Small angles for grand actions

Small-Angle Neutron Scattering method: basics and examples

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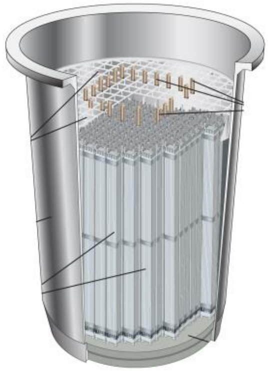
Small-Angle Neutron Scattering (SANS)

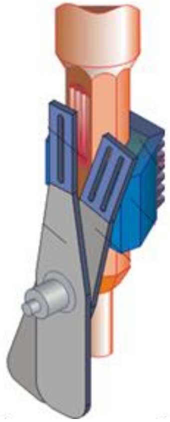
elastic scattering on inhomogeneities of matter, the sizes of which are much larger than the radiation wavelength

Brumberger H. (*Ed.*), Modern Aspects of Small-Angle Scattering, (1995).

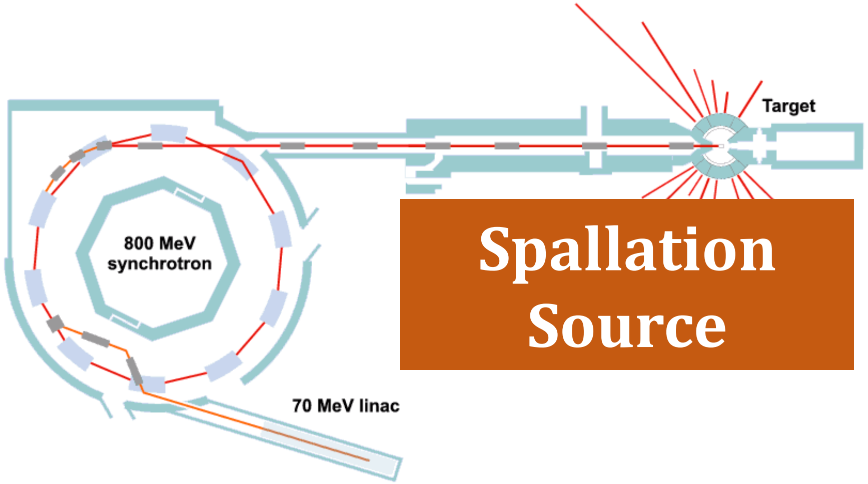
Thermal (slow) neutrons for condensed matter research



Steady-state Reactor



Pulsed Reactor



Spallation Source

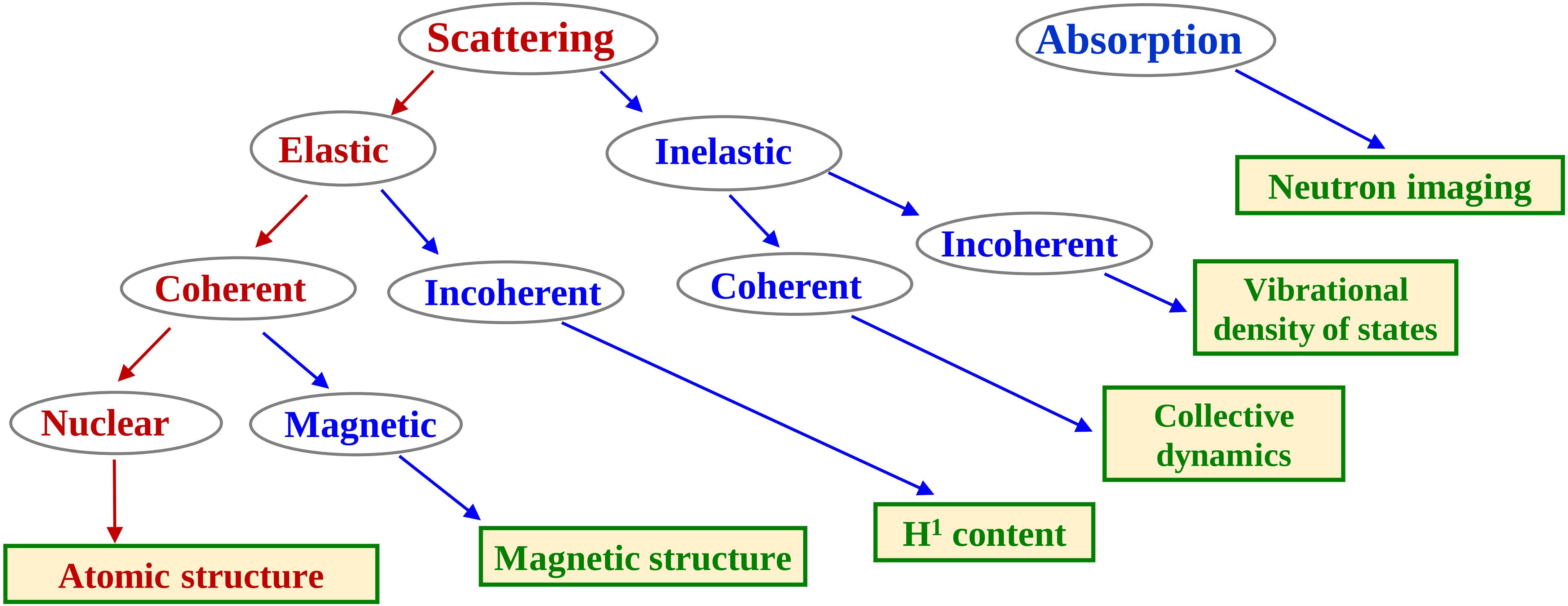
Moderation (speed reduction)

$\lambda \approx 1 - 10\ \text{Å}$

$$\lambda\,[\text{Å}] = \frac{h}{\sqrt{2mE}} \approx \frac{0.286}{\sqrt{E\ [\text{eV}]}}$$

$E \approx 1 - 50\ \text{meV}$

Interaction of thermal neutrons with matter

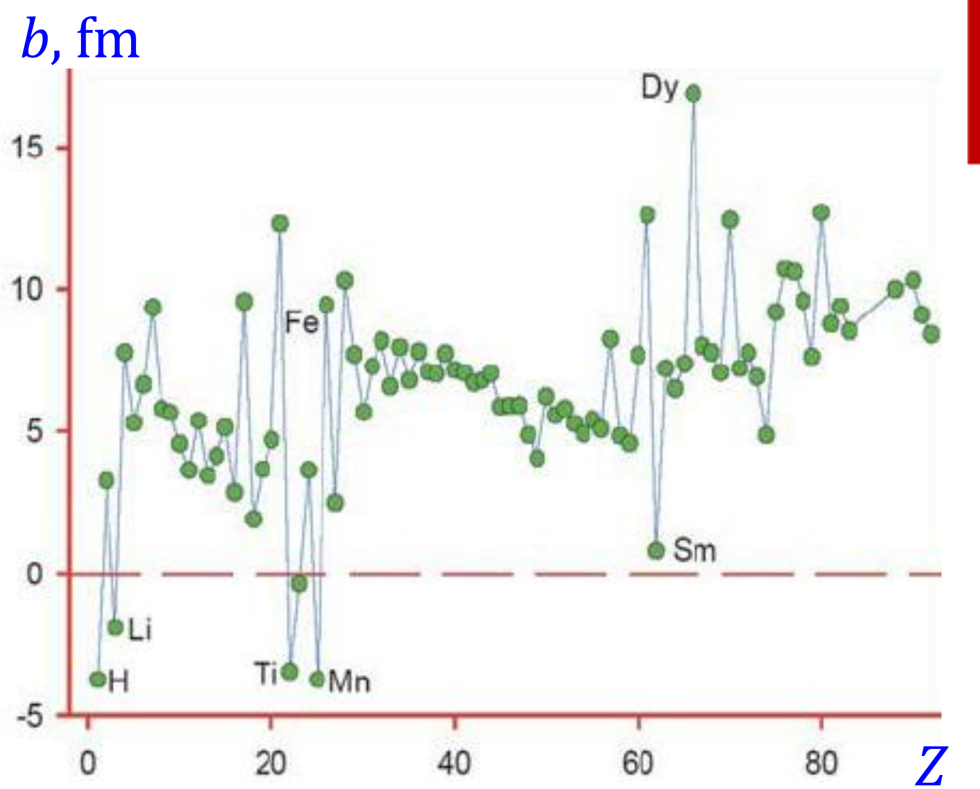


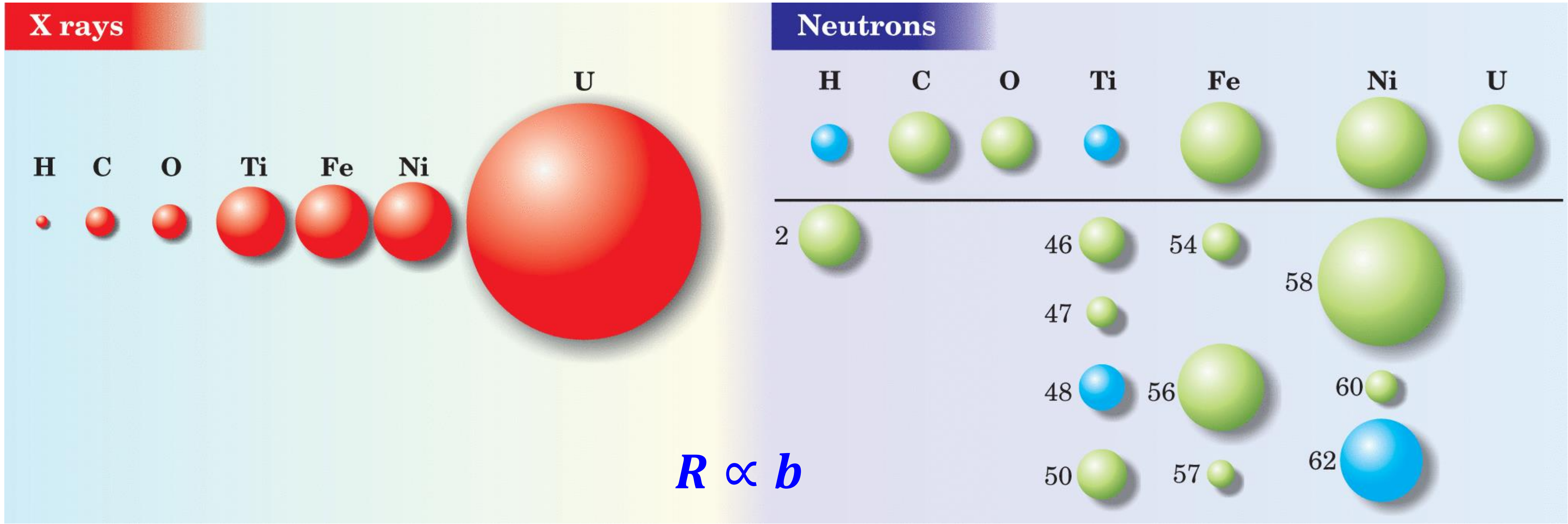
The experiments use absorption and 8 different types of neutron scattering

Neutron scattering length

Fermi pseudopotential

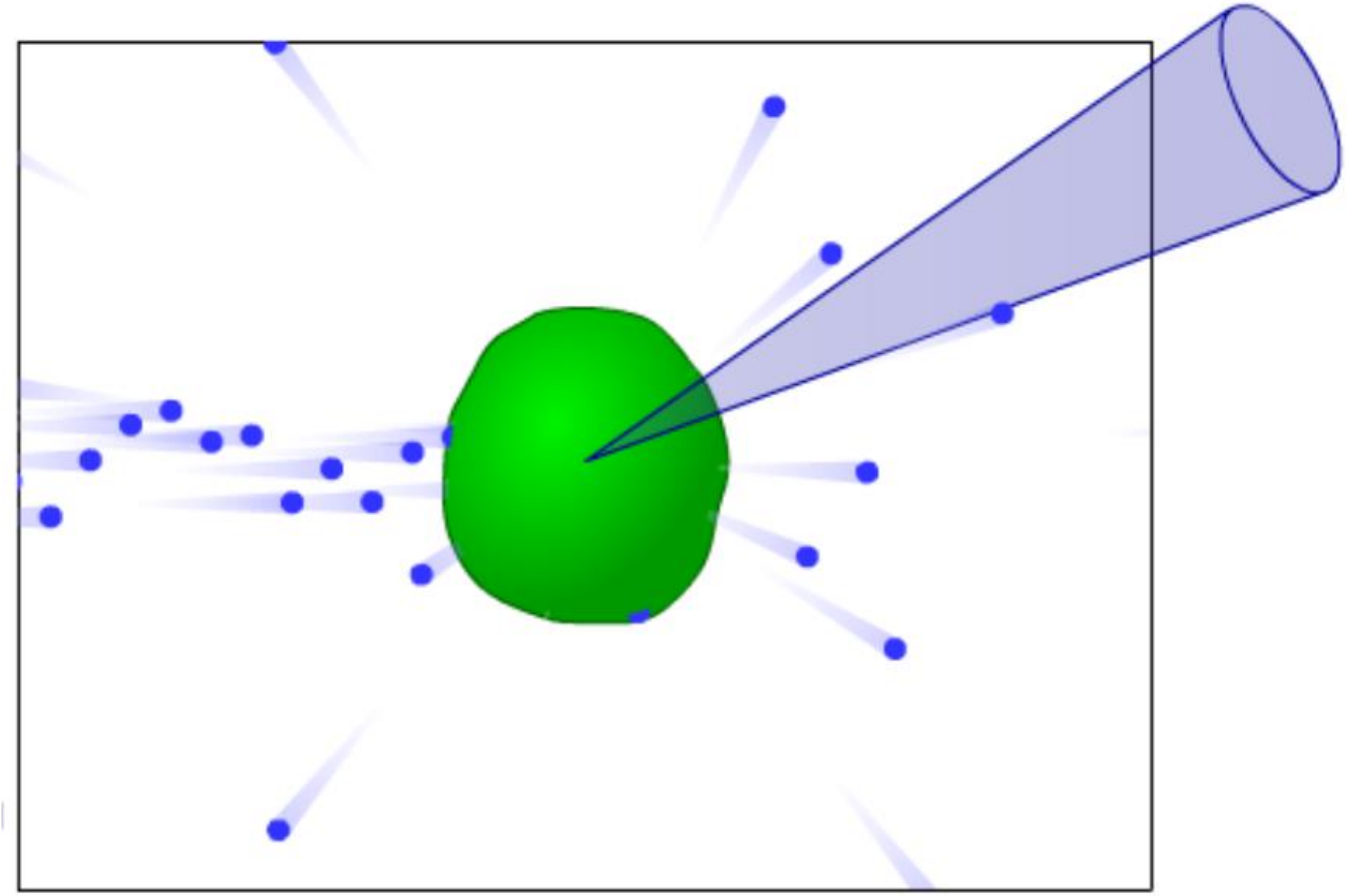
$$U(\vec{r}) = \frac{2\pi\hbar^2}{m}\sum_j b_j \delta(\vec{r} - \vec{R_j})$$

