Small-Angle Neutron Scattering

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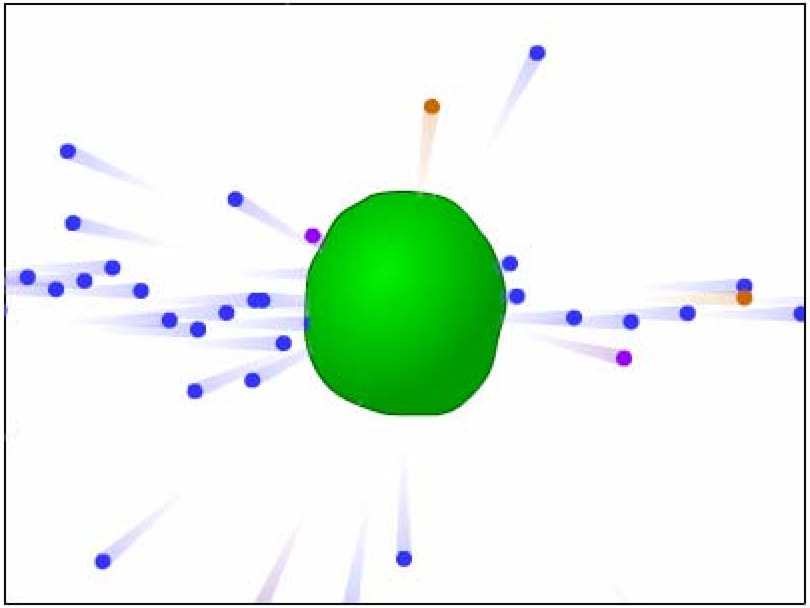
Flash design by Julia Emelina

Contents

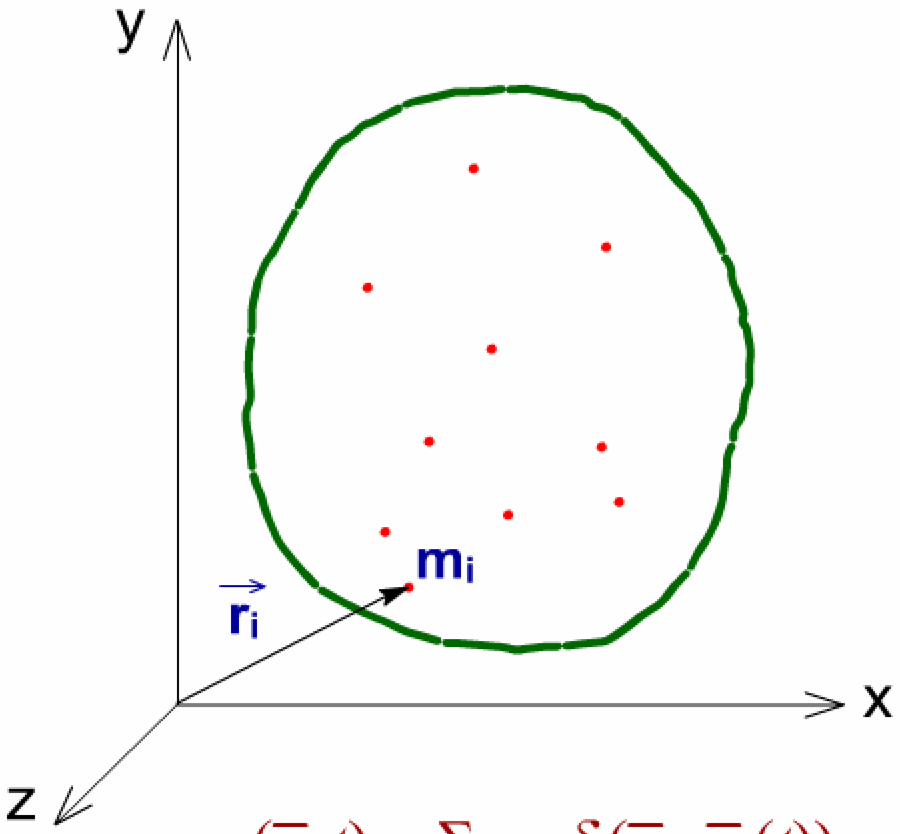
Scattering experiment



☒ Incident beam ☒ Scattering

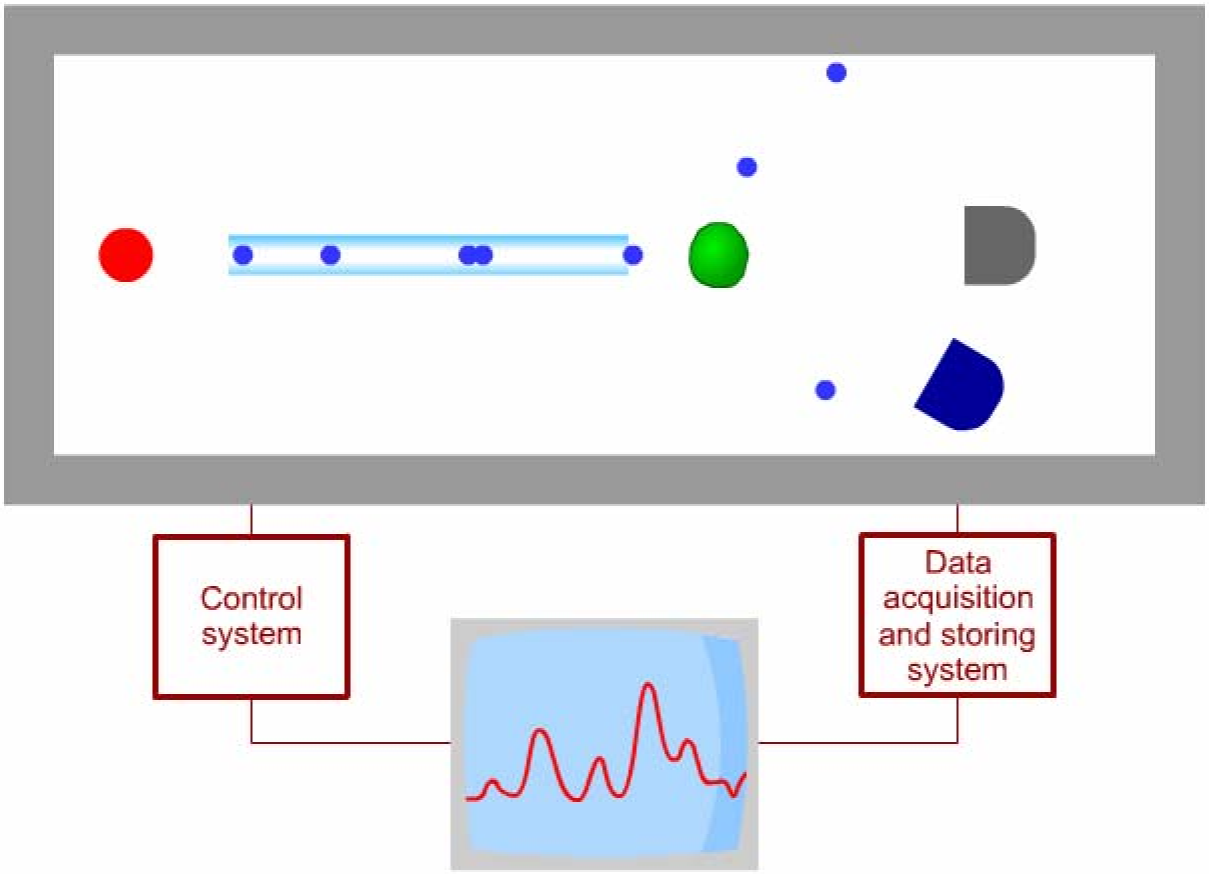
☒ Transmitted beam ☒ Absorption and secondary radiation

The task is to find $\rho_m(\bar{r}, t)$

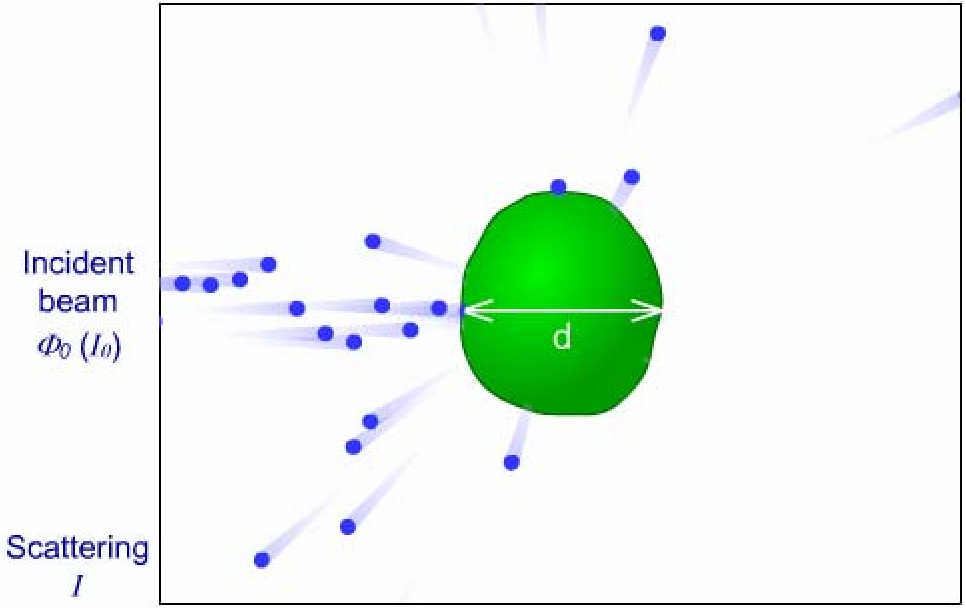


$$\rho_m(\bar{r}, t) = \Sigma\, m_i\, \delta(\bar{r} - \bar{r}_i(t))$$

Main elements of the scattering setup



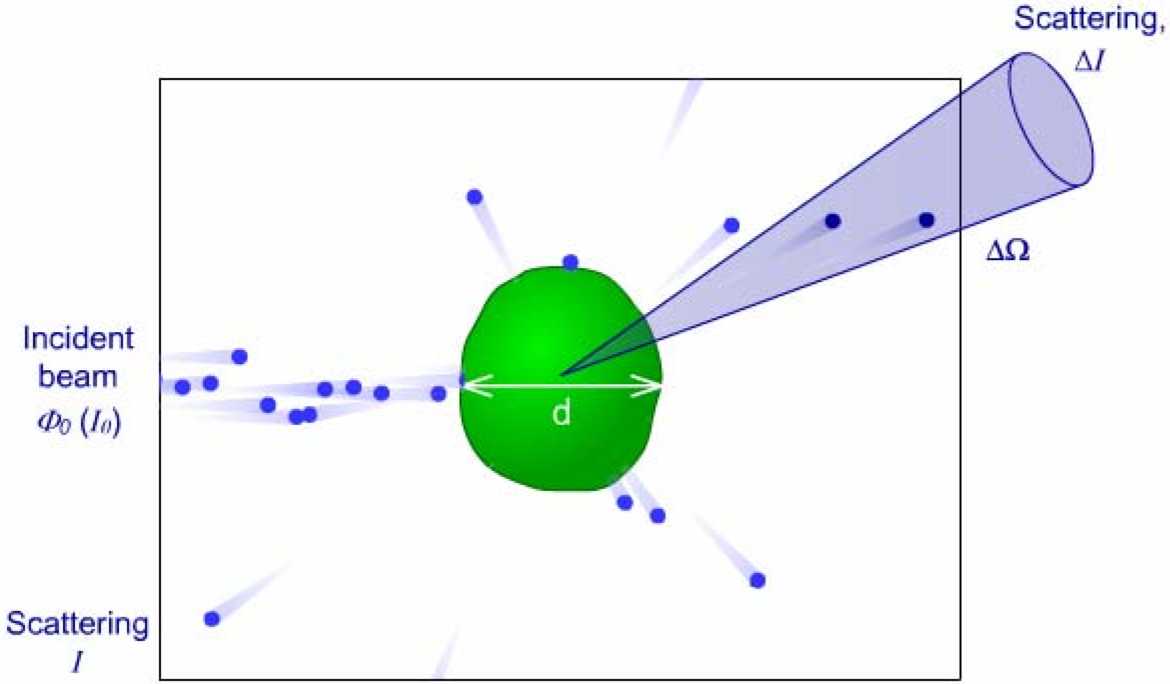
Scattering-cross section



$$\sigma\,[\mathrm{cm}^2] = \frac{I\,[\mathrm{c}^{-1}]}{\Phi_0\,[\mathrm{cm}^{-2}\mathrm{c}^{-1}]}$$ cross-section

$$\Sigma\,[\mathrm{cm}^{-1}] = \frac{I\,[\mathrm{c}^{-1}]}{I_0\,[\mathrm{c}^{-1}]\,d\,[\mathrm{cm}]}$$ cross-section per sample volume

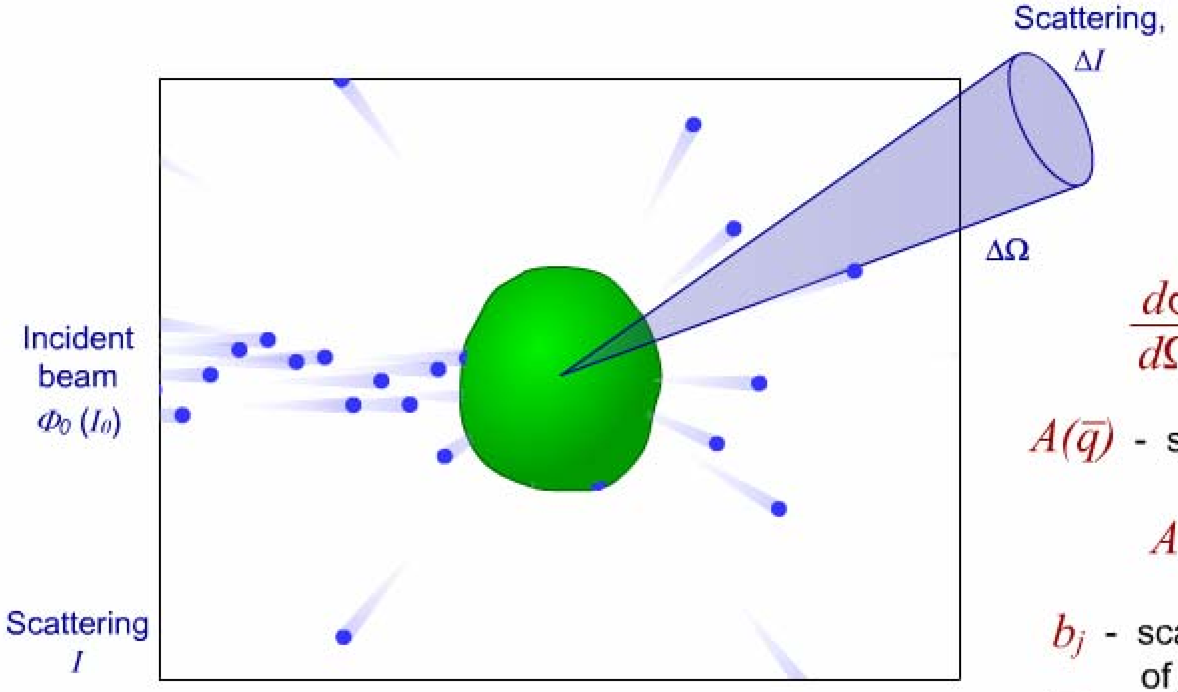
Differential scattering cross-section



$$\frac{\Delta\sigma}{\Delta\Omega}[\text{cm}^2] = \frac{\Delta I\ [\text{c}^{-1}]}{\Phi_0\ [\text{cm}^{-2}\text{c}^{-1}]}$$ differential cross-section

$$\frac{\Delta\Sigma}{\Delta\Omega}[\text{cm}^{-1}] = \frac{\Delta I\ [\text{c}^{-1}]}{I_0\ [\text{c}^{-1}]\ d\ [\text{cm}]}$$ differential cross-section per sample volume

Elastic scattering of thermal neutrons



$$\frac{d\sigma}{d\Omega} = f(\bar{q})$$

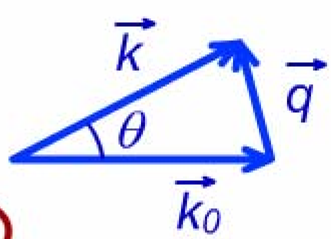
$$\frac{d\sigma}{d\Omega} = A(\bar{q})A^*(\bar{q})$$

