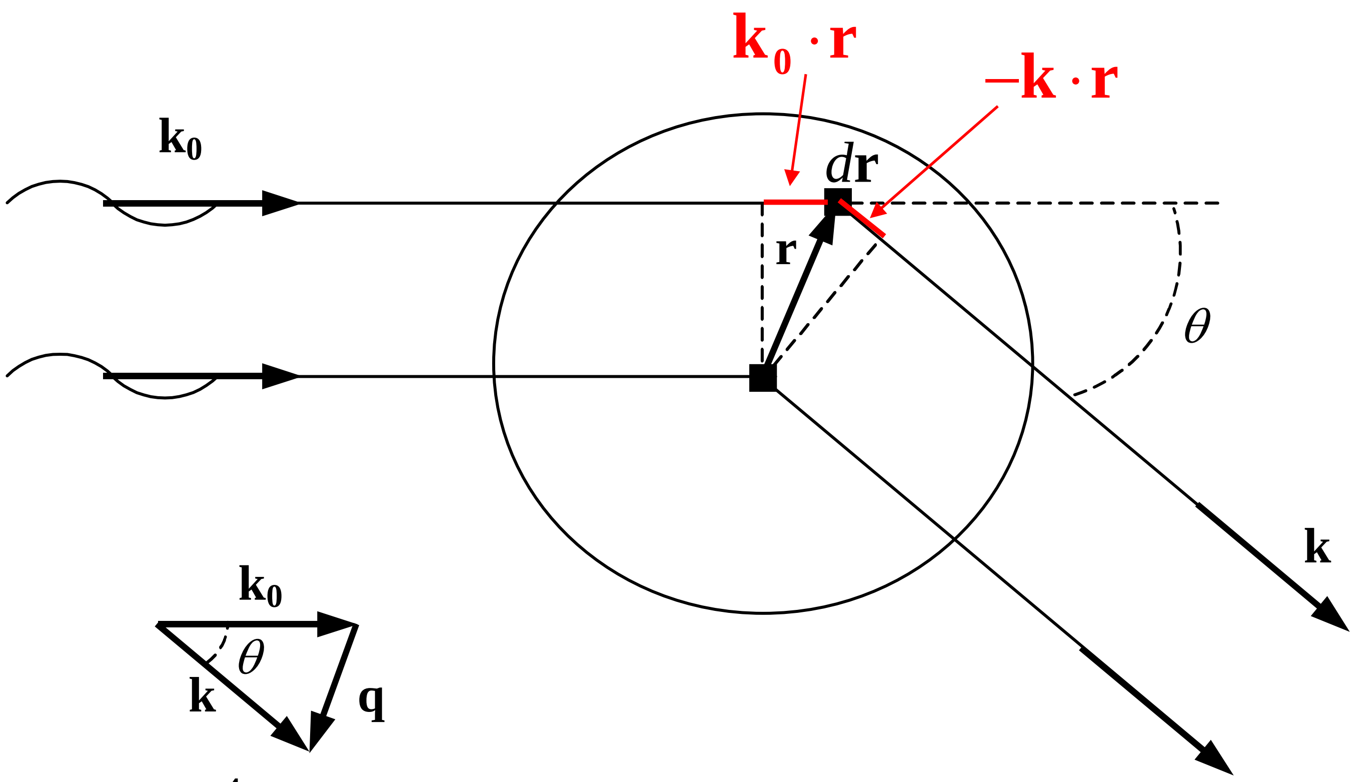
Divide particle into pointlike subunits and sum all wavelets.



Valid if:

- *each subunit responds only to incident field:* $|m-1| << 1$
- *wave inside particle suffers no phase lag relative to a wave passing the particle by:* $kd\,|m-1| << 1$

$$\Delta\phi = -\mathbf{k}\cdot\mathbf{r} + \mathbf{k_0}\cdot\mathbf{r} = -\left(\mathbf{k}-\mathbf{k_0}\right)\cdot\mathbf{r} \equiv -\mathbf{q}\cdot\mathbf{r}$$



$$q = |\mathbf{q}| = \frac{4\pi}{\lambda}\sin\left(\theta/2\right)$$

$$dE_s^{\perp} = \frac{k^2}{2\pi R}\left(m(\mathbf{r})-1\right)E_0^{\perp}e^{ikR-i\omega t-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r}$$

$$(m^2-1)/(m^2+2) \approx \tfrac{2}{3}(m-1)$$

Integrate over the particle:

$$E_s^{\perp} = \frac{k^2}{2\pi R} E_0^{\perp} e^{ikR - i\omega t} f(\mathbf{q})$$

$$f(\mathbf{q}) = \int_{V_p} \left(m(\mathbf{r}) - 1\right) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

Take the modulus squared:

$$I_s = I_0 \frac{k^4 V_p^2 \left|\bar{m} - 1\right|^2}{8\pi^2 R^2} P(\mathbf{q}) \left(1 + \cos^2\theta\right)$$

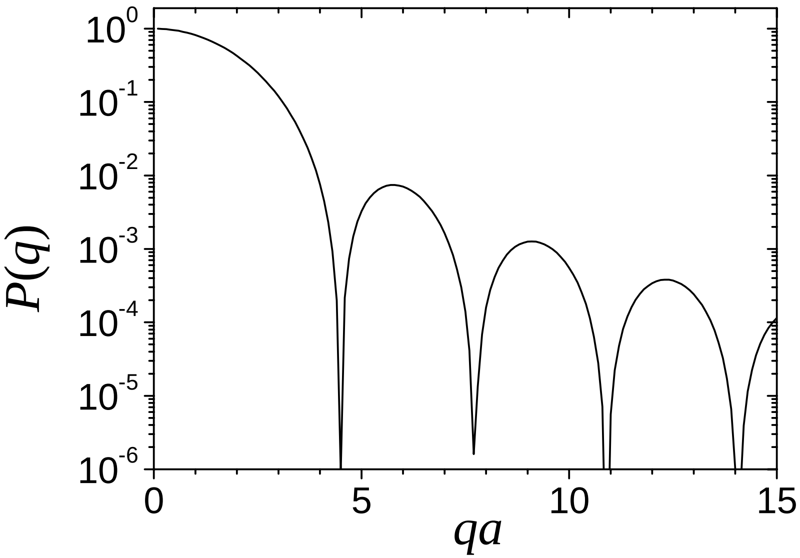
$$P(\mathbf{q}) = \left|\frac{f(\mathbf{q})}{f(\mathbf{0})}\right|^2 = \left|\frac{\int_{V_p} \left(m(\mathbf{r}) - 1\right) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}}{\int_{V_p} \left(m(\mathbf{r}) - 1\right) d\mathbf{r}}\right|^2$$

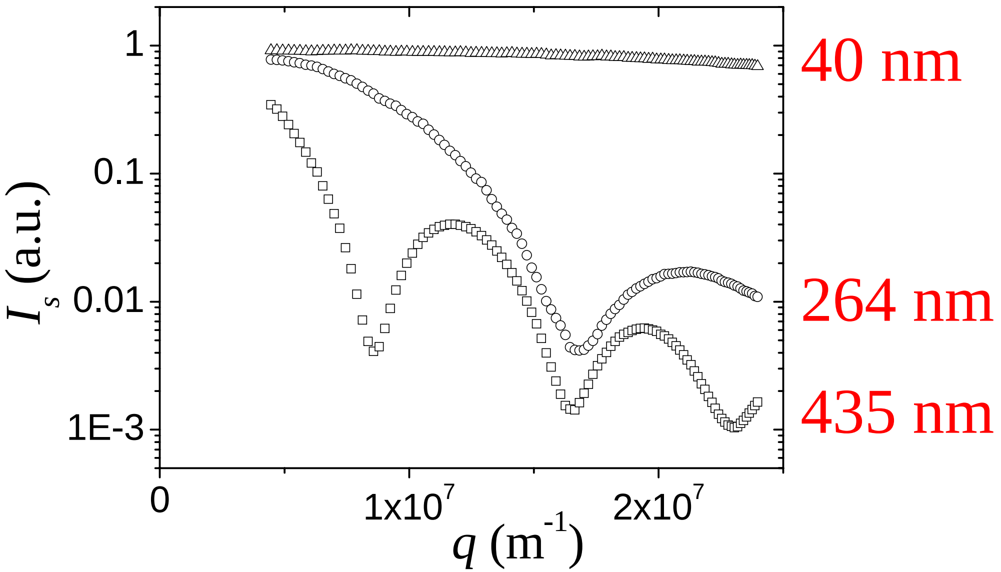
Particle form factor

Compare with a model.

Form factor of a sphere

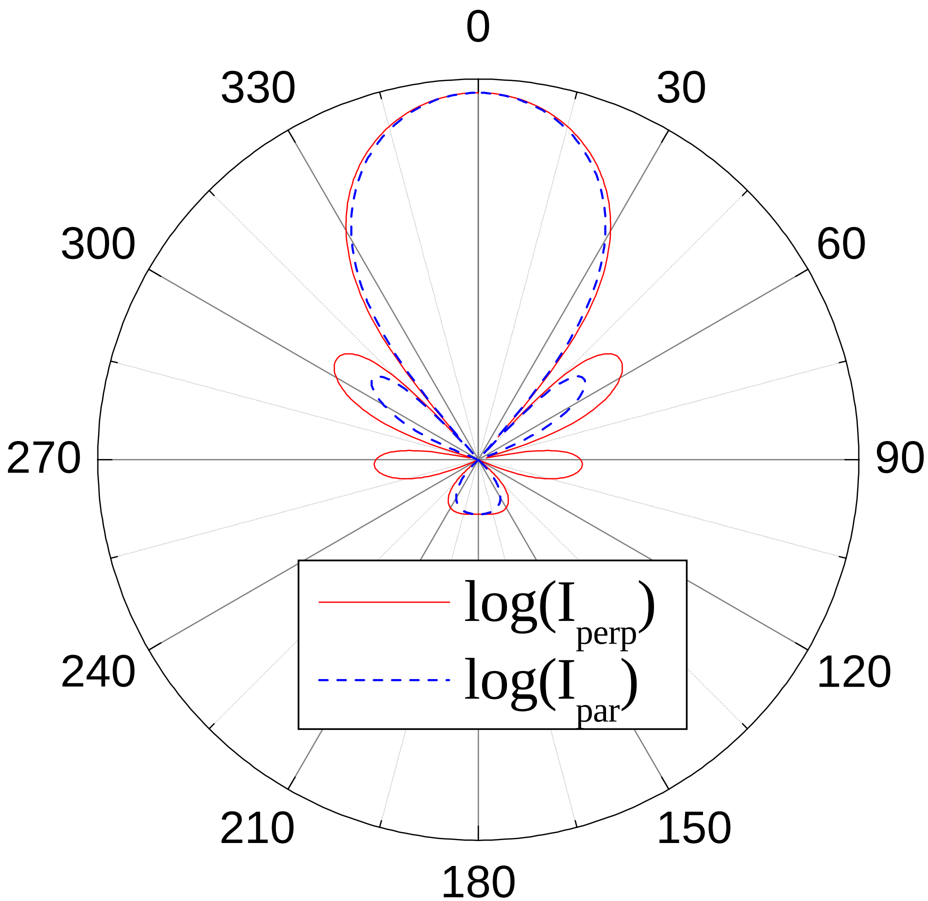
$$P(q)=\left[3\frac{\sin(qa)-qa\cos(qa)}{(qa)^3}\right]^2 \qquad q=|\mathbf{q}|=\frac{4\pi}{\lambda}\sin(\theta/2)$$