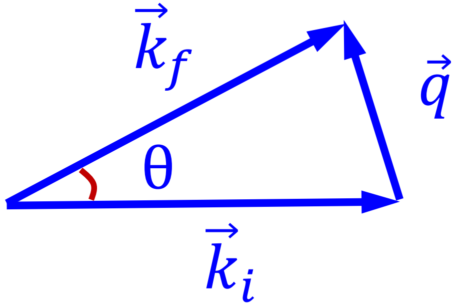




$R \propto b$

Elastic scattering of thermal neutrons





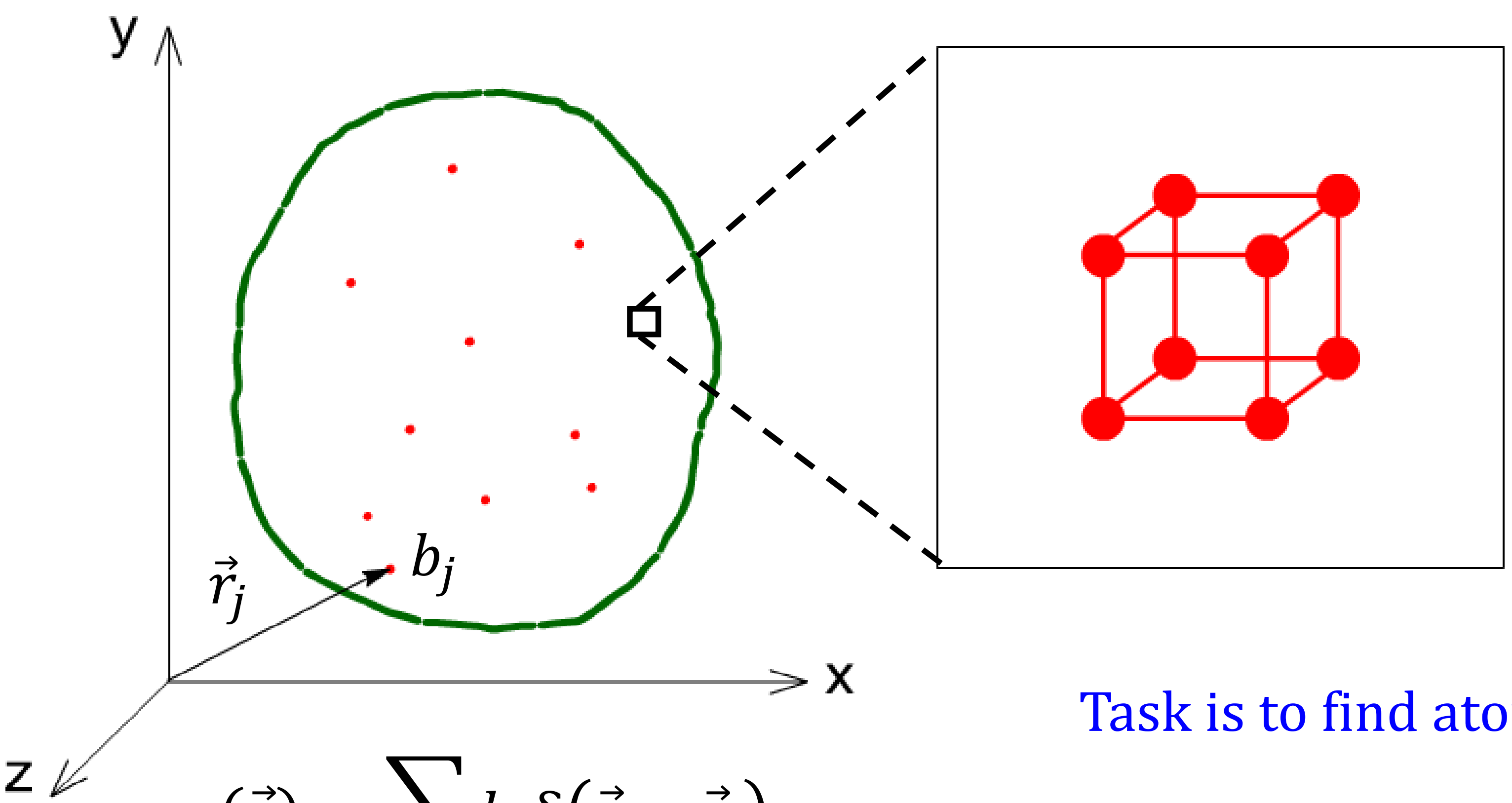
$$q = \frac{4\pi}{\lambda} \sin\frac{\theta}{2}$$

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

$$\frac{d\sigma}{d\Omega}(q) = \langle |A(\vec{q})|^2 \rangle_\Omega$$

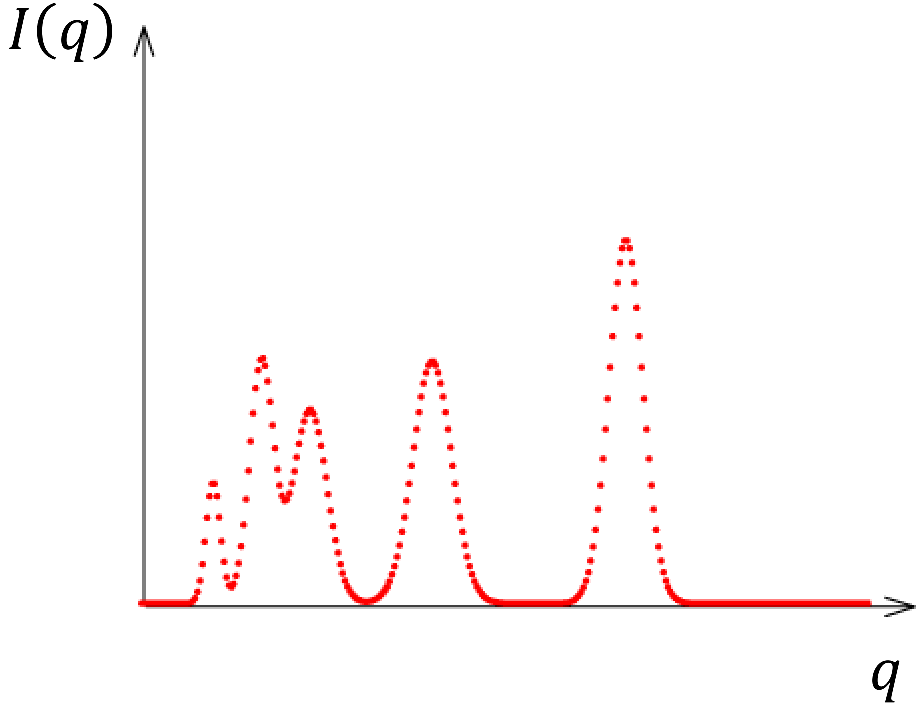
$$I(q) = n \frac{d\sigma}{d\Omega}(q)$$

Point scattering centers



$$\rho(\vec{r}) = \sum_j b_j \delta(\vec{r} - \vec{r}_j)$$

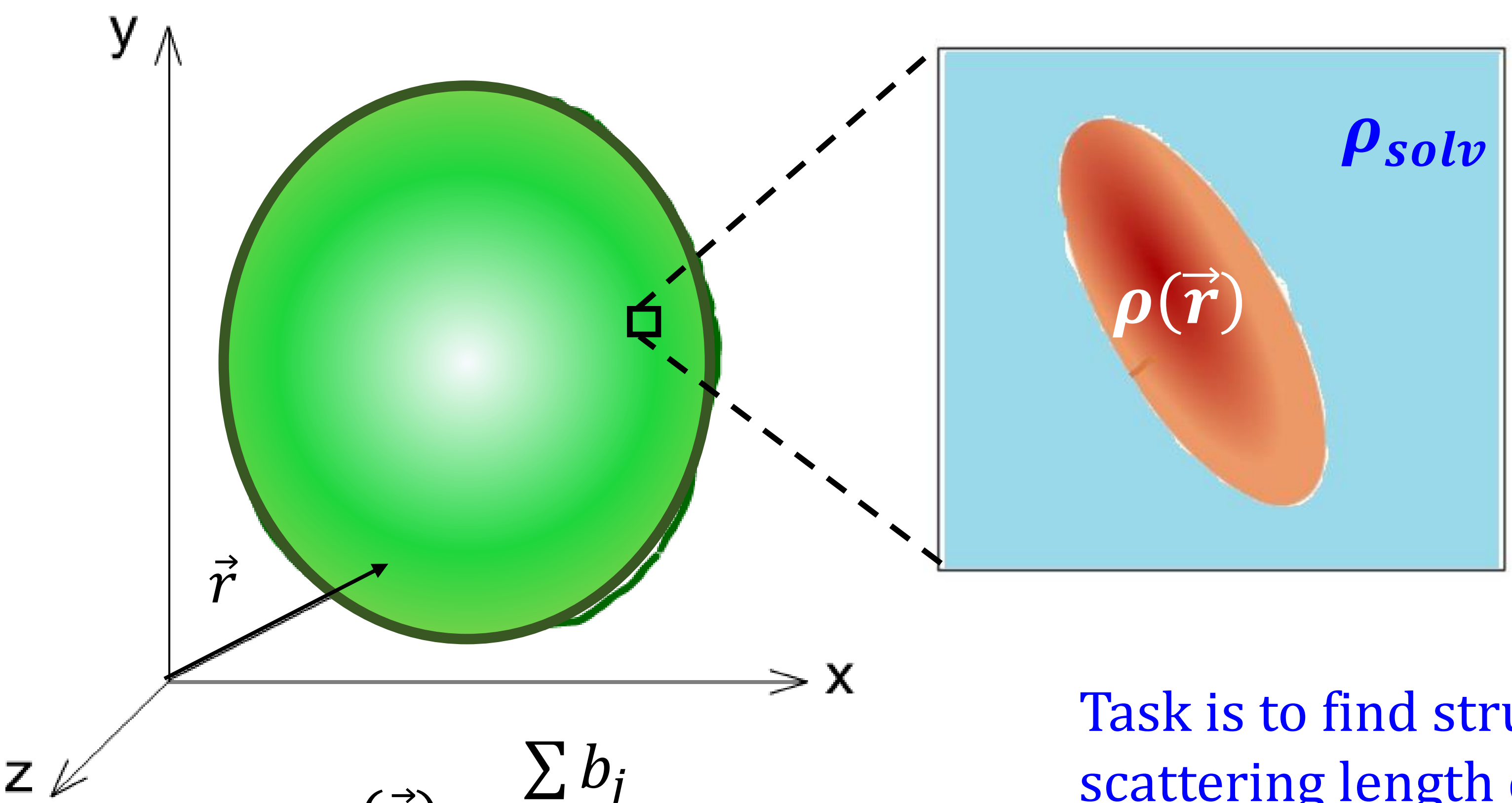
Diffraction on crystal

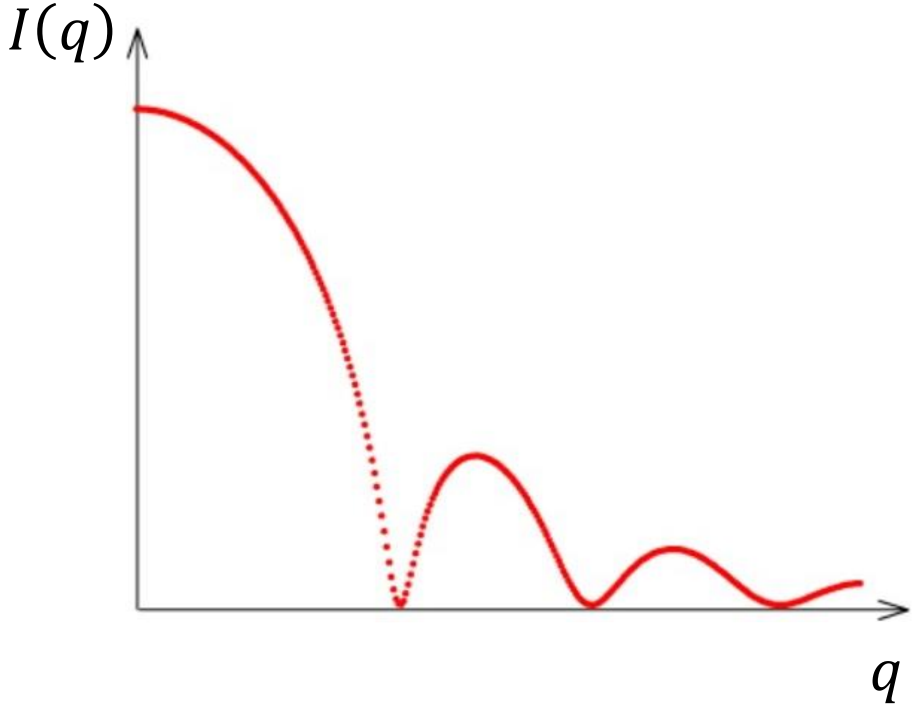


Task is to find atomic coordinates

Continuous medium

Diffraction on inhomogeneity





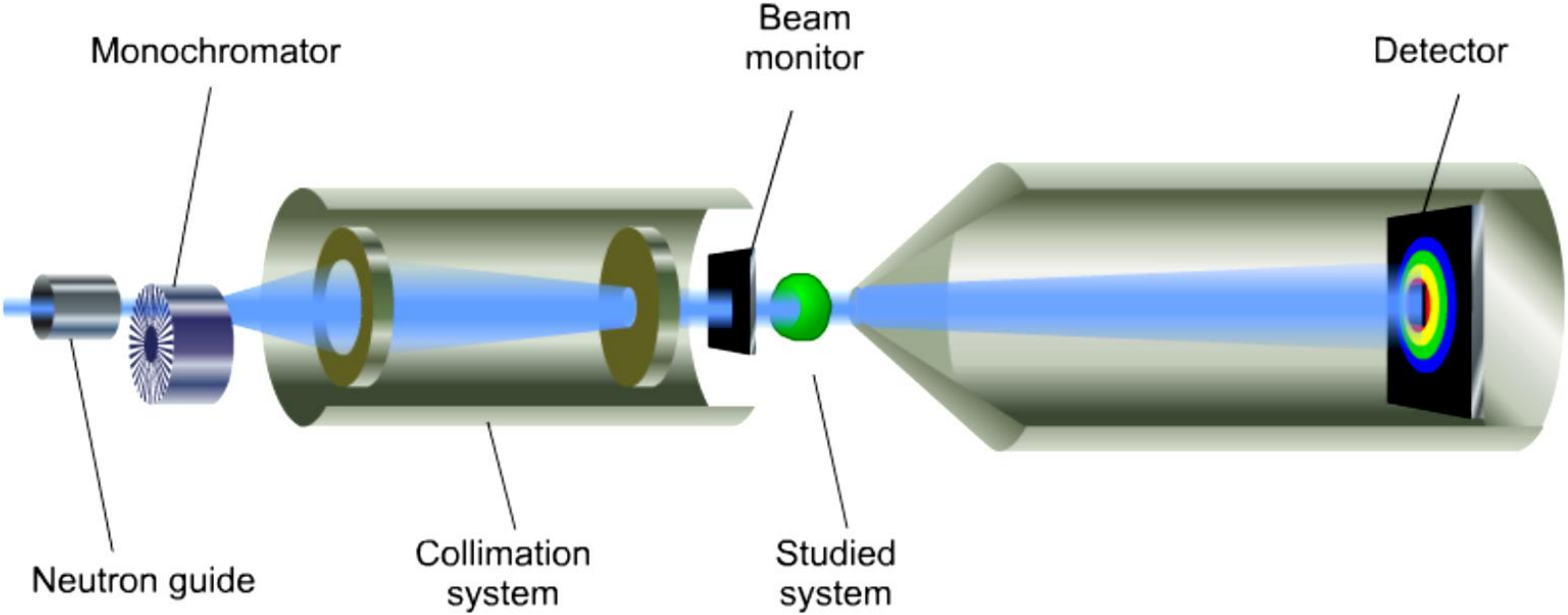
$$\rho(\vec{r}) = \frac{\sum b_j}{\Delta v}$$

Task is to find structural characteristics in terms of scattering length density $\rho(\vec{r})$

Neutron contrast $\Delta\rho = \bar{\rho} - \rho_{solv}$

Small–angle neutron scattering method

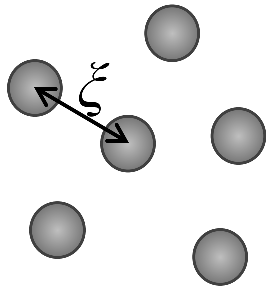
L = nm – μm　　λ = 1 – 10 Å　　q = 0.0001 – 1 $Å^{-1}$　　$\theta < 10°$

