Diffraction from non-crystalline materials

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Outline

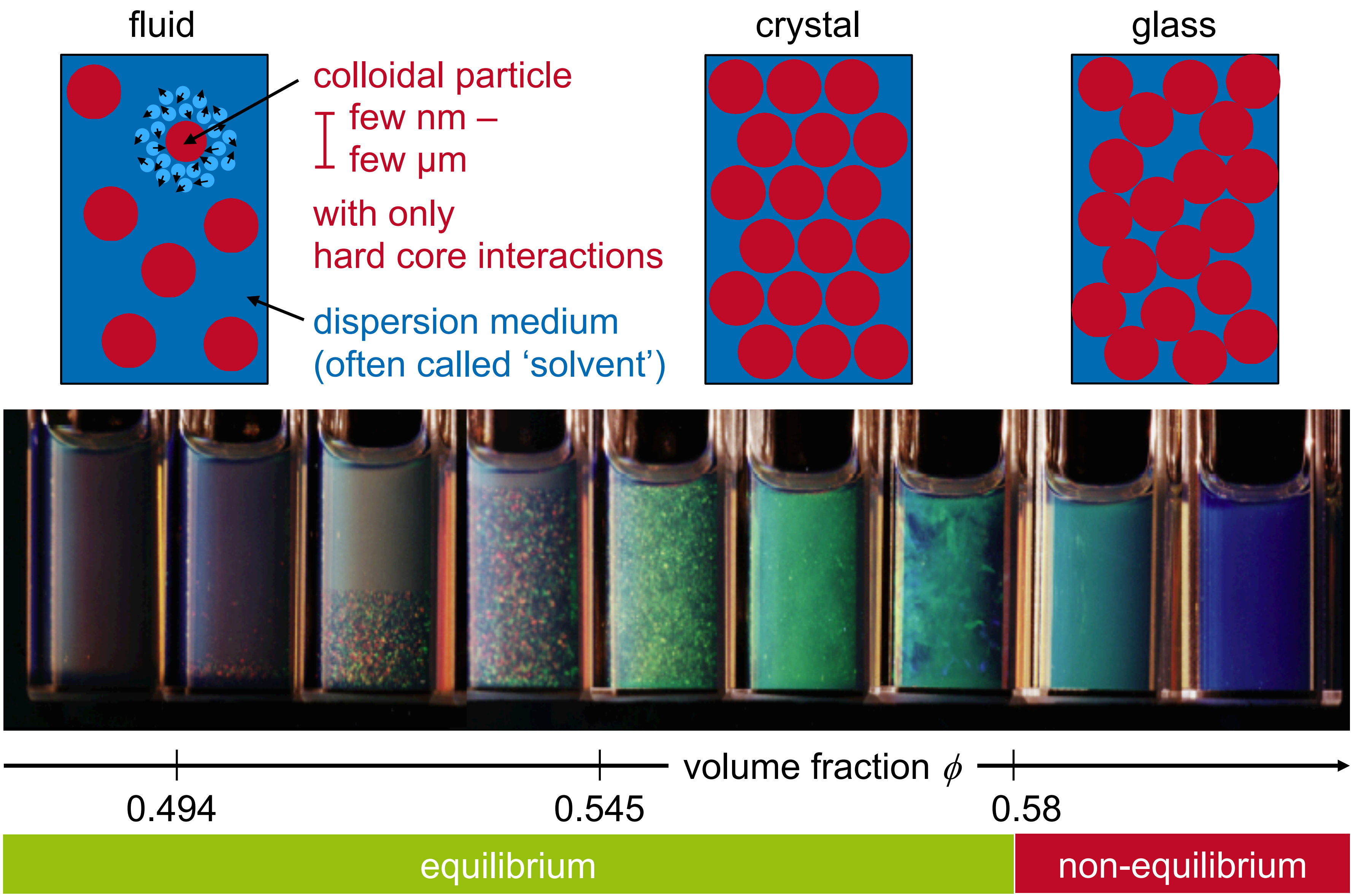
examples of non-crystalline materials

characterization of non-crystalline materials

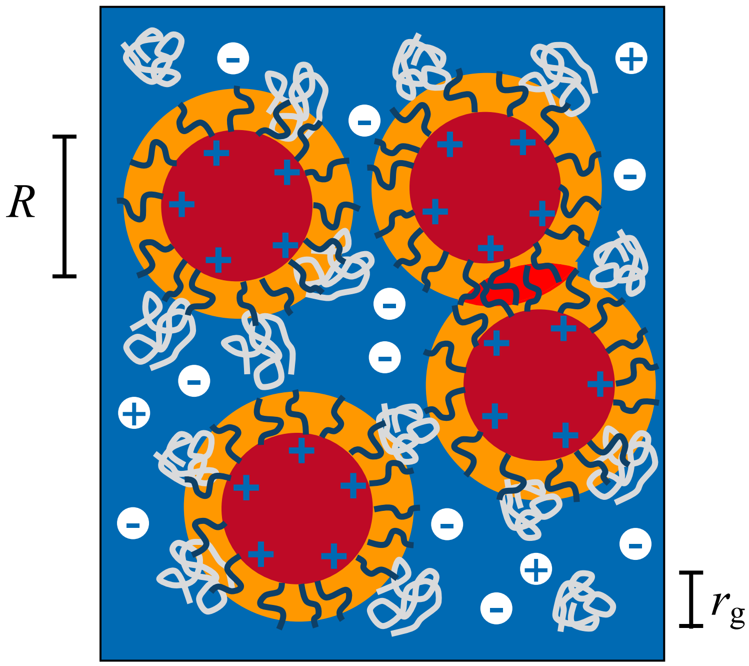
diffraction from non-crystalline materials

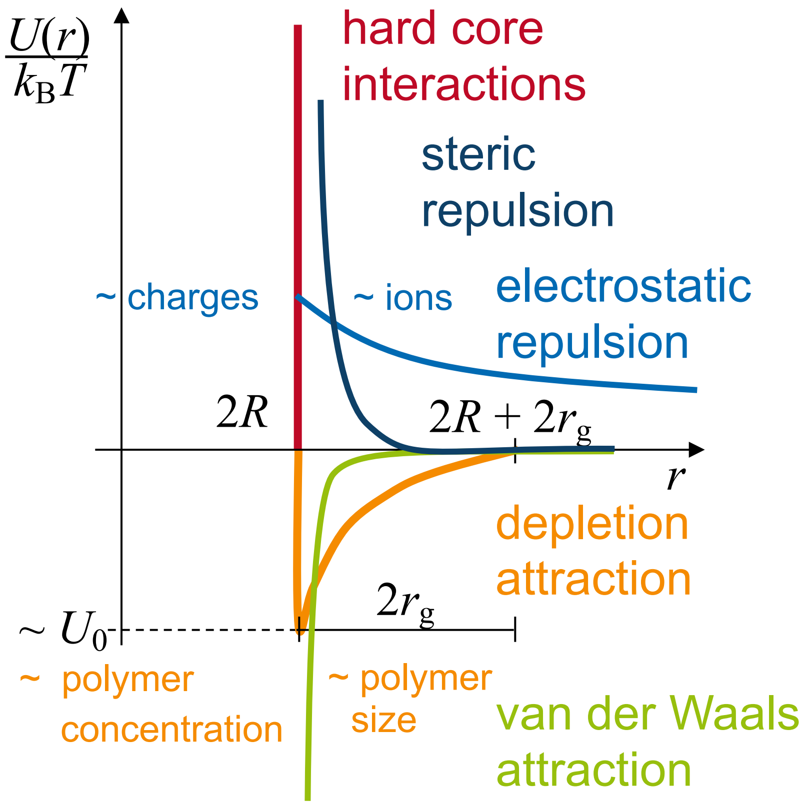
- general concept
- form factor – particle properties
- structure factor – particle arrangements
- ‘prefactor’ – contrast variaton