Homogeneous sphere

(radius $a = \lambda$)



Radius of gyration

At small angles or for small particles: $e^{-i\mathbf{q}\cdot\mathbf{r}} \approx 1 - i\mathbf{q}\cdot\mathbf{r} - \tfrac{1}{2}\left(\mathbf{q}\cdot\mathbf{r}\right)^2 + \dots$

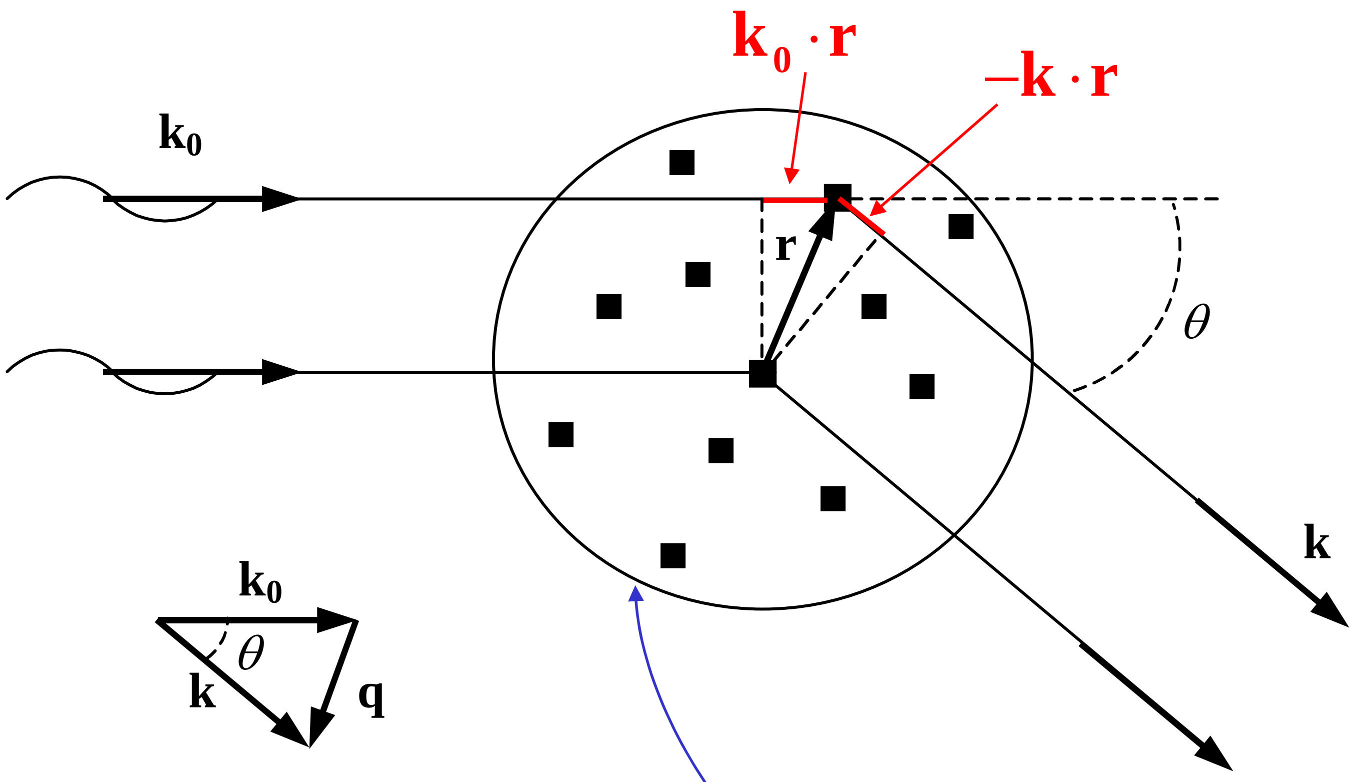
$$P\left(\mathbf{q}\right) \approx \left| 1 - \frac{\int_{V_p}\left(m-1\right) i\mathbf{q}\cdot\mathbf{r}\, d\mathbf{r}}{\int_{V_p}\left(m-1\right) d\mathbf{r}} - \frac{1}{2}\left\langle \frac{\int_{V_p}\left(m-1\right)\left(\mathbf{q}\cdot\mathbf{r}\right)^2 d\mathbf{r}}{\int_{V_p}\left(m-1\right) d\mathbf{r}} \right\rangle \right|^2$$

$$= 1 - \frac{\int_{V_p}\left(m-1\right) q^2 r^2 \left\langle \cos^2\theta \right\rangle d\mathbf{r}}{\int_{V_p}\left(m-1\right) d\mathbf{r}}$$

$$= 1 - \frac{1}{3} q^2 R_g^2 + \dots \qquad R_g^2 = \frac{\int_{V_p}\left(m-1\right) r^2 d\mathbf{r}}{\int_{V_p}\left(m-1\right) d\mathbf{r}}$$

Sphere: $R_g = \sqrt{3/5}\,a$ *Rodlike:* $R_g = L/\sqrt{12}$ *Polymer:* $R_g = l\sqrt{n/6}$

Scattering by many particles



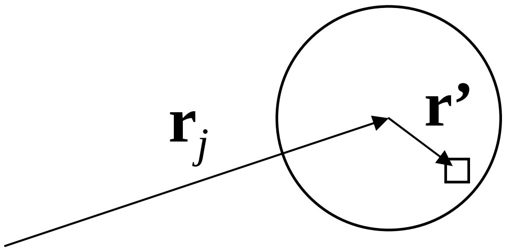
$$E_s^{\perp} \sim E_0^{\perp} \int_{V_s} \left(m(\mathbf{r}) - 1\right) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

= 0 if **r** in medium

$$E_s^{\perp} \sim E_0^{\perp} \int_{V_s} \left(m(\mathbf{r}) - 1 \right) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

$$= E_0^{\perp} \sum_{j=1}^{N} \int_{V_j} \left(m(\mathbf{r}) - 1 \right) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

$$\mathbf{r} = \mathbf{r}_j + \mathbf{r}'$$



$$= E_0^{\perp} \sum_{j=1}^{N} e^{-i\mathbf{q}\cdot\mathbf{r}_j} \int_{V_j} \left(m(\mathbf{r}') - 1 \right) e^{-i\mathbf{q}\cdot\mathbf{r}'} d\mathbf{r}'$$

$$= E_0^{\perp} \sum_{j=1}^{N} e^{-i\mathbf{q}\cdot\mathbf{r}_j} f_j(\mathbf{q})$$

$$I_s^{\perp} \sim \left\langle \left| E_s^{\perp} \right|^2 \right\rangle = I_0 \left\langle \left| \sum_{j=1}^{N} f_j(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{r}_j} \right|^2 \right\rangle = N I_0 P(\mathbf{q}) S(\mathbf{q})$$

Identical particles

$$S(\mathbf{q}) = \frac{1}{N} \left\langle \sum_{j=1}^{N} \sum_{k=1}^{N} e^{i\mathbf{q}\cdot(\mathbf{r}_k - \mathbf{r}_j)} \right\rangle$$

Structure factor

$$= 1 + \rho \int \left[g(r) - 1 \right] e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

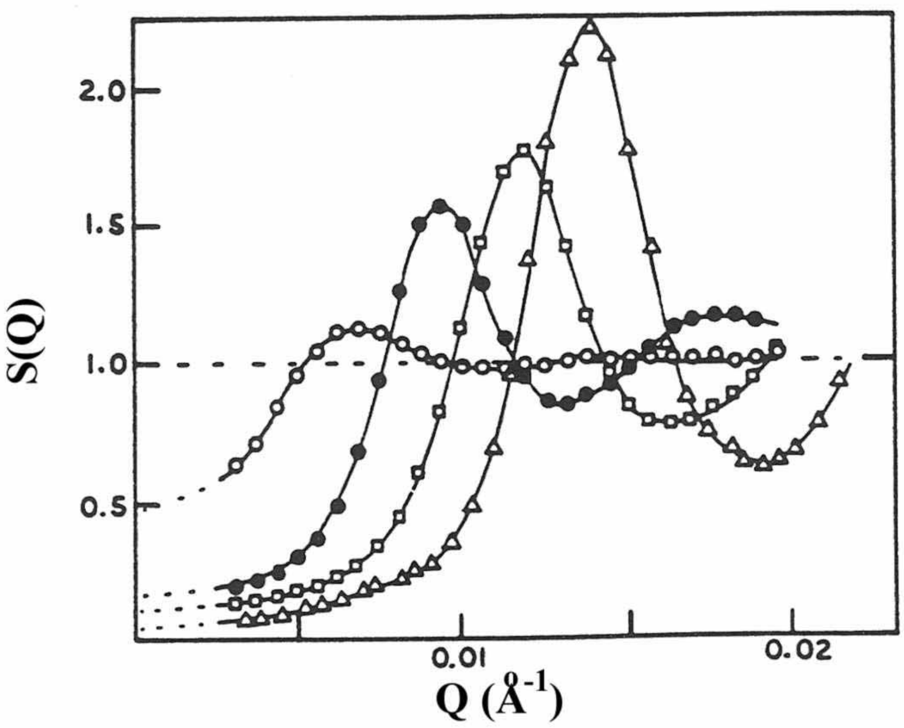
Radial distribution function

Measuring structure factors

Dilute sample: $I_{dil}(\mathbf{q}) \sim \rho_{dil} P(\mathbf{q})$

Concentrated sample: $I(\mathbf{q}) \sim \rho P(\mathbf{q}) S(\mathbf{q})$

$$S(\mathbf{q}) = \frac{\rho_{\mathrm{dil}}}{\rho} \frac{I(\mathbf{q})}{I_{\mathrm{dil}}(\mathbf{q})}$$