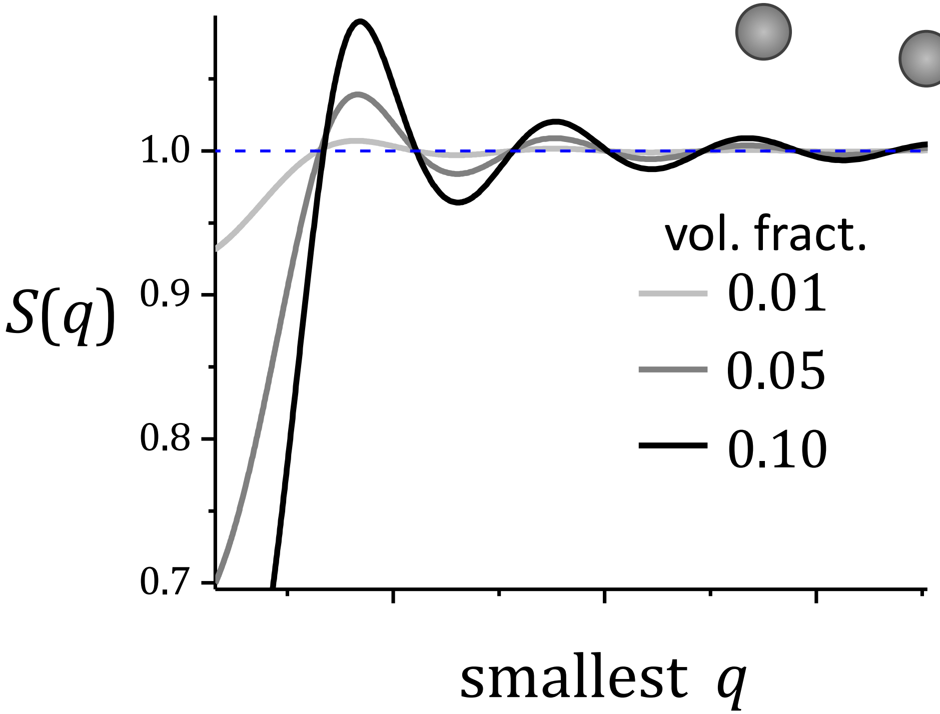


Information that can be obtained using SANS

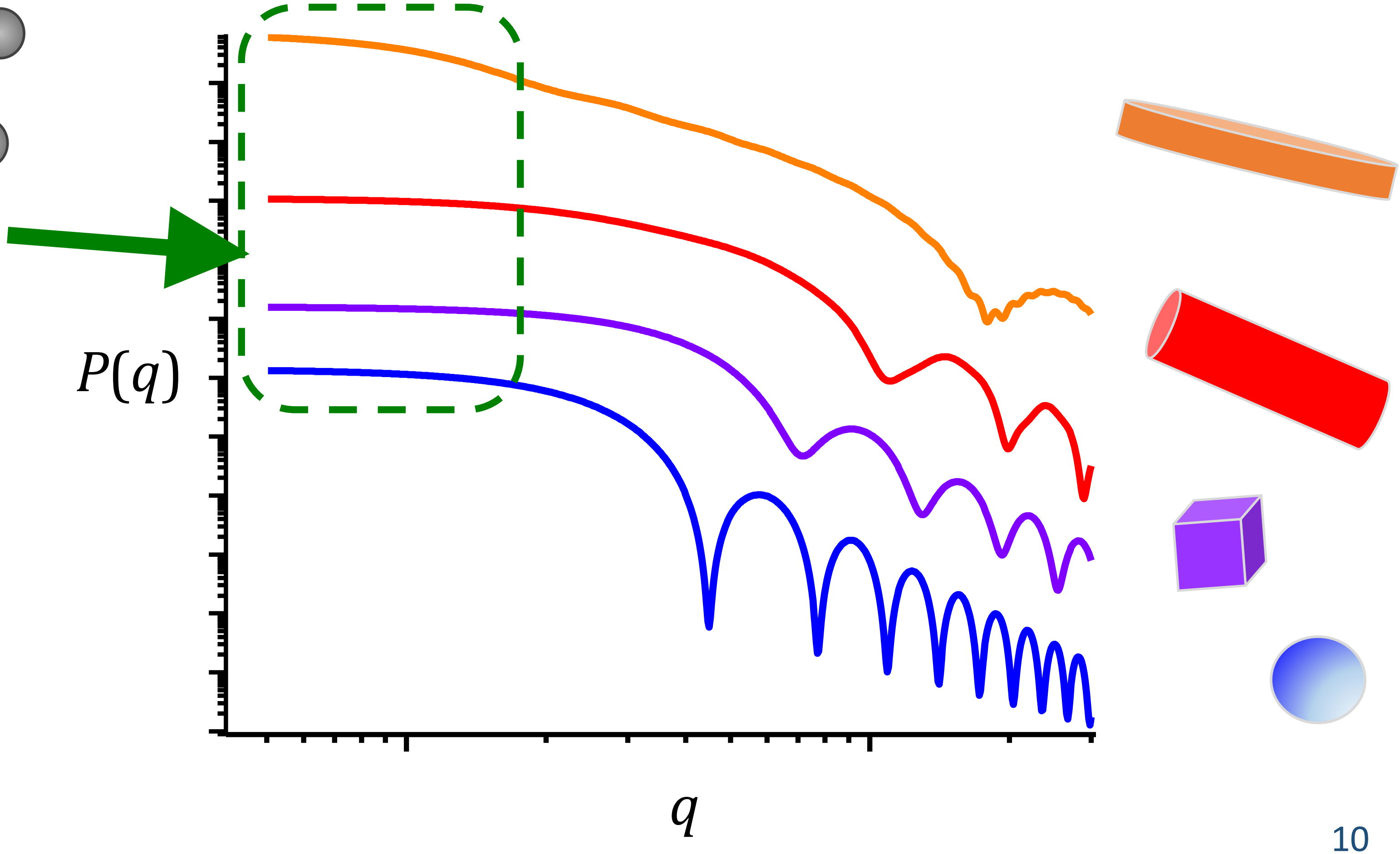
$$I(q) = nV^2(\Delta\rho)^2 S(q) P(q)$$

Structure factor:
inter-particle interaction



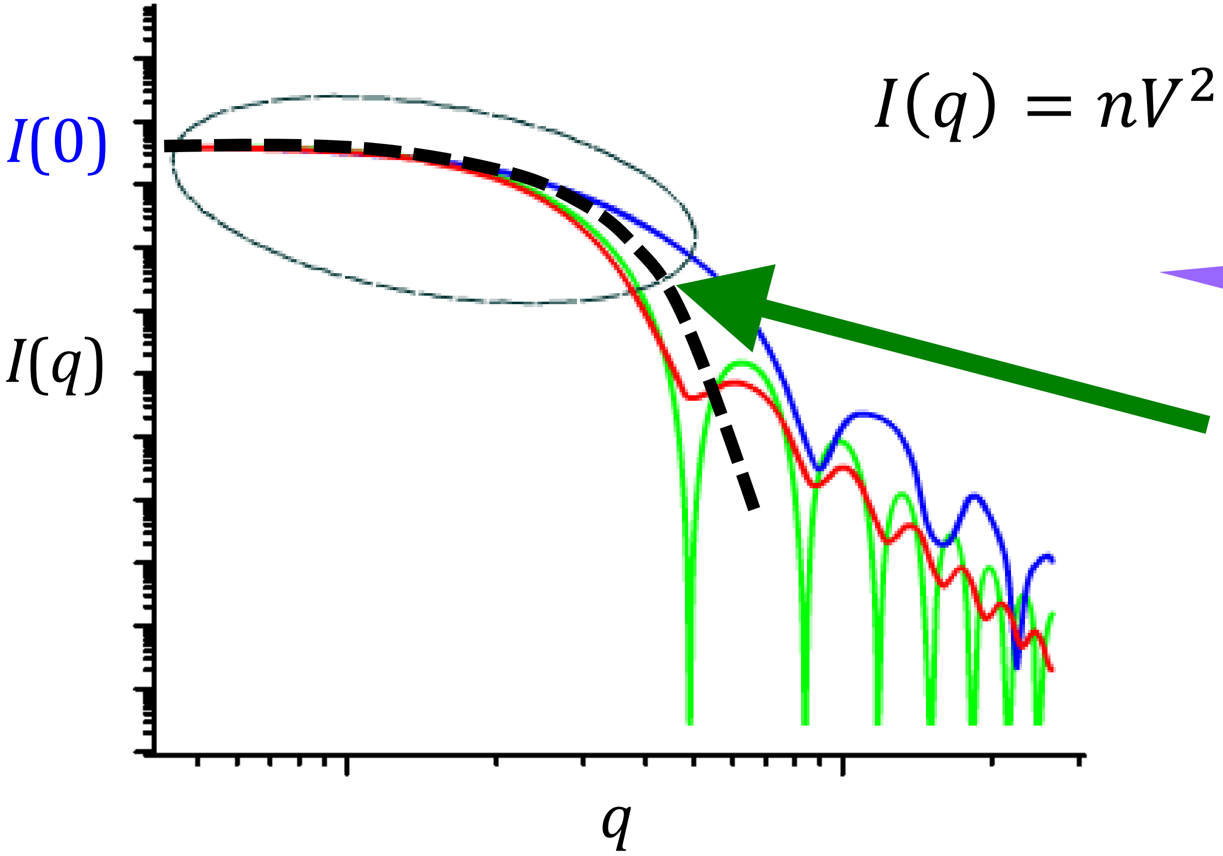


Form-factor: shape, size & polydispersity



Fourier transform of the
radial distribution function

Characteristic size: Radius of gyration



$$I(q) = nV^2(\Delta\rho)^2 S(q)P(q)$$

$S(q) \rightarrow 1$
$q \rightarrow 0$

$$I(q) = I(0)\exp\left(-q^2 R_g^2/3\right)$$ Guinier law

$$I(0) = nV^2(\Delta\rho)^2$$ Forward scattering intensity

$$R_g^2 = \frac{\int r^2 \rho(\vec{r})d\vec{r}}{\int \rho(\vec{r})d\vec{r}}$$ Gyration radius

sphere

$$R_g^2 = \frac{3}{5}R^2$$

spherical shell

$$R_g^2 = \frac{3}{5}\frac{R_1^5 - R_2^5}{R_1^3 - R_2^3}$$

ellipsoid

$$R_g^2 = \frac{a^2 + b^2 + c^2}{5}$$

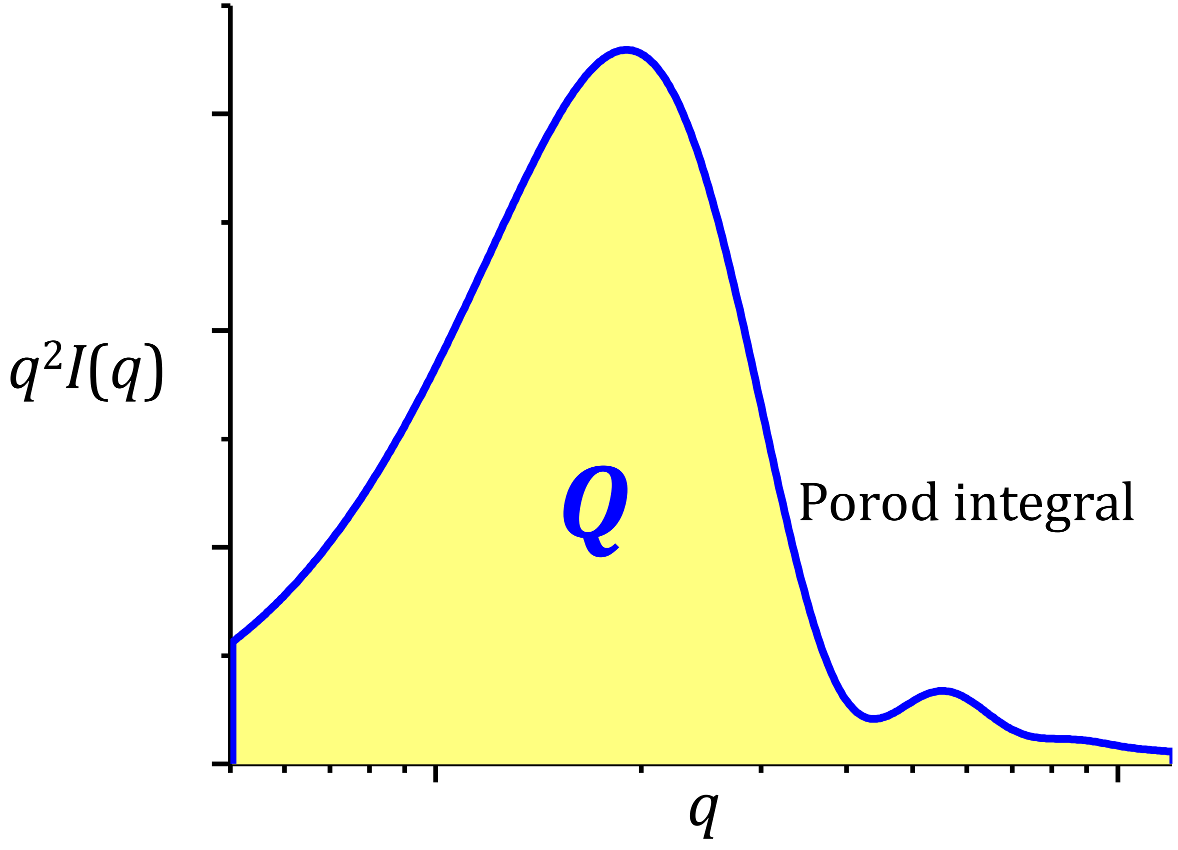
parallelepiped

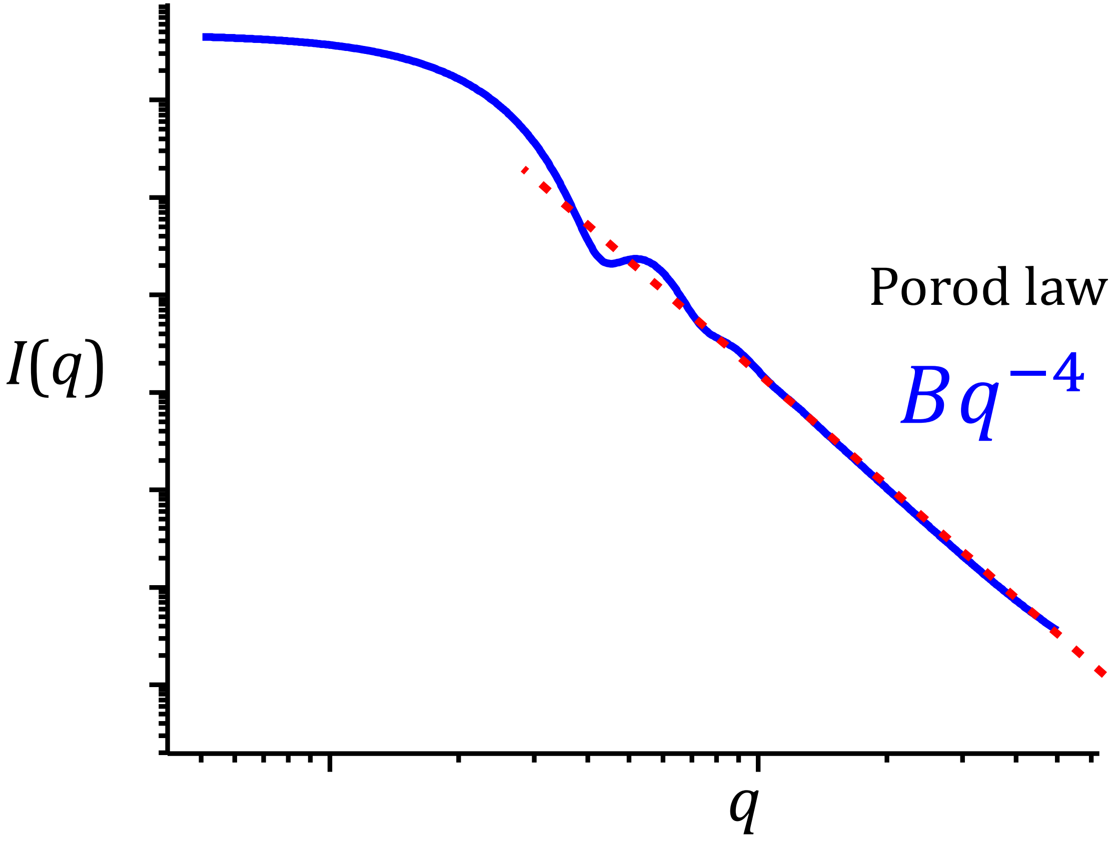
$$R_g^2 = \frac{A^2 + B^2 + C^2}{12}$$

cylinder

$$R_g^2 = \frac{R^2}{2} + \frac{L^2}{12}$$

Specific area





Characteristic volume

Characteristic area

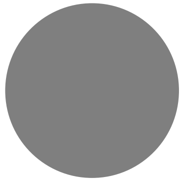
$$Q = \int_0^\infty q^2\, I(q)dq = 2\pi^2\rho^2 nV$$