Colloidal Suspensions



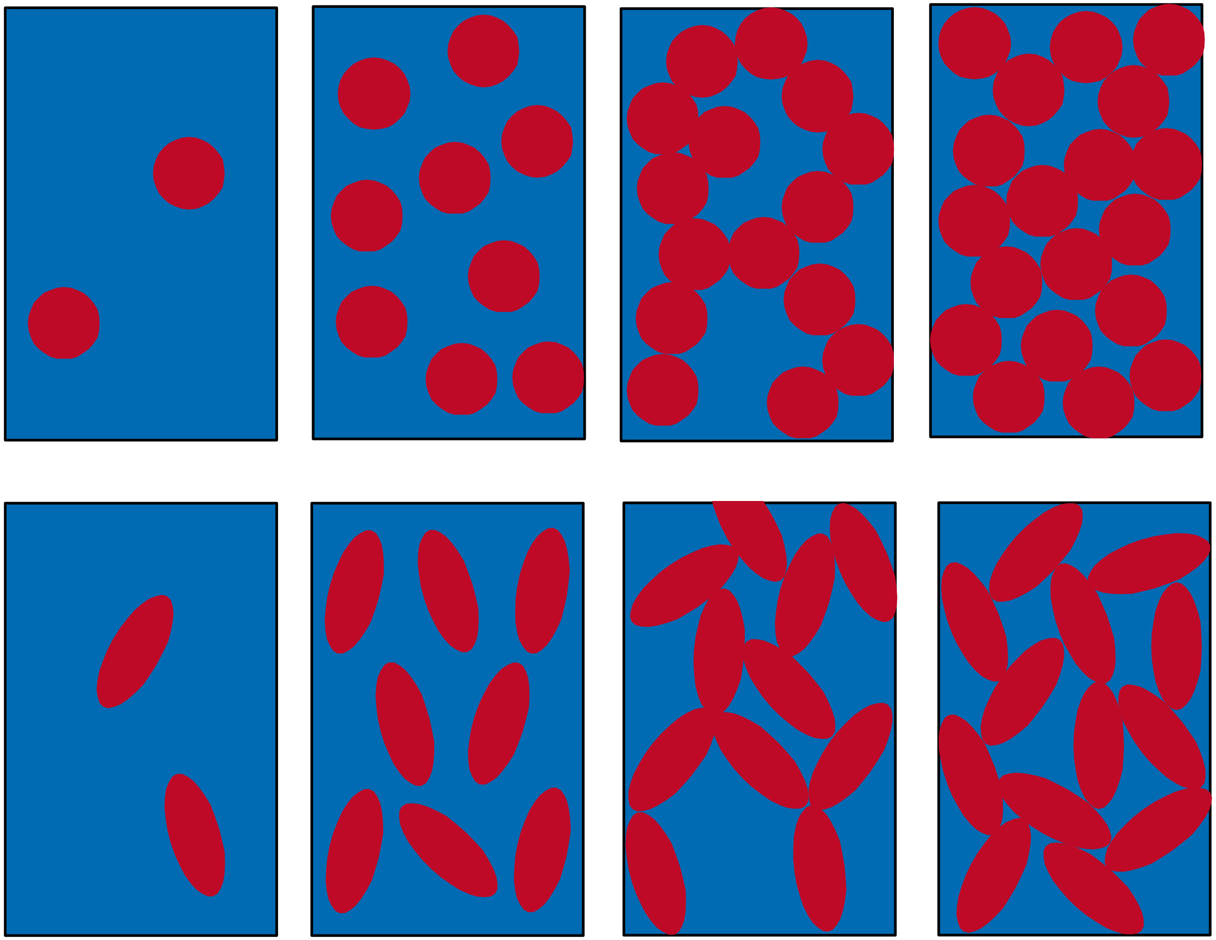
Particle interactions



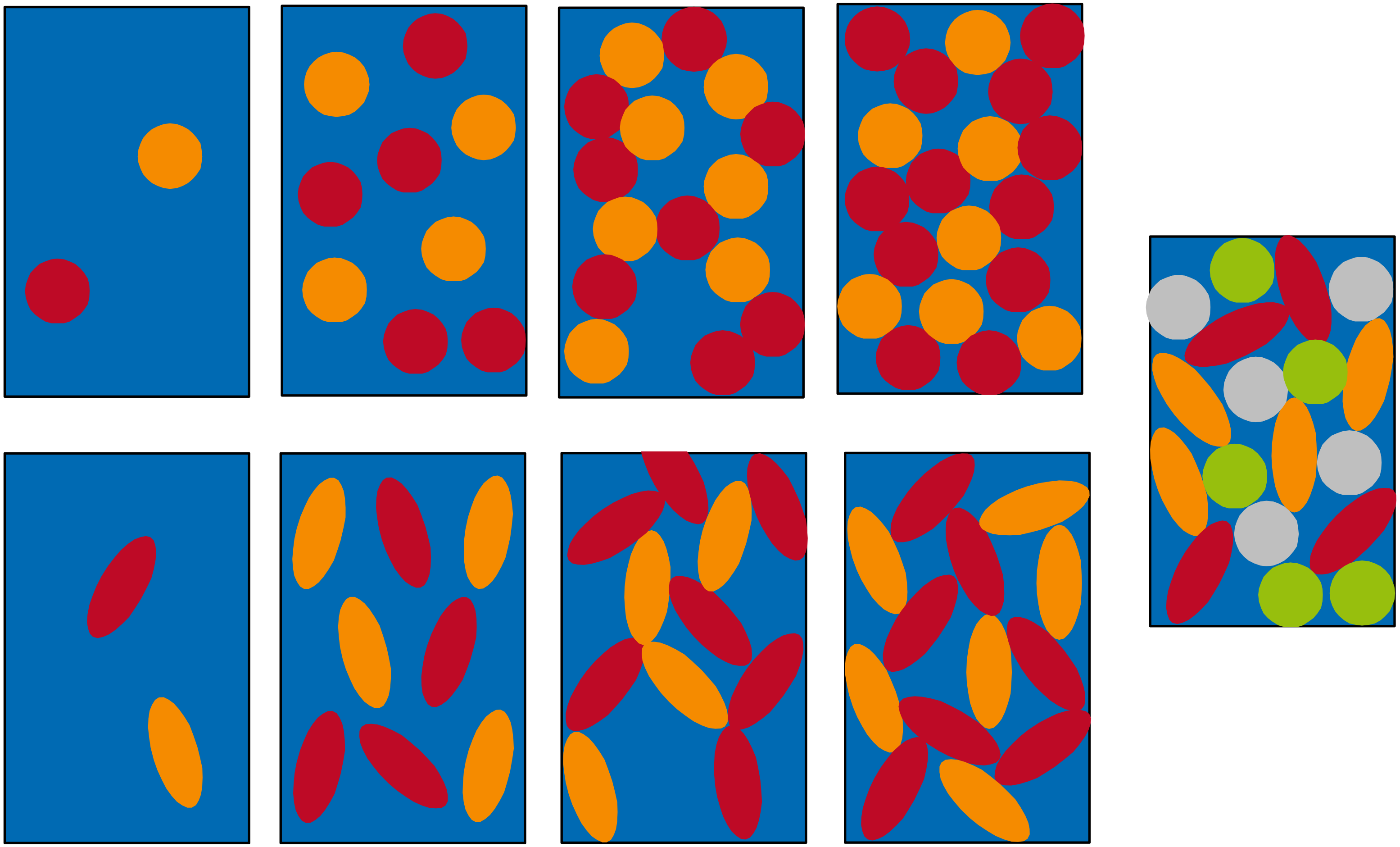


as well as anisotropic interactions,
(e.g. dipol or ‘patchy’ interactions)

Non-crystalline materials



Non-crystalline materials



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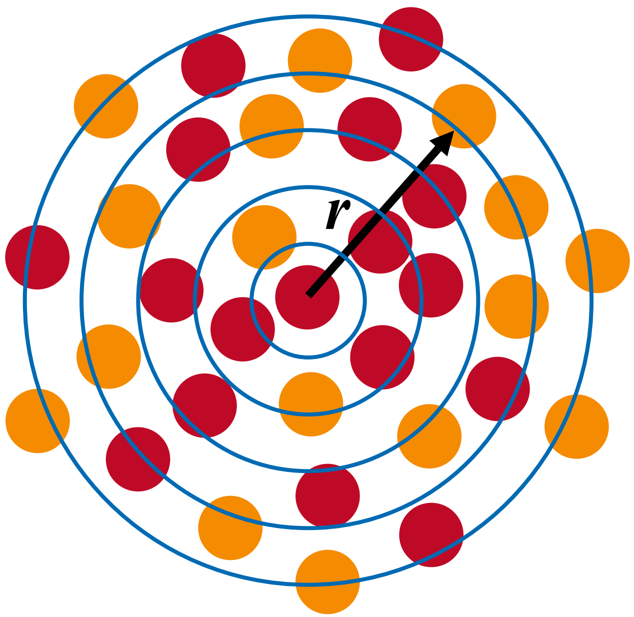
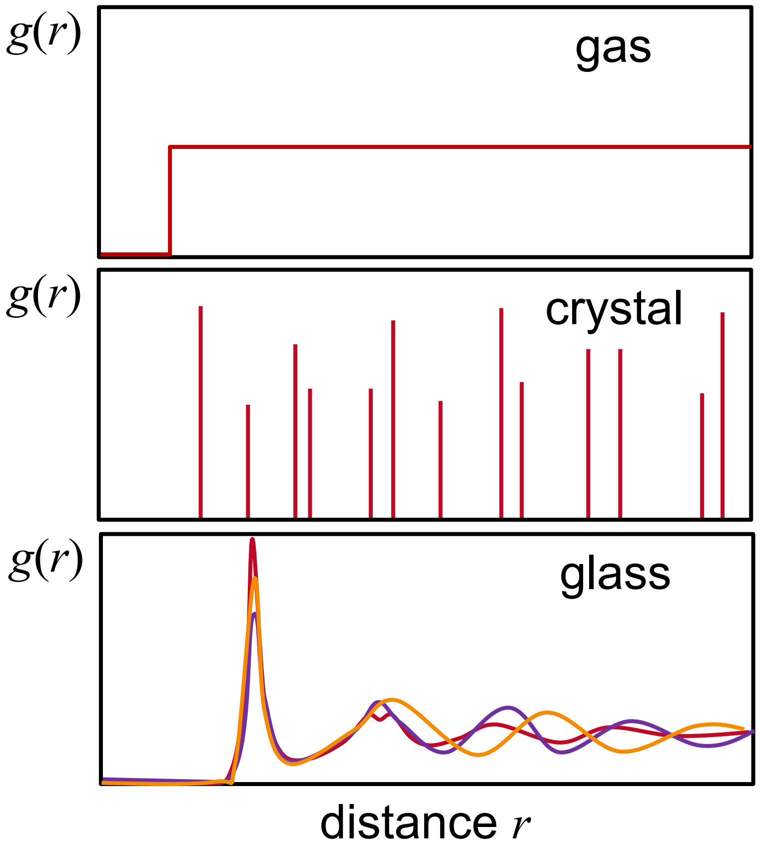
Characterization - arrangement

radial distribution function $g(r)$

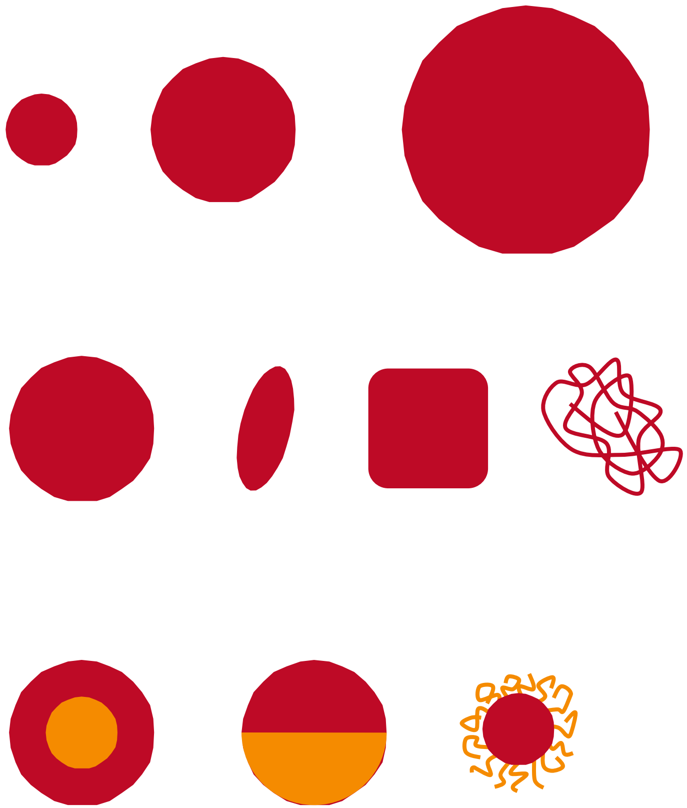
$(N/V)\, g(r)\, d^3r$ is the number of particles in d^3r at r





contains information on interactions

Characterization – particle



particle size

particle shape

particle structure

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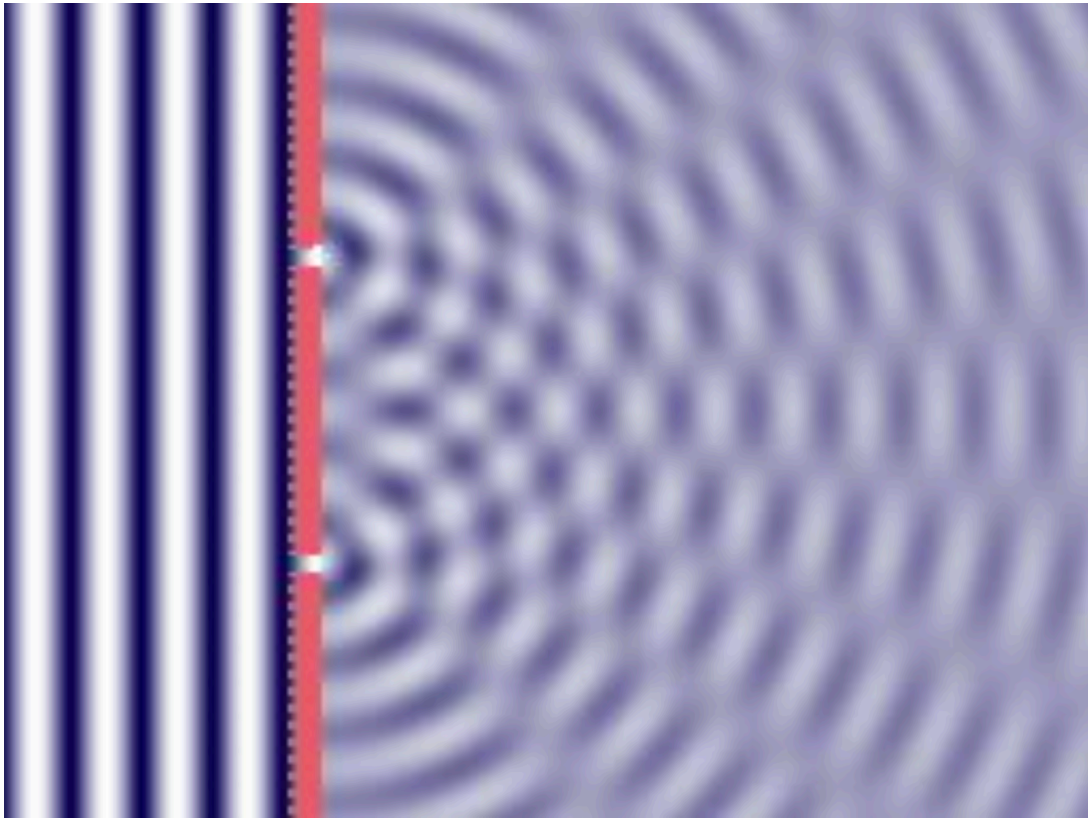
Two-slit experiment