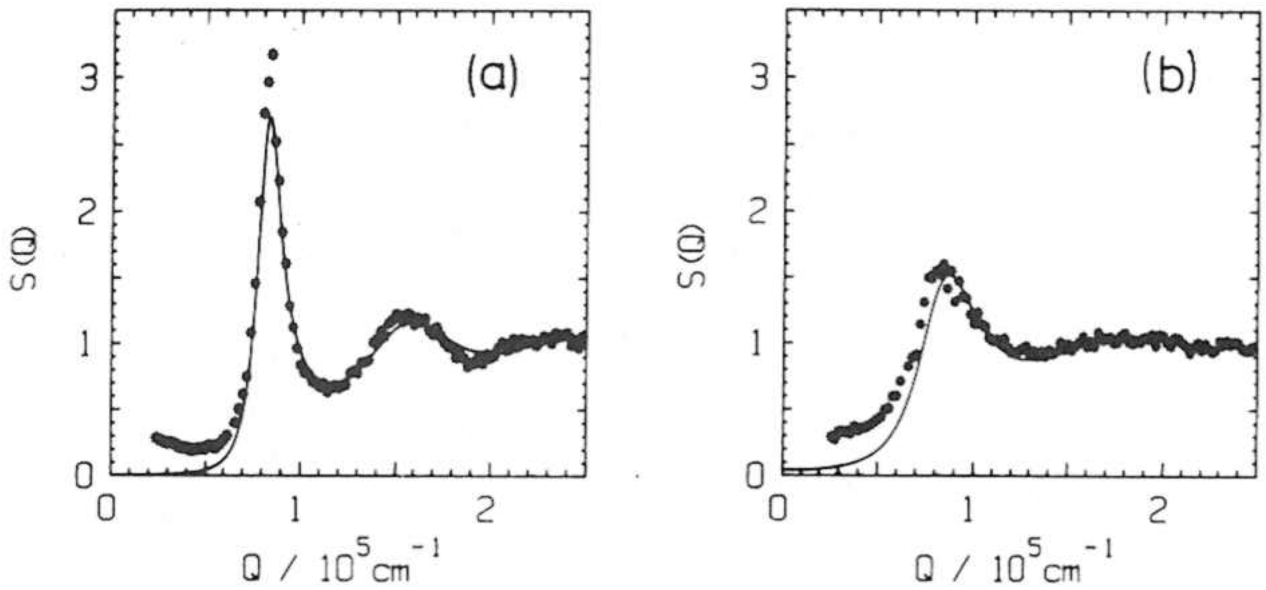
31 nm polystyrene spheres + 0.1 mmol/L NaCl

Volume fractions: 0.01, 0.04, 0.08, 0.13

(SANS, Ottewill et al.)

80 nm polystyrene spheres with –SO_3H surface groups

(SLS, Härtl and Versmold, 1992)



3.1 μmol/L NaOH

3.1 μmol/L NaCl

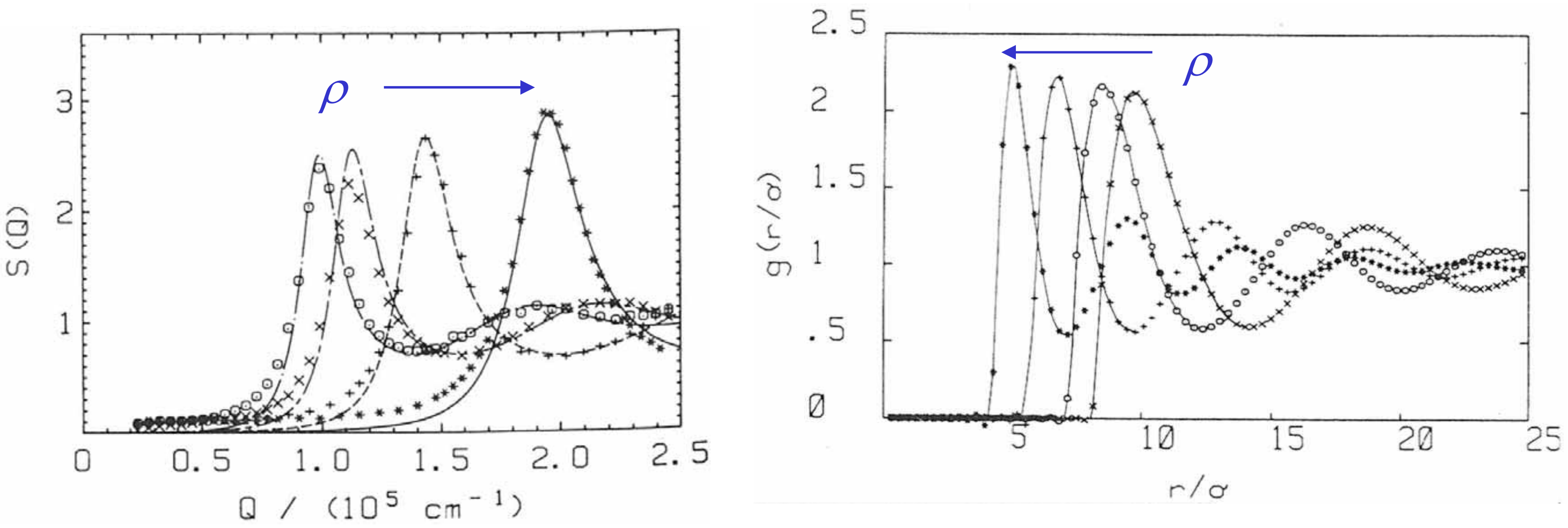
model fits: $Z_{eff} = 503\ e^-$ $Z_{eff} = 474\ e^-$

$\kappa\sigma = 0.21$ $\kappa\sigma = 0.50$

Inverting structure factors

1) Fourier inversion (limited **q**-range)

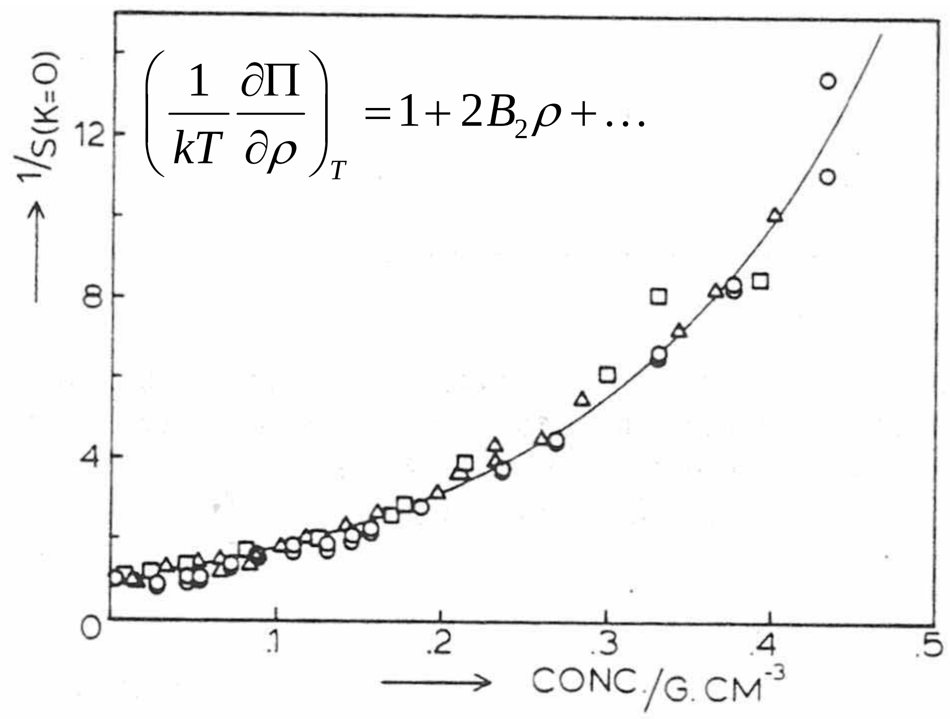
2) Fit with model; then Fourier invert the fit curve



(80 nm PS spheres, deionized, Härtl and Versmold, 1992)

Low *q* scattering

$$S(q=0) = kT\left(\frac{\partial\rho}{\partial\Pi}\right)_T$$ → Equation of state



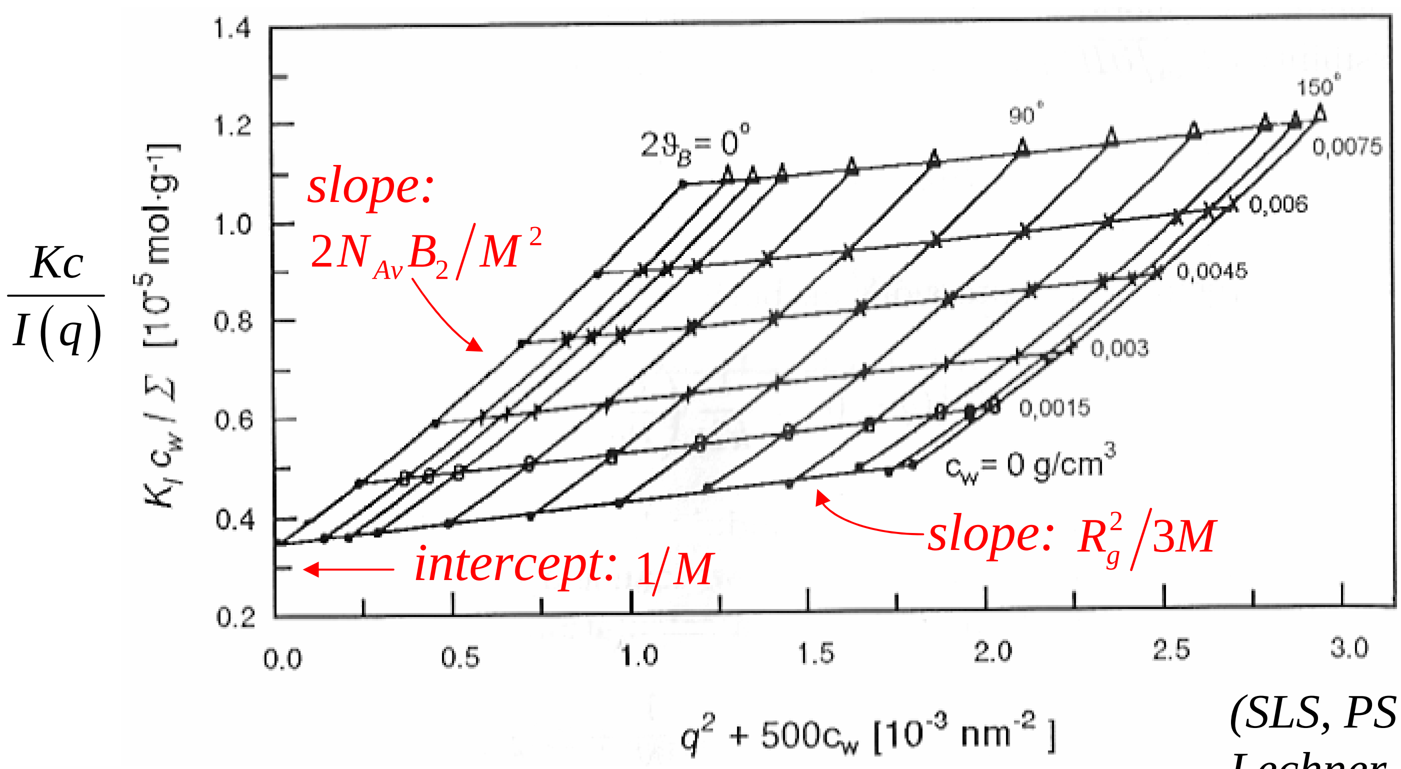
Hard-sphere particles

(silica coated with stearyl alcohol, suspended in cyclohexane)