$$I(q) = \frac{1}{q^4}B = \frac{1}{q^4}2\pi\rho^2 nS$$

$$\frac{S}{V} = \frac{\pi B}{Q}$$

Surface scattering

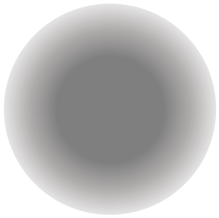
$\alpha = 4$ smooth surface

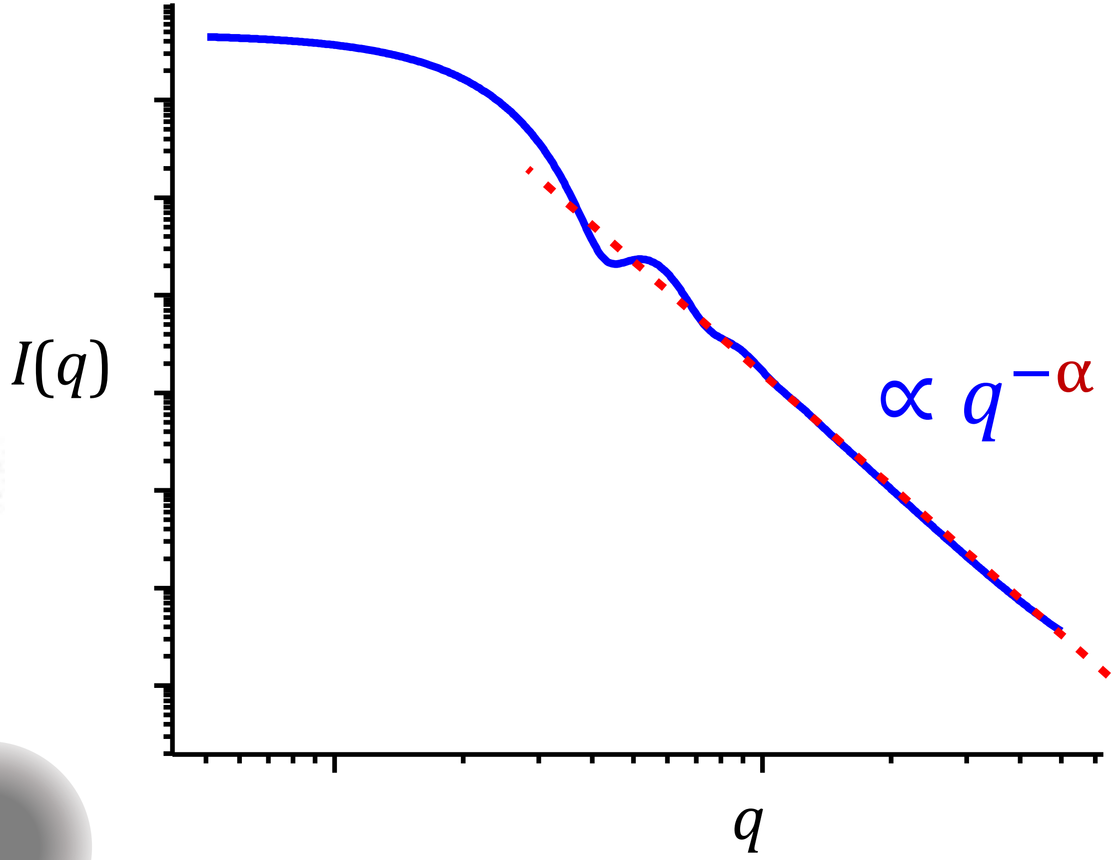


$3 < \alpha < 4$ fractal surface, $D_S = 6 - \alpha$

$4 < \alpha < 6$ diffusive shell, $\beta = (\alpha - 4)/2$

$$\rho(r) = \rho_0 \left(\frac{R-r}{d}\right)^{\beta}$$

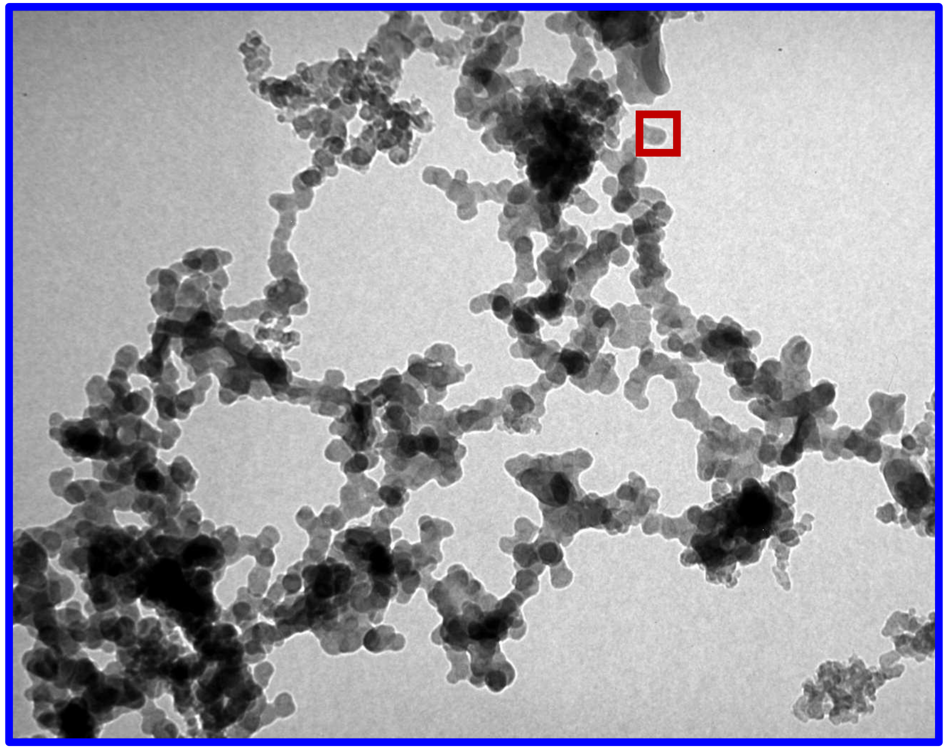


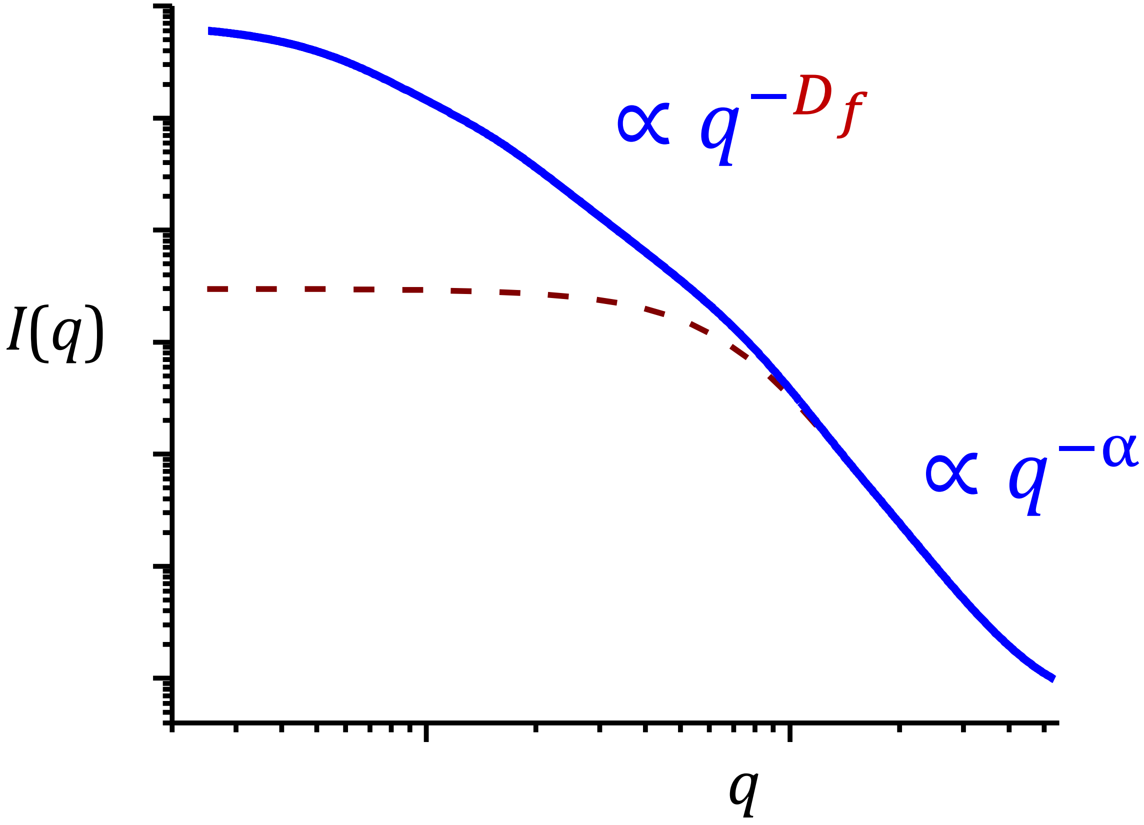


Scattering exponent → Surface type

Scattering by mass fractals

$$I(q) = nV^2(\Delta\rho)^2 P(q) S(q)$$



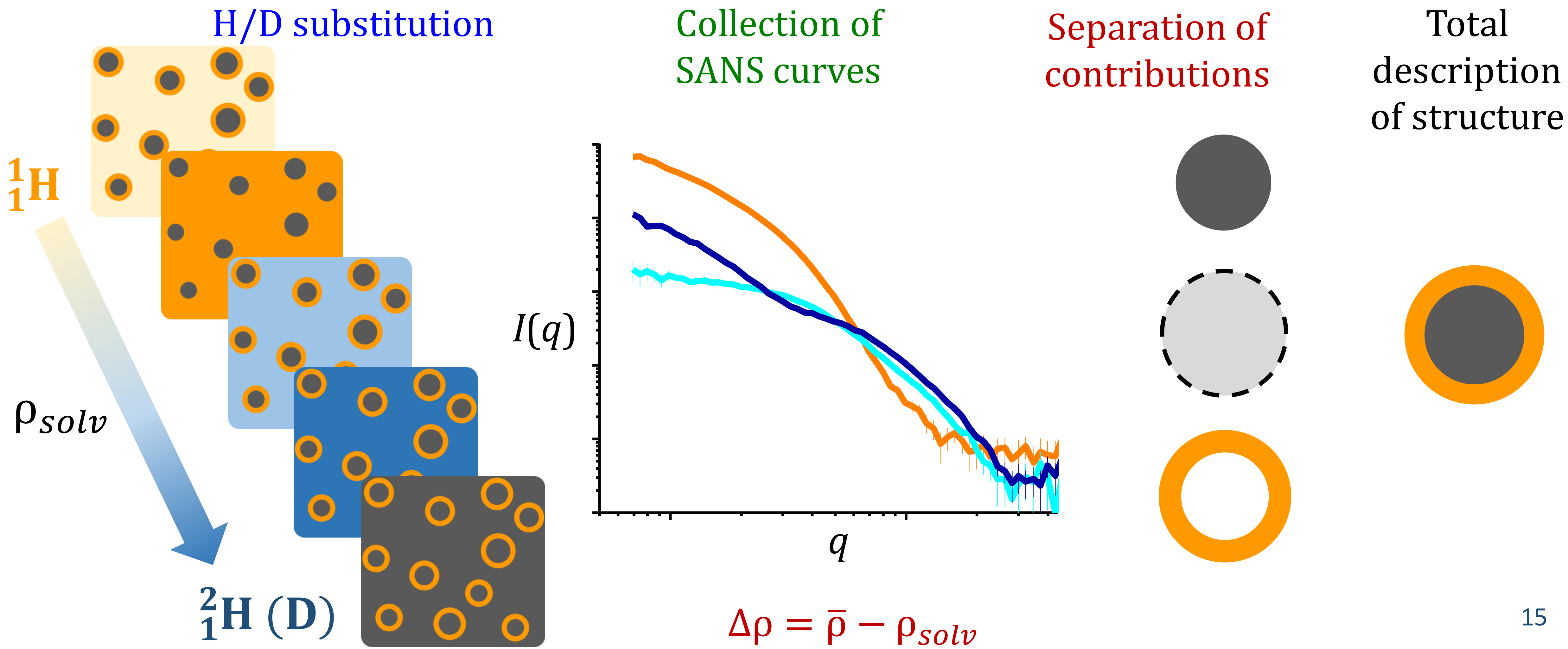


Non-compact, self-similar agglomeration $N(r) \propto r^{D_f}$ $1 < D_f < 3$

Scattering exponent → Fractal dimension

Contrast variation

$$I(q) = nV^2(\Delta\rho)^2P(q)S(q)$$



Applications of SANS

Material Science

Soft condensed matter

Biology

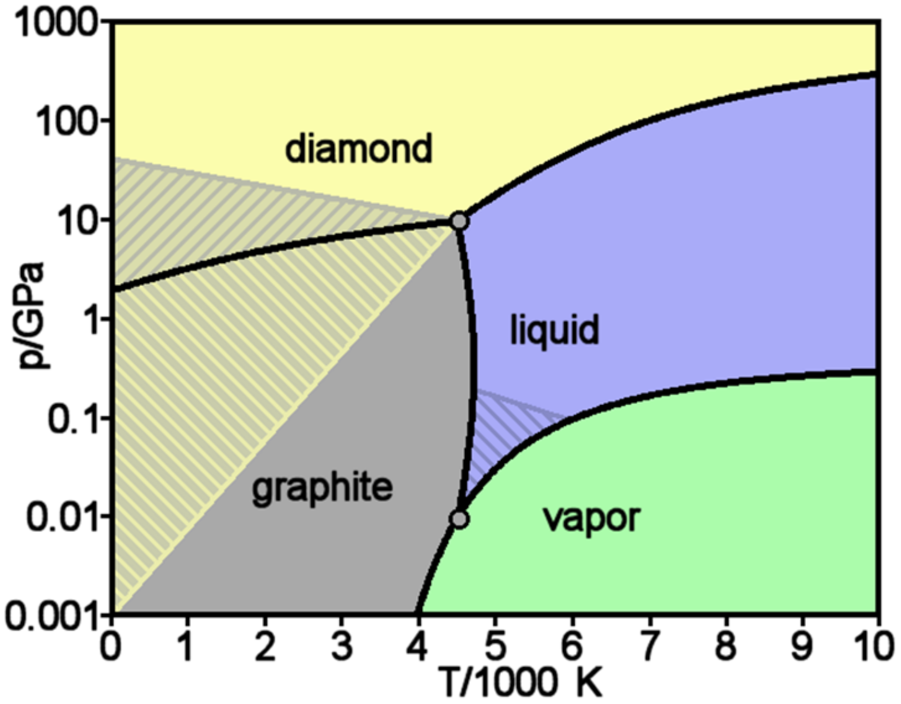
Magnetic properties

Fuel cells

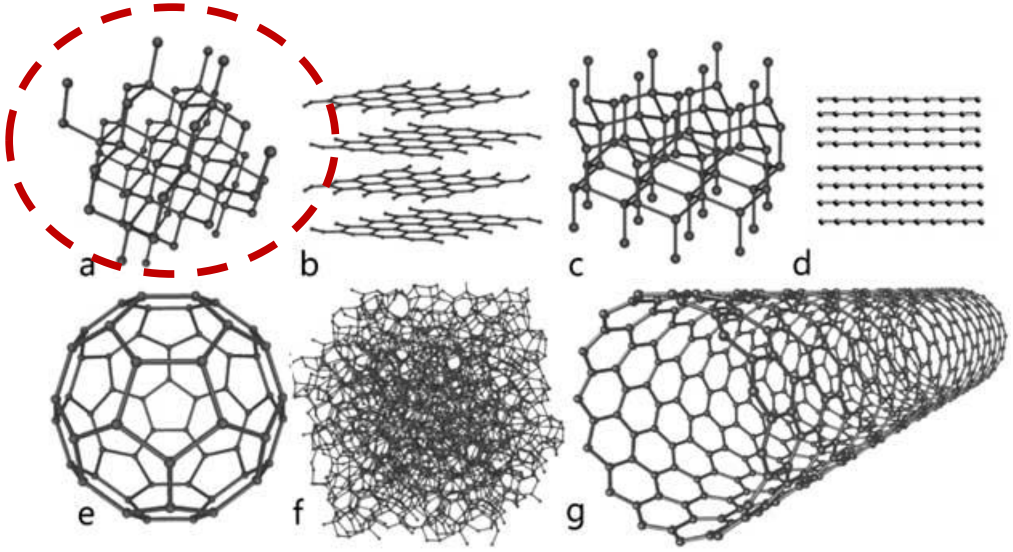
Lithium batteries

etc.