$A(\bar{q})$ - scattering amplitude

$$A(\bar{q}) = \sum_j b_j e^{i\bar{q}\bar{r}_j}$$

b_j - scattering length of j-th scattering center

$\bar{r}_j$ - radius-vector of j-th scattering center

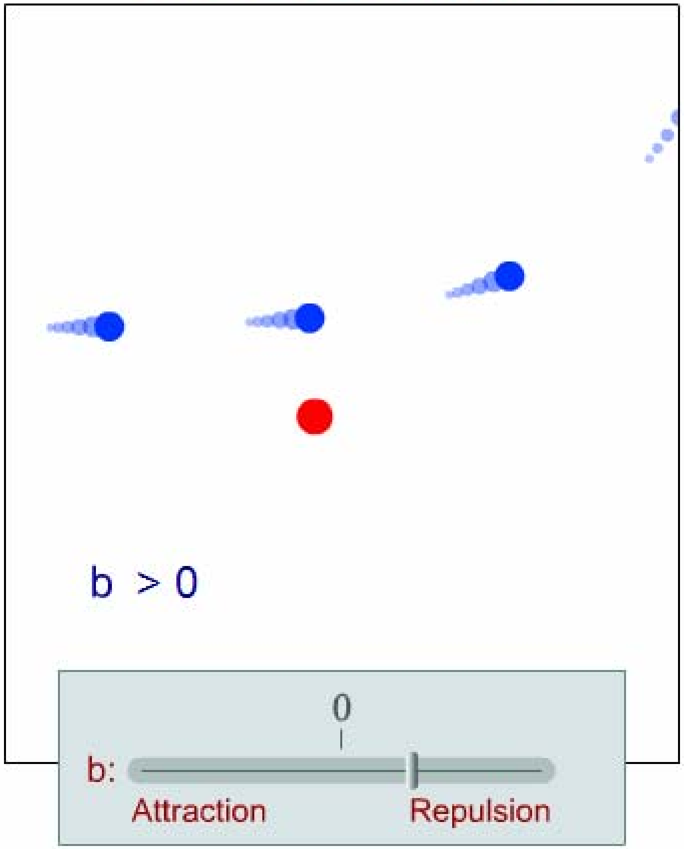


$$\vec{q} = \vec{k} - \vec{k_0}$$

$$q = 2k * \sin\frac{\theta}{2} = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

Scattering length

Effective interaction



Nuclear scattering length

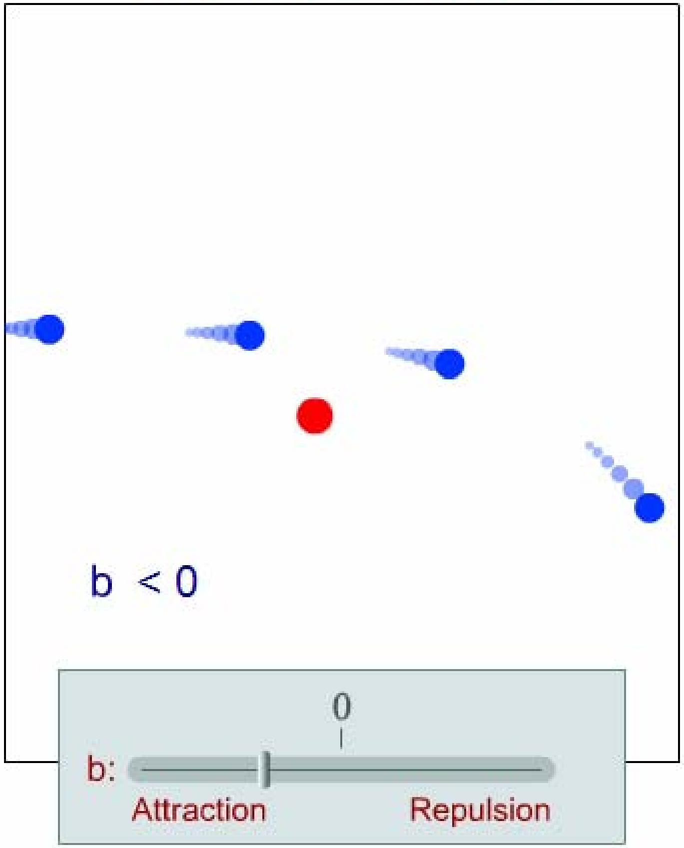
Element	b_{cn}, cm^{-12}
H	-0.374
D	0.667
^{12}C	0.665
^{14}N	0.94
O	0.58

Magnetic scattering length

Element	Term	p(0), cm^{-12}
Fe^{3+}	$^6S_{5/2}$	1.35
Fe^{2+}	$^5D_4$	1.62
Co	$^4F_{9/2}$	1.62
Ni	$^3F_4$	1.35

Scattering length

Effective interaction



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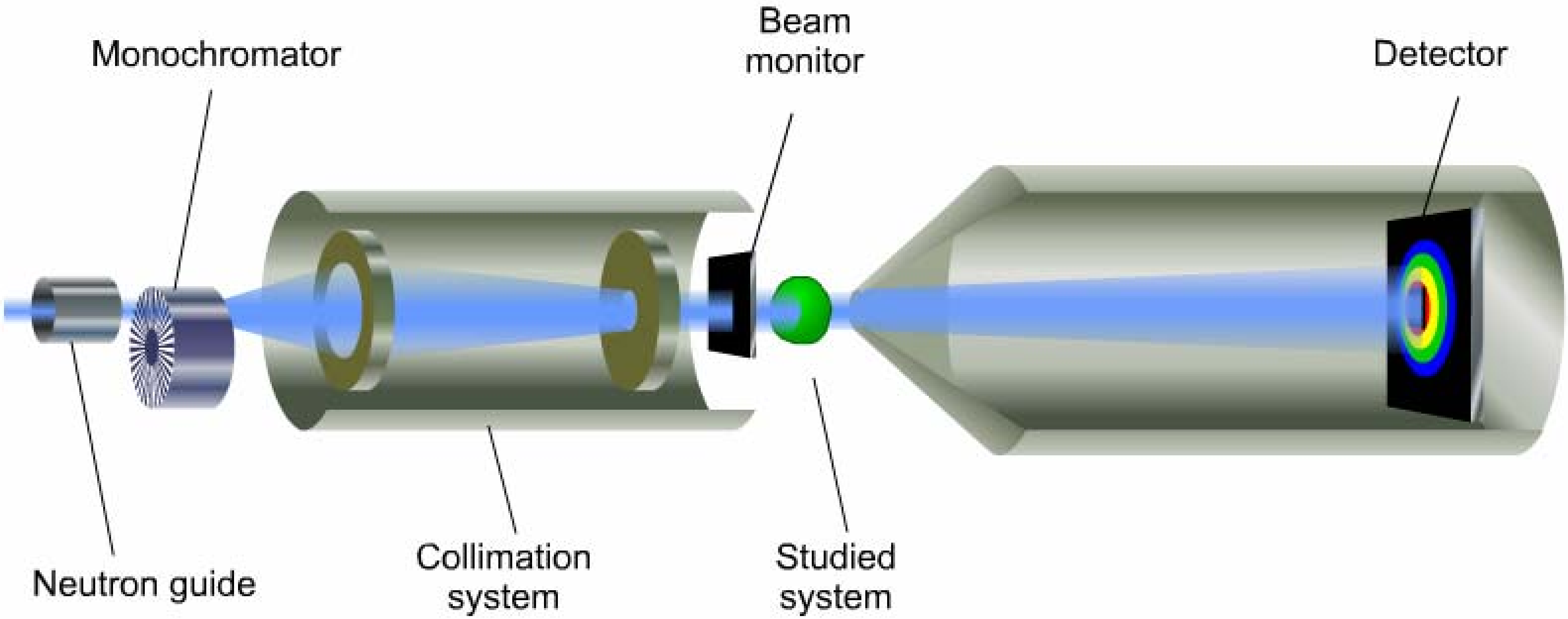
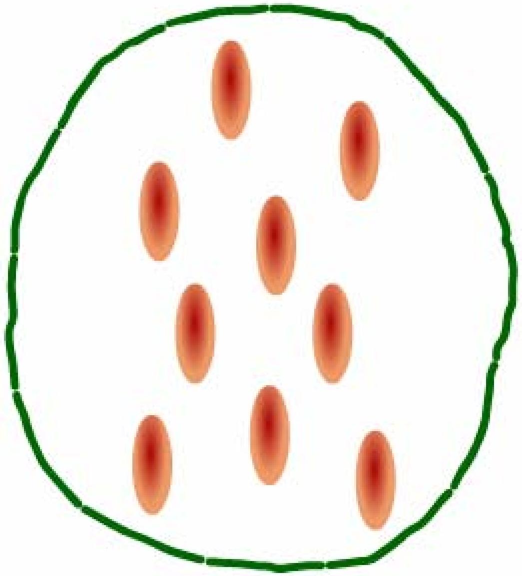
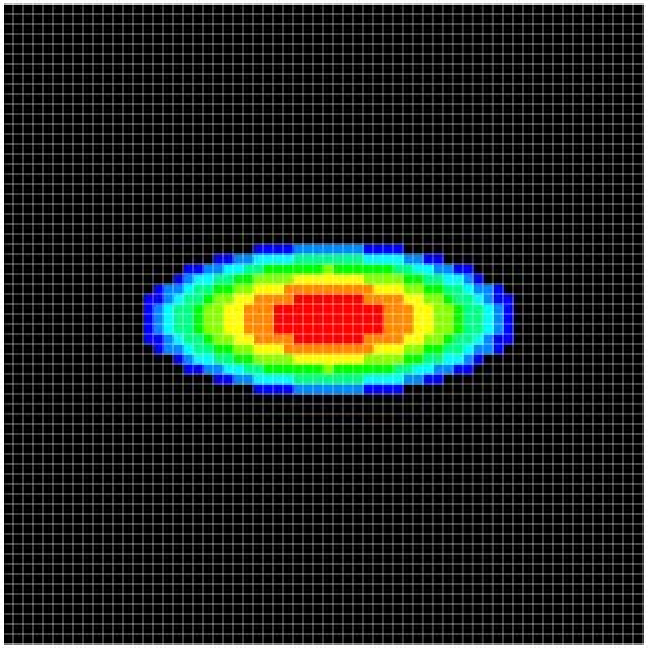
Small-angle neutron scattering (SANS)



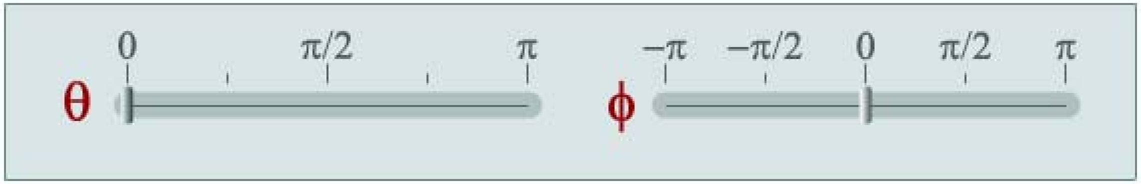
Anisotropic case



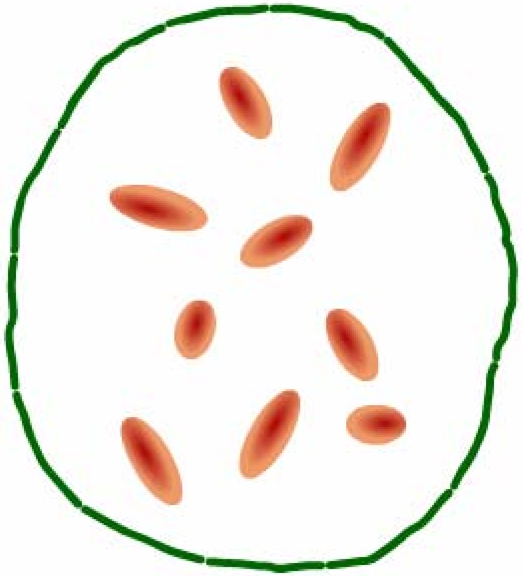
Preferable orientation
in the system

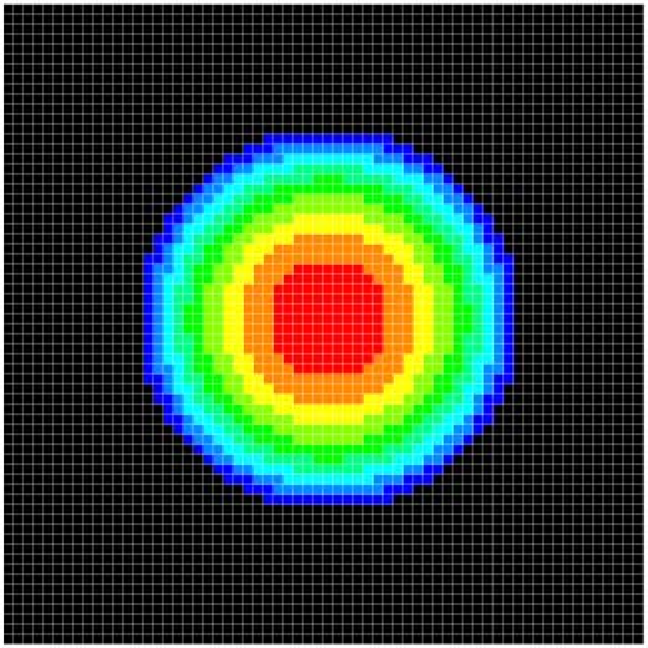


Long axis is rotated by $\pi/2$
in respect to preferable orientation



Isotropic case

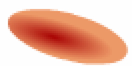


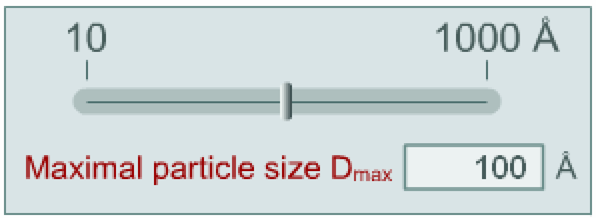


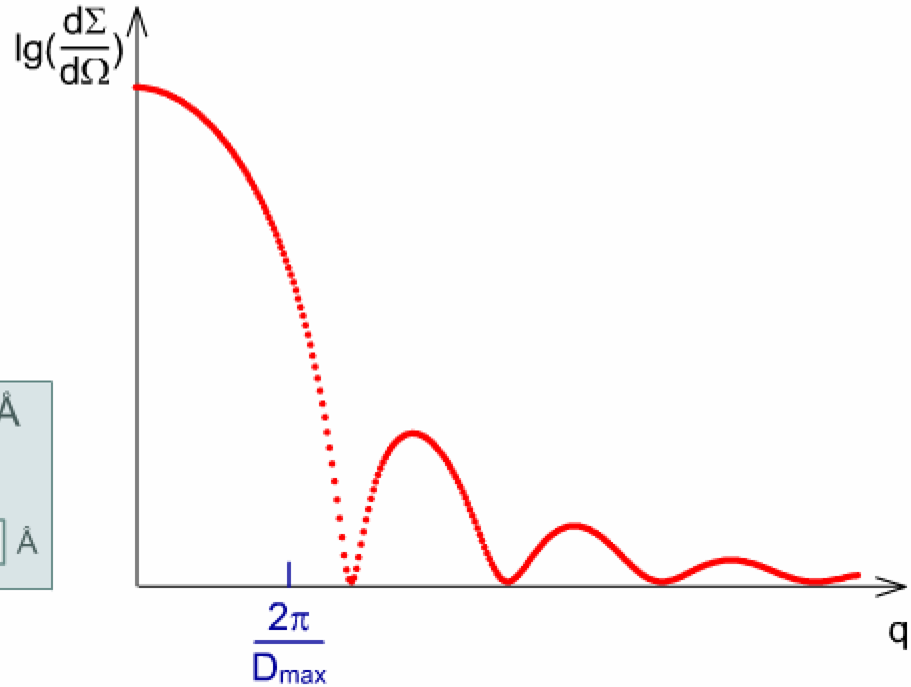
Averaging over all orientations !