Polymer solutions – Zimm plot

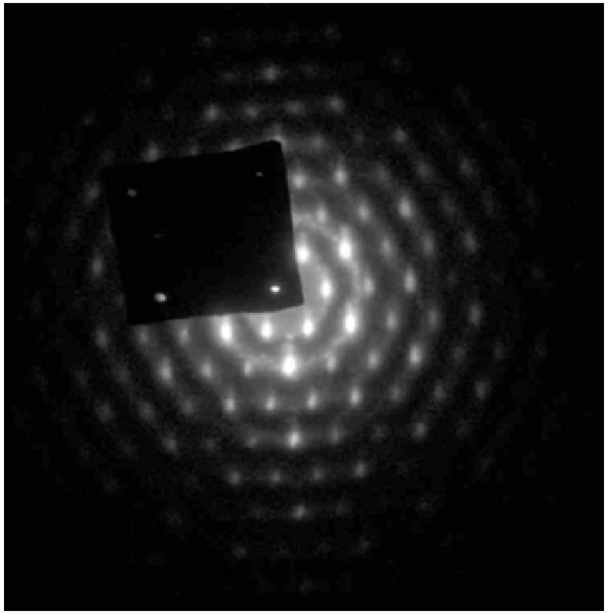
$$I_s(q) = KM^2 \rho P(q) S(q) \quad \Rightarrow \frac{K\rho}{I(q)} = \frac{1}{M^2}\frac{1}{P(q)}\frac{1}{S(q)} \approx \frac{1}{M^2}\left(1+\frac{1}{3}R_g^2 q^2\right)(1+2B_2\rho)$$

$$\text{with: } \rho = \frac{cN_{Av}}{M} \quad \Rightarrow \frac{Kc}{I(q)} \approx \left(1+\frac{1}{3}R_g^2 q^2\right)\left(\frac{1}{M}+\frac{2N_{Av}B_2}{M^2}c\right)$$

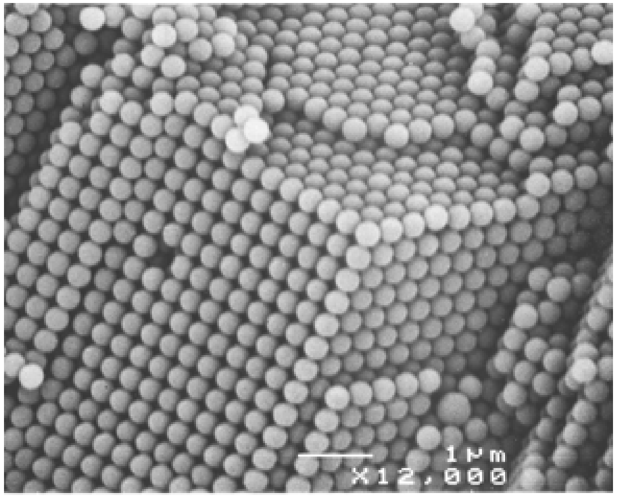


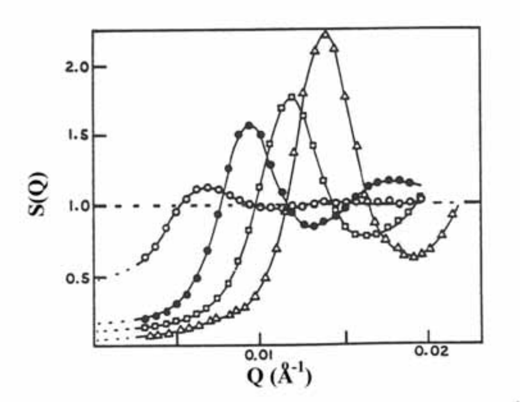
(SLS, PS in toluene, Lechner 1993.)

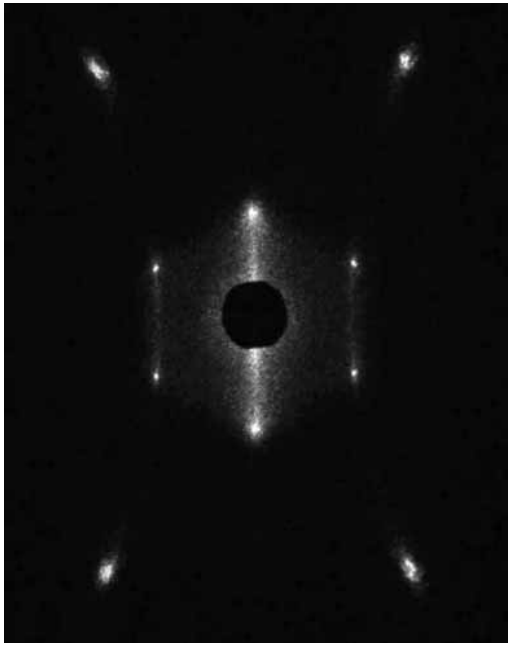
Scattering from crystals



SAXS





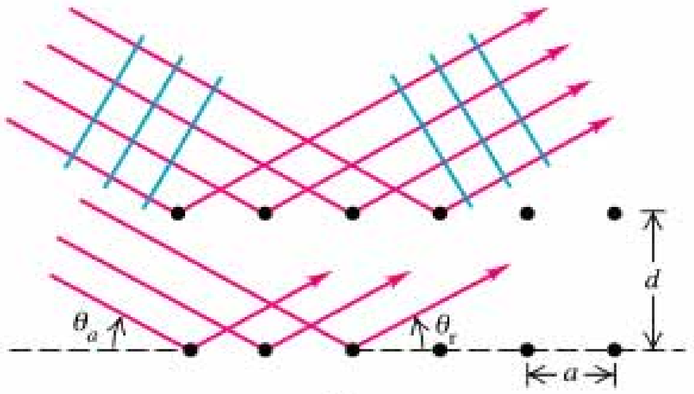


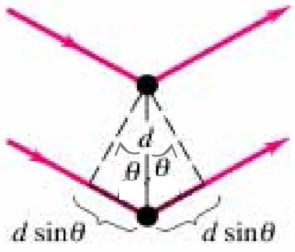
Light scattering

- Opals and colloidal crystals:

The Bragg law:

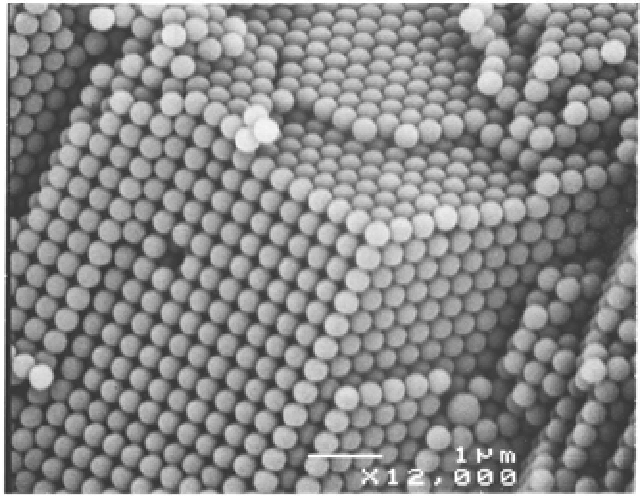
$$2d\sin\theta = m\lambda$$



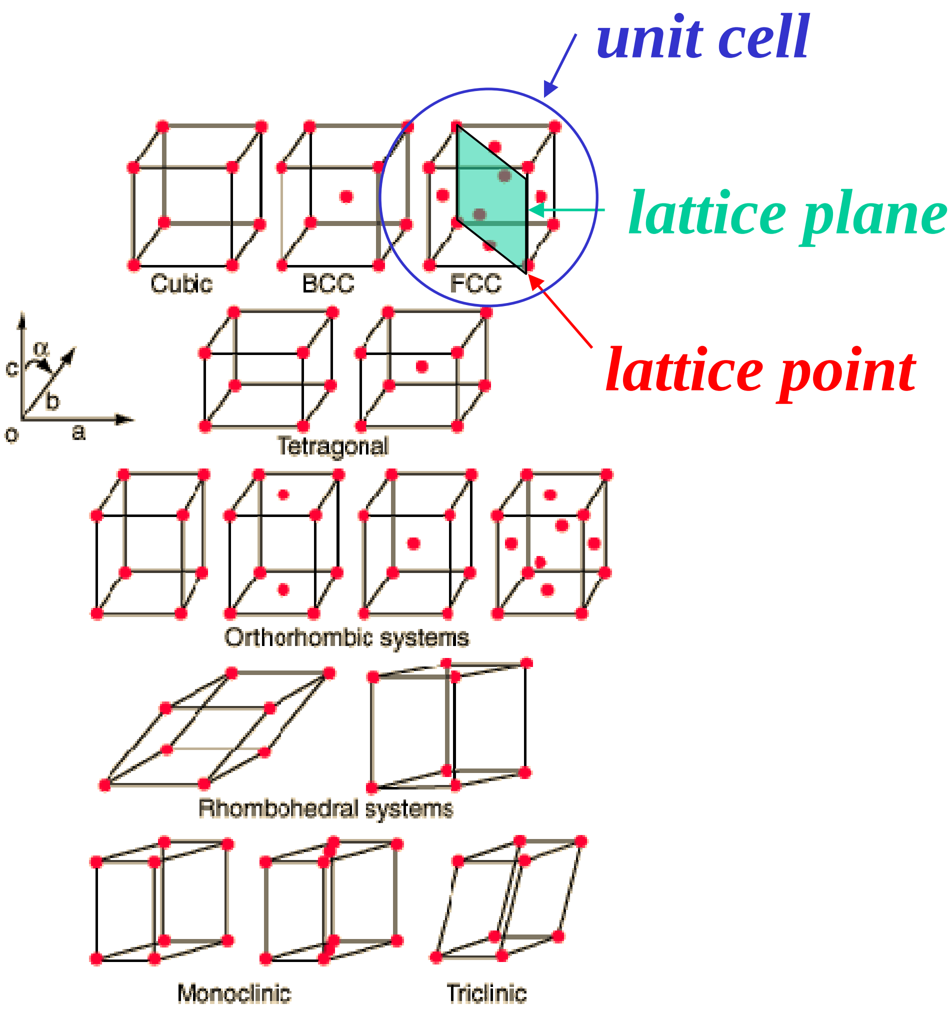


Crystal lattices

- Crystal: periodic lattice of equivalent points

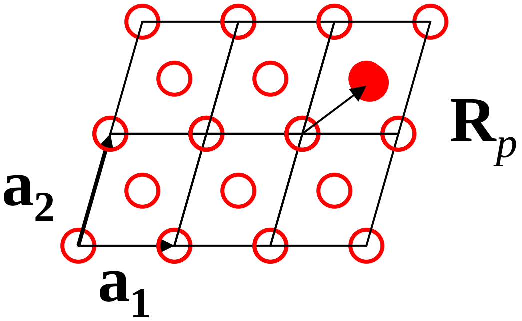


diameter ~ 300 nm



Diffraction

- Position of particle p in unit cell number m_1, m_2, m_3:



$$\mathbf{r}_j = \mathbf{R}_p + m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3$$