Diamond

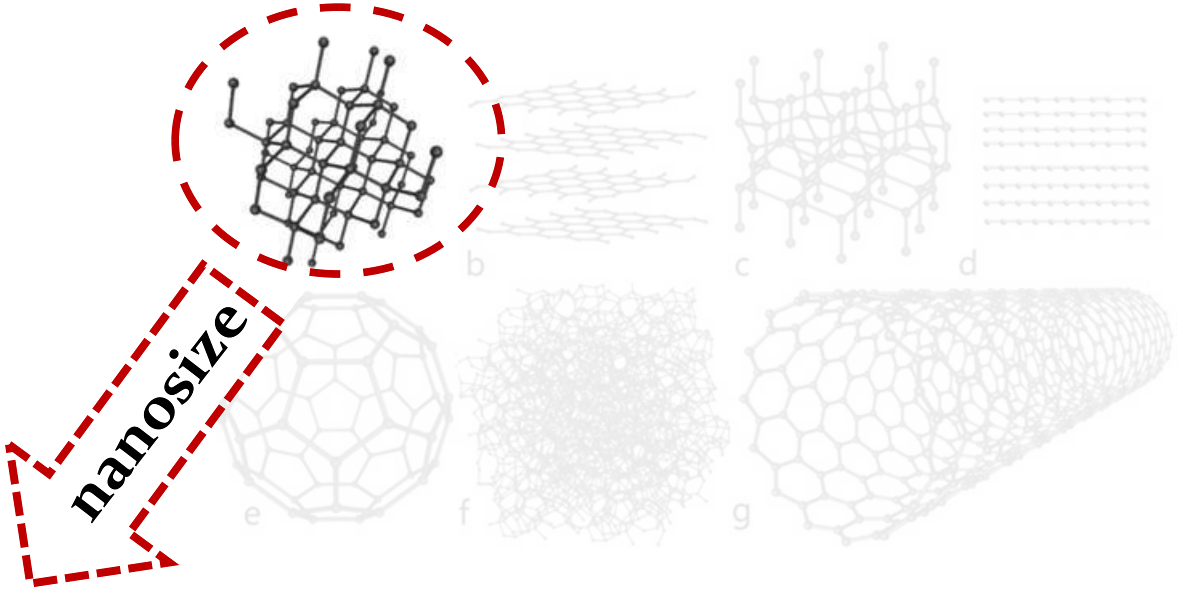


Carbon allotropes



Nanodiamond

Applications



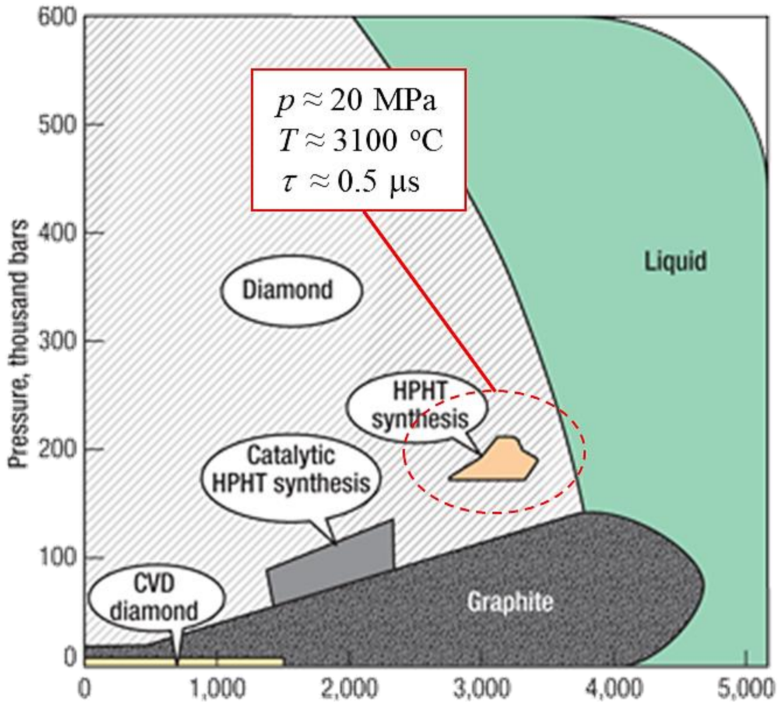
NDs in the **industry**

- Coatings
- Abrasives
- Electrodes
- Superhard composites

NDs in the **biomedical** field

- Agents for local delivery
- Labeling / Bioimaging
  - Fluorescent biomarkers
  - Photoacoustic microscopy
  - Magnetic resonance imaging
- Tissue scaffolds and surgical implants

Detonation NanoDiamond (DND)

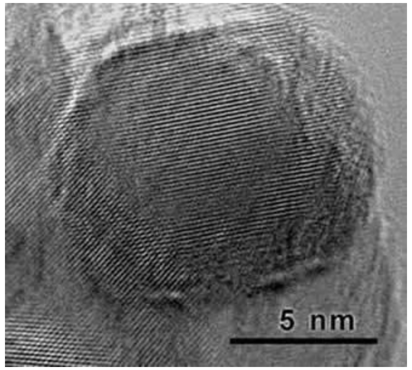


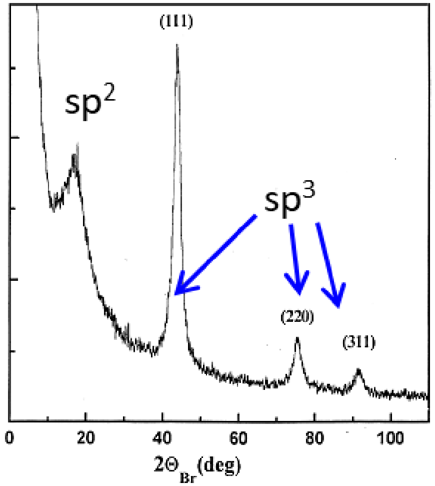
T, °C

Detonation synthesis

TNT + RDX

carbon-oxygen balance
C/O > 1

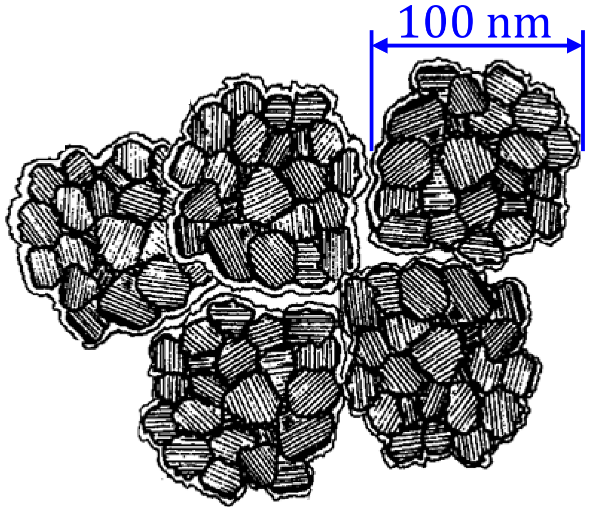




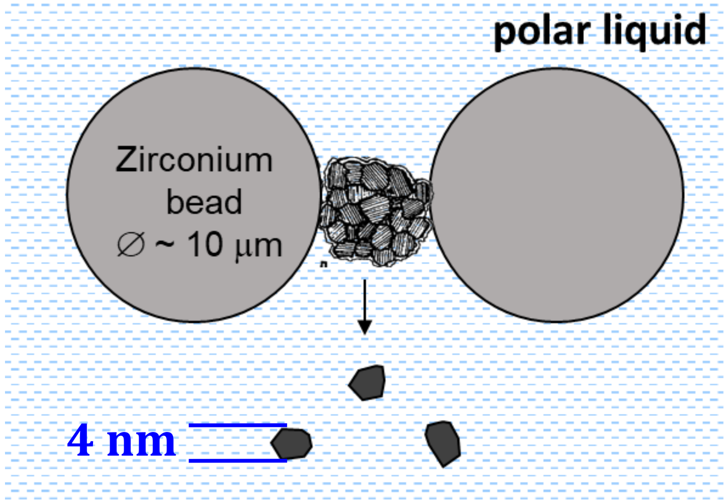
Greiner N. *et al.*, Nature 333 (1988) 440

Detonation Nanodiamond dispersion

Agglutinates

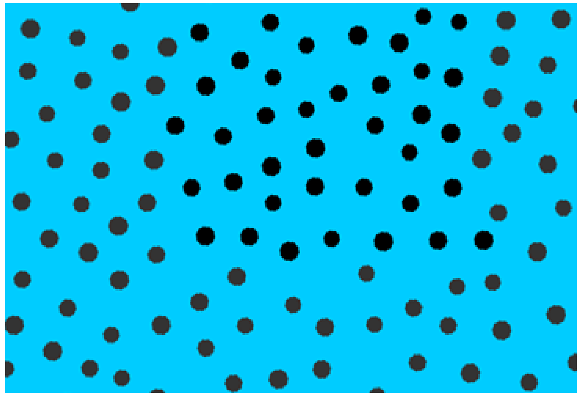


'Wet' milling

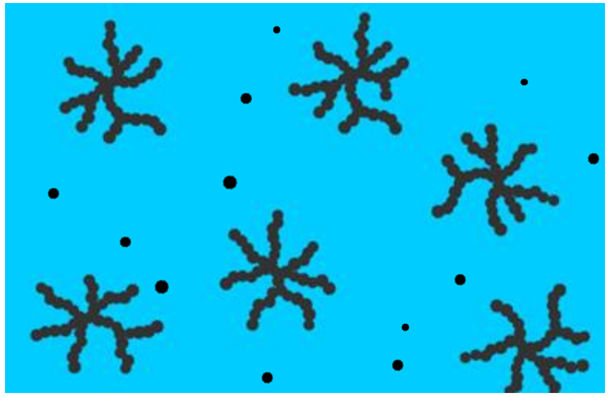


Suspension

< 0.01 wt. %

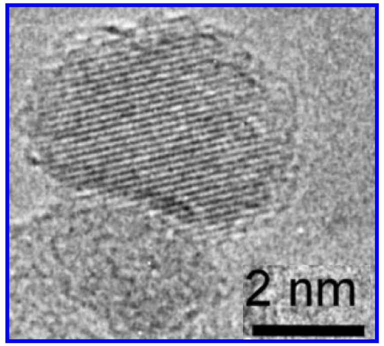


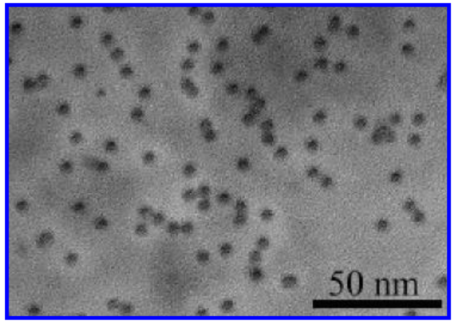
> 0.1 wt. %

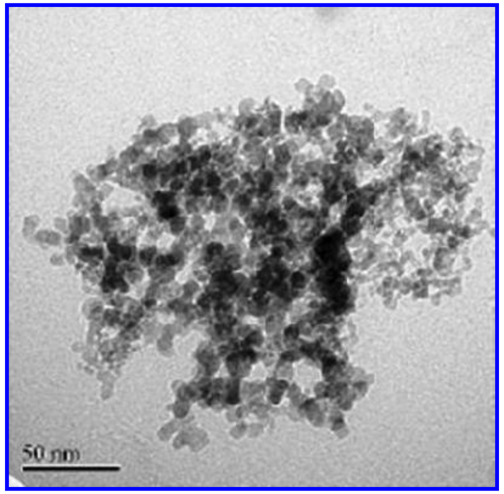


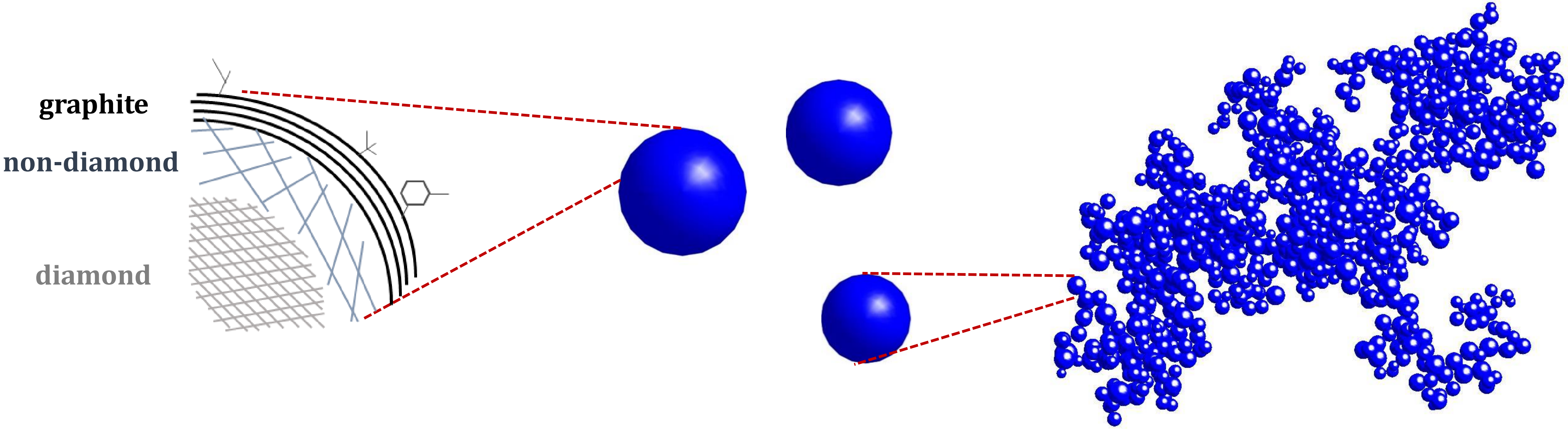
Krüger A. *et al.*, Carbon 43 (2005) 1722