$$\frac{d\sigma}{d\Omega} = \langle A(\bar{q})A^*(\bar{q})\rangle_\Omega$$

Scattering curve







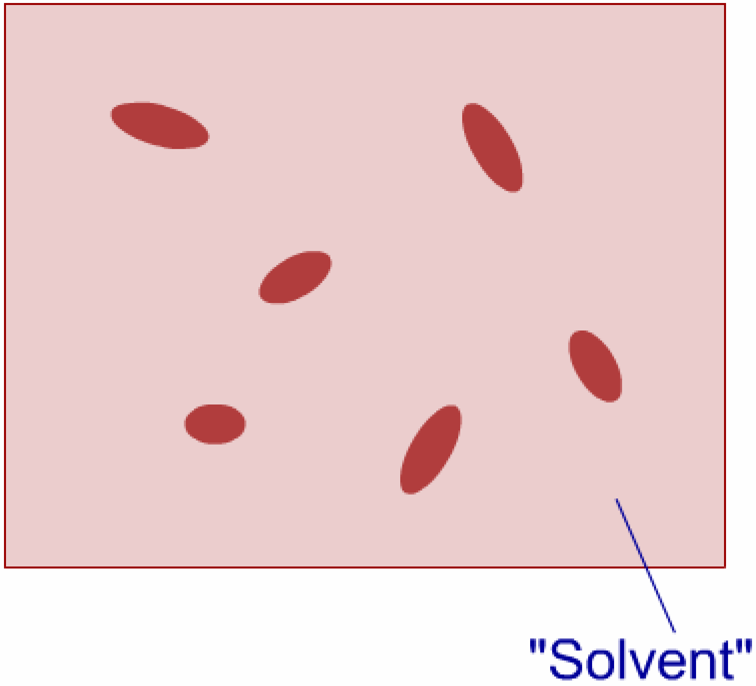
$D_{max} \sim 10 - 1000$ Å

$q < 10^{-3} - 10^{-1}$ Å^{-1}

$\lambda \sim 1 - 10$ Å

$\theta < \sim 1.6\ 10^{-4} - 1.6\ 10^{-1} < 10^{0}$

Homogeneous approximation



Differential cross-section per volume (scattering intensity $I(q)$):

$$\frac{d\Sigma}{d\Omega} = n\, V^2\, \Delta\rho^2\, P(q)$$

n - particle concentration

V - particle volume

$\Delta\rho^2$ - contrast

$P(q)$ - particle form-factor

Contrast

SANS experiment:
"solution" scattering - "solvent" scattering

$$\Delta\rho^2 = (\bar{\rho} - \rho_s)^2$$

$\bar{\rho}$ - mean scattering length density of the "particle"

ρ_s - mean scattering length density of the "solvent"

$\bar{\rho}$ for several systems

Element	$\bar{\rho} \cdot 10^{10}$, cm^{-2}
H_2O	-0.559
D_2O	6.349
protein in H_2O	1.9
protein in D_2O	2.95

Contrast

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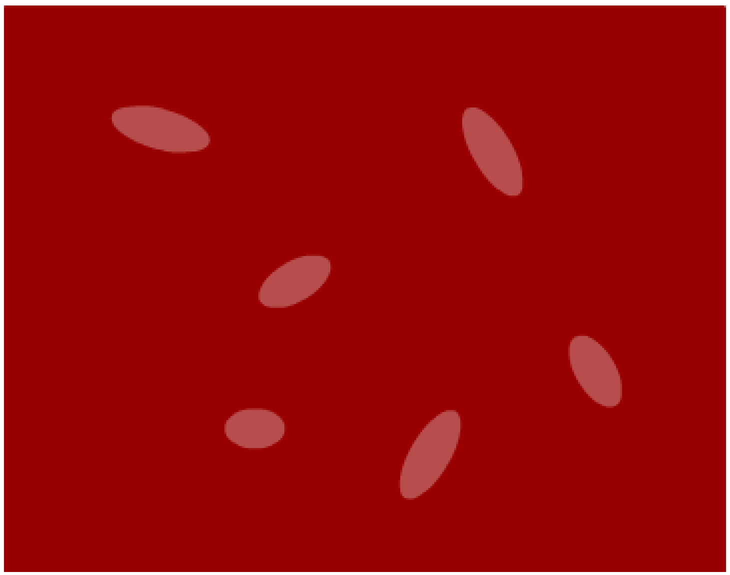

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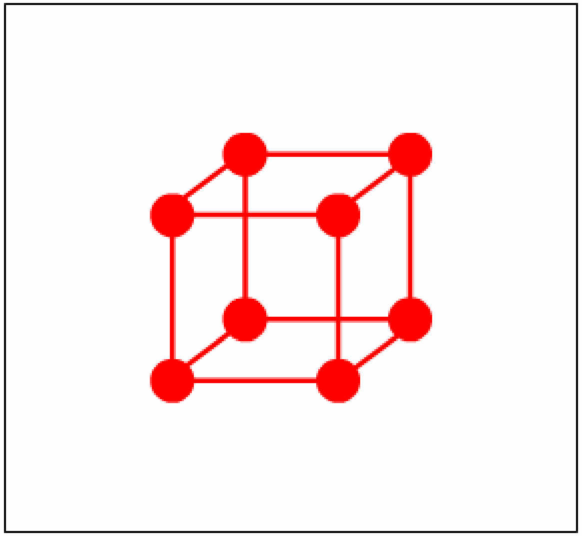
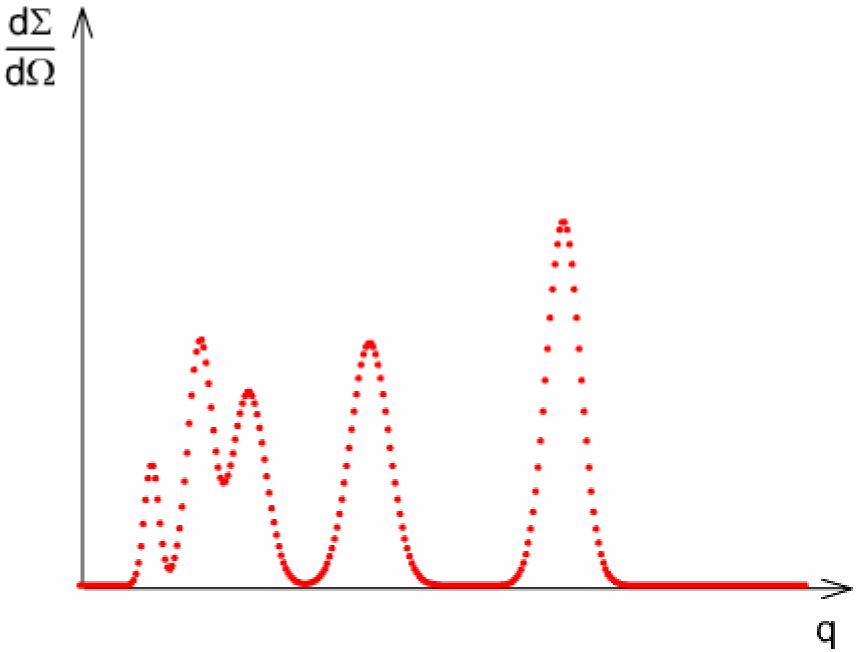
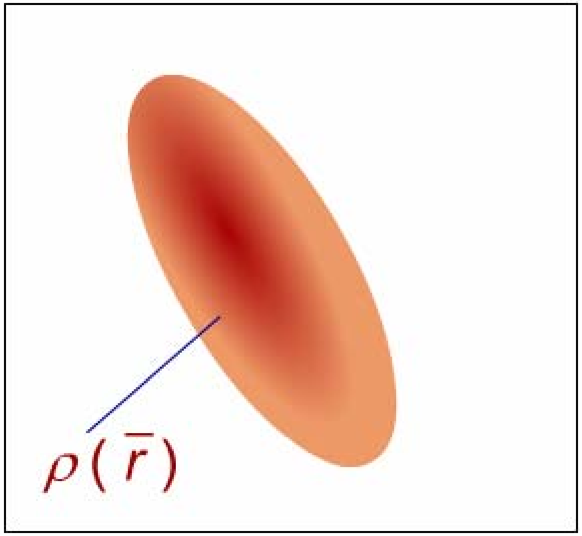
Diffraction on crystal

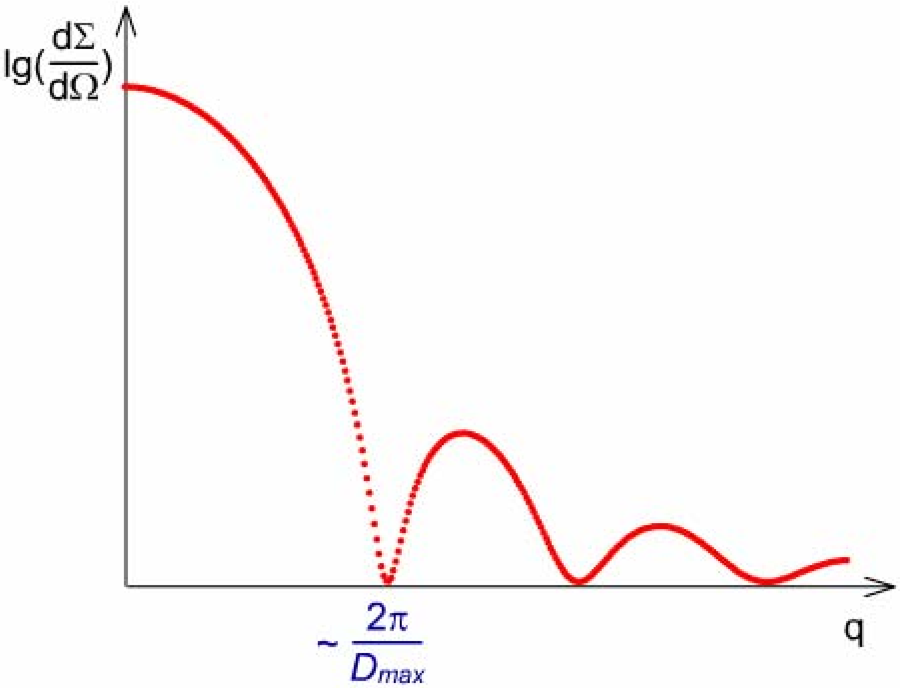




Task is to find atomic coordinates

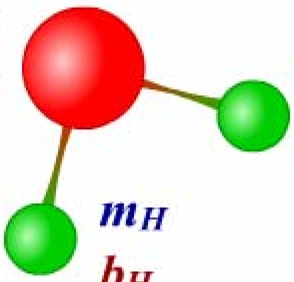
Diffraction on inhomogeneity





Task is to find scattering length density $\bar{\rho}(r)$

H_2O



Mass	Scattering length
$m_{H_2O} = 2m_H + m_O$	$b_{H_2O} = 2b_H + b_O$
Mass density	**Scattering length density**
$\rho = n\, m_{H_2O}$	$\rho = n\, b_{H_2O}$
$m > 0$ **always**	b **may be negative**

Form-factor

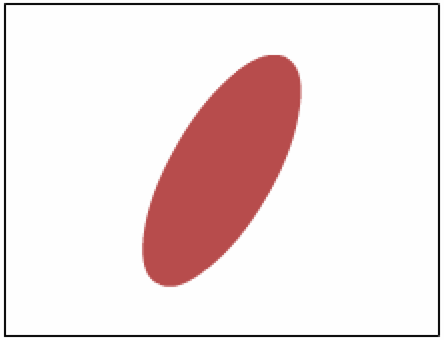
Form-factor is the scattering from the shape of the particle.

Debye formule (P.Debye, 1915):

$$P(q) = \frac{1}{V^2} \int_V \int_V \hat{\rho}(\bar{r}_1)\hat{\rho}(\bar{r}_2) \frac{\sin q|\bar{r}_1 - \bar{r}_2|}{q|\bar{r}_1 - \bar{r}_2|} dV_1 dV_2$$

$$P(0) = 1$$

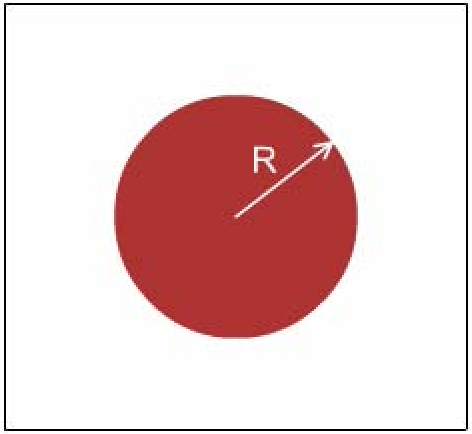
$$\hat{\rho}(\bar{r}) = \begin{cases} 0, \text{ outside particle} \\ 1, \text{ inside particle} \end{cases}$$

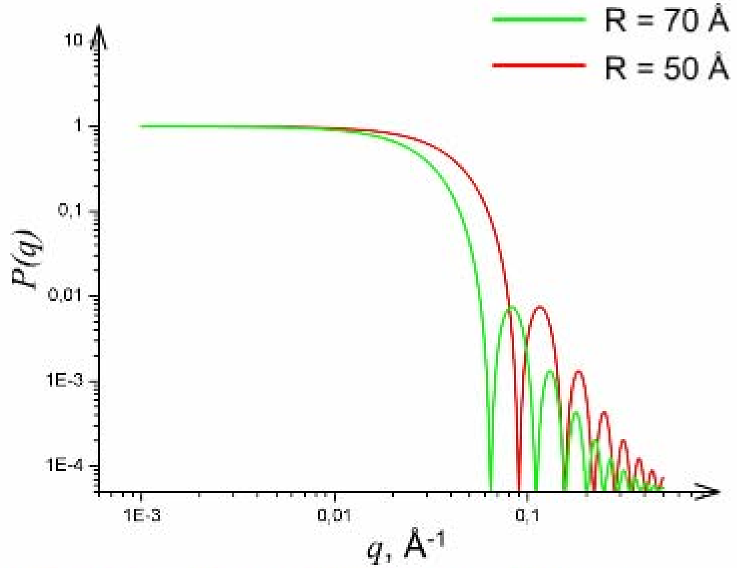


Form-factor from different shapes

Sphere (R)	Ellipsoid of revolution (a, a, μa)	Cylinder (R, H)

$$P(q) = \Phi^2(qR), \quad \Phi(x) = 3\,\frac{\sin x - x\cos x}{x^3}$$

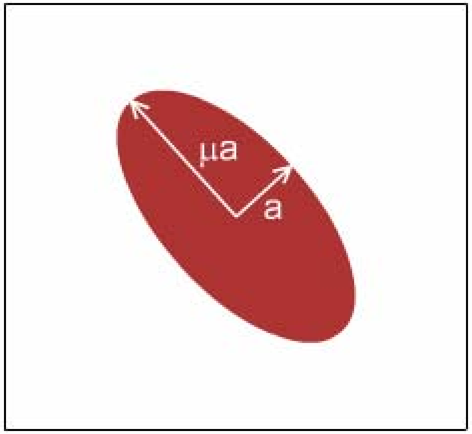


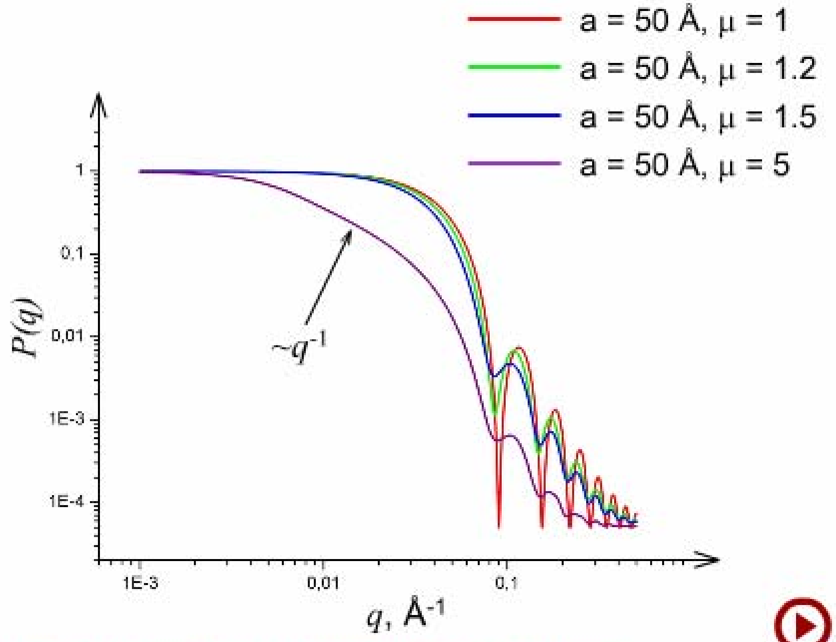


Form-factor from different shapes

Sphere (R)	Ellipsoid of revolution (a, a, μa)	Cylinder (R, H)

$$P(q) = \int_0^1 \Phi^2\left(qa\sqrt{1 + x^2(\mu^2 - 1)}\right) dx, \quad \Phi(x) = 3\,\frac{\sin x - x\cos x}{x^3}$$