- Substitute in structure factor $(N=nM_1M_2M_3$ particles$)$:

$$\sum_{j=1}^{N} e^{-i\mathbf{q}\cdot\mathbf{r}_j} = \sum_{p=1}^{n} e^{-i\mathbf{q}\cdot\mathbf{R}_p} \sum_{m_1=0}^{M_1-1} e^{-im_1\mathbf{q}\cdot\mathbf{a_1}} \sum_{m_2=0}^{M_2-1} e^{-im_2\mathbf{q}\cdot\mathbf{a_2}} \sum_{m_3=0}^{M_3-1} e^{-im_3\mathbf{q}\cdot\mathbf{a}_3}$$

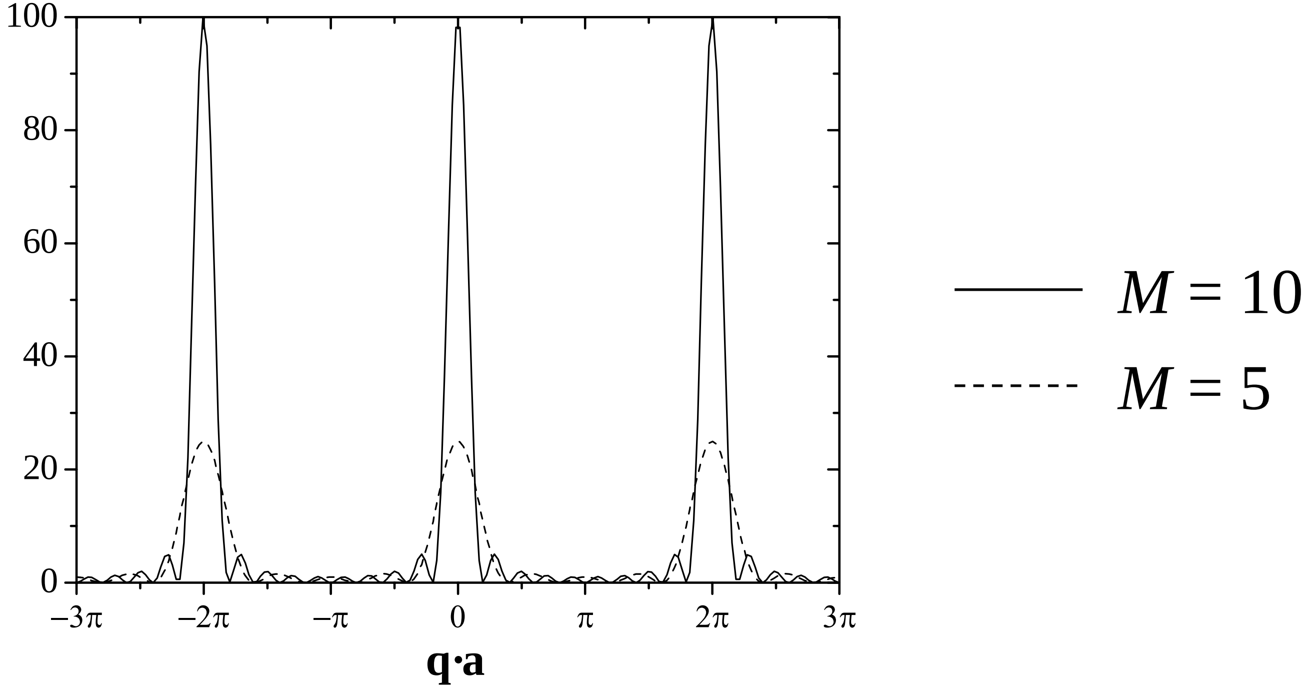
$$\sum_{m=0}^{M-1} x^m = \frac{1-x^M}{1-x} = \frac{1-e^{-iM\mathbf{q}\cdot\mathbf{a}}}{1-e^{-i\mathbf{q}\cdot\mathbf{a}}}$$

$$I_s = \left| E_s \right|^2$$
$$= \frac{1}{M_1 M_2 M_3} F(\mathbf{q}) \frac{\sin^2\left(\frac{1}{2} M_1 \mathbf{q}\cdot\mathbf{a}_1\right)}{\sin^2\left(\frac{1}{2}\mathbf{q}\cdot\mathbf{a}_1\right)} \frac{\sin^2\left(\frac{1}{2} M_2 \mathbf{q}\cdot\mathbf{a}_2\right)}{\sin^2\left(\frac{1}{2}\mathbf{q}\cdot\mathbf{a}_2\right)} \frac{\sin^2\left(\frac{1}{2} M_3 \mathbf{q}\cdot\mathbf{a}_3\right)}{\sin^2\left(\frac{1}{2}\mathbf{q}\cdot\mathbf{a}_3\right)}$$

$$F(\mathbf{q}) = \frac{1}{n} \left| \sum_{p=1}^{n} e^{-i\mathbf{q}\cdot\mathbf{R}_p} \right|^2$$

Structure factor of a unit cell

The function $$\frac{\sin^2\left(\frac{1}{2}M\mathbf{q}\cdot\mathbf{a}\right)}{\sin^2\left(\frac{1}{2}\mathbf{q}\cdot\mathbf{a}\right)}$$



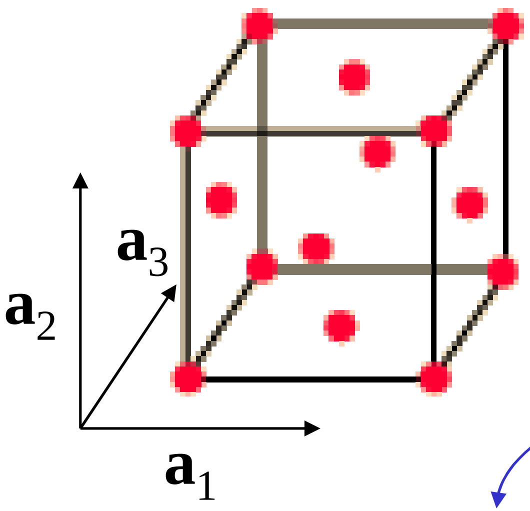
<u>Only</u> diffraction if:

$$\mathbf{q}\cdot\mathbf{a}_1 = 2\pi h$$
$$\mathbf{q}\cdot\mathbf{a}_2 = 2\pi k$$
$$\mathbf{q}\cdot\mathbf{a}_3 = 2\pi l$$

h, k, l integers

“Laue conditions”

Structure factor of *fcc* lattice



$$\mathbf{R}_p = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$$

$$(x,y,z) = (0,0,0)\ ;\ (½,½,0)\ ;\ (½,0,½)\ ;\ (0,½,½)$$

$$\mathbf{q}\cdot\mathbf{R}_p = 2\pi\left(hx + ky + lz\right)$$

$$F(\mathbf{q}) = \frac{1}{n}\left|\sum_{p=1}^{n} e^{-i\mathbf{q}\cdot\mathbf{R}_p}\right|^2 = \frac{1}{4}\left|1 + e^{-i\pi(k+l)} + e^{-i\pi(h+l)} + e^{-i\pi(h+k)}\right|^2$$

$$= \frac{1}{4}\left(1 + (-1)^{k+l} + (-1)^{h+l} + (-1)^{h+k}\right)^2$$

$$= \begin{cases} 4 & hkl \text{ all even or all odd} \\ 0 & \text{otherwise} \end{cases}$$

"systematic vanishings"

Scattering recap

$$E_s^{\perp} \propto E_0^{\perp} \sum_{j=1}^{N} f_j(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{r}_j}$$

"weak scattering"

$$I_s(\mathbf{q}) \propto N I_0 P(\mathbf{q}) S(\mathbf{q}) \left(1+\cos^2\theta\right)$$