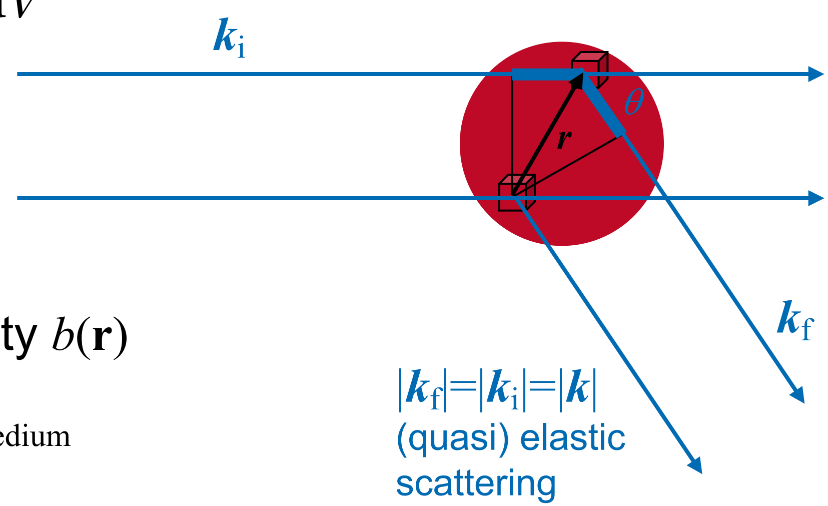
Scattering by a particle

particle = ensemble of small volume elements $\mathrm{d}V$ (using Born approx.)

$$\delta L = \delta L_1 + \delta L_2$$

$$\psi_{\mathrm{p}}^{\mathrm{sc}} = \int_V \mathrm{e}^{i\delta\phi}\mathrm{d}\psi^{\mathrm{sc}} \sim \int_V \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{r}}\Delta b(\mathbf{r})\mathrm{d}V$$

Fourier transform

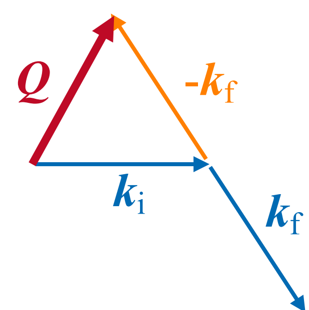


$$\delta\phi = \frac{2\pi}{\lambda}\delta L = \mathbf{k}_{\mathrm{i}}\cdot\mathbf{r} - \mathbf{k}_{\mathrm{f}}\cdot\mathbf{r} = \mathbf{Q}\cdot\mathbf{r}$$

$\mathrm{d}\psi^{\mathrm{sc}} \sim \Delta b(\mathbf{r})\,\mathrm{d}V$ scatt. length density $b(\mathbf{r})$

$$\Delta \mathrm{b}(\mathbf{r}) = b_{\mathrm{part}}(\mathbf{r}) - b_{\mathrm{medium}}$$

with scattering vector $\mathbf{Q} = \mathbf{k}_{\mathrm{i}}$ - $\mathbf{k}_{\mathrm{f}}$



$$|\mathbf{Q}| = 2k\sin\frac{\theta}{2} = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} = \frac{4\pi n}{\lambda_0}\sin\frac{\theta}{2}$$

$$|\mathbf{Q}| \sim (\text{length} \quad \text{scale})^{-1}$$

Scattering by many particles

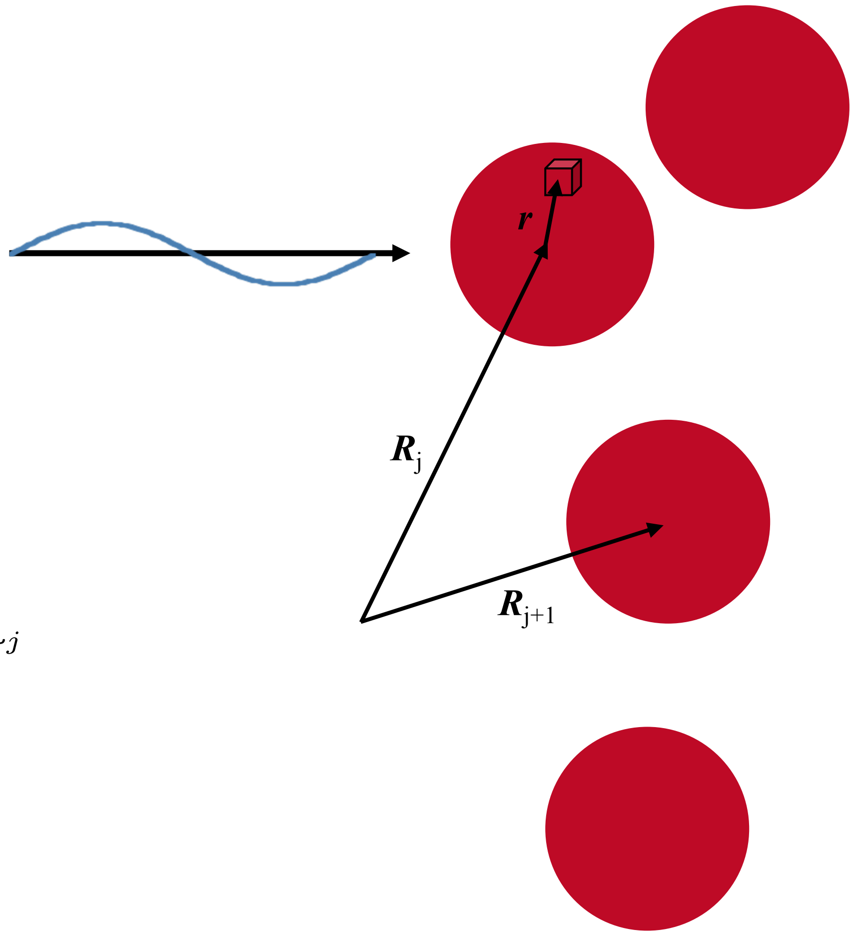
many particles = ensemble of particles j=1..N (using Born approx.)

$$\psi^{\mathrm{sc}} = \sum_j \psi^{\mathrm{sc}}_{\mathrm{p},j}\, \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{R}_j}$$

'Fourier transform'

$$\psi^{\mathrm{sc}}_{\mathrm{p},j} \sim \int_{V_j} \Delta b(\mathbf{r})\, \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{r}} \mathrm{d}V$$

Fourier transform



$$\psi^{\mathrm{sc}} \sim \sum_j \int_{V_j} \Delta b(\mathbf{r})\, \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{r}} \mathrm{d}V\, \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{R}_j}$$

$$\sim \sum_j \int_{V_j} \Delta b(\mathbf{r})\, \mathrm{e}^{i\mathbf{Q}\cdot(\mathbf{r}+\mathbf{R}_j)}\, \mathrm{d}V$$

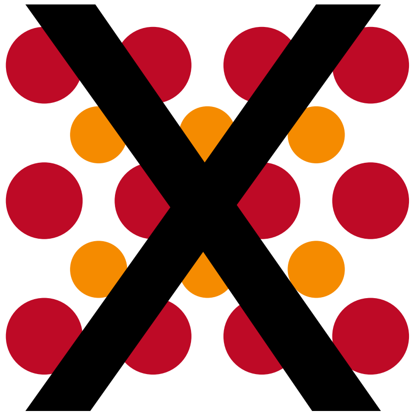
Differential cross section

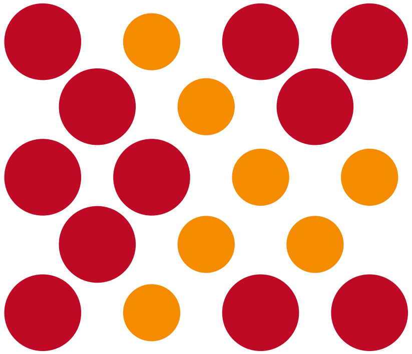
time-averaged (or ensemble-averaged) differential cross section is detected

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{Q}) \sim |\psi^{\mathrm{sc}}|^2 \sim \sum_k \sum_j \left\langle \psi^{\mathrm{sc}}_{\mathrm{p},j}(\mathbf{Q})\, \psi^{\mathrm{sc}\,\star}_{\mathrm{p},k}(\mathbf{Q})\; \mathrm{e}^{i\mathbf{Q}\cdot(\mathbf{R}_j - \mathbf{R}_k)} \right\rangle$$

assumption: all particles are identical, i.e. $\psi^{\mathrm{sc}}_{\mathrm{p},j}(\mathbf{Q}) = \psi^{\mathrm{sc}}_{\mathrm{p},k}(\mathbf{Q}) = \psi^{\mathrm{sc}}_{\mathrm{p}}(\mathbf{Q})$

(important: particle properties must not be linked to their positions)





Differential cross section

time-averaged (or ensemble-averaged) differential cross section is detected

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{Q}) \sim |\psi^{\mathrm{sc}}|^2 \sim \sum_k \sum_j \left\langle \psi^{\mathrm{sc}}_{\mathrm{p},j}(\mathbf{Q})\, \psi^{\mathrm{sc}\,\star}_{\mathrm{p},k}(\mathbf{Q})\; \mathrm{e}^{i\mathbf{Q}\cdot(\mathbf{R}_j - \mathbf{R}_k)} \right\rangle$$

assumption: all particles are identical, i.e. $\psi^{\mathrm{sc}}_{\mathrm{p},j}(\mathbf{Q}) = \psi^{\mathrm{sc}}_{\mathrm{p},k}(\mathbf{Q}) = \psi^{\mathrm{sc}}_{\mathrm{p}}(\mathbf{Q})$