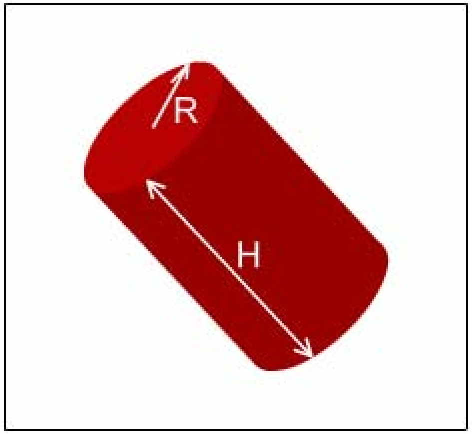


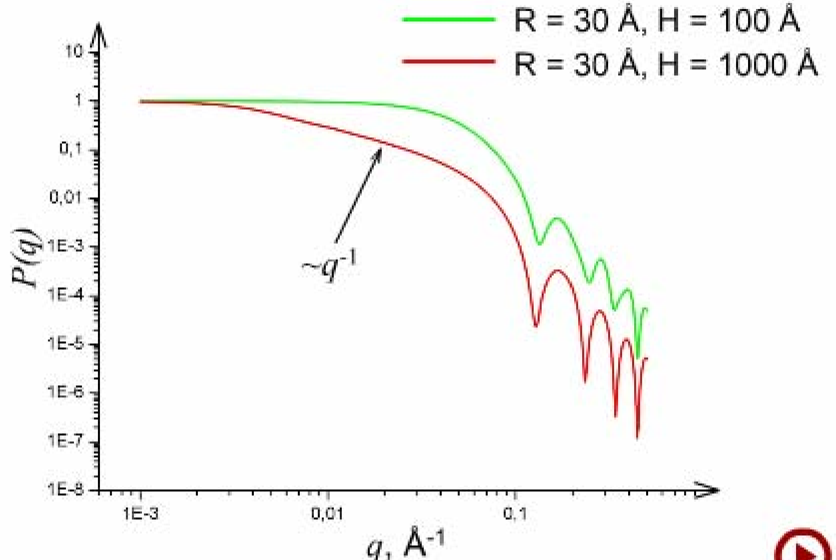
Form-factor from different shapes

Sphere (R)	Ellipsoid of revolution (a, a, μa)	Cylinder (R, H)

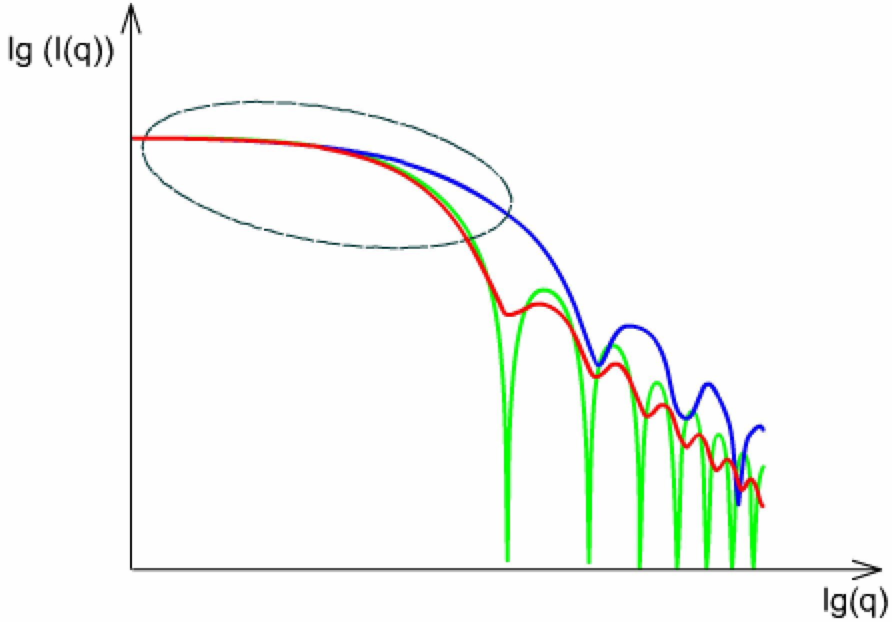
$$P(q) = 4\int_0^1 \frac{J_1^2\left(qR\sqrt{1-x^2}\right)}{\left(qR\sqrt{1-x^2}\right)^2}\, S^2\left(\frac{qHx}{2}\right) dx, \quad S(x) = \frac{\sin x}{x}$$

J_1 - Bessel function of the 1st order





Guinier law



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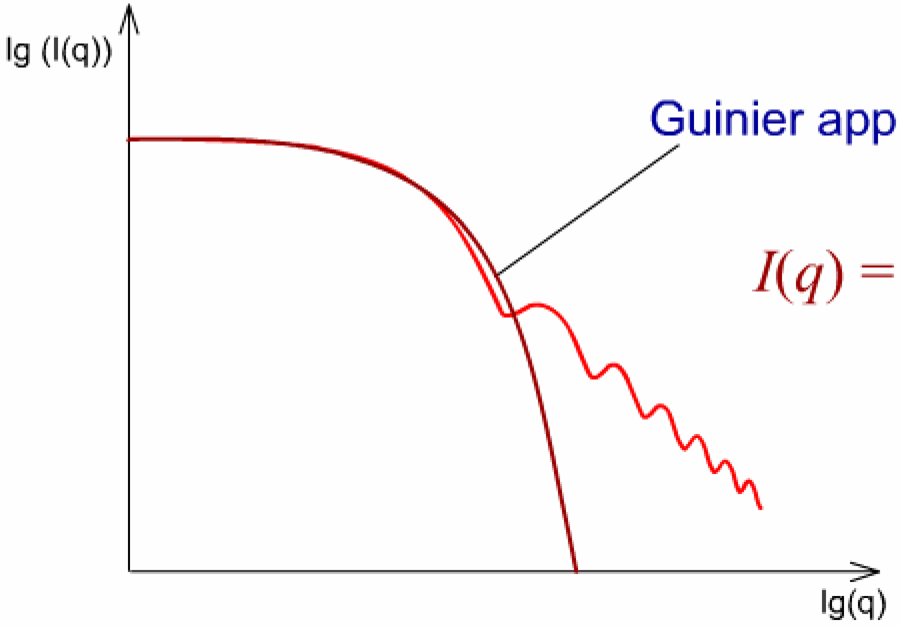


$$I(q) = I(0)\, exp\,(-\frac{1}{3} q^2 R_g{}^2)$$

$$q < \frac{1}{R_g}$$

$I(0) = n\, V^2\, (\rho - \rho_s)^2$ - intensity in zero angle

R_g - radius of gyration

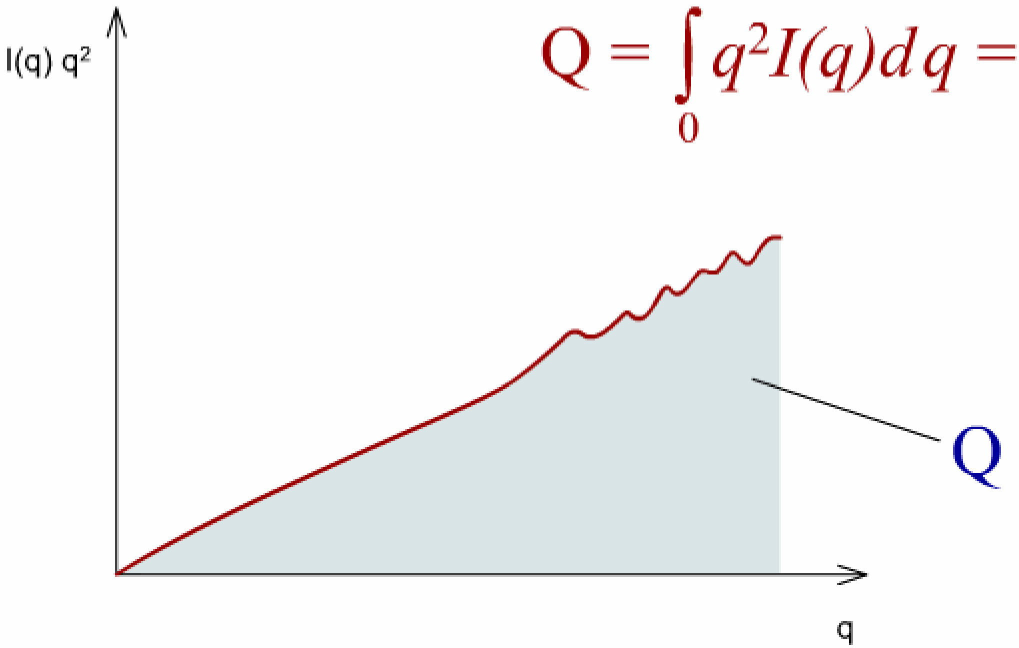
Radius of gyration

$$R_g^2 = \frac{\int_{V_0} r^2 \rho(\bar{r})\, d\bar{r}}{\int_{V_0} \rho(\bar{r})\, d\bar{r}}$$

sphere (R)	$R_g^2 = \frac{3}{5} R^2$
ellipsoid of revolution (a, a, μa)	$R_g^2 = \frac{a^2}{5}(2 + \mu^2)$
cylinder (R, H)	$R_g^2 = \frac{R^2}{5} + \frac{H^2}{12}$

Radius of gyration $\Rightarrow$ characteristic particle size

Porod integral

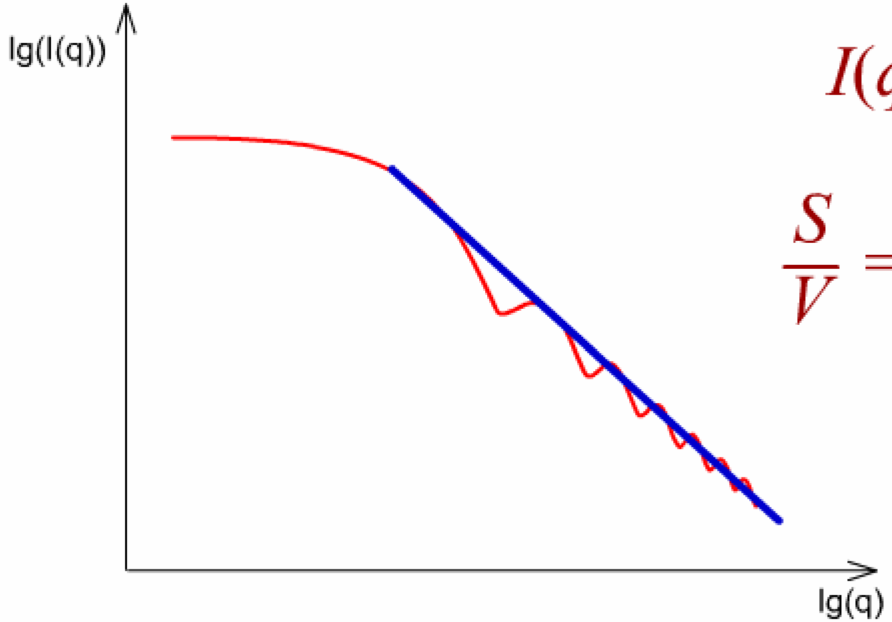


$$Q = \int_0^\infty q^2 I(q)\,dq = 2\pi^2\rho^2 Vn$$

Porod integral $\Rightarrow$ particle volume

Porod law

for low-symmetric forms



$$I(q) \underset{q\to\infty}{=} n\frac{2\pi}{q^4}\rho^2 S$$

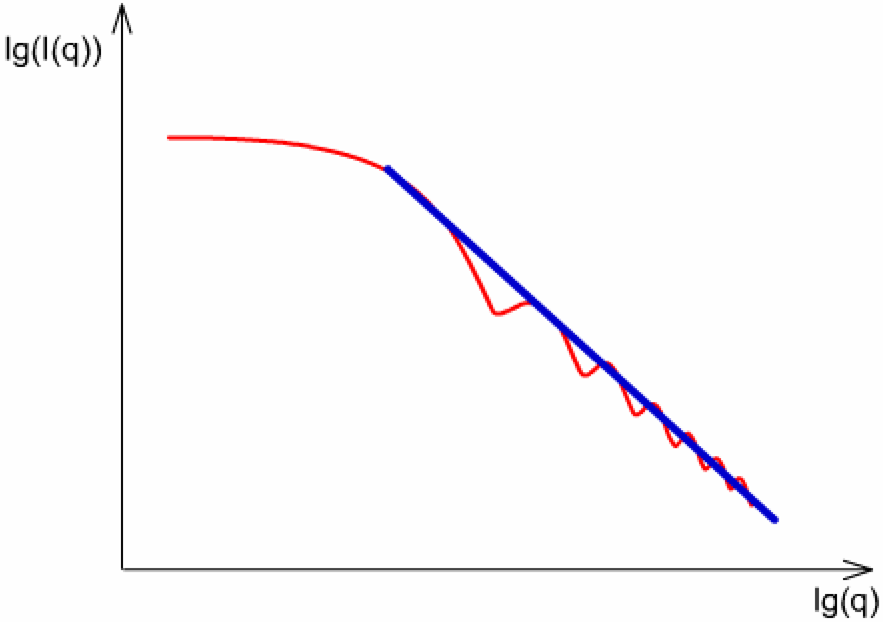
$$\frac{S}{V} = \frac{\pi}{Q}\lim_{q\to\infty}[q^4 I(q)]$$

S - surface area

Porod law $\Rightarrow$ specific area

Surface fractal dimension

for rough surface



$$I(q) \underset{q\to\infty}{\sim} \frac{1}{q^{\alpha}}$$

$$\alpha = 6 - D_S$$

D_S - surface fractal dimention

Power-law scattering $\Rightarrow$ surface fractal dimension

Interparticle correlation

No interaction

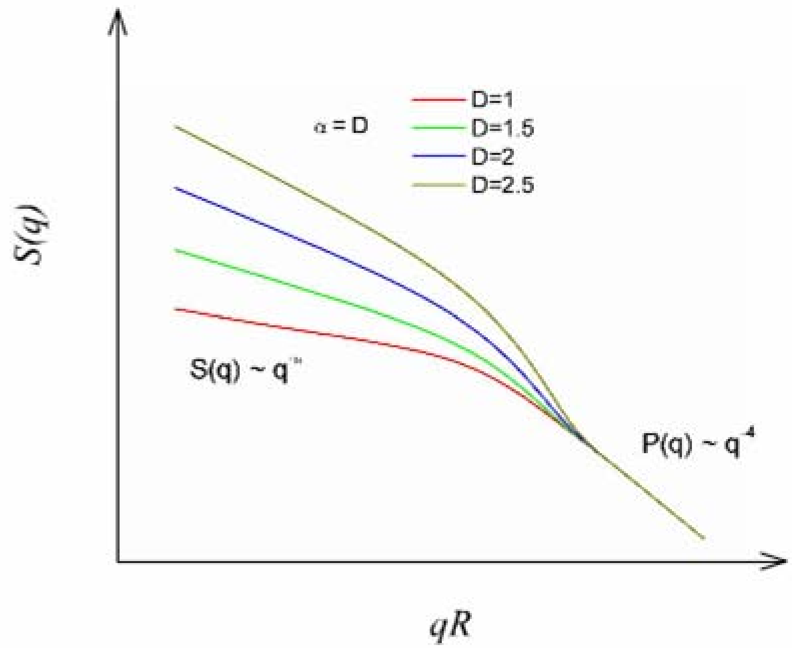
$$\frac{d\Sigma}{d\Omega} = n\, V^2\, \Delta\rho^2\, P(q)$$

Interaction

$$\frac{d\Sigma}{d\Omega} = n\, V^2\, \Delta\rho^2\, P(q)\, S(q)$$

$S(q)$ - structure-factor (F.Zernike, G.Prince, 1927)