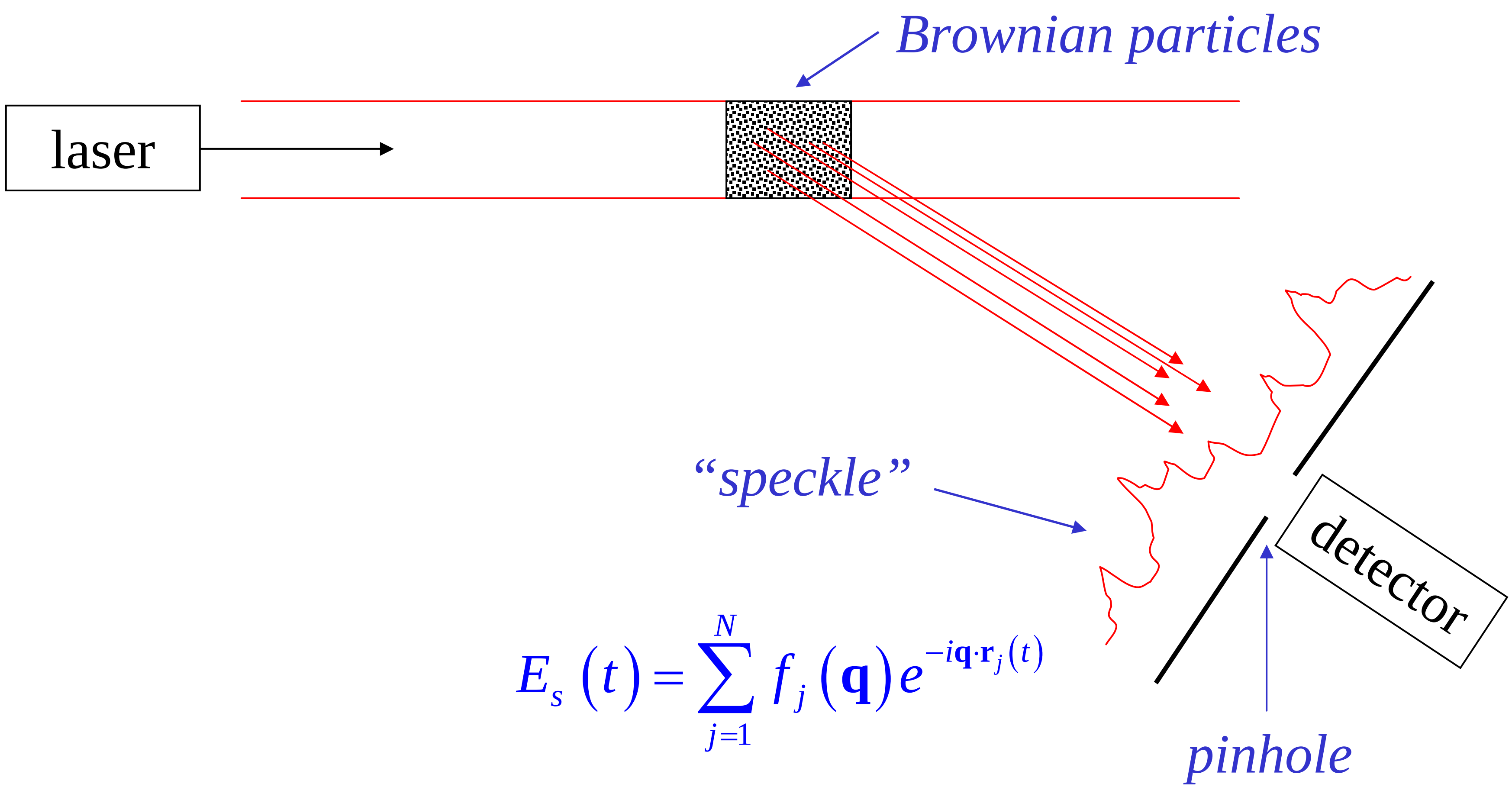
Form factor:

$$P(\mathbf{q}) = \left| \frac{f(\mathbf{q})}{f(\mathbf{0})} \right|^2 = \left| \frac{\int_{V_p} \left(m(\mathbf{r})-1\right) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}}{\int_{V_p} \left(m(\mathbf{r})-1\right) d\mathbf{r}} \right|^2$$

Structure factor:

$$S(\mathbf{q}) = \frac{1}{N} \left\langle \sum_{j=1}^{N} \sum_{k=1}^{N} e^{i\mathbf{q}\cdot\left(\mathbf{r}_k-\mathbf{r}_j\right)} \right\rangle$$

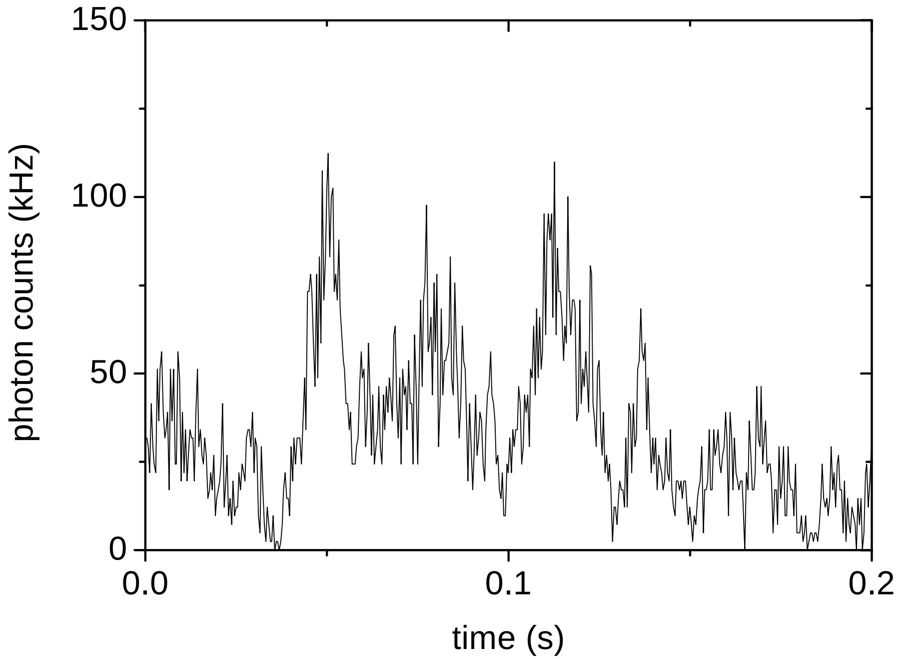
Dynamic light scattering



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

(random variable)

How to quantify fluctuating speckle?

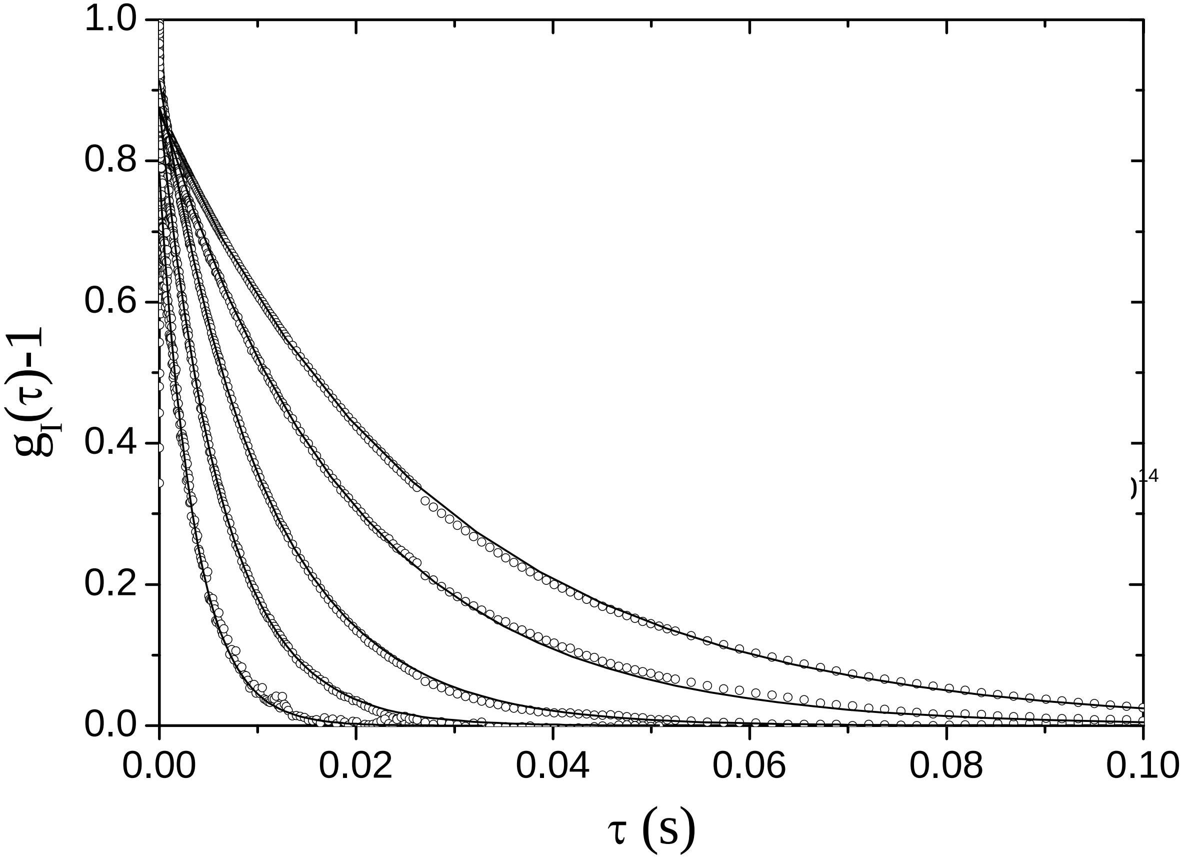


Almost random…

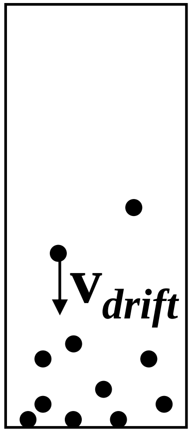
"intensity autocorrelation function"

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

$$g_I(0) = \langle I^2 \rangle \quad > \quad g(\tau \to \infty) = \langle I \rangle^2$$


1.0
0.8
0.6
0.4
0.2
0.0
g_I(τ)-1
0.00
0.02
0.04
0.06
0.08
0.10
τ (s)
)[14]

Brownian motion



Einstein's argument:

System of a particles with external force: $\mathbf{K} = -\nabla\Phi$

In equilibrium Boltzmann says: $P(\mathbf{r}) = P_0 \exp(-\Phi / kT)$

Probability density function (~ concentration)

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

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

(friction factor: γ) $P\mathbf{K}/\gamma$

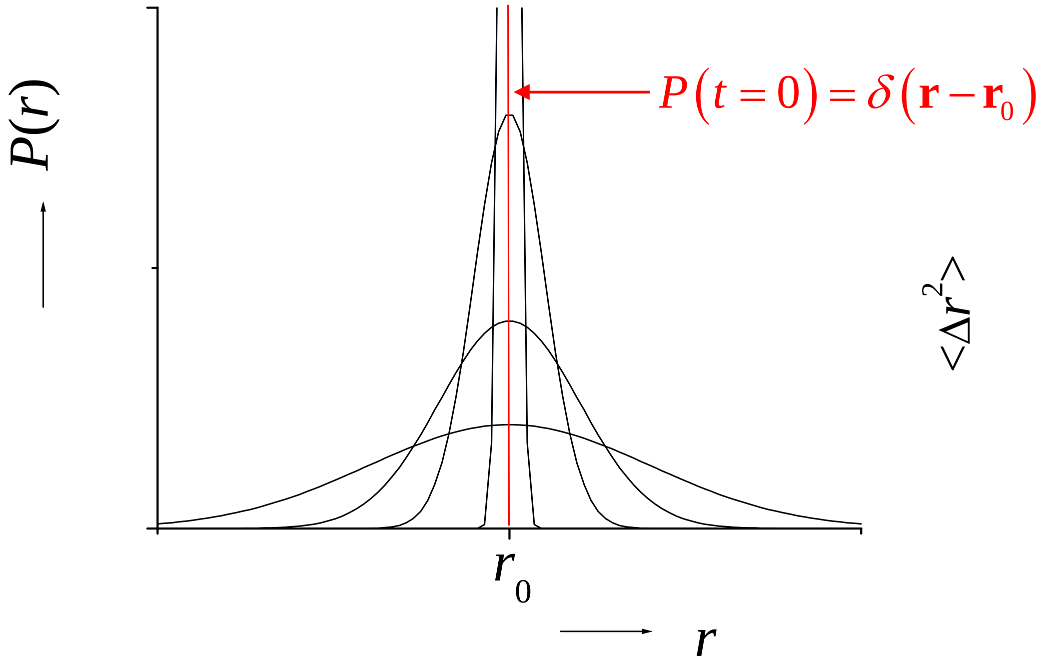
$$\mathbf{J} = -(P/\gamma)\nabla\Phi \quad -D_0\nabla P \quad = \quad 0 \Rightarrow \boxed{D_0 = \frac{kT}{\gamma}} = \frac{kT}{6\pi\eta_0 a}$$