(important: particle properties must not be linked to their positions)

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{Q}) \sim \qquad |\psi^{\mathrm{sc}}_{\mathrm{p}}(\mathbf{Q})|^2 \qquad \sum_k \sum_j \left\langle \mathrm{e}^{i\mathbf{Q}(\mathbf{R}_j(t) - \mathbf{R}_k(t))} \right\rangle$$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{Q}) \sim N|\psi^{\mathrm{sc}}_{\mathrm{p}}(0)|^2 \frac{|\psi^{\mathrm{sc}}_{\mathrm{p}}(\mathbf{Q})|^2}{|\psi^{\mathrm{sc}}_{\mathrm{p}}(0)|^2}\; \frac{1}{N} \sum_k \sum_j \left\langle \mathrm{e}^{i\mathbf{Q}(\mathbf{R}_j(t) - \mathbf{R}_k(t))} \right\rangle$$

‘prefactor’ scattering by N particles (random walk)

$= P(\boldsymbol{q})$ form factor (intraparticle)

$= S(\boldsymbol{q})$ structure factor (interparticle)

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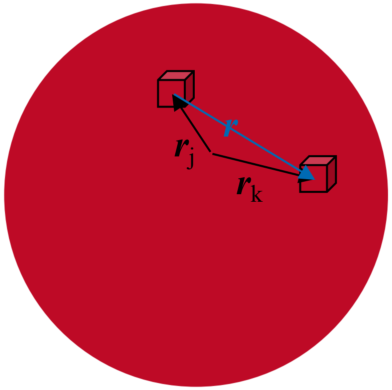
Form factor $P(Q)$

intraparticle interference
depends on particle size and shape



$$P(\mathbf{Q}) = \frac{|\psi_\mathrm{p}^\mathrm{sc}(\mathbf{Q})|^2}{|\psi_\mathrm{p}^\mathrm{sc}(0)|^2}$$

with $\psi_\mathrm{p}^\mathrm{sc}(\mathbf{Q}) \sim \int_V \Delta b(\mathbf{r})\, \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{r}} \mathrm{d}V$

$$\vdots$$

$$|\psi_\mathrm{p}^\mathrm{sc}(\mathbf{Q})|^2 = 4\pi \int_0^\infty p(r) \frac{\sin(qr)}{qr} \mathrm{d}r$$

pair distance distribution function

$$p(\mathbf{r}) = r^2 \int_V \Delta b(\mathbf{r}') \Delta b(\mathbf{r}-\mathbf{r}'))\, \mathrm{d}^3\mathbf{r}$$

Form factor $P(Q)$

any shape – Guinier approximation

for small Q ($Q < R_\mathrm{g}^{-1}$):

$$P(Q) = 1 - \frac{1}{3}(QR_\mathrm{g})^2$$

with radius of gyration R_g

$$R_\mathrm{g}^2 = \int_V \rho(\mathbf{r})\,(\mathbf{r} - \mathbf{r}_\mathrm{cm})^2 \mathrm{d}\mathbf{r}$$

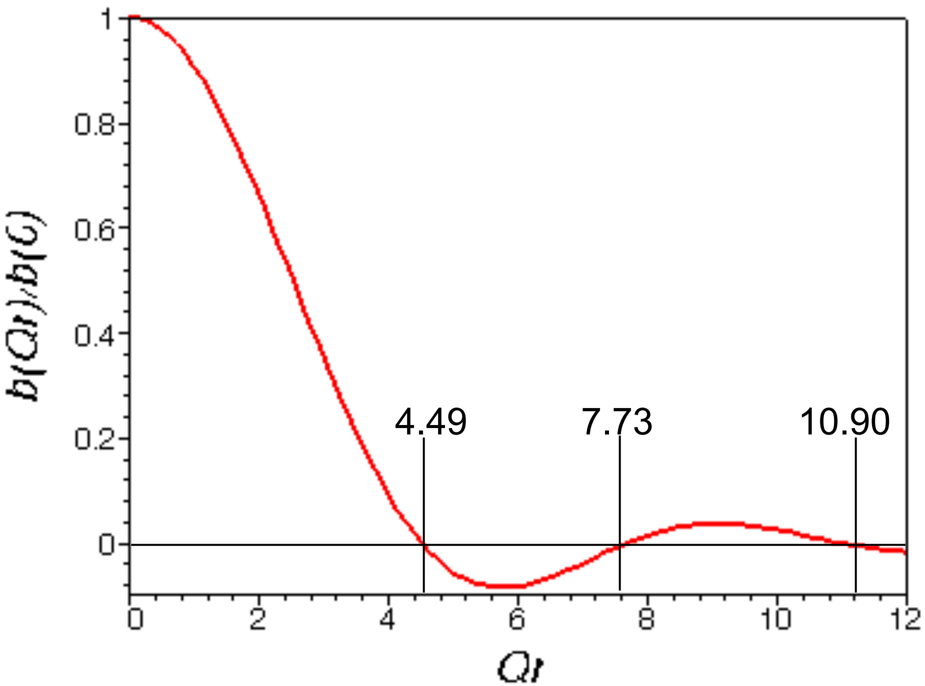
Form factor $P(Q)$

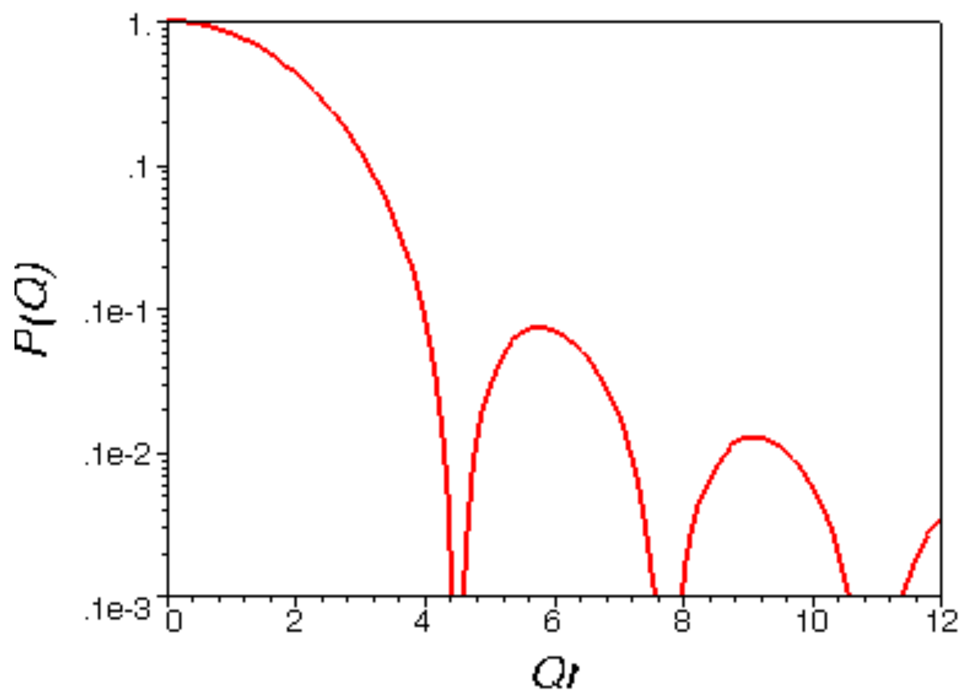
homogenous sphere

$$\psi_{\mathrm{p}}^{\mathrm{sc}}(\mathbf{Q}) = \int \Delta b(\mathbf{r}) \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{r}} \mathrm{dV} = \Delta b \int_{V_{\mathrm{sphere}}} \mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{r}} \mathrm{dV} = \Delta b \int \mathrm{d}\phi \int r^2 \mathrm{d}r \int \mathrm{e}^{iQr\cos\theta} \sin\theta \mathrm{d}\theta$$

$$\vdots$$

$$\sim \frac{3}{(QR)^3} \left(\sin(QR) - QR\cos(QR)\right)$$





Form factor $P(Q)$

polydisperse homogenous spheres

radius of gyration

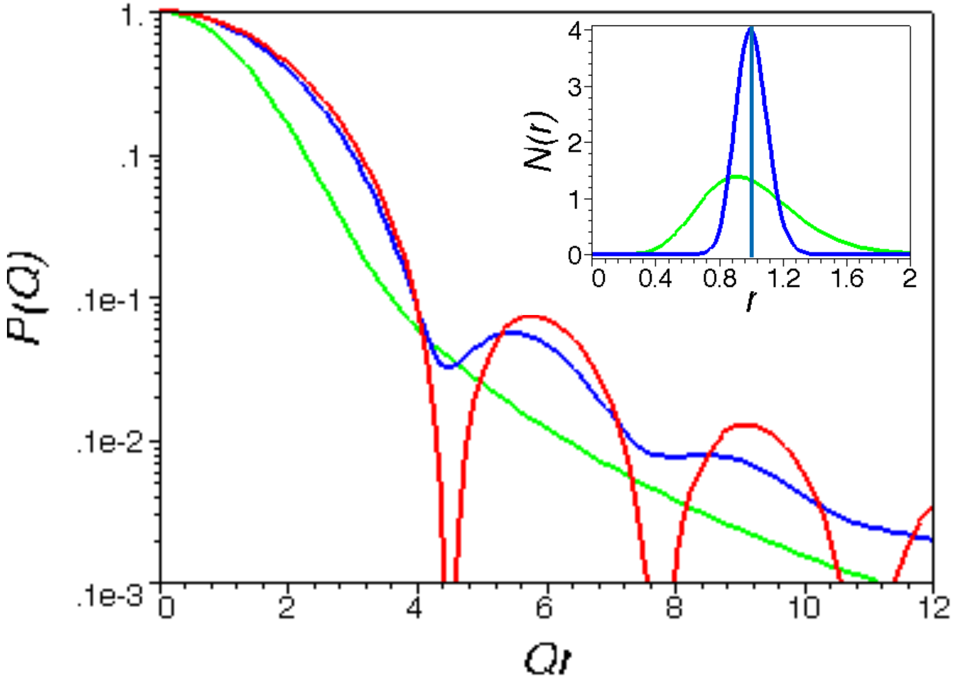
$$\langle R_g^2 \rangle = \frac{\int_0^\infty N(r) M^2(r) R_g^2 \, dr}{\int_0^\infty N(r) M^2(r) \, dr}$$

molar mass

$$\langle M \rangle = \frac{\int_0^\infty N(r) M^2(r) \, dr}{\int_0^\infty N(r) M(r) \, dr}$$

form factor

$$\langle P(\mathbf{q}) \rangle = \frac{\int_0^\infty N(r) M^2(r) P(\mathbf{q}, r) \, dr}{\int_0^\infty N(r) M^2(r) \, dr}$$