Fractal clusters



Gauss coil, *D* = 2 (P.Debye, 1947)

$$S(q) = 2\,\frac{e^{-x} + x - 1}{x^2}$$

$$x = \zeta^2 q^2, \quad S(q) \sim q^{-2}$$

ζ - radius of gyration of the coil

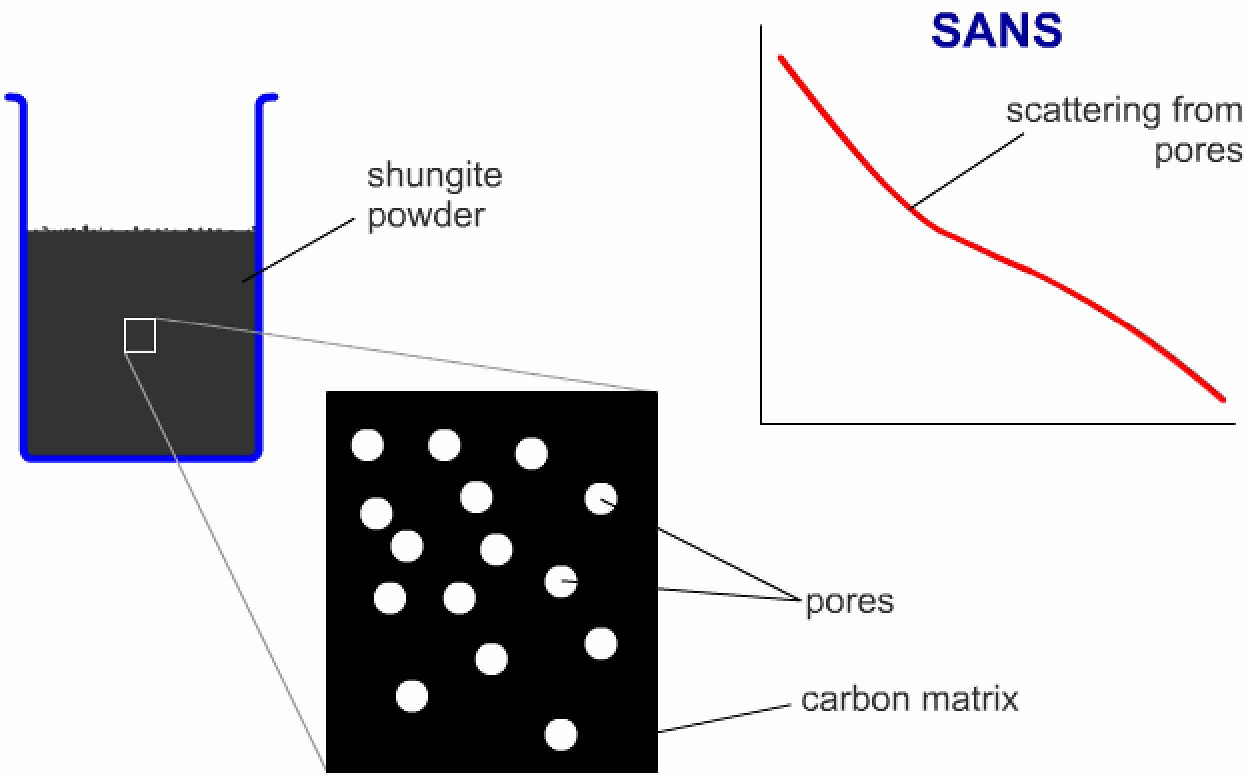
Arbitrary mass fractal

$$S(q) \sim \frac{1}{q^D} \quad 1 < D < 3$$

Structure-factor ⇒ mass fractal dimension

Matching of open pores in natural carbon

(shungites)



Matching of open pores in natural carbon

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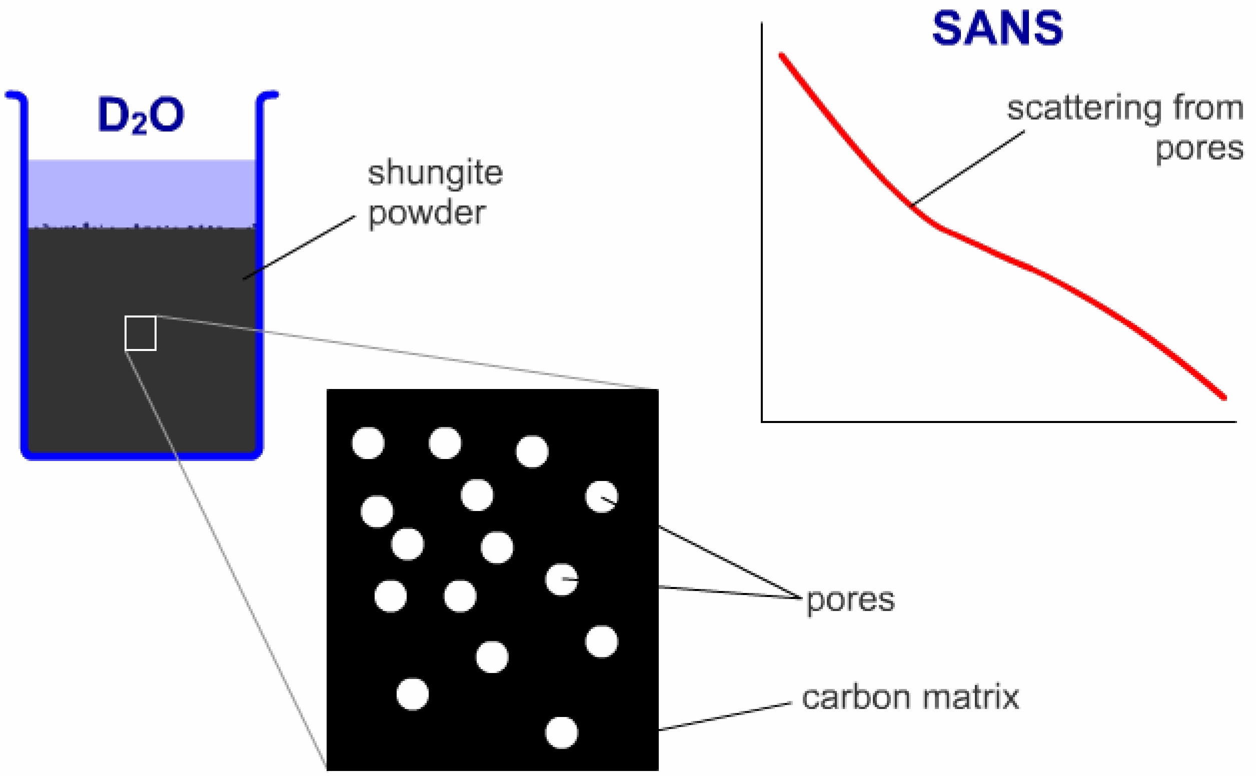

Matching of open pores in natural carbon

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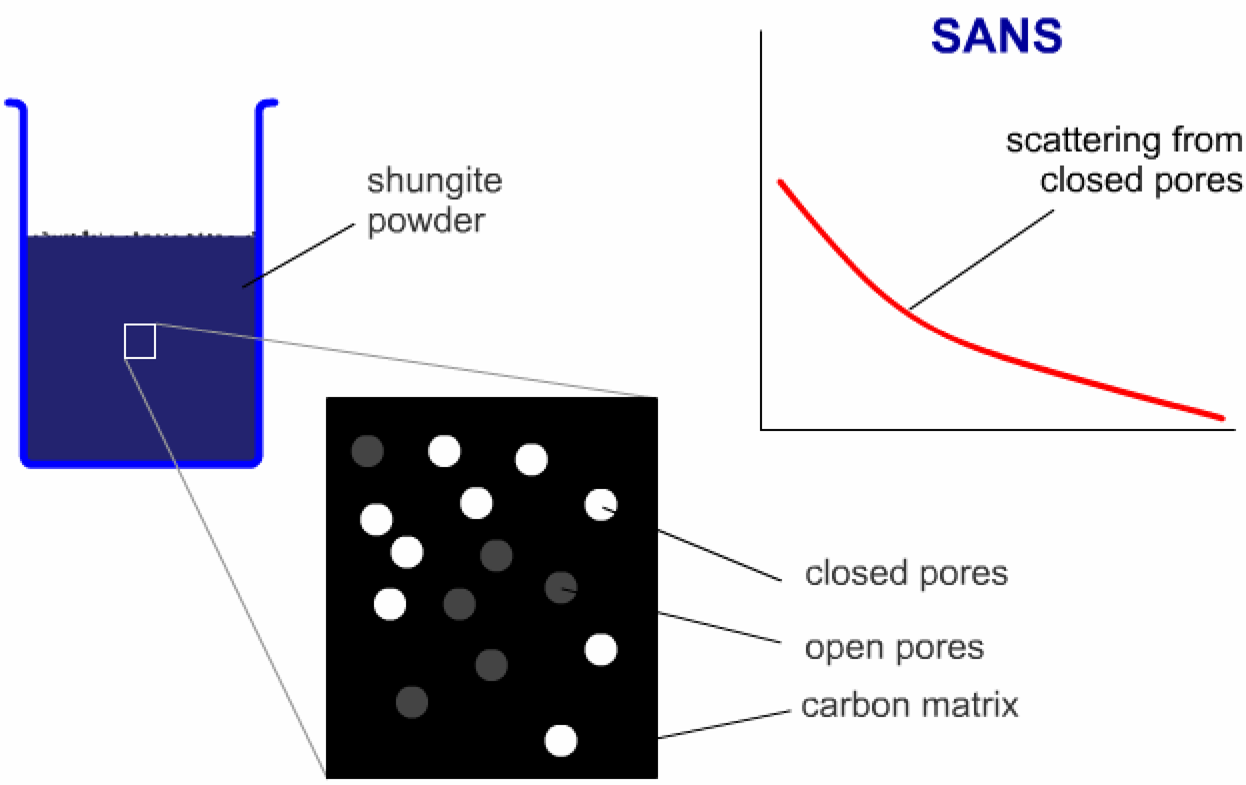
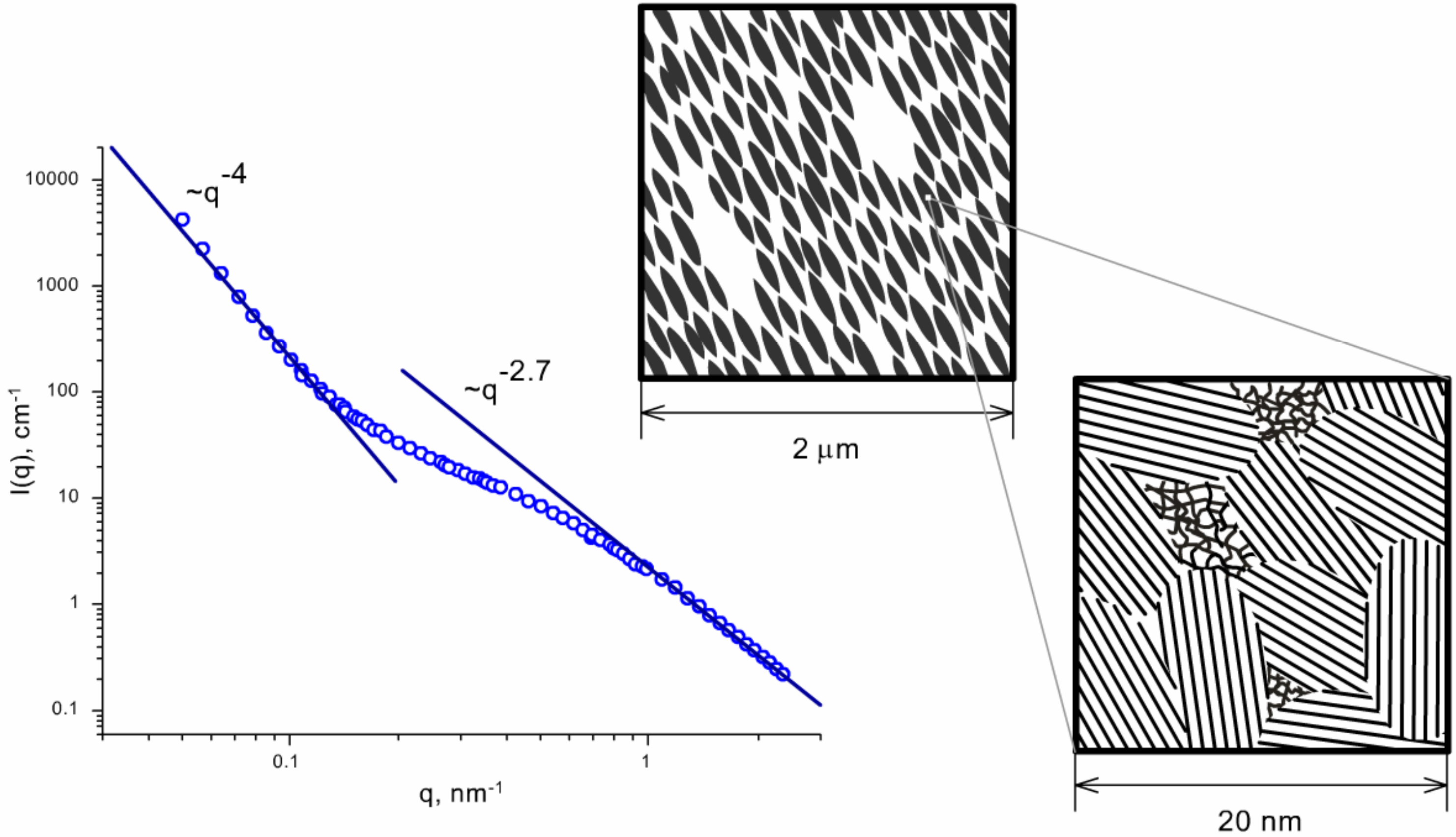


Analysis of SANS curves

(Shungite Maksovo, Russian Karelia)