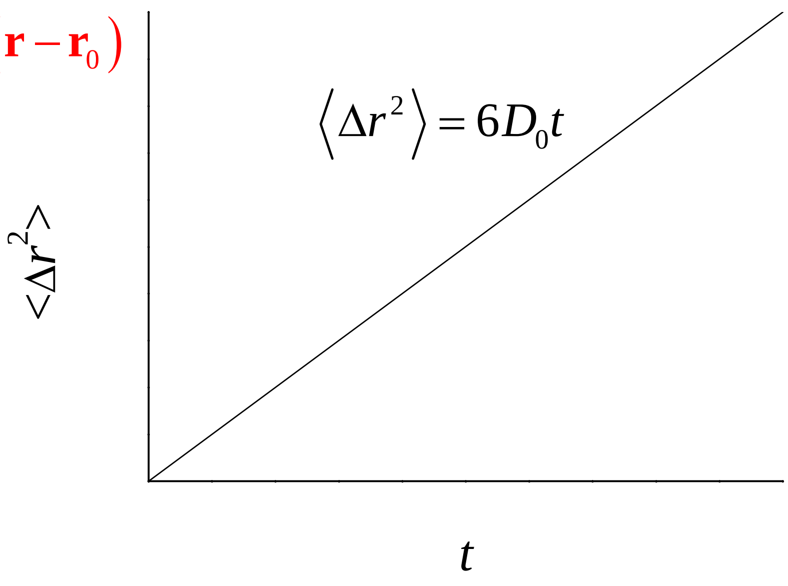
Now <u>remove</u> the external force:

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

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

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





Dilute dispersions

(particles are statistically independent)

$$g_I(\tau) = \left\langle f^4 \sum_{j,k,l,m=1}^{N} \exp\left(-i\mathbf{q}\cdot\left[\mathbf{r}_j(0) - \mathbf{r}_k(0) - \mathbf{r}_l(\tau) + \mathbf{r}_m(\tau)\right]\right)\right\rangle$$

Statistical independence means: $\langle ABCD \rangle = \langle A \rangle \langle B \rangle \langle C \rangle \langle D \rangle$

But $\left\langle \exp\left(-i\mathbf{q}\cdot\mathbf{r}_j(\tau)\right)\right\rangle = 0$ …so most terms equal <u>zero</u>!

$$g_I(\tau) = \left\langle f^4 \sum_{j,k,l,m=1}^{N} \exp\left(-i\mathbf{q}\cdot\left[\mathbf{r}_j(0) - \mathbf{r}_k(0) - \mathbf{r}_l(\tau) + \mathbf{r}_m(\tau)\right]\right)\right\rangle$$

<u>Surviving terms are:</u>

i. N^2 terms $j=k$, $l=m$

these terms give: 1

ii. $N^2 - N$ terms $j=m$, $k=l$, $j \neq k$

$$\left\langle \exp\left(i\mathbf{q}\cdot\left[\mathbf{r}_j(\tau) + \mathbf{r}_j(0)\right]\right)\right\rangle \left\langle \exp\left(-i\mathbf{q}\cdot\left[\mathbf{r}_k(\tau) + \mathbf{r}_k(0)\right]\right)\right\rangle = 0$$

iii. $N^2 - N$ terms $j=l$, $k=m$, $j \neq k$

$$\left\langle \exp\left(i\mathbf{q}\cdot\underbrace{\left[\mathbf{r}_j(\tau) - \mathbf{r}_j(0)\right]}_{\text{particle displacement}}\right)\right\rangle \left\langle \exp\left(-i\mathbf{q}\cdot\left[\mathbf{r}_k(\tau) - \mathbf{r}_k(0)\right]\right)\right\rangle$$

particle displacement

$$g_I(\tau) = N^2 f^4 + \left(N^2 - N\right) f^4 \left| \left\langle \exp\left(i\mathbf{q}\cdot\Delta\mathbf{r}_j(\tau)\right)\right\rangle \right|^2$$

$\langle I \rangle = Nf^2$ $\quad\approx N^2\quad$ $\Delta\mathbf{r}_j(\tau) = \mathbf{r}_j(\tau) - \mathbf{r}_j(0)$

$$g_I(\tau) = \langle I \rangle^2 \left[1 + \left| \left\langle \exp\left(i\mathbf{q}\cdot\Delta\mathbf{r}_j(\tau)\right)\right\rangle \right|^2 \right]$$

Displacements are described by the diffusion equation:

$$\begin{cases} \dfrac{\partial P(\Delta\mathbf{r}, t)}{\partial t} = D_0 \nabla^2 P(\Delta\mathbf{r}, t) \\ P(\Delta\mathbf{r}, t=0) = \delta(\Delta\mathbf{r}) \end{cases}$$

but we only need: $\left\langle \exp\left(-i\mathbf{q}\cdot\Delta\mathbf{r}\right)\right\rangle = \int P(\Delta\mathbf{r}, t) \exp\left(-i\mathbf{q}\cdot\Delta\mathbf{r}\right) d(\Delta\mathbf{r})$

Fourier transformation of diffusion equation:

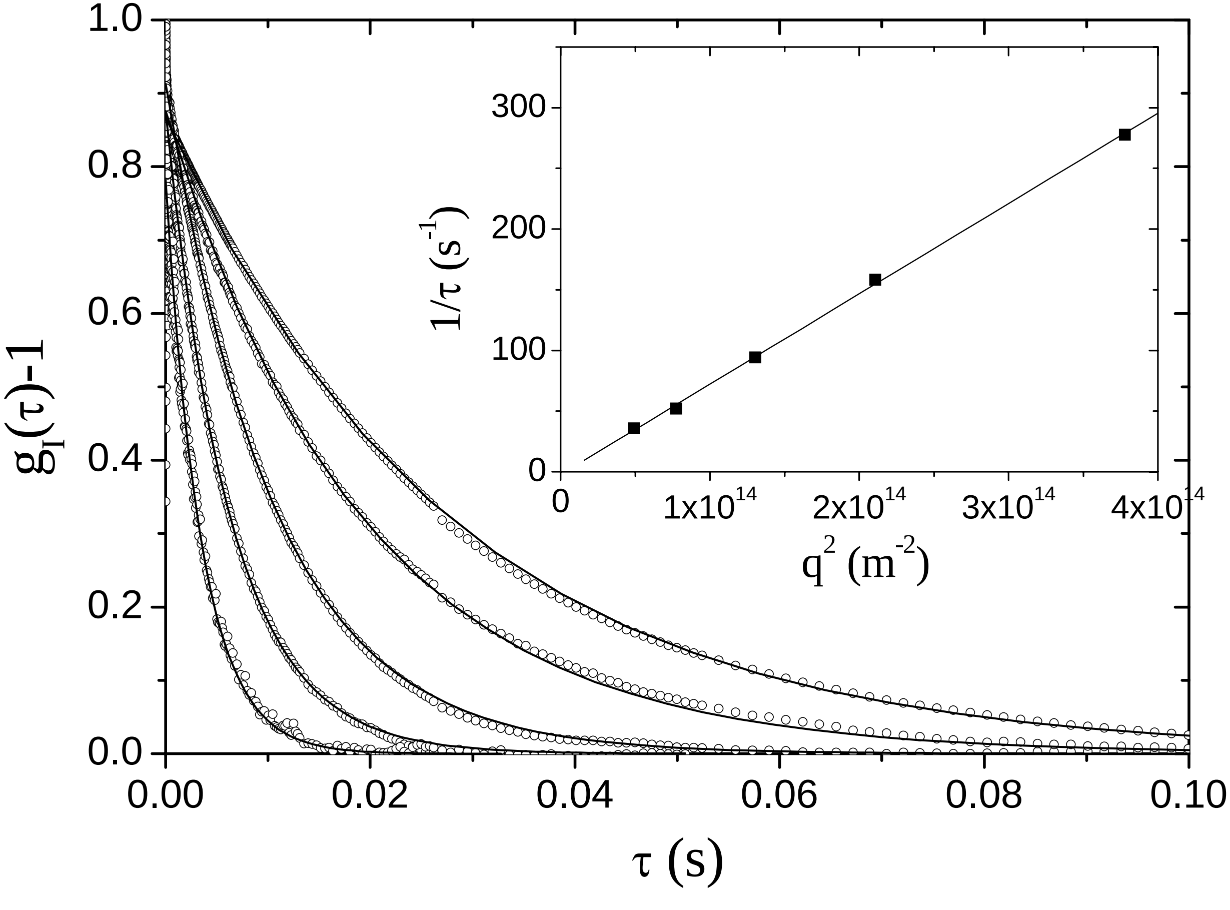
$$\begin{cases} \dfrac{\partial P(\mathbf{q},t)}{\partial t} = -q^2 D_0 P(\mathbf{q},t) \\ P(\mathbf{q},t) = 1 \end{cases} \quad \Rightarrow \quad P(\mathbf{q},t) = \exp\left(-q^2 D_0 t\right)$$

So, finally: $$g_I(\tau) = \langle I \rangle^2 \left[1 + \exp\left(-2q^2 D_0 t\right)\right]$$

"Stokes-Einstein": $D_0 = \dfrac{kT}{6\pi\eta R}$ *(for spheres)*

Determination of particle size

$$g_I(\tau) = \langle I \rangle^2 \left[1 + \exp\left(-2q^2 D_0 t\right)\right]$$



Concentrated dispersions

(particles are ***not*** statistically independent)