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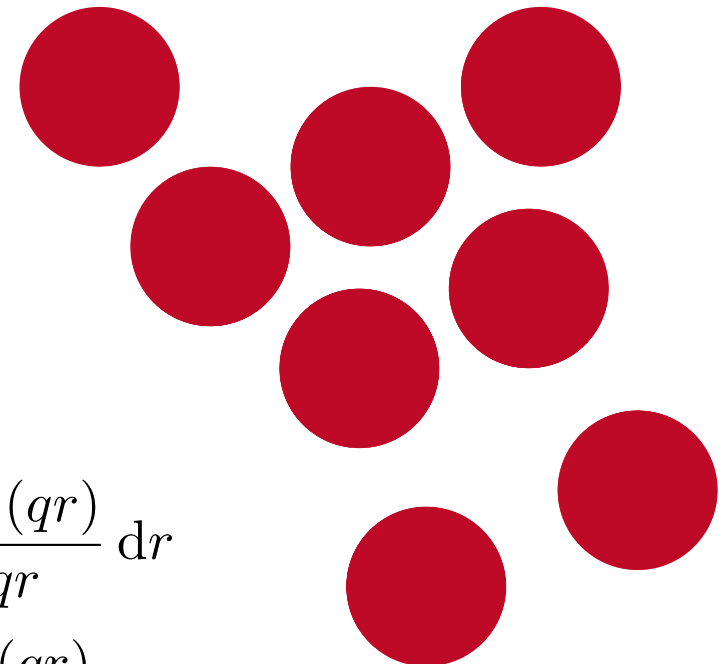
Structure factor $S(Q)$

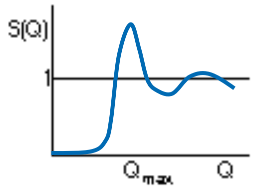


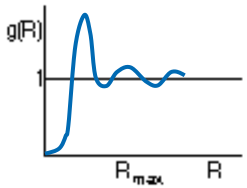
interparticle interference
depends on particle arrangement

$$S(\mathbf{Q}) = \frac{1}{N} \sum_j \sum_k \left\langle \mathrm{e}^{i\mathbf{Q}\cdot(\mathbf{R}_j - \mathbf{R}_k)} \right\rangle$$

$$S(\mathbf{Q}) = 1 + 4\pi \frac{N}{V} \int (g(\mathbf{r}) - 1)\, r^2 \frac{\sin(qr)}{qr}\, \mathrm{d}r$$

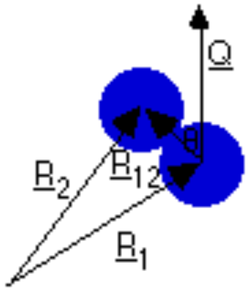
$$S(\mathbf{Q}) - 1 = 4\pi \frac{N}{V} \int (g(\mathbf{r}) - 1)\, r^2 \frac{\sin(qr)}{qr}\, \mathrm{d}r$$





Structure factor $S(Q)$

dumbbell



$$S(\mathbf{Q}) = \frac{1}{N}\sum_j\sum_k \left\langle e^{i\mathbf{Q}\cdot(\mathbf{R}_j-\mathbf{R}_k)}\right\rangle = \frac{1}{2}\sum_{j=1}^{2}\sum_{k=1}^{2}\left\langle e^{i\mathbf{Q}\cdot(\mathbf{R}_j-\mathbf{R}_k)}\right\rangle$$

$$= \frac{1}{2}\left\langle 1 + e^{i\mathbf{Q}\cdot(\mathbf{R}_1-\mathbf{R}_2)} + e^{i\mathbf{Q}\cdot(\mathbf{R}_2-\mathbf{R}_1)} + 1\right\rangle$$

$$= \langle 1 + \cos(\mathbf{Q}\cdot\mathbf{R}_{12})\rangle$$

↓ spherical averaging

$$S(\mathbf{Q}) = 1 + \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}\cos(\mathbf{Q}\cdot\mathbf{R}_{12})\sin\theta \,\mathrm{d}\theta\,\mathrm{d}\phi$$

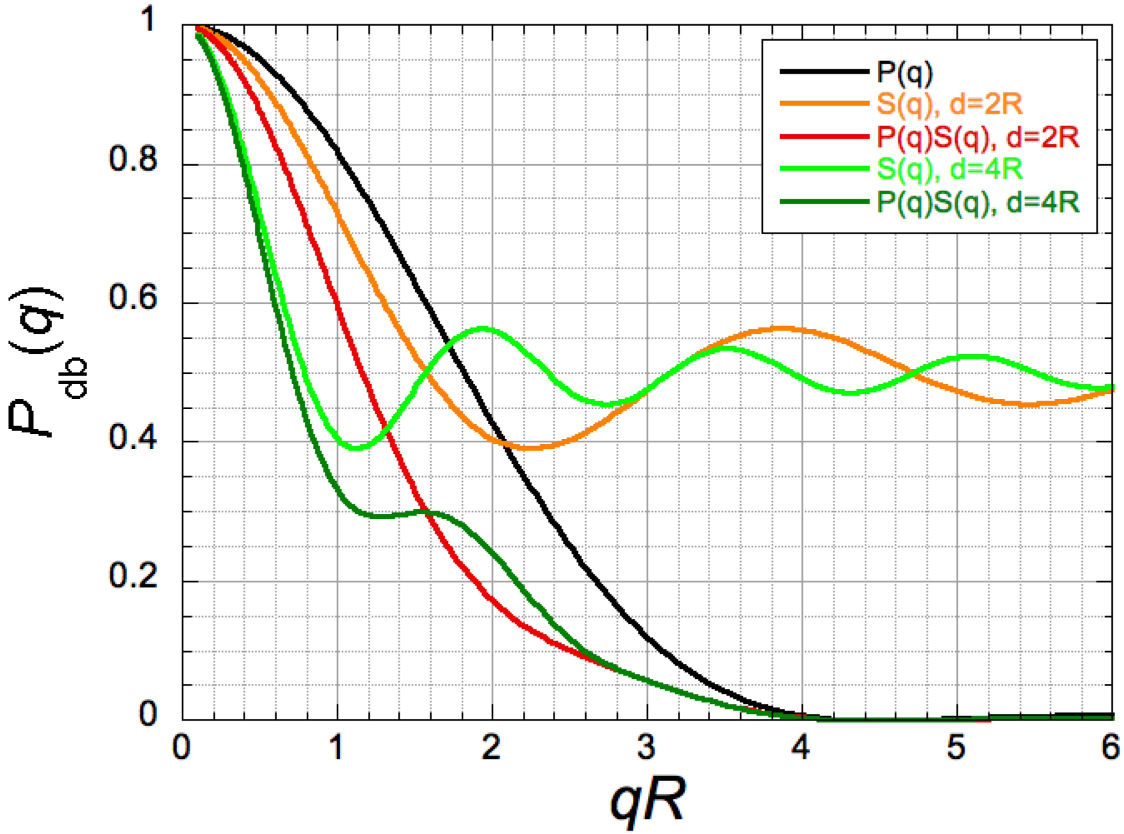
$$= 1 + \frac{\sin(2QR_{12})}{2QR_{12}}$$

↓ $P(q)$ of a sphere
dumbbell = 2 spheres

…..

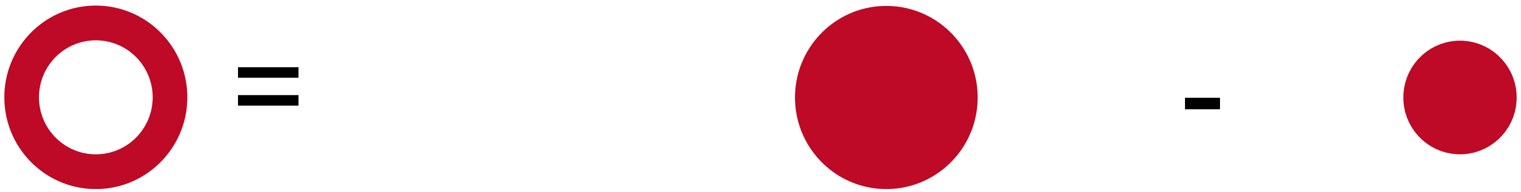
Structure factor $S(Q)$

dumbbell

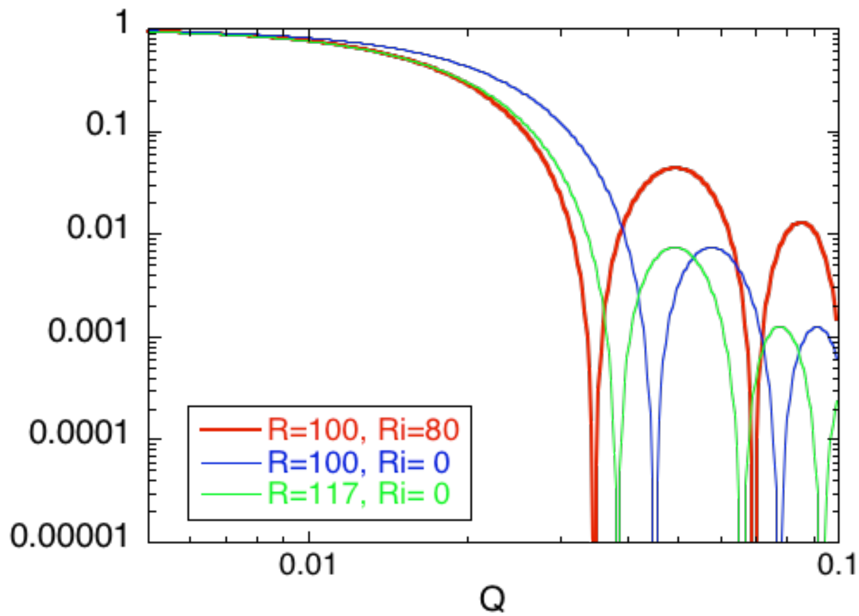


Form factor $P(Q)$

inhomogenous sphere (core-shell



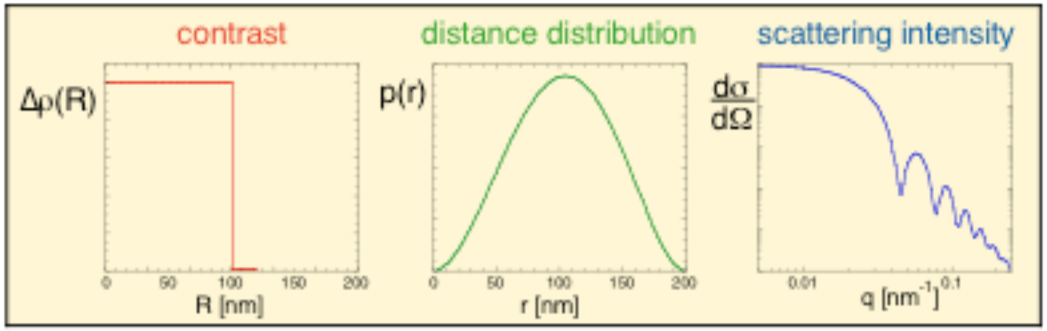
$$P(q) = \left(\frac{3}{(QR_\mathrm{s})^3 - (QR_\mathrm{c})^3} \left\{ (\sin(QR_\mathrm{s}) - QR_\mathrm{s}\cos(QR_\mathrm{s})) - (\sin(QR_\mathrm{c}) - QR_\mathrm{c}\cos(QR_\mathrm{c})) \right\} \right)^2$$