Structure of DND suspensions



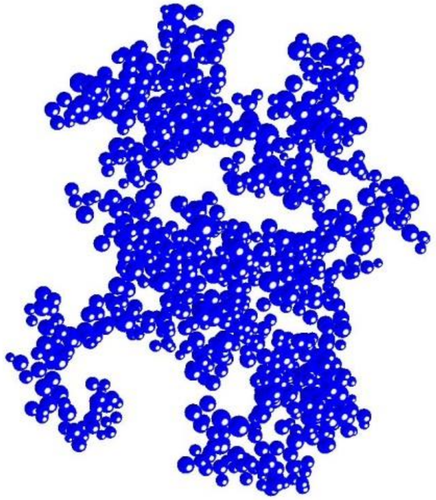


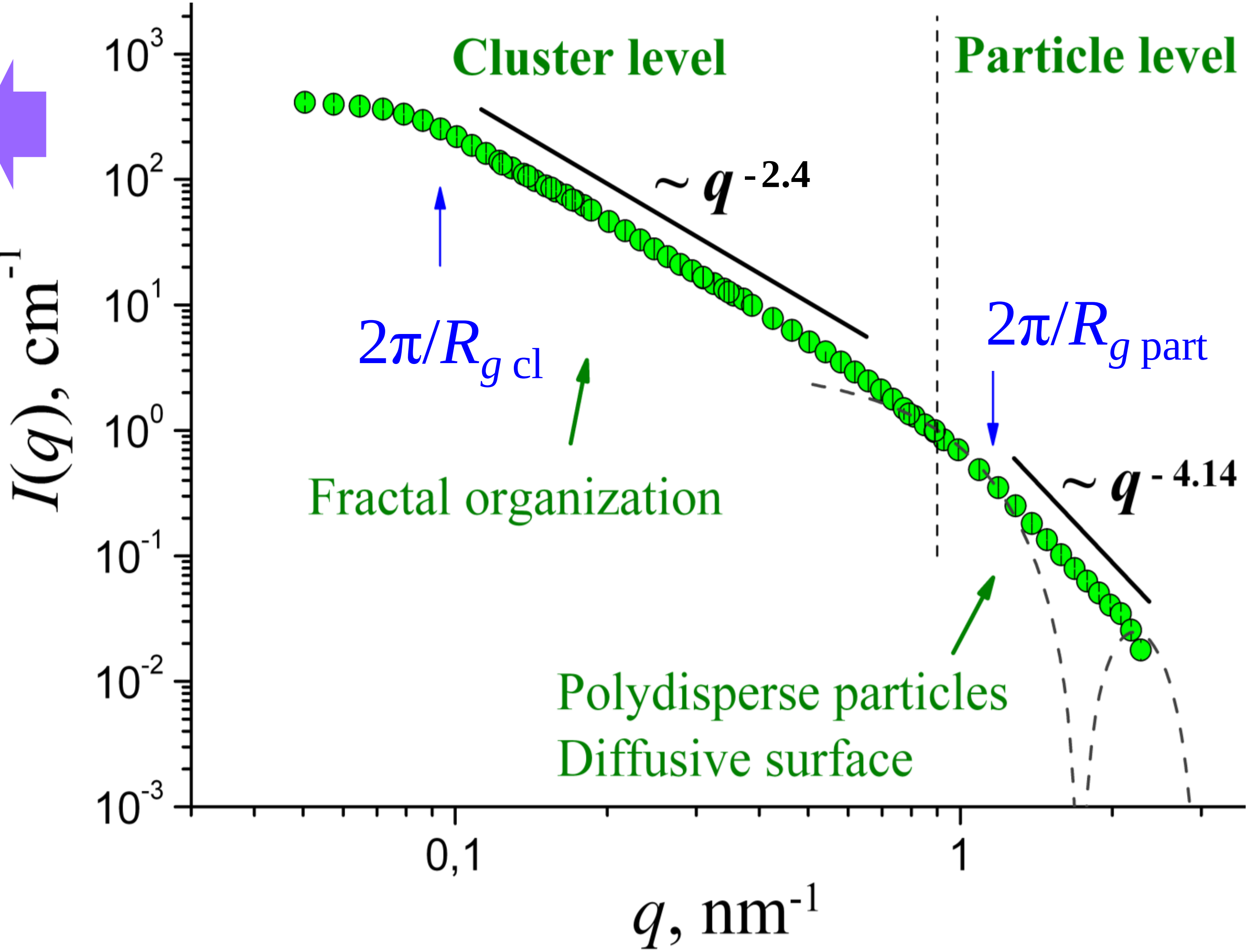


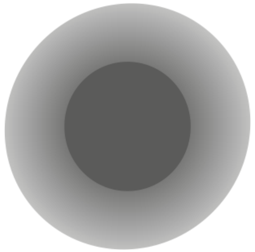


Surface Particle Cluster

SANS on DND suspensions



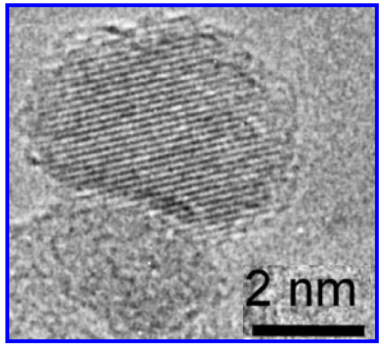


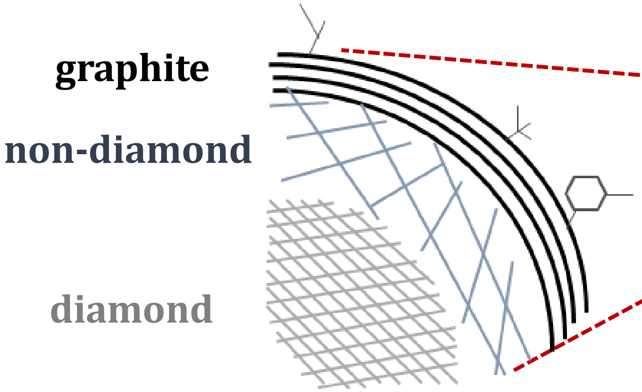


Tomchuk O.V. *et al.*, J. Phys. Chem. C 119 (2015) 794

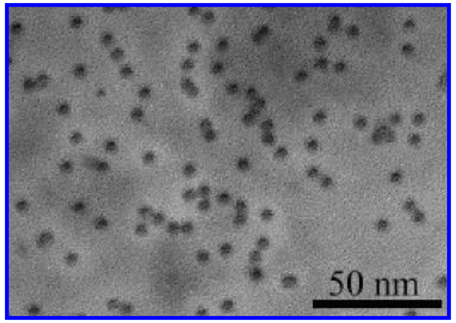
Tomchuk O.V. *et al.*, Springer Proc. Phys. 223 (2019) 201

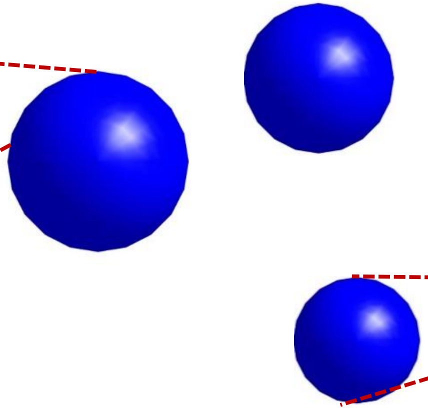
Structure of DND suspensions



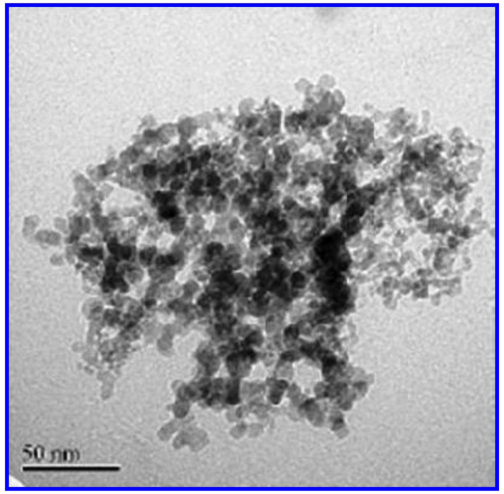


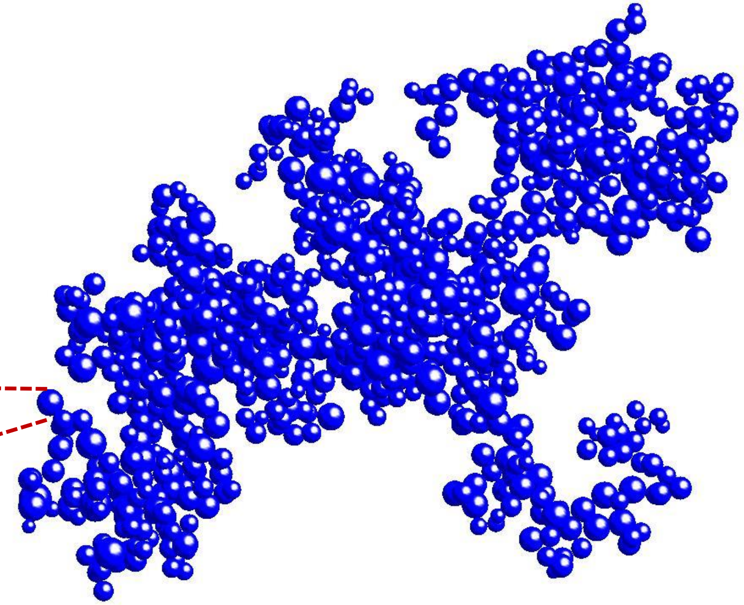
Surface





Particle





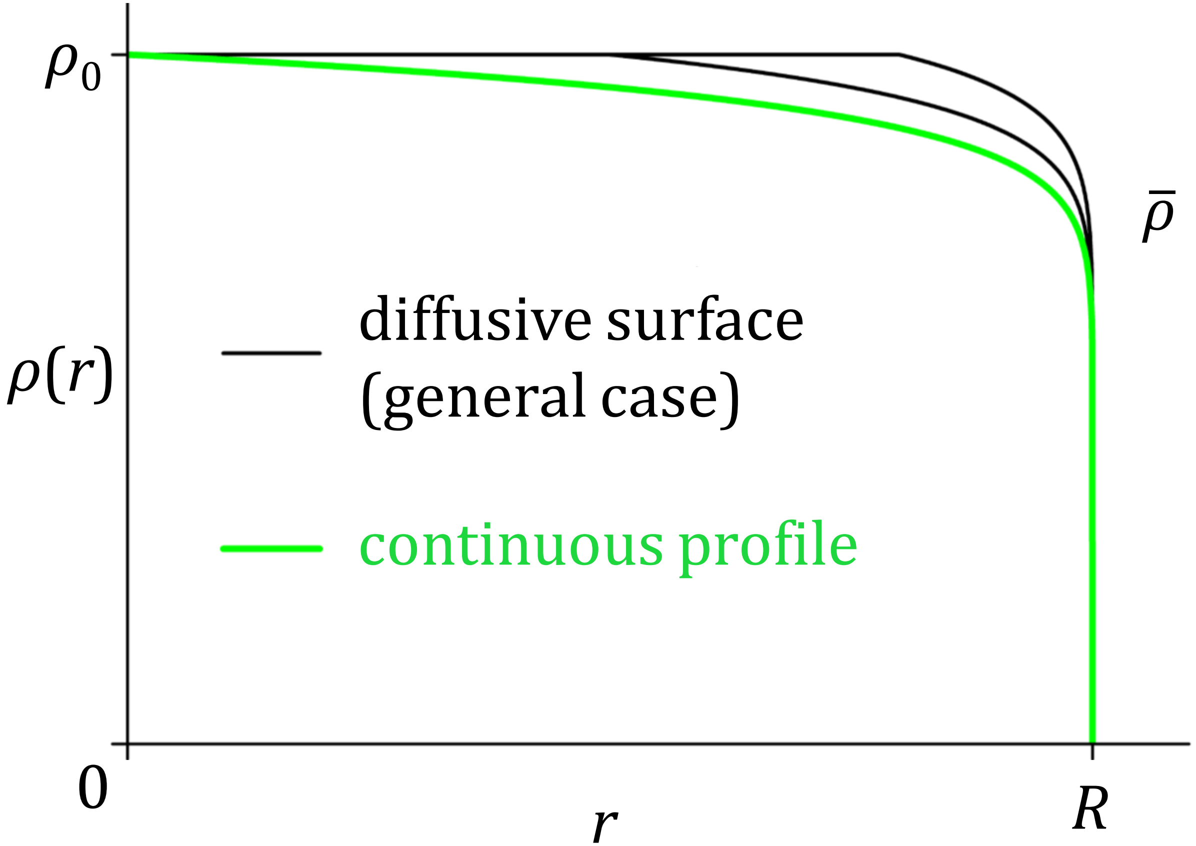
Cluster

Continuous diffusive radial profile model

$$I(q) \propto q^{-(4+2\beta)}$$

$\beta \ll 1 \qquad d \approx R$

$$\boldsymbol{\rho(r) = \rho_0 \left(1 - \frac{r}{R}\right)^{\beta}}$$



$$\bar{\rho} = \frac{6\rho_0}{(\beta+1)(\beta+2)(\beta+3)}$$

Does not depend on the size!