If scattering volume >> "correlation volume" then the electric field is still a random variable:

Siegert relation:

$$g_I(\tau) = \langle I \rangle^2 + \left| g_E(\tau) \right|^2$$

$$g_E(\tau) = \left\langle E_s(t) E_s^*(t+\tau) \right\rangle$$

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

"electric field autocorrelation function"

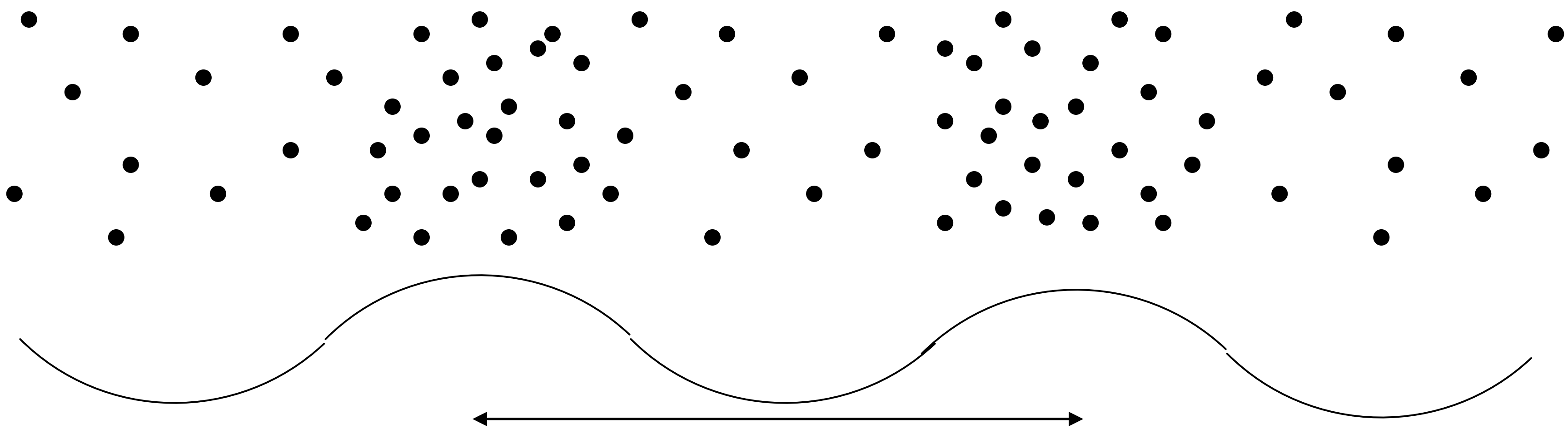
"dynamic structure factor"

Let's again write: $$g_I(\tau) = \langle I \rangle^2 \left[1 + \exp\left(-2q^2 D_c(q,t)\,t\right)\right]$$

<u>Definition</u> of $D_c(q,t)$

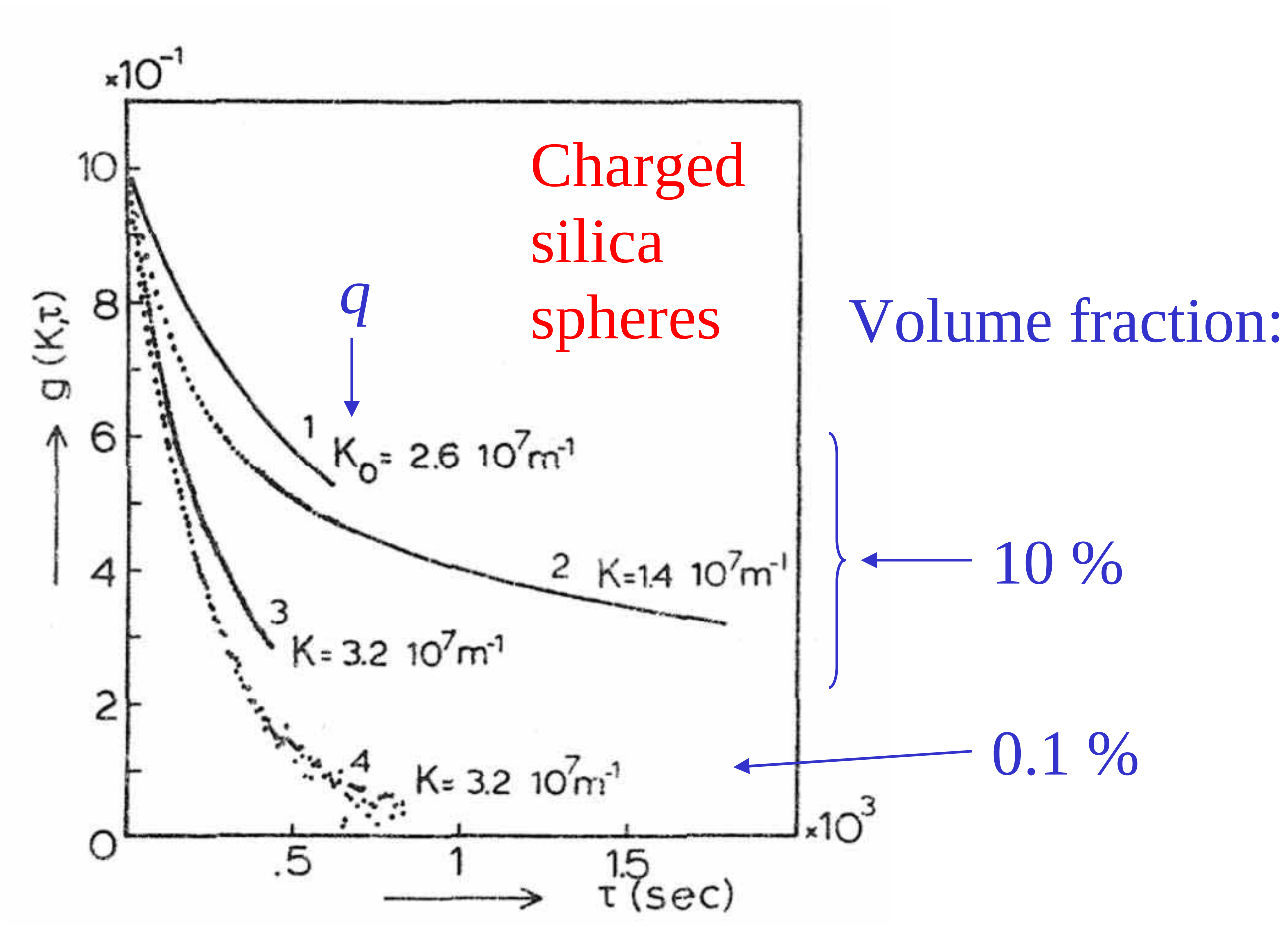
("collective diffusion coeff.")

<u>Interpretation</u>: *decay of density fluctuations*



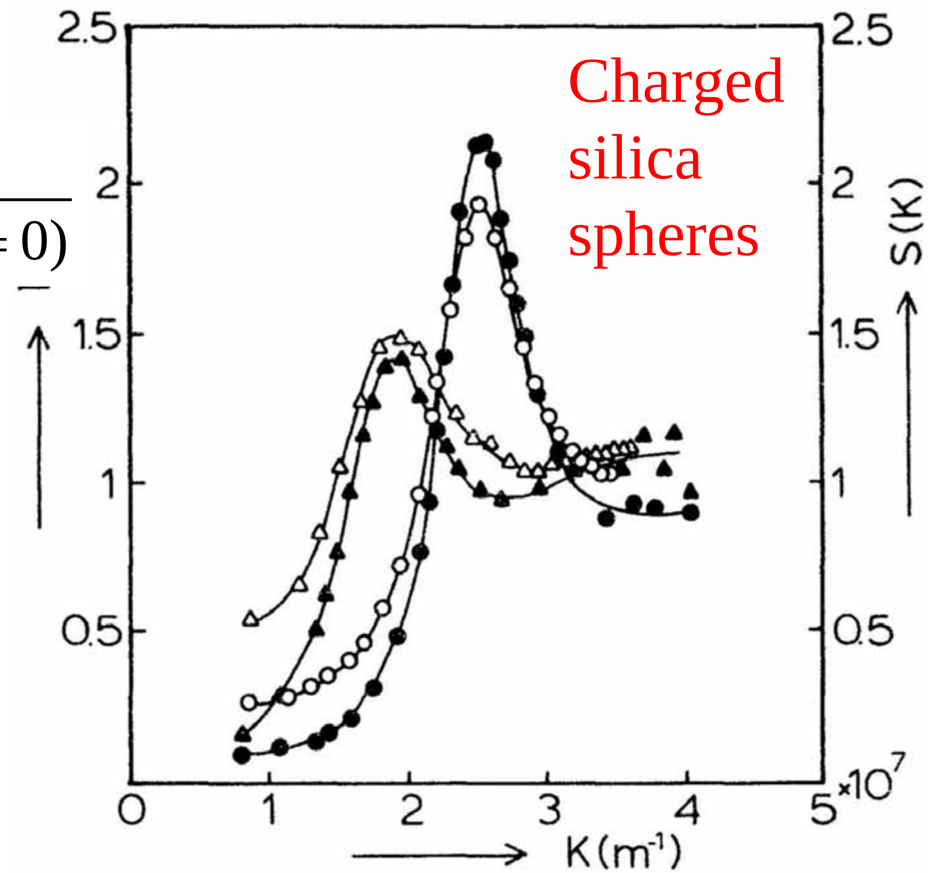
$\frac{2\pi}{q}$

Time dependence: no longer pure exponential



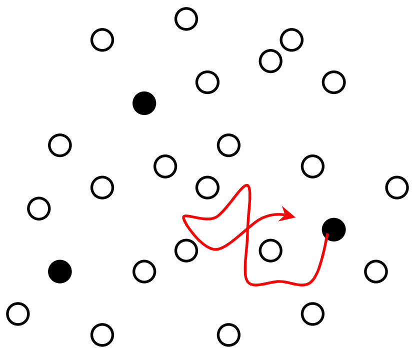
longer times → slower motion → particles collide

q-dependence: no longer pure q_2



$1/D_c(t=0)$ looks like $S(q)$

Self-diffusion



Diffusion of
"*tracer particles*"

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

(Sum over tracers)

$$= \langle I \rangle \left\langle \exp\left(i\mathbf{q} \cdot \Delta\mathbf{r}(\tau) \right) \right\rangle$$

$$= \langle I \rangle \exp\left(-q^2 D_s(t) t \right)$$

Tracers are independent:
only terms $j=k$ survive

Definition of $D_s(t)$ no q-dependence

(self-diffusion coefficient)

Measuring mean-square displacements