Data analysis

hhu

indirect Fourier transformation



model fitting (analytical, numerical, simulations)

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‘Prefactor’

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{Q}) \sim N|\psi_{\mathrm{p}}^{\mathrm{sc}}(0)|^2$$

$$\psi_{\mathrm{p}}^{\mathrm{sc}}(\mathbf{Q}) = \int \Delta b(\mathbf{r})\mathrm{e}^{i\mathbf{Q}\cdot\mathbf{r}}\mathrm{dV} \quad \rightarrow \quad \psi_{\mathrm{p}}^{\mathrm{sc}}(0) \sim \Delta b V \quad \text{with } \Delta b = \langle \Delta b(\boldsymbol{r})\rangle$$

$$\sim (b_{\mathrm{part}} - b_{\mathrm{medium}})V$$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(0) \sim (b_{\mathrm{part}} - b_{\mathrm{medium}})^2$$

consider that solvent consists of a mixture of solvent A (b_{A}) and solvent B (b_{B}) with volume fraction ϕ_{B} of solvent B:

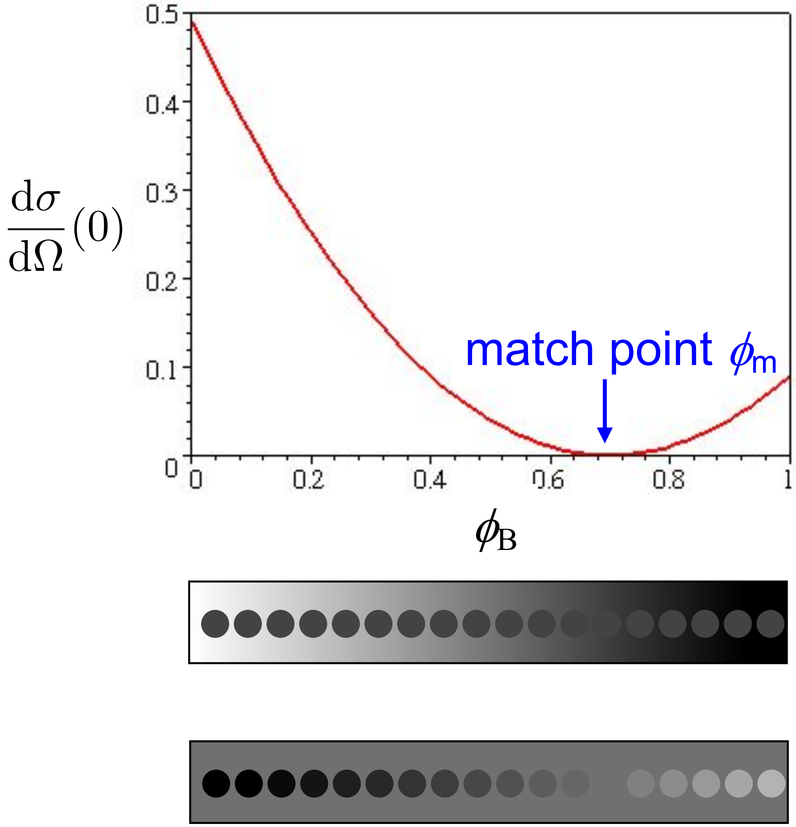
$$b_{\mathrm{medium}} = (1-\phi_{\mathrm{B}})b_{\mathrm{A}} + \phi_{\mathrm{B}}b_{\mathrm{B}} = b_{\mathrm{A}} + \phi_{\mathrm{B}}(b_{\mathrm{B}} - b_{\mathrm{A}})$$

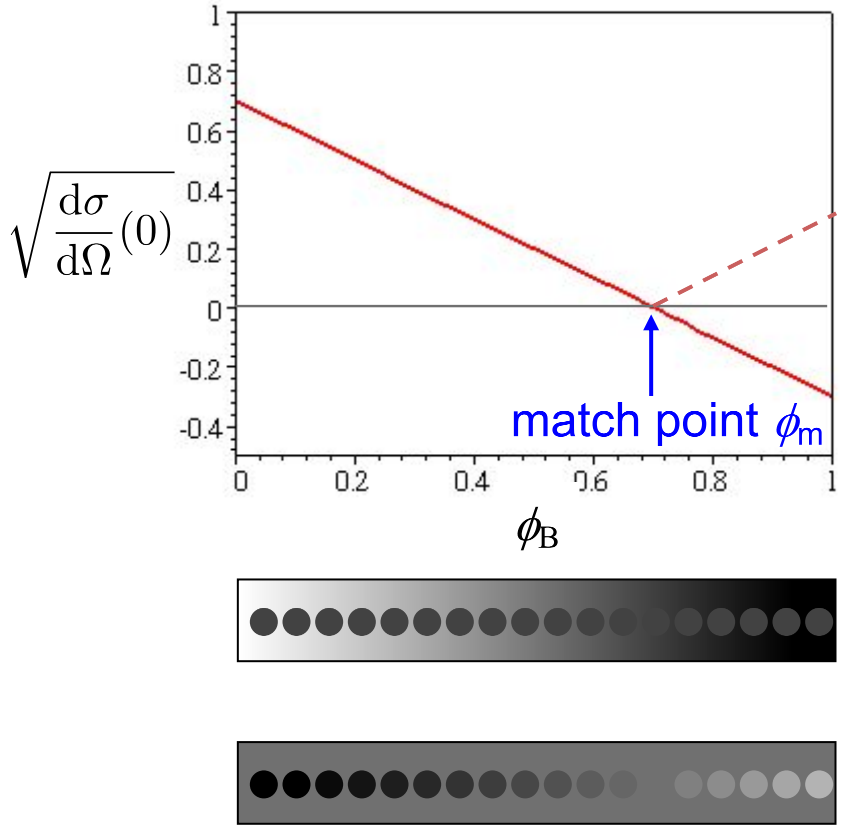
$$\downarrow$$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \sim (b_{\mathrm{part}} - b_{\mathrm{medium}})^2 = (b_{\mathrm{part}} - \{b_{\mathrm{A}} + \phi_{\mathrm{B}}(b_{\mathrm{A}} - b_{\mathrm{A}})\})^2$$

$$\sim (b_{\mathrm{B}} - b_{\mathrm{A}})^2(\phi_{\mathrm{m}} - \phi_{\mathrm{B}})^2\ , \quad \phi_{\mathrm{m}} = \frac{b_{\mathrm{part}} - b_{\mathrm{A}}}{b_{\mathrm{B}} - b_{\mathrm{A}}}$$

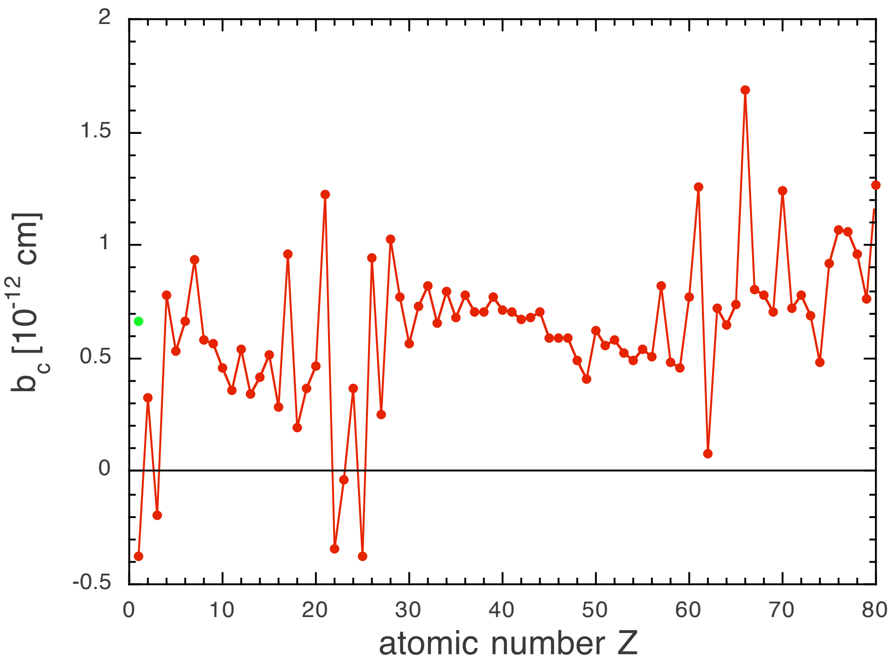
(Solvent) contrast variation

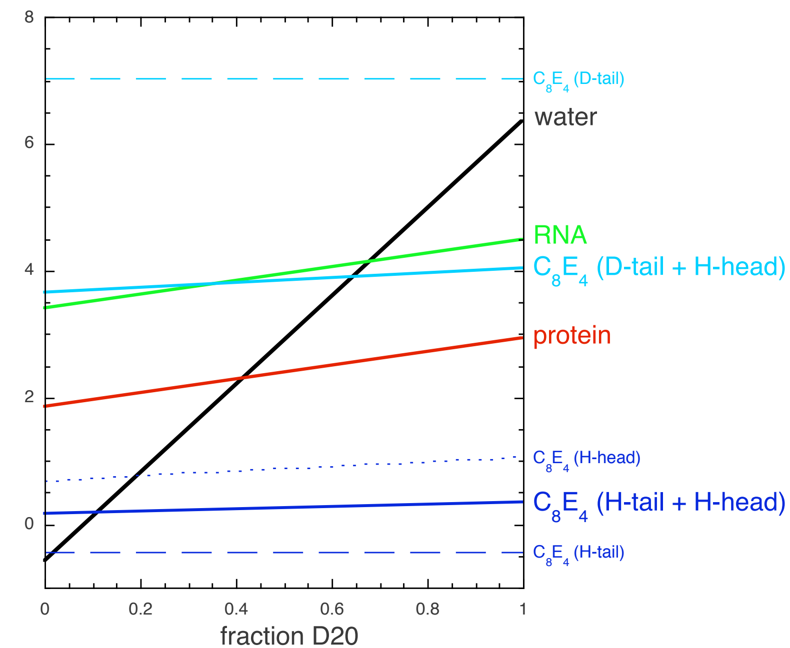




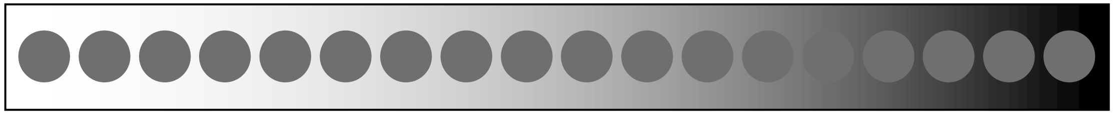
‘Prefactor’

scattering length depends on:
- nucleus, i.e. isotope (non-systematic)
- nuclear spin (magnetic scattering)





Applications



- increase signal

  improve statistics

- reduce signal

  reduce multiple scattering

- reduce ‘noise’

  reduce background due to solvent

Optimize measurement

example: dilute polystyrene spheres in cyclohexane
with $R = 10$ nm, $c = 10$ mg/ml ($\approx 1\%$)

substance	formula	molar mass M (g/mol)	density $\bar{v}^{-1}$ (g/cm^3)	scatt. length dens. b (10^{10} cm^{-2})
polystyrene	$(C_8H_8)_n$	$(104.2)_n$	1.04	1.44
	$(C_8D_8)_n$	$(112.2)_n$	~1.12	6.44
cyclohexane	C_6H_{12}	84.2	0.779	- 0.24
	C_6D_{12}	96.2	0.893	6.74