Avdeev M.V., Tomchuk O.V. *et al.*, J. Phys.: Cond. Matt. 25 (2013) 445001

Tomchuk O.V. *et al.*, J. Appl. Cryst. 47 (2014) 642

Contrast variation on DND suspensions

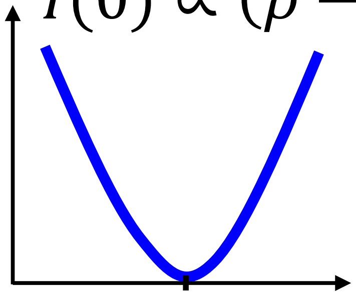
Comparison of theory and experiment

mean scattering length density

$$\bar{\rho}_{\mathrm{theor}} = \frac{6\rho_0}{(\beta+1)(\beta+2)(\beta+3)}$$

vs.

$$I(0) \propto (\bar{\rho} - \rho_{\mathrm{solv}})^2$$



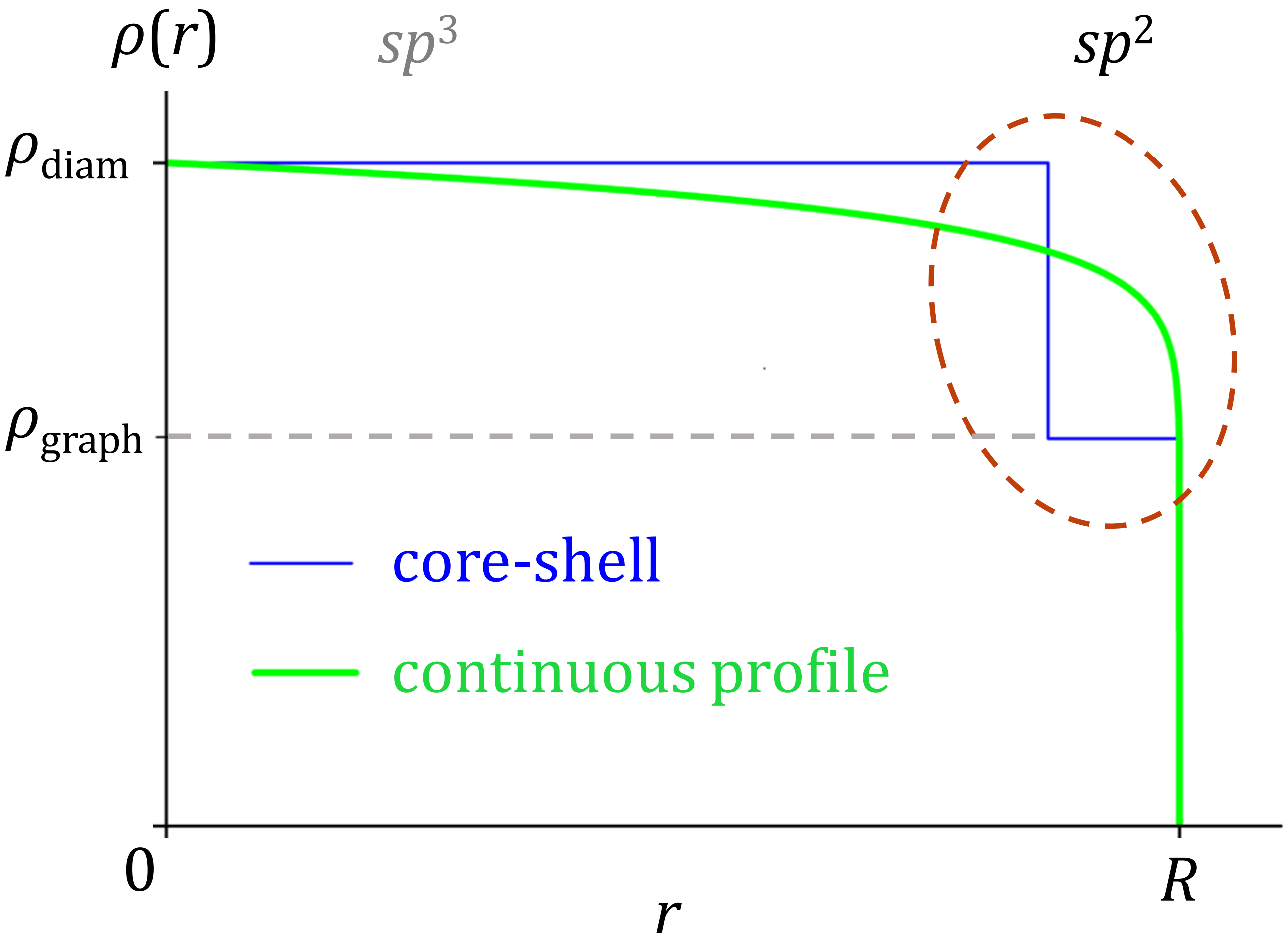
match-point
$\Delta\rho = 0$

	1	***2***	***3***	***4***
	water	water	water	DMSO
$\bar{\boldsymbol{\rho}}_{\mathrm{exper}}$	10.5(5)	11.0(4)	10.8(6)	10.2(4)
$\bar{\boldsymbol{\rho}}_{\mathrm{theor}}$	10.4(3)	10.8(3)	10.6(5)	10.4(3)
	1%	1.8%	1.9%	2%

The continuous profile of particles with a diffuse interface describes the experiment

Avdeev M.V., Tomchuk O.V. *et al.*, J. Phys.: Cond. Matt. 25 (2013) 445001
Tomchuk O.V. *et al.*, J. Appl. Cryst. 47 (2014) 642

Structure of DND surface by SANS

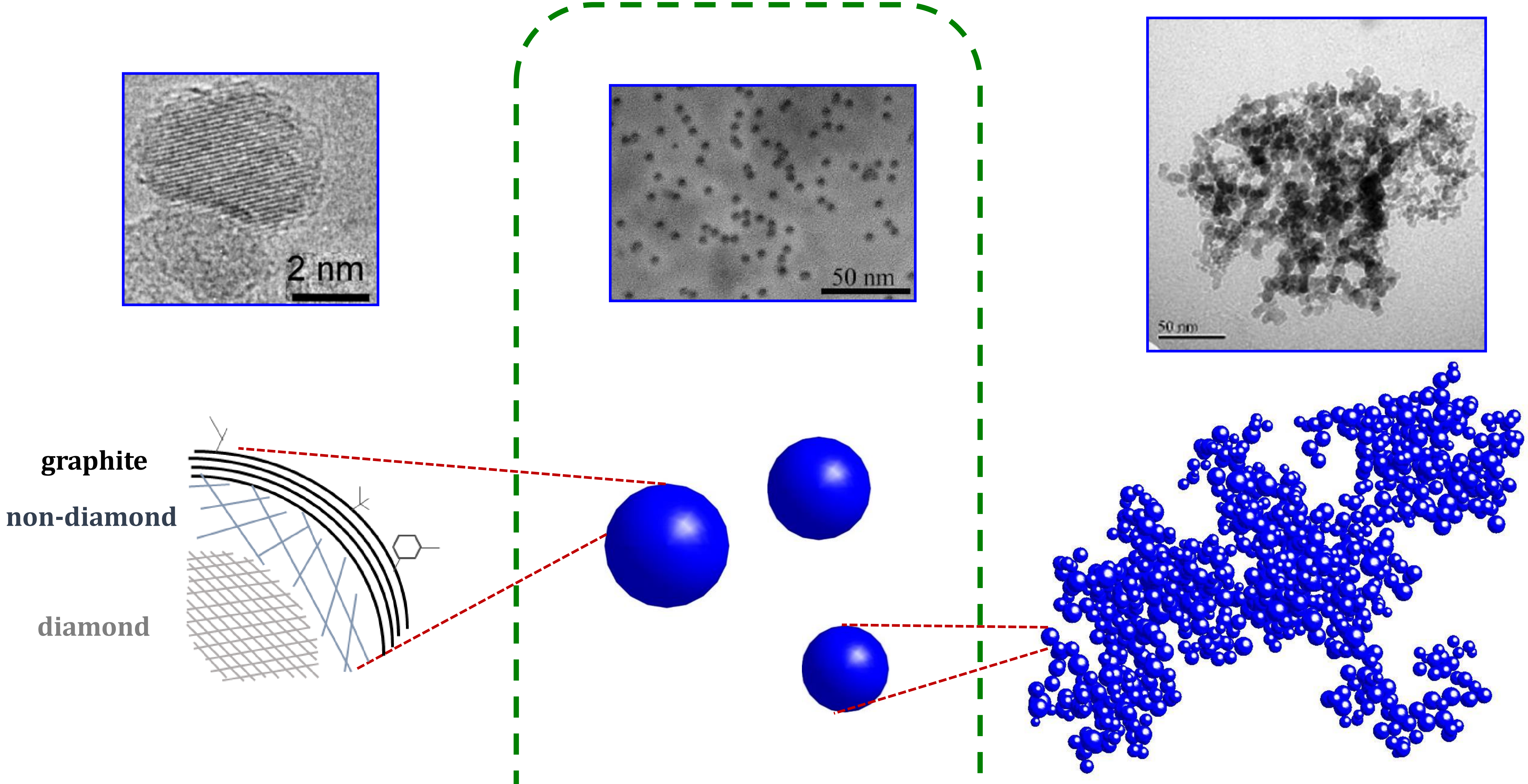


Continuous transition from diamond to grapheme-like state of carbon

Avdeev M.V., Tomchuk O.V. *et al*., J. Phys.: Cond. Matt. 25 (2013) 445001

Tomchuk O.V. *et al*., J. Appl. Cryst. 47 (2014) 642

Structure of DND suspensions



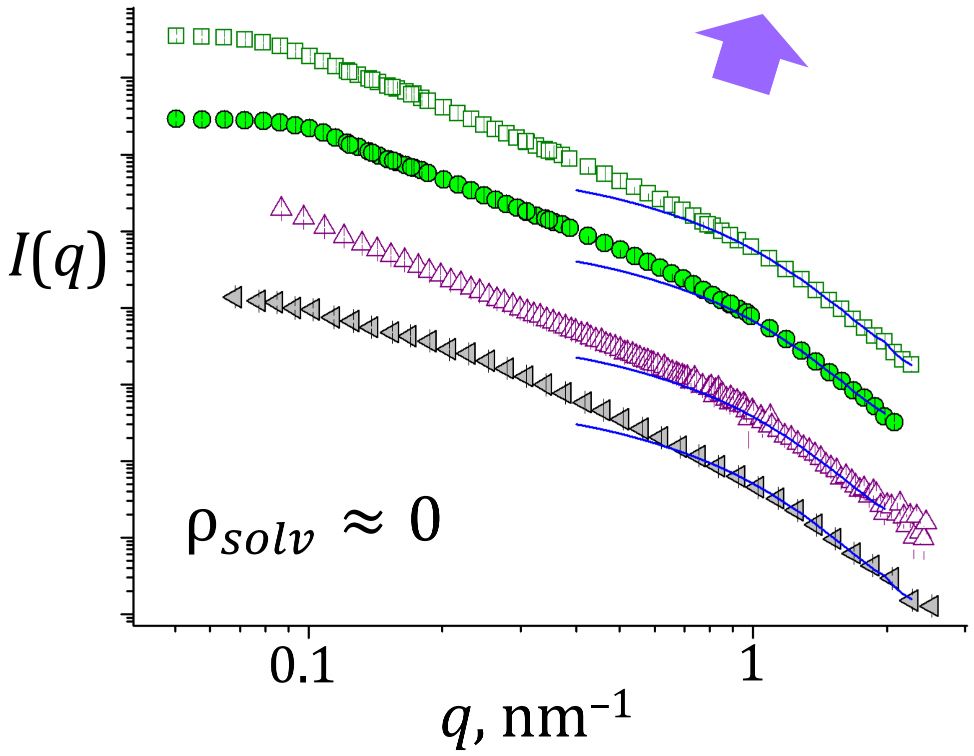
Surface

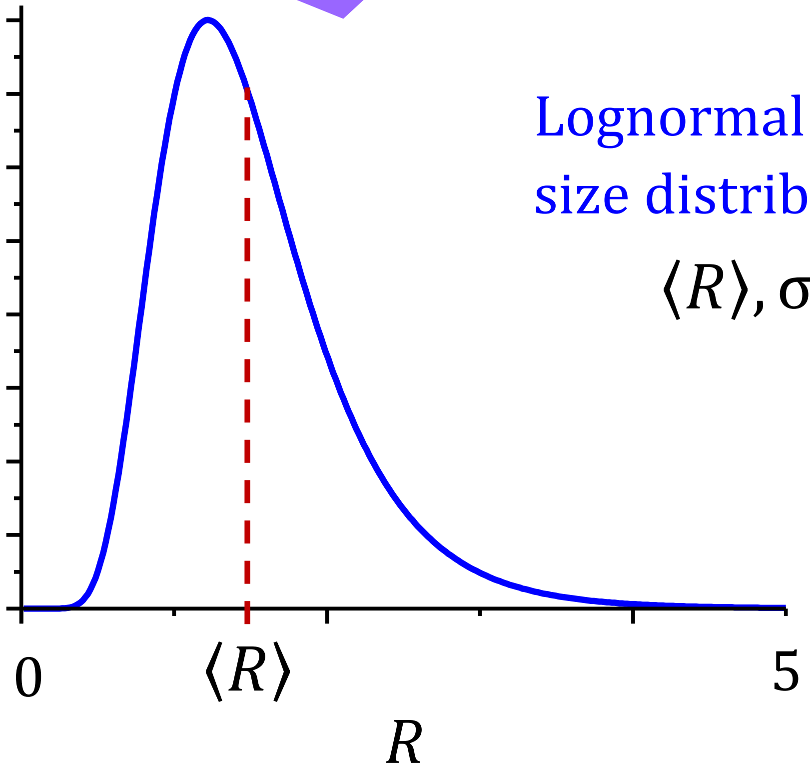
Particle

Cluster

Analysis of polydispersity of particles with a diffuse surface

$$I(0), R_g, B, \beta \quad \Rightarrow \quad PDI = \frac{B\left(R_g\right)^{4+2\beta}}{I(0)f(\beta)}$$





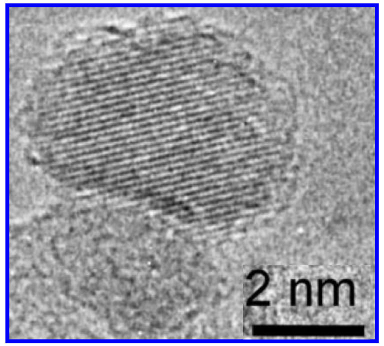
Lognormal size distribution

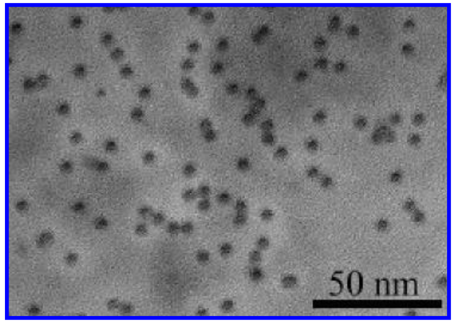
$\langle R \rangle, \sigma$

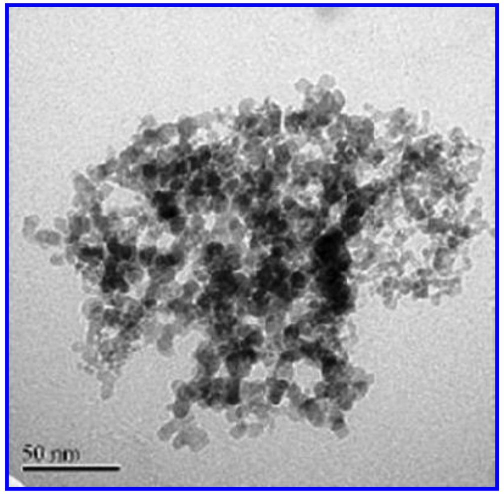
Polydispersity ≈ 40%

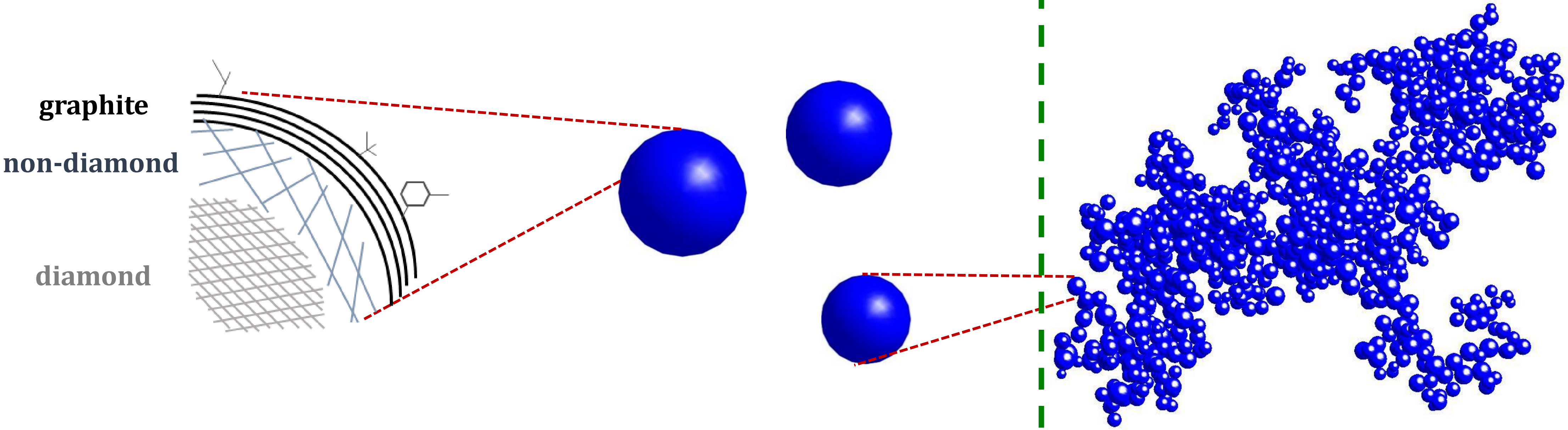
Tomchuk O.V. *et al.*, J. Appl. Cryst. 47 (2014) 642