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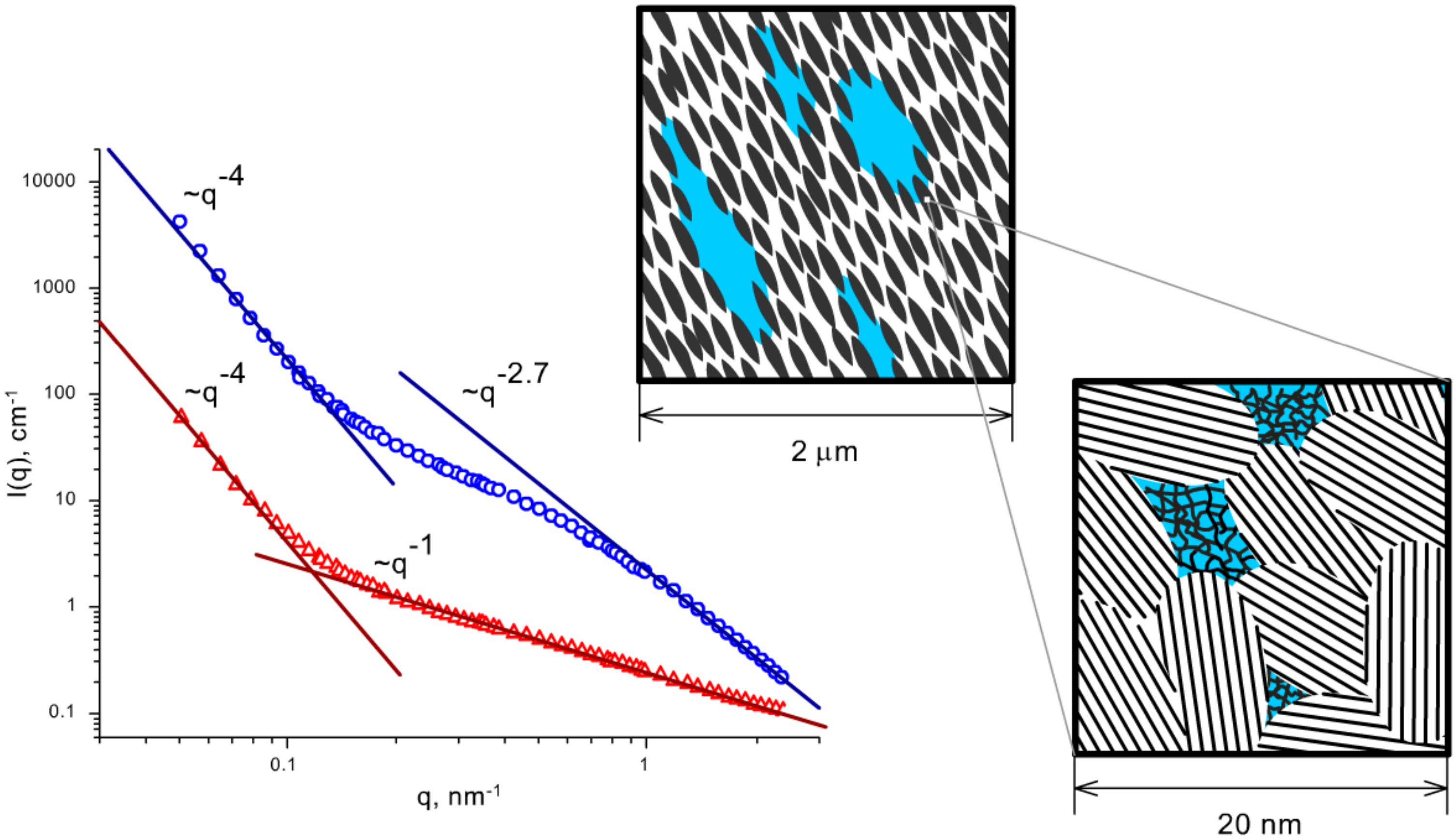
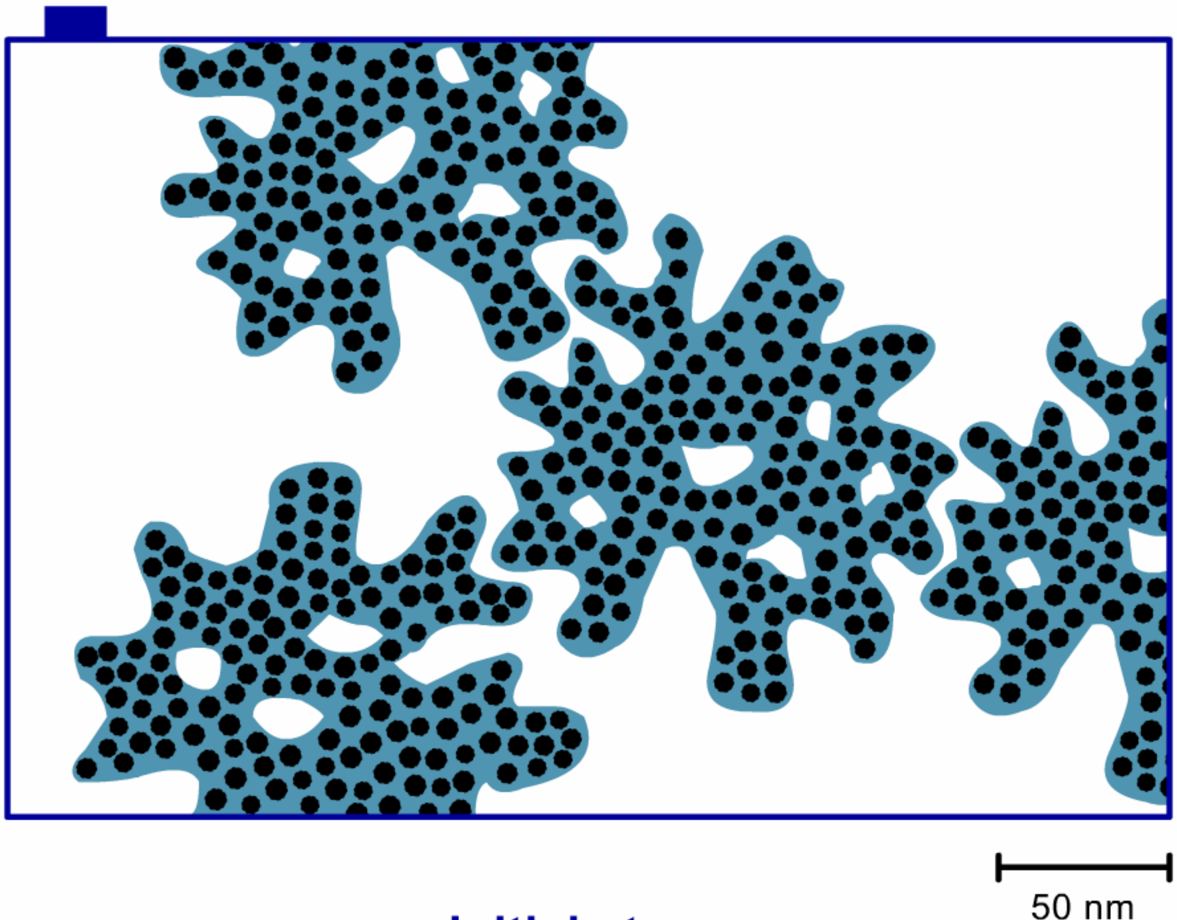


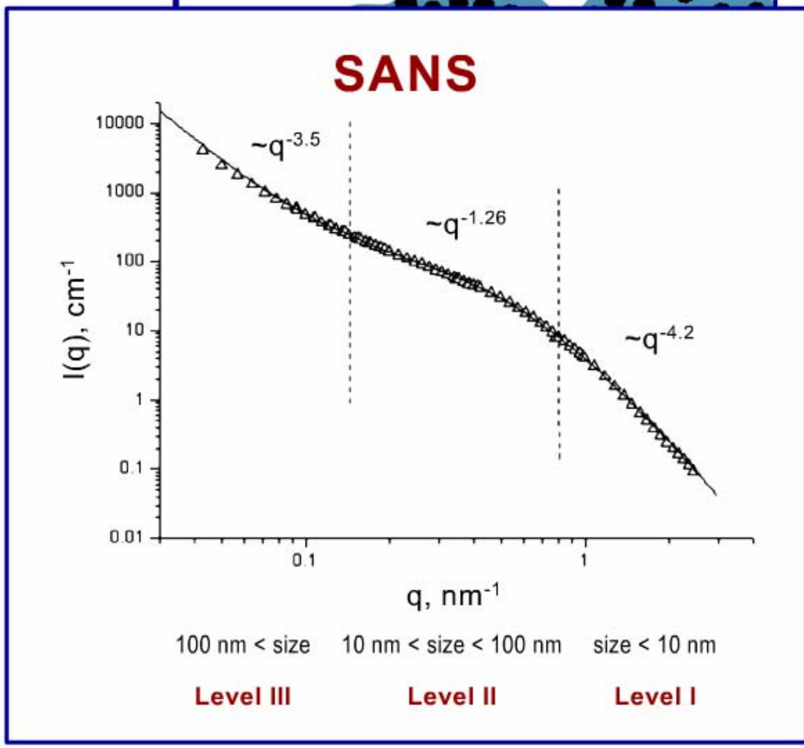
M.V.Avdeev, et al., Carbon (2006)

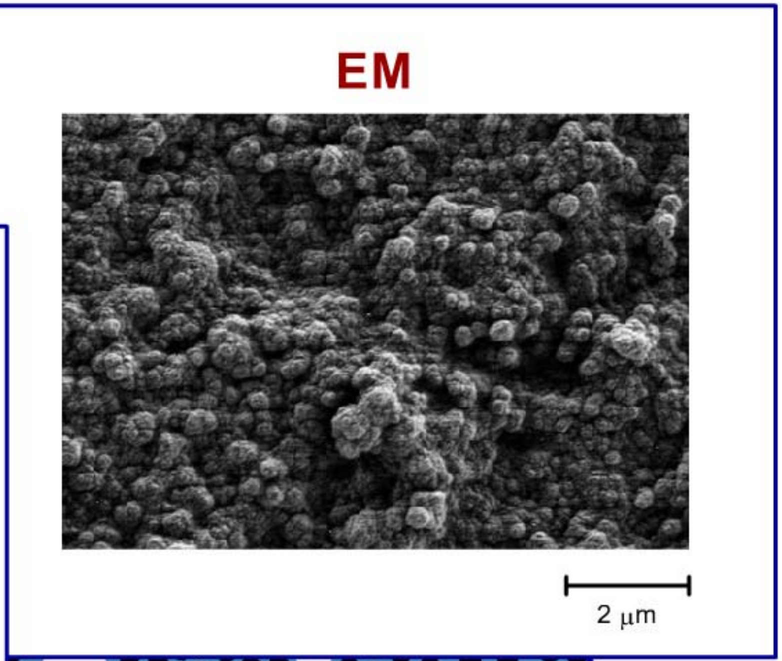
Nanodiamond dispersion



Initial stage

Nanodiamond dispersion





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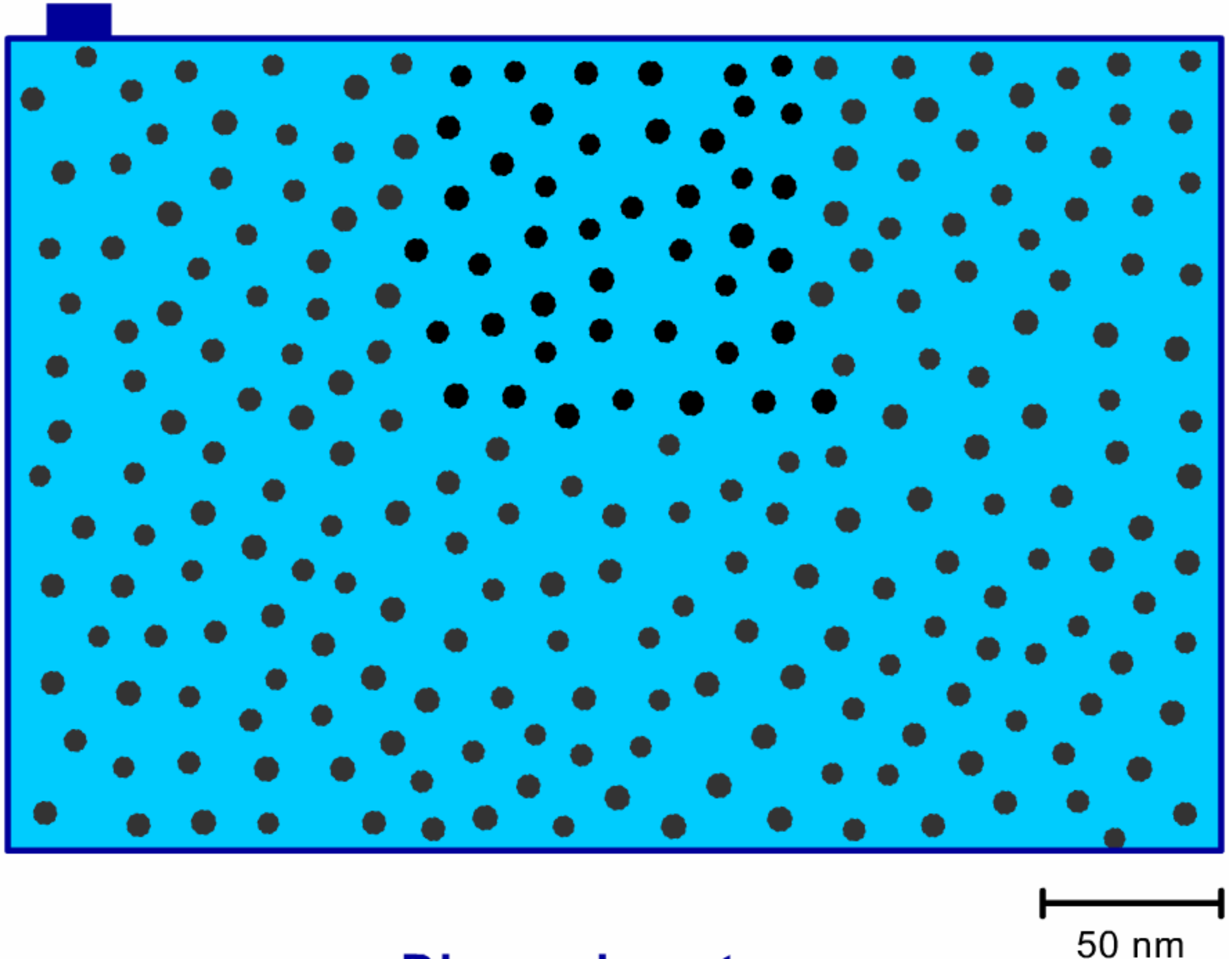
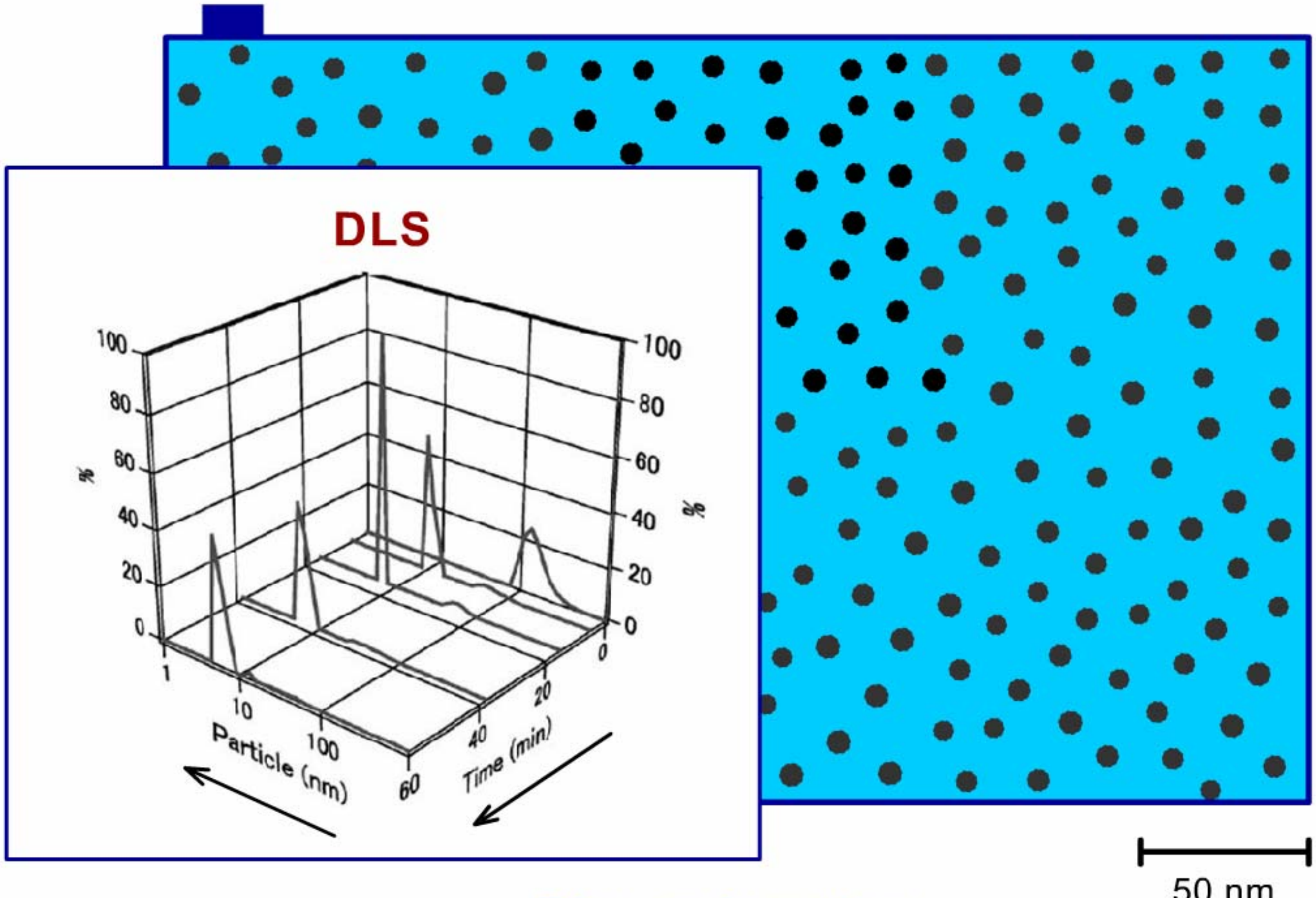


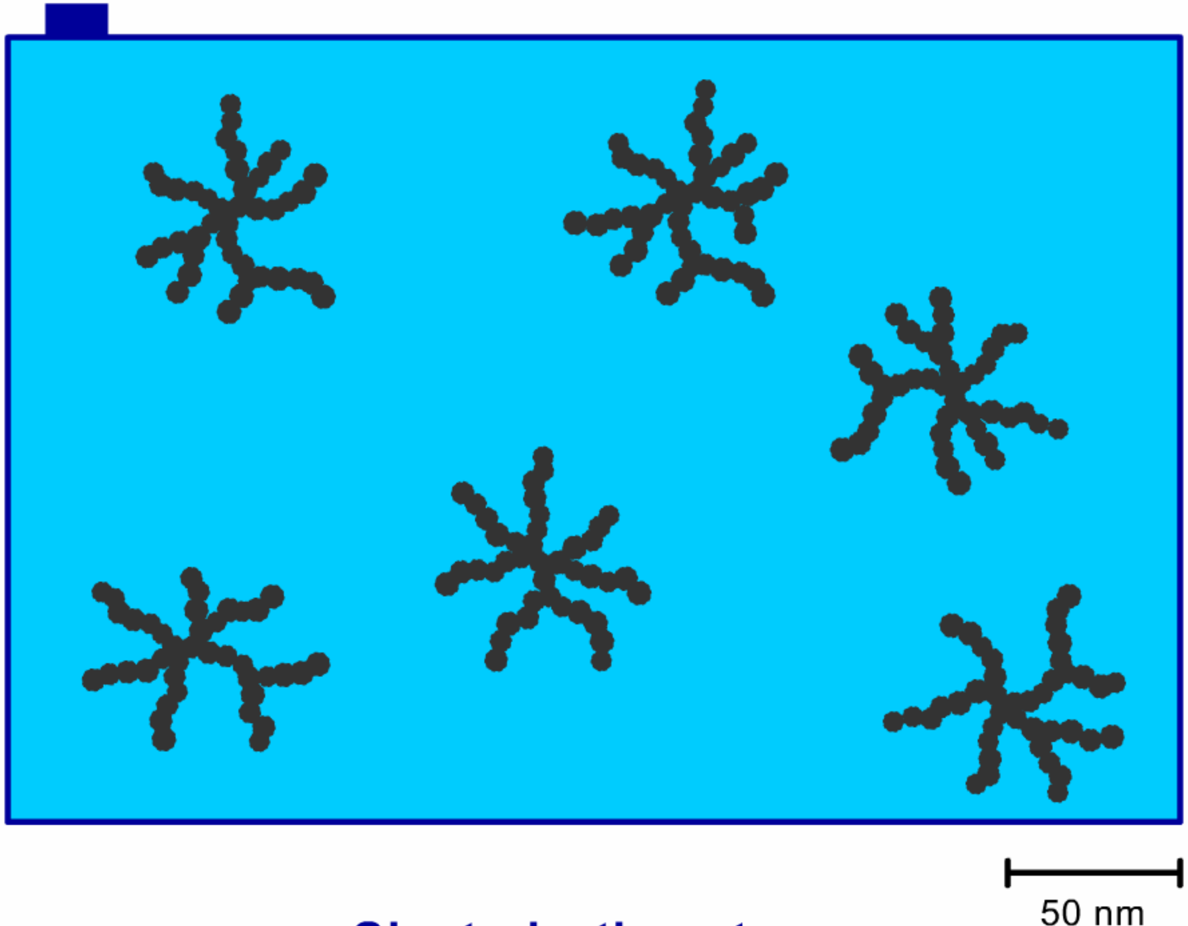
Dispersing stage

Nanodiamond dispersion



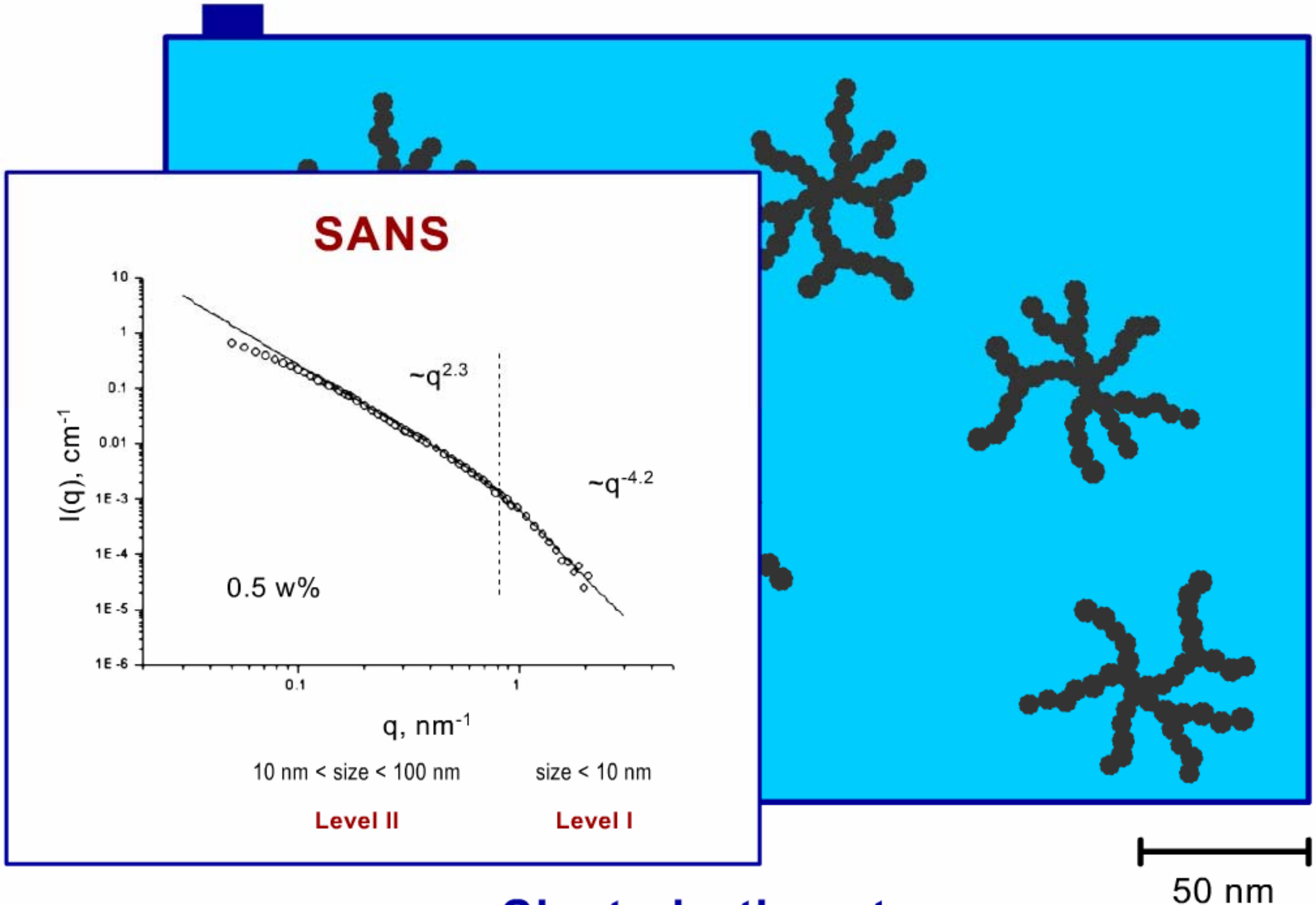
Dispersing stage

Nanodiamond dispersion



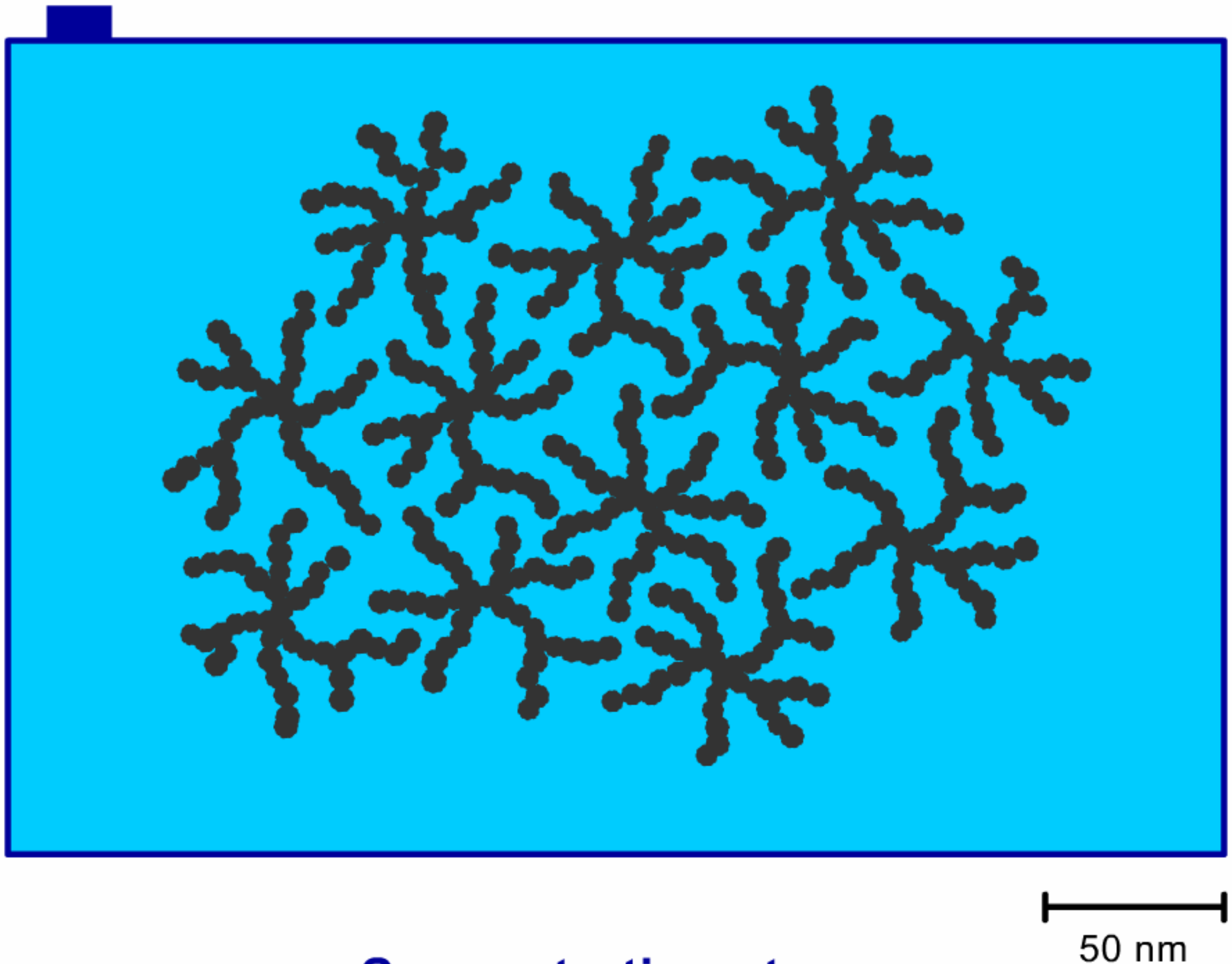
Clusterization stage

Nanodiamond dispersion



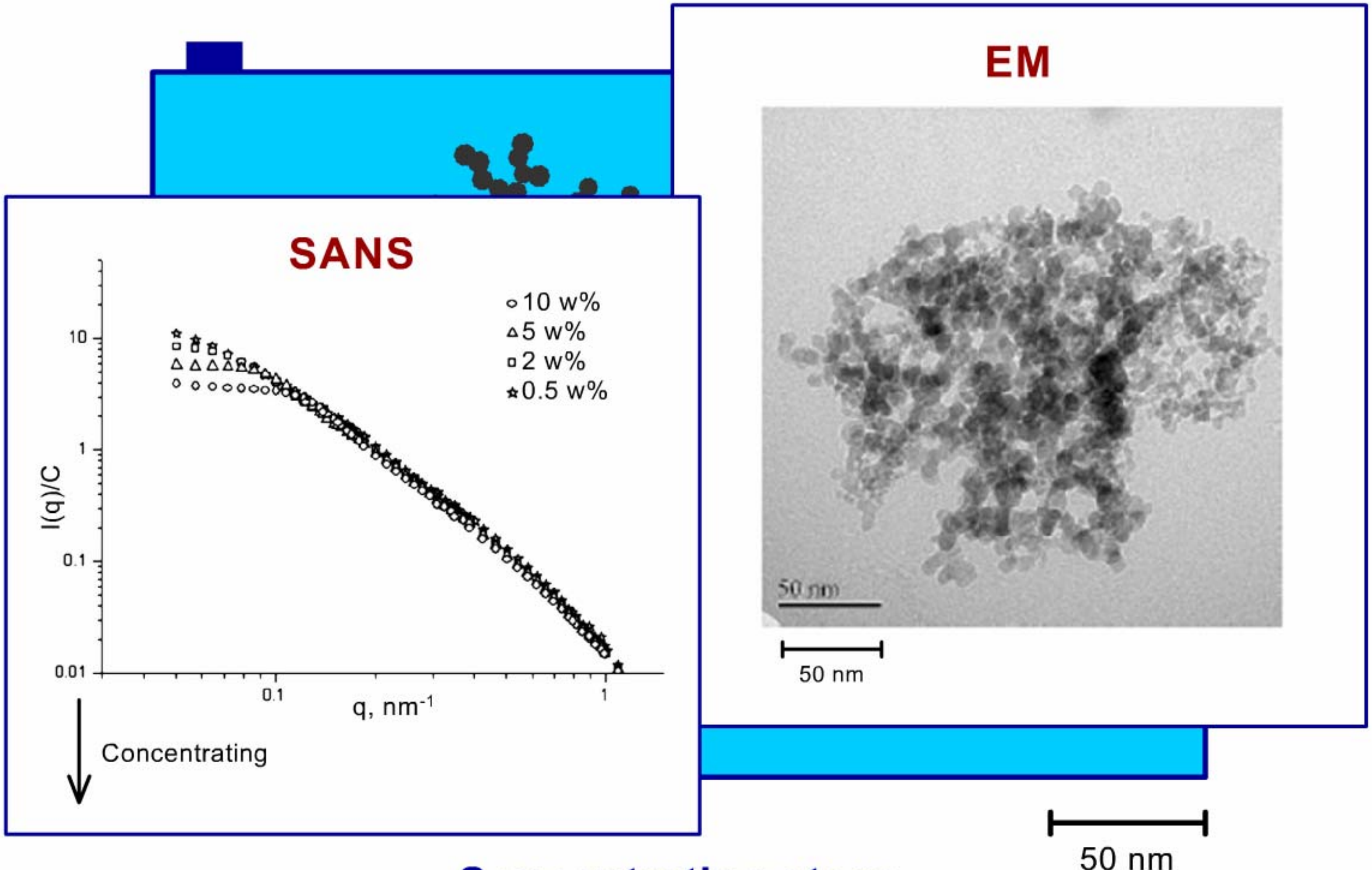
Clusterization stage

Nanodiamond dispersion



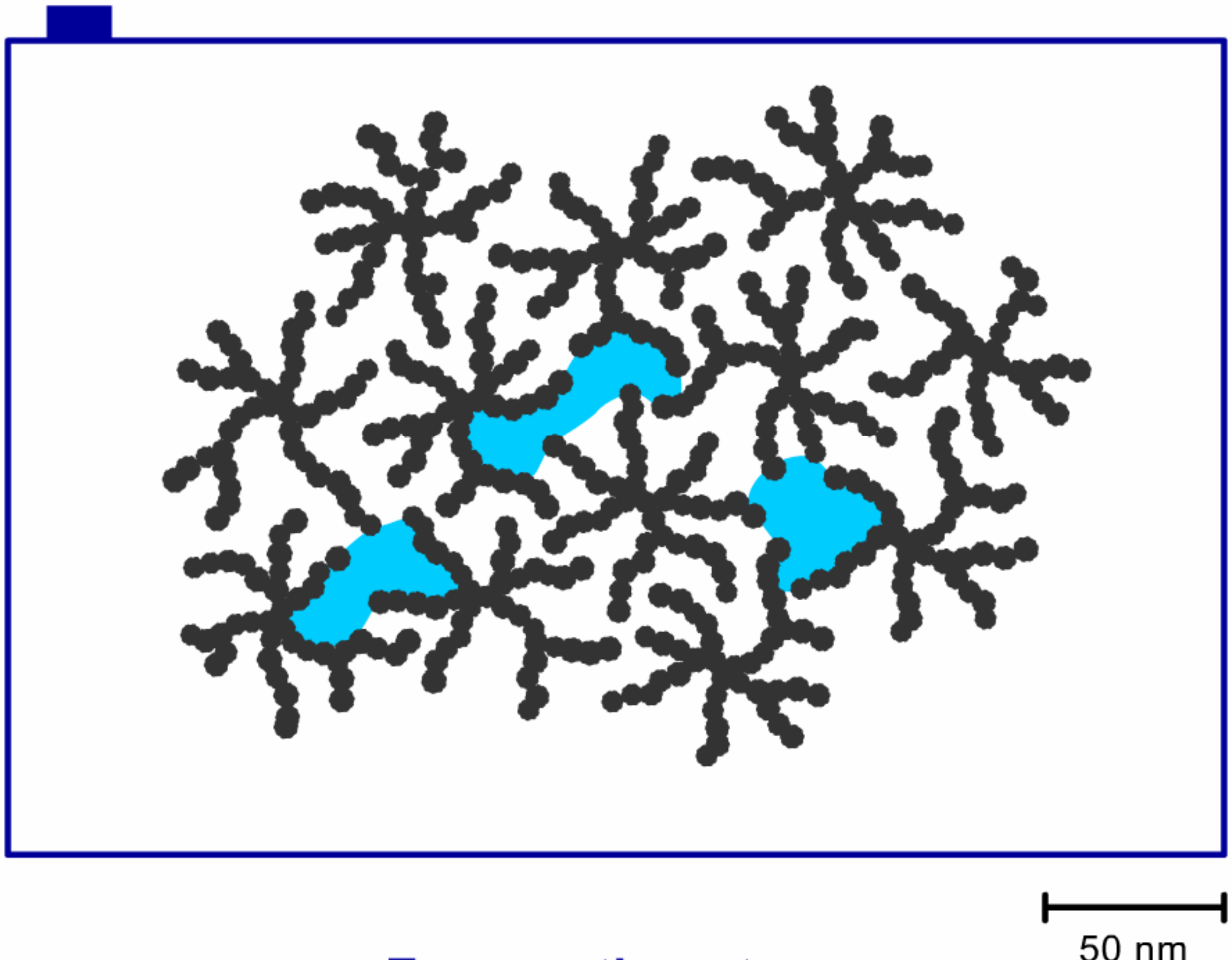
Concentrating stage

Nanodiamond dispersion



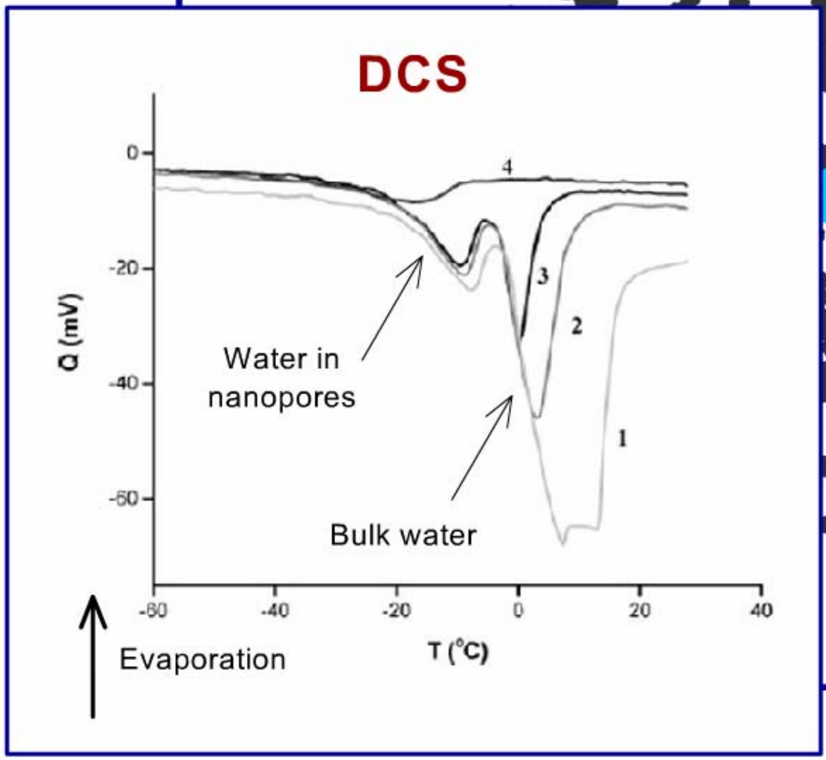
Concentrating stage

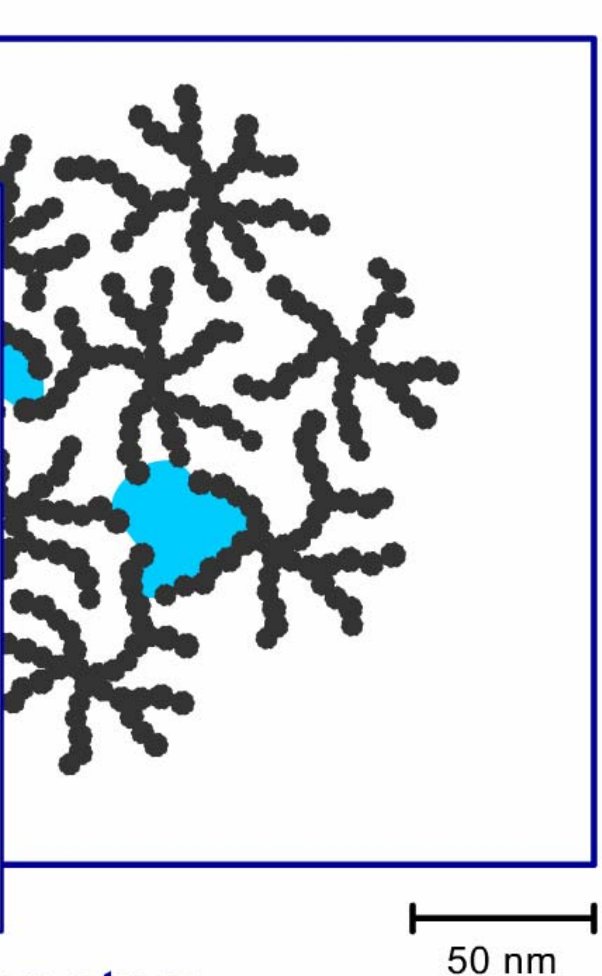
Nanodiamond dispersion



Evaporation stage

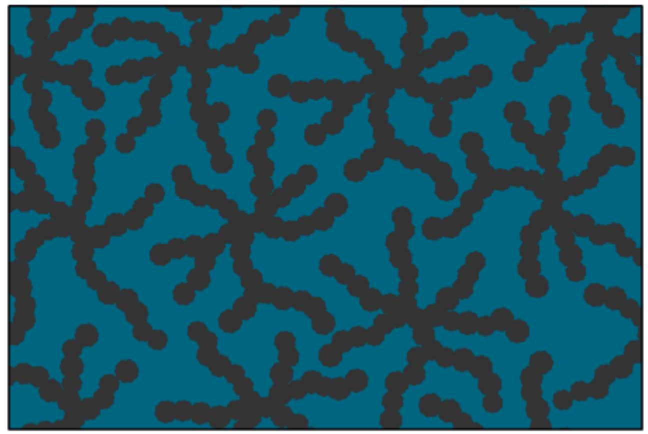
Nanodiamond dispersion



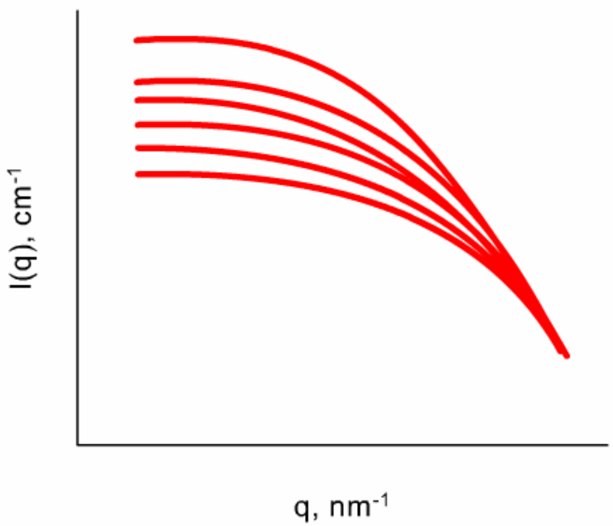


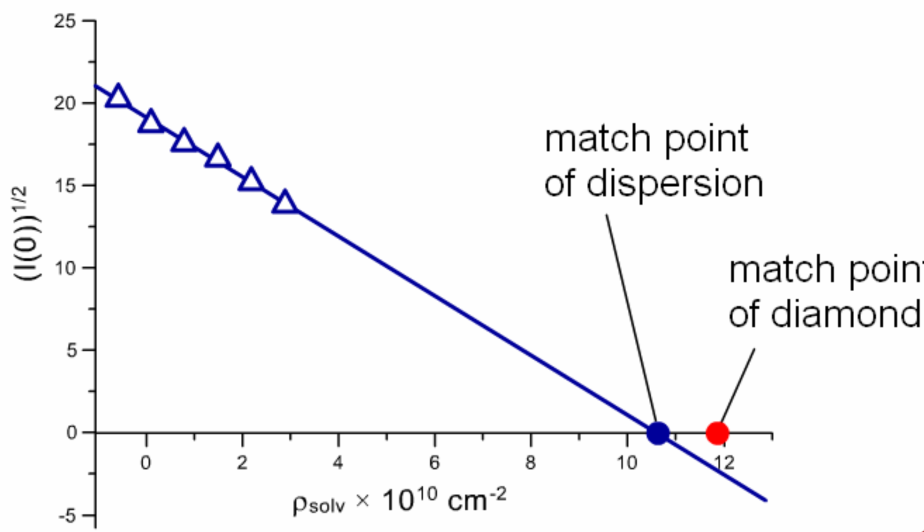
Evaporation stage

Contrast variation

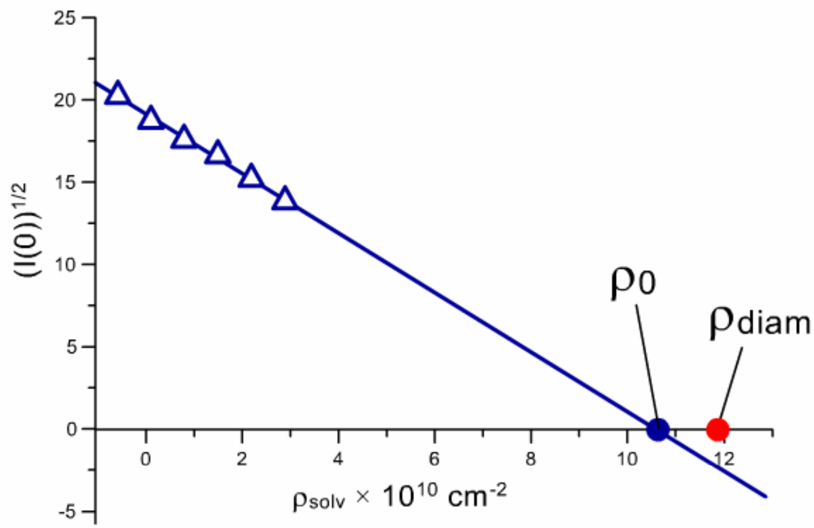


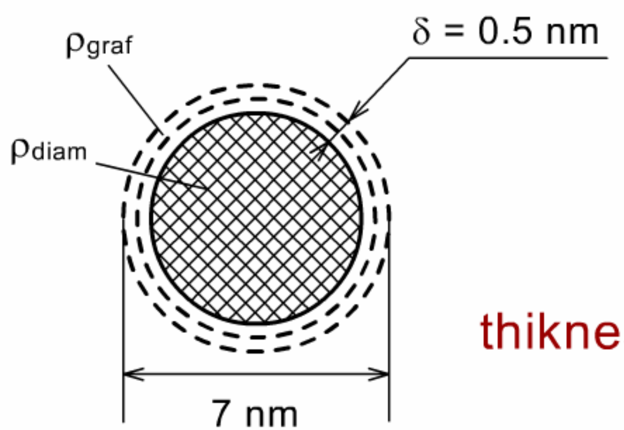
D_2O
0 %
10 %
20 %
30 %
40 %
50 %





Non-diamond shell





$\rho_0 = 10.4(5) \times 10^{10}$ cm^{-2}

$\rho_0 = \varepsilon\rho_{graph} + (1 - \varepsilon)\rho_{diam}$

$\rho_{graf} = 7.0 \times 10^{10}$ cm^{-2}

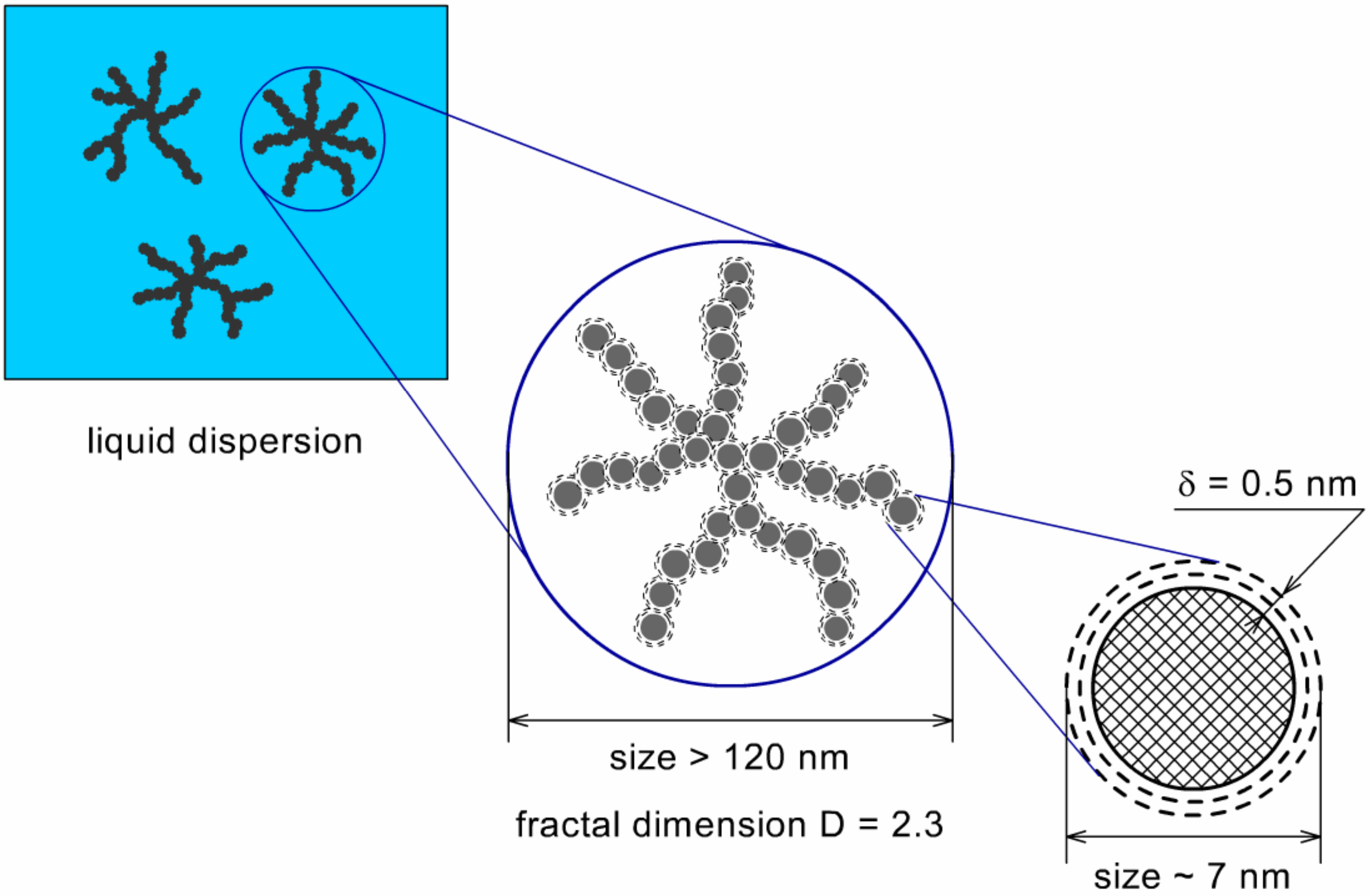
$\rho_{diam} = 11.8 \times 10^{10}$ cm^{-2}

volume fraction
of non-diamond
component (ρ_{graph})
$\varepsilon = 0.3$

thikness of non-diamond shell δ = 0.5 nm

M.V.Avdeev, et al., J Phys Chem C (2009)

Nanodiamond cluster structure



Complex study of nanostructures

Electron microscope

Dynamic light scattering

Static light scattering

Quasy elastic neutron scattering

X-ray and neutron diffraction

X-ray and neutron reflectometry

Small angle X-ray and neutron scattering

Sedimentation analysis

Spectrometry

Photometry

Calorimetry