Optimize measurement

hhu

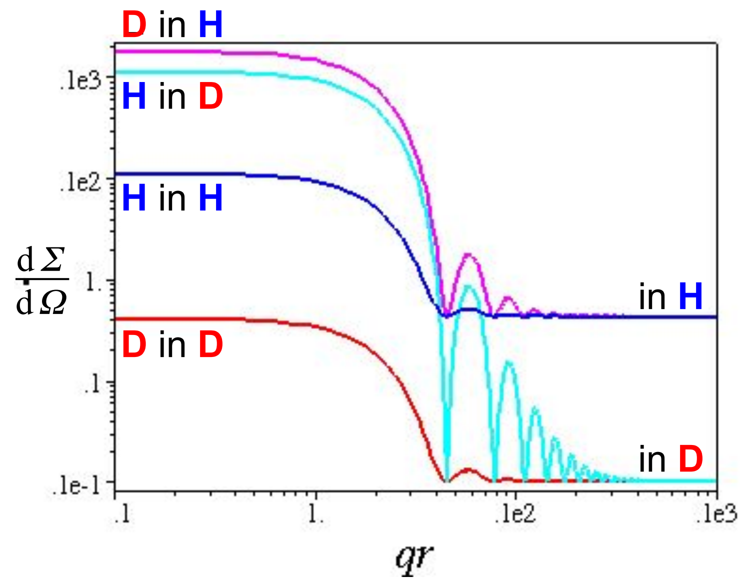
example: dilute polystyrene spheres in cyclohexane
with R = 10 nm, c = 10 mg/ml (≈ 1%)

excess spheres ('signal')

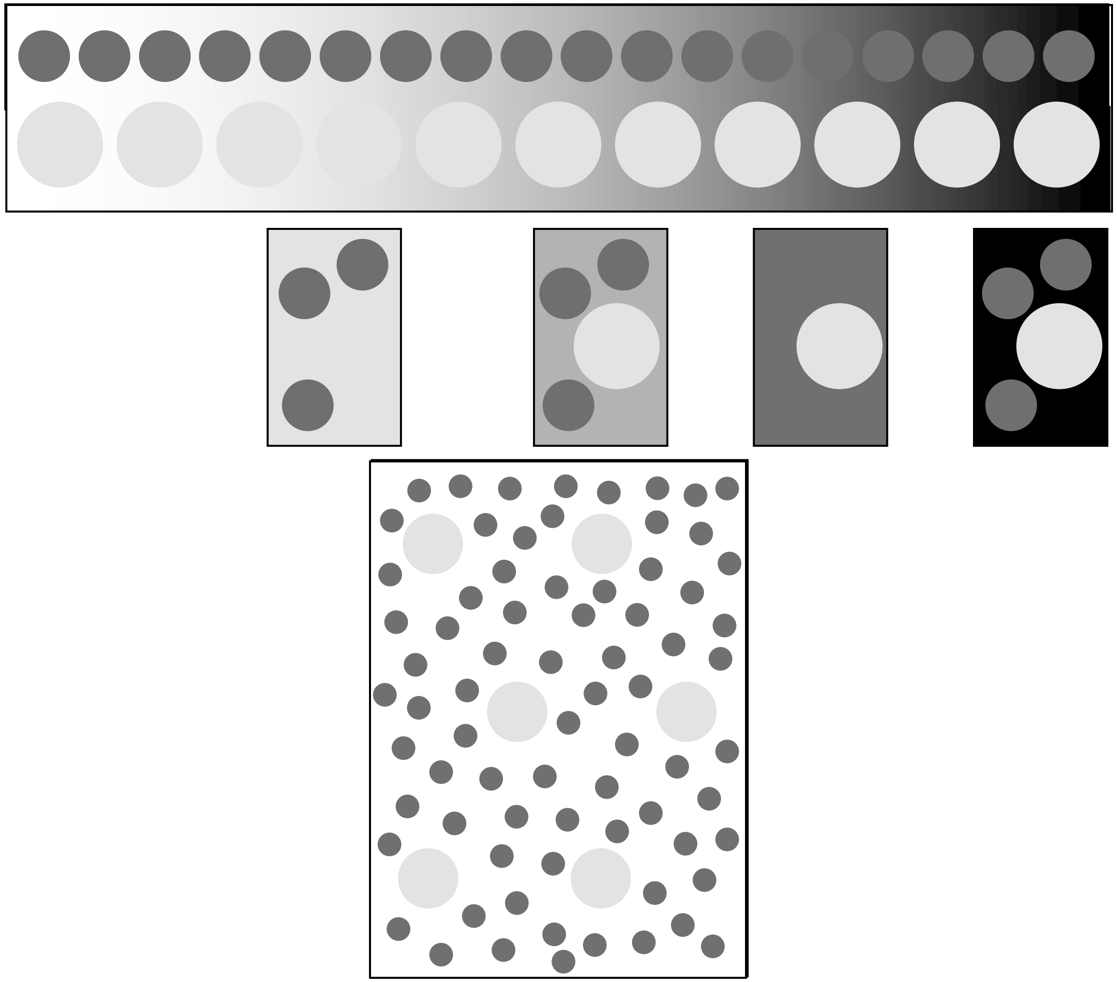
H in H: 10.8 cm^{-1}
H in D: 113.1 cm^{-1}
D in H: 179.7 cm^{-1}
D in D: 0.4 cm^{-1}

solvent ('noise')