Structure of DND suspensions









Surface

Particle

Cluster

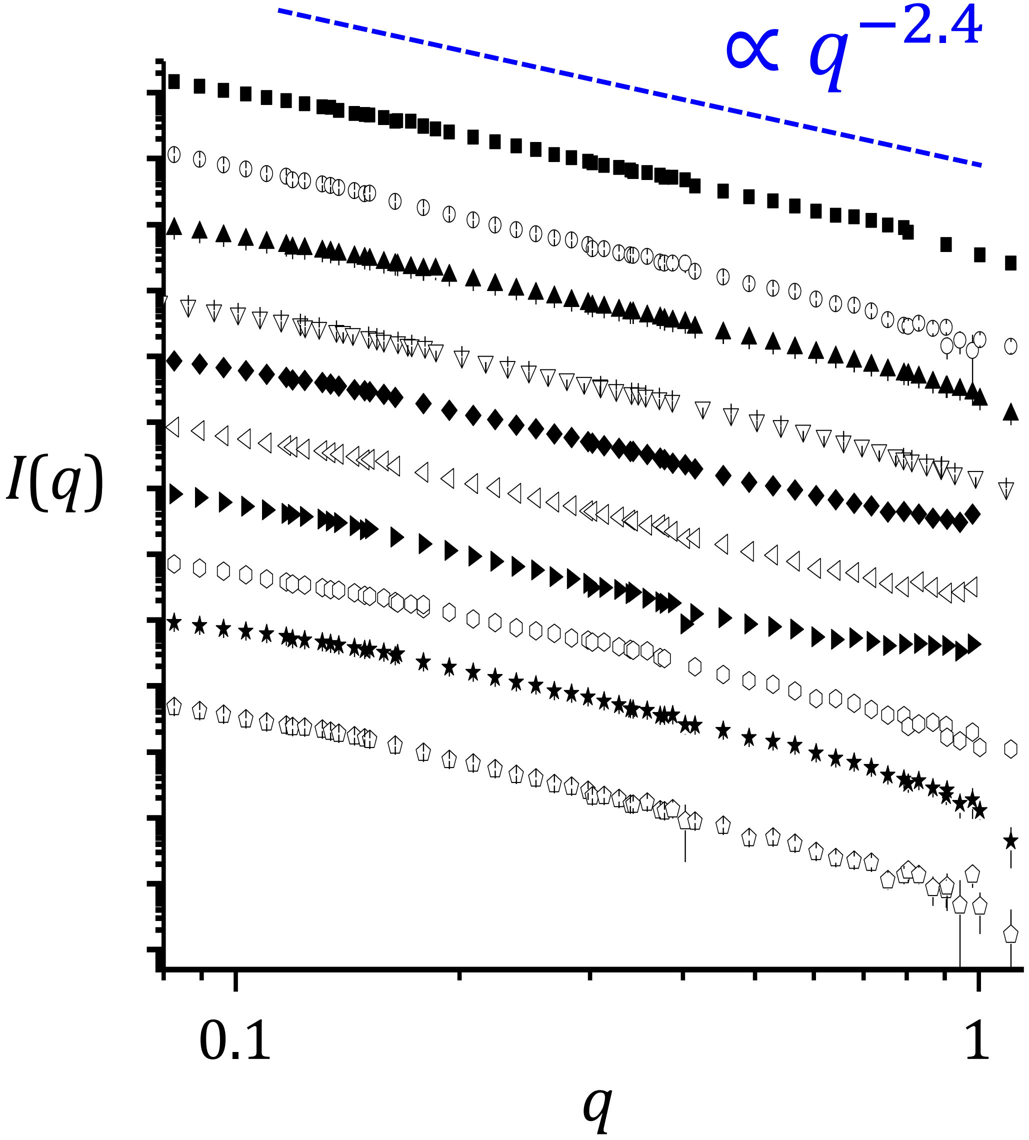
Repeatable cluster structure

$I(q) \propto q^{-D_f}$

$\boldsymbol{D_f = 2.3 - 2.5}$

Common clustering mechanism:

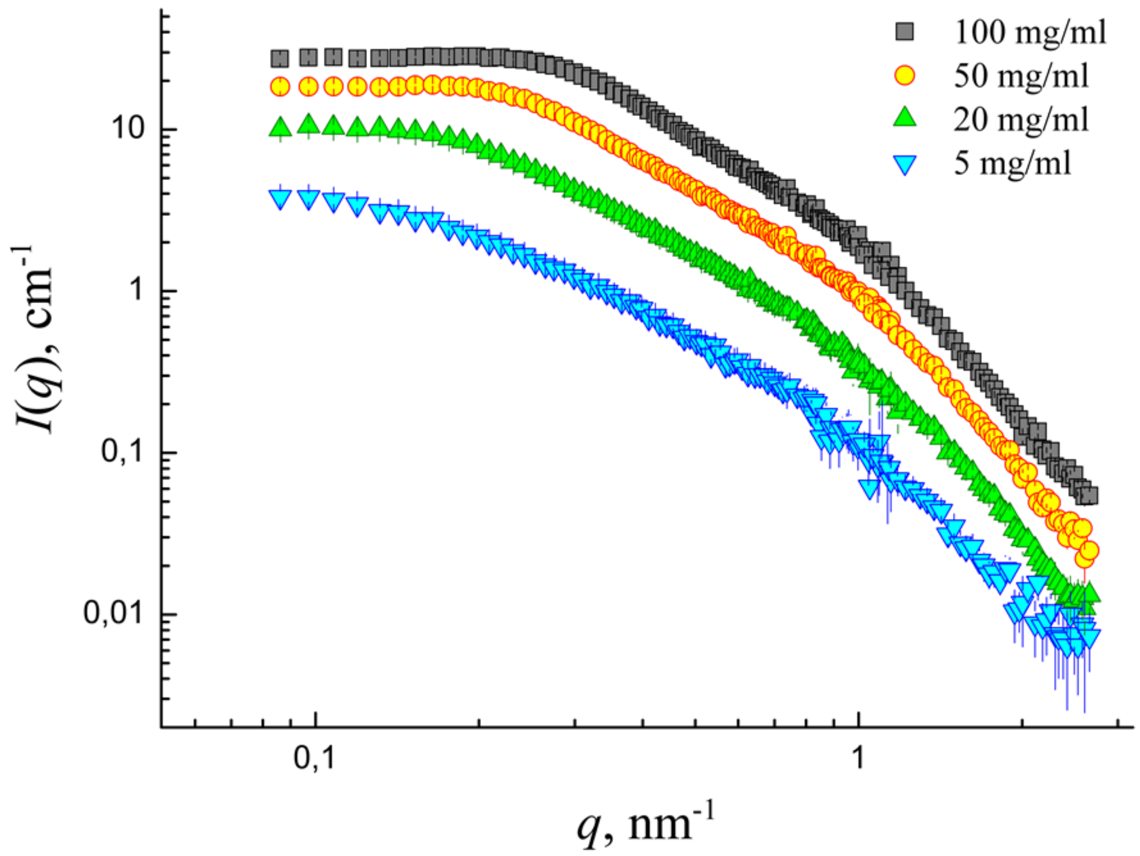
Diffusion-limited aggregation

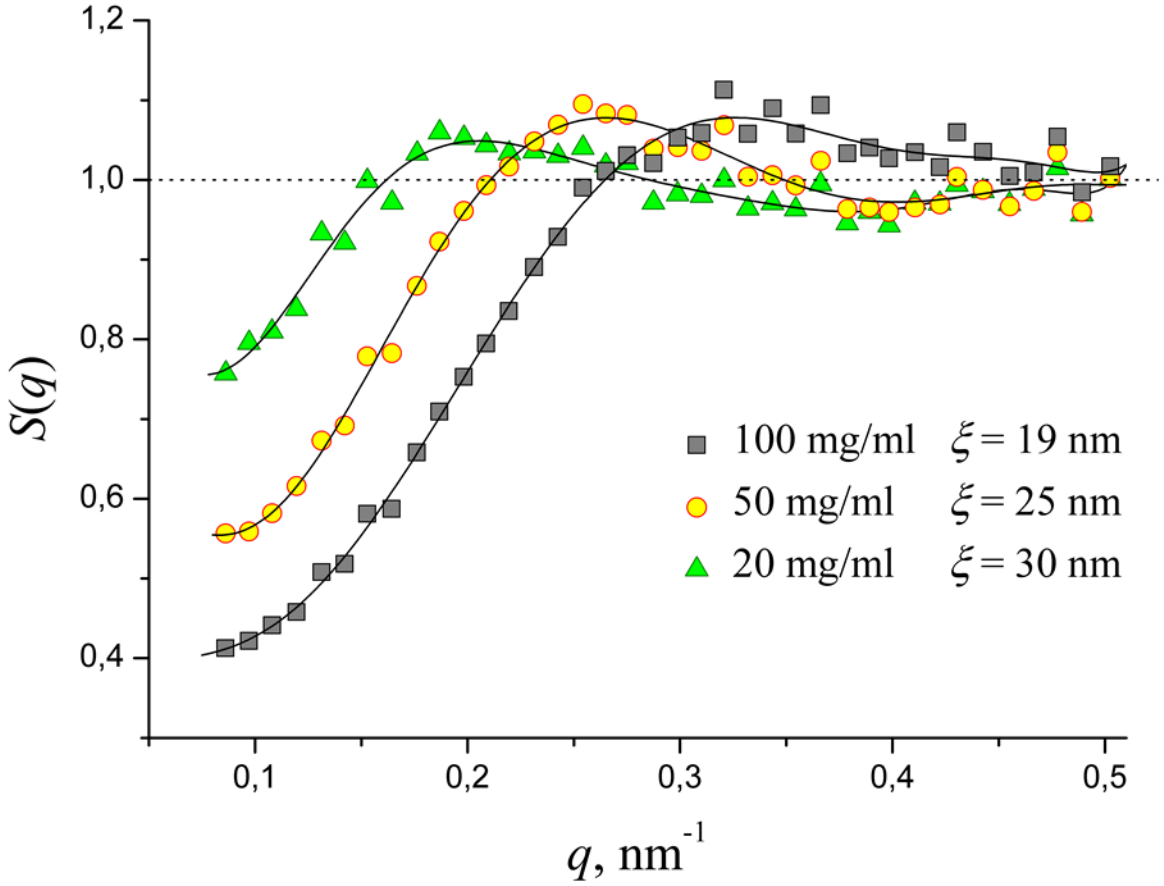


Tomchuk O.V. *et al.*, J. Surf. Inv. 6 (2012) 821

Avdeev M.V., Tomchuk O.V. *et al.*, Chem. Phys. Lett. 658 (2016) 58

Interaction of nanodiamond clusters in suspensions





repulsion prevails in the system

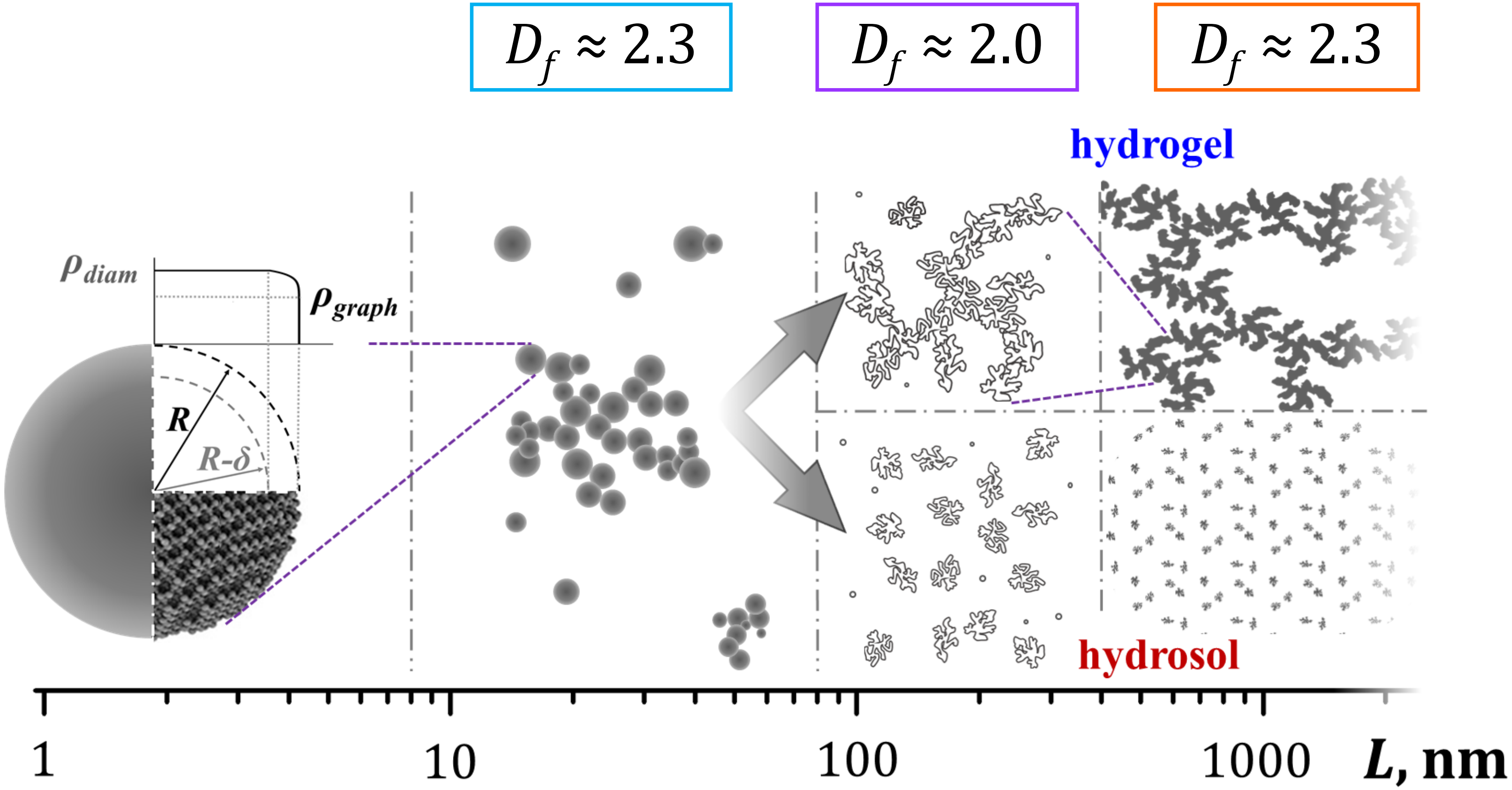
overlapping is possible at high concentrations

Tomchuk O.V. *et al.*, Springer Proc. Phys., 223 (2019) 201

Tomchuk O.V. *et al.*, J. Mol. Liq. 354 (2022) 118816

Reversible sol-gel transition in DND dispersions

Thixotropy



Two-stage gelation is the basis of the thixotropy effect

Tomchuk O.V. *et al.*, J. Phys. Chem. C 123 (2019) 18028

Conclusions on nanodiamond particles

- ♦ Continuous diamond-graphite interface in detonation nanodiamond particles
- ♦ Both particles and clusters are characterized by high polydispersity
- ♦ Cluster formation is well described by the diffusion-limited aggregation model
- ♦ Suspension stability is determined by the repulsive inter-cluster interaction
- ♦ Branched structure suggests their overlapping at high concentrations
- ♦ Further concentrating leads to reversible gelation effect

Summary on SANS