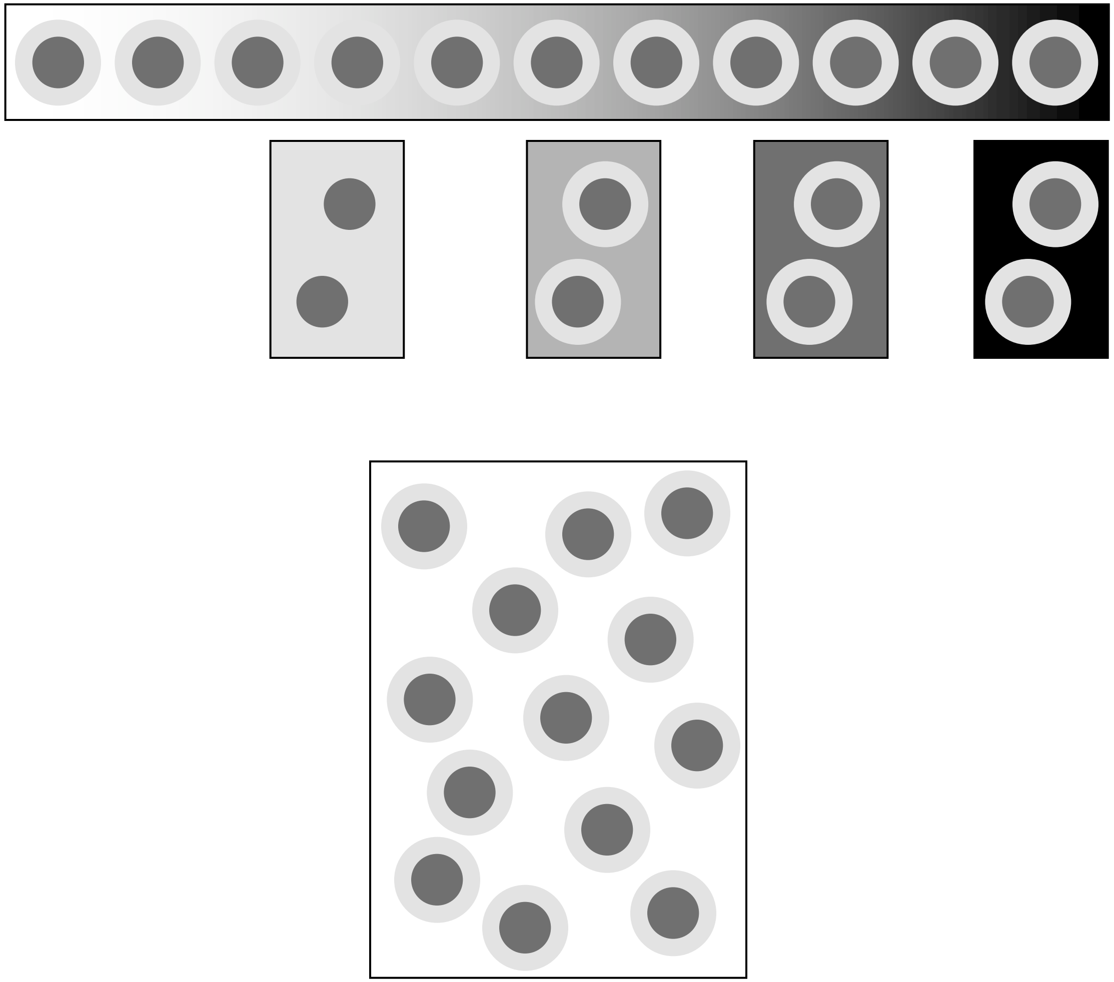
in H: 0.43 cm^{-1}
in D: 0.01 cm^{-1}



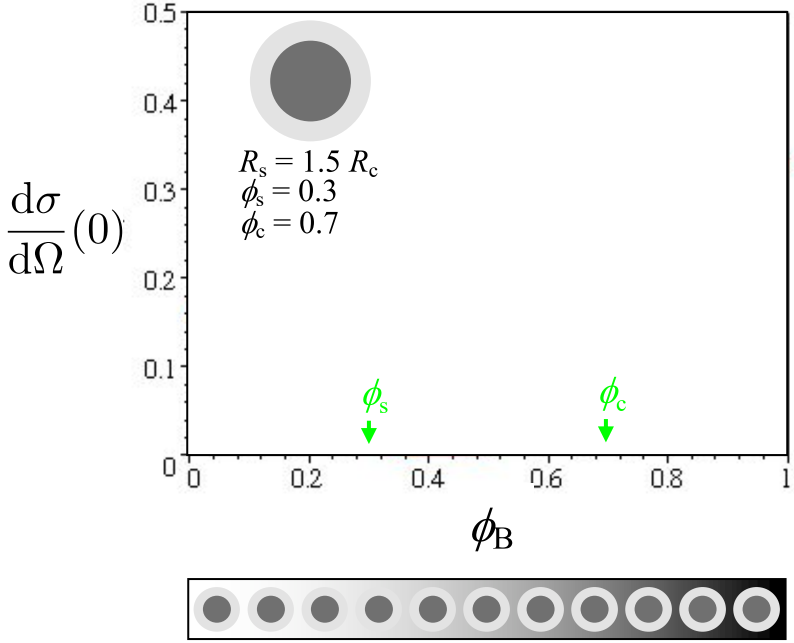
Heterogeneous samples

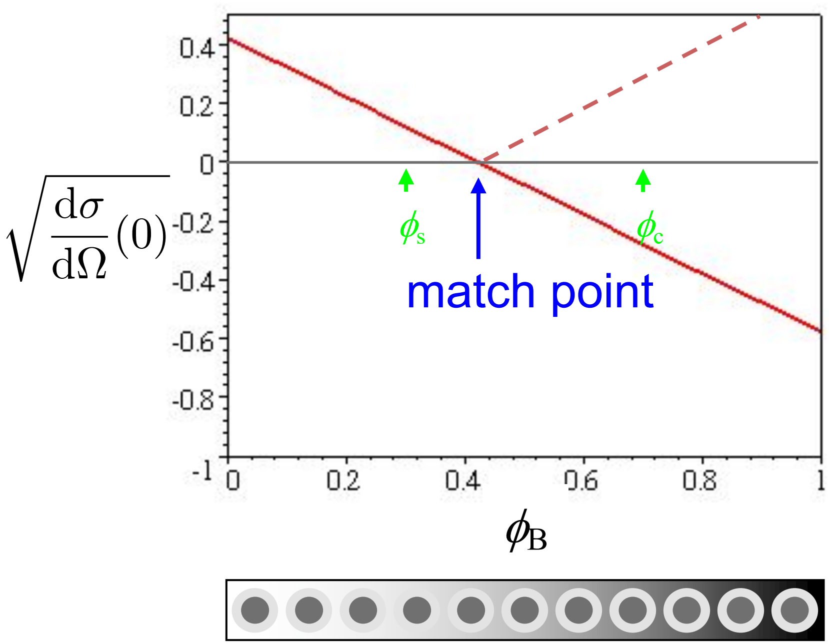


Heterogeneous particles



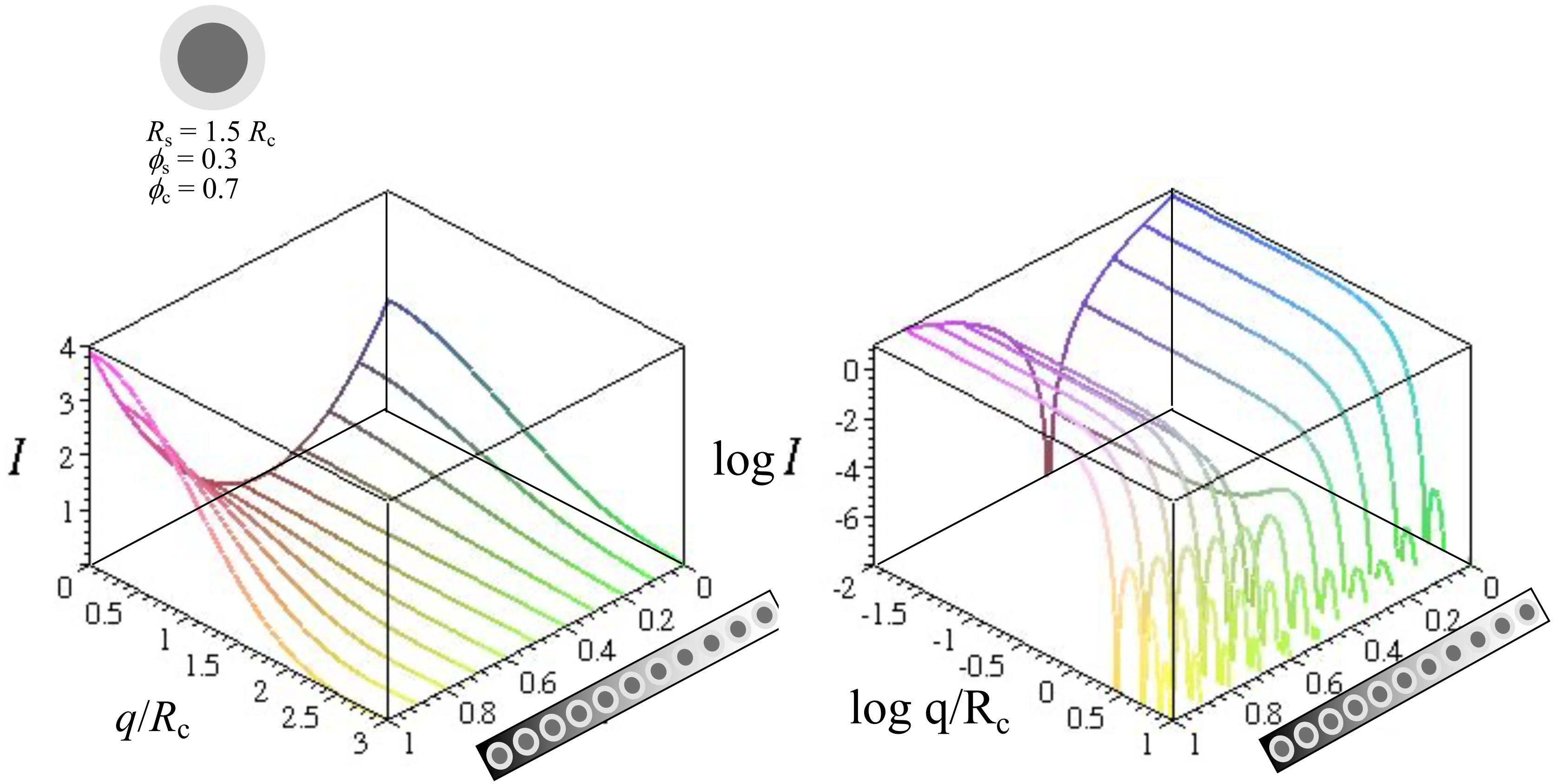
(Solvent) contrast variation





$$\phi_{part} = \frac{\phi_s (V_s - V_c) + \phi_c V_c}{V_s} = \frac{0.3 \times (1.5^3 - 1^3) + 0.7 \times 1^3}{1.5^3} = 0.42$$

(Solvent) contrast variation



Differential cross section

$$\frac{d\sigma}{d\Omega}(\mathbf{Q}) \sim |\psi^{sc}|^2 \sim \sum_k \sum_j \left\langle \psi^{sc}_{p,j}(\mathbf{Q})\, \psi^{sc\,\star}_{p,k}(\mathbf{Q})\; e^{i\mathbf{Q}\cdot(\mathbf{R}_j - \mathbf{R}_k)} \right\rangle$$

↓ identical scatterers

$$\frac{d\sigma}{d\Omega}(\mathbf{Q}) \sim N|\psi^{sc}_p(0)|^2 \frac{|\psi^{sc}_p(\mathbf{Q})|^2}{|\psi^{sc}_p(0)|^2} \frac{1}{N} \sum_k \sum_j \left\langle e^{i\mathbf{Q}(\mathbf{R}_j(t) - \mathbf{R}_k(t))} \right\rangle$$

but b_j, b_k depend on nucleus (isotope) and spin

thus for same isotope

$$j \neq k : \; \langle b_j\, b_k\, e^{i\mathbf{Q}\cdot\mathbf{r}_{jk}} \rangle = \langle b_j \rangle \langle b_k \rangle \langle e^{i\mathbf{Q}\cdot\mathbf{r}_{jk}} \rangle = \langle b \rangle^2 \langle e^{i\mathbf{Q}\cdot\mathbf{r}_{jk}} \rangle$$

$$j = k : \; \langle b_j\, b_k\, e^{i\mathbf{Q}\cdot\mathbf{r}_{jk}} \rangle = \langle b_j^2 \rangle = \langle b^2 \rangle$$

↓

$$\frac{d\sigma}{d\Omega} \sim \sum_j \sum_k \langle b_j\, b_k\, e^{i\mathbf{Q}\cdot\mathbf{r}_{jk}} \rangle = \sum_j \sum_{k \neq j} \langle b_j\, b_k\, e^{i\mathbf{Q}\cdot\mathbf{r}_{jk}} \rangle + \sum_j \langle b_j\, b_j\, e^{i\mathbf{Q}\cdot\mathbf{r}_{jk}} \rangle$$

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \sum_j \sum_{k \neq j} \langle e^{i\mathbf{Q}\cdot\mathbf{r}_{jk}} \rangle + N \langle b^2 \rangle$$

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \sum_j \sum_k \langle e^{i\mathbf{Q}\cdot\mathbf{r}_{jk}} \rangle \qquad + N \left\{ \langle b^2 \rangle - \langle b \rangle^2 \right\}$$

Differential cross section

coherent cross section

$$\sigma_{coh} = 4\pi \langle b \rangle^2$$

- contains structural information on particles & arrangement ($e^{i\boldsymbol{Q}\boldsymbol{r}}$ term)
- collective properties of particles ($S(\boldsymbol{Q})$, D_c)

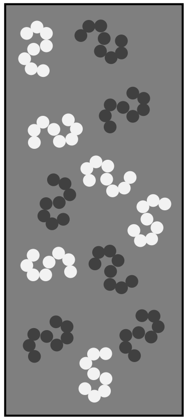
incoherent cross section

$$\sigma_{incoh} = 4\pi \left(\langle b^2 \rangle - \langle b \rangle^2 \right)$$

- contains no structural information on arrangement (no interference term, missing phase relation)
- properties of individual particles (D_s)

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \langle b \rangle^2 \sum_j \sum_k \langle \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{r}_{jk}} \rangle \qquad + N \left\{ \langle b^2 \rangle - \langle b \rangle^2 \right\}$$

Zero average contrast



identical particles, but hydrogenated (b_H) and deuterated (b_D) species in H/D-solvent such that $\Delta b_\mathrm{H} = - \Delta b_\mathrm{D}$

$\Rightarrow$ $\langle b \rangle = \frac{1}{2}(\Delta b_H + \Delta b_D) = 0$

$\Rightarrow$ coherent contribution = 0
(i.e. structural contribution)

$\langle b^2 \rangle = \frac{1}{2}(\Delta b_H^2 + \Delta b_D^2) = \Delta b_H^2 = \Delta b_D^2$

incoherent contribution ≠ 0
(i.e. individual particle contribution)

coherent cross section

$$\sigma_{coh} = 4\pi \langle b \rangle^2$$

- contains structural information on particles & arrangement (e^{iQr} term)
- collective properties of particles ($S(Q)$, D_c)

incoherent cross section

$$\sigma_{incoh} = 4\pi \left(\langle b^2 \rangle - \langle b \rangle^2 \right)$$

- contains no structural information on arrangement (no interference term, missing phase relation)
- properties of individual particles (D_s)

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \langle b \rangle^2 \sum_j \sum_k \langle \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{r}_{jk}} \rangle \quad + N \left\{ \langle b^2 \rangle - \langle b \rangle^2 \right\}$$

Isotope substitution

solvent isotope substitution can cause

- shift in cmc (generally higher in H_2O)
- shift in Θ temperature (±4°C for PS in cyclohexane) or critical point
- shift in melting point (6°C for polyethylene)
- selective adsorption
- exchange of particle H/D with solvent (e.g. OH, NH, COOH groups, scattering length density becomes a function of the solvent H/D ratio)
- …

'particle' isotope substitution can cause

- phase separation (e.g. H- and D-polymer)
- …

Conclusions

non-crystaline materials are wonderful

Literature

K. Paul, V. Thomas, *Oxford University Press* (1987)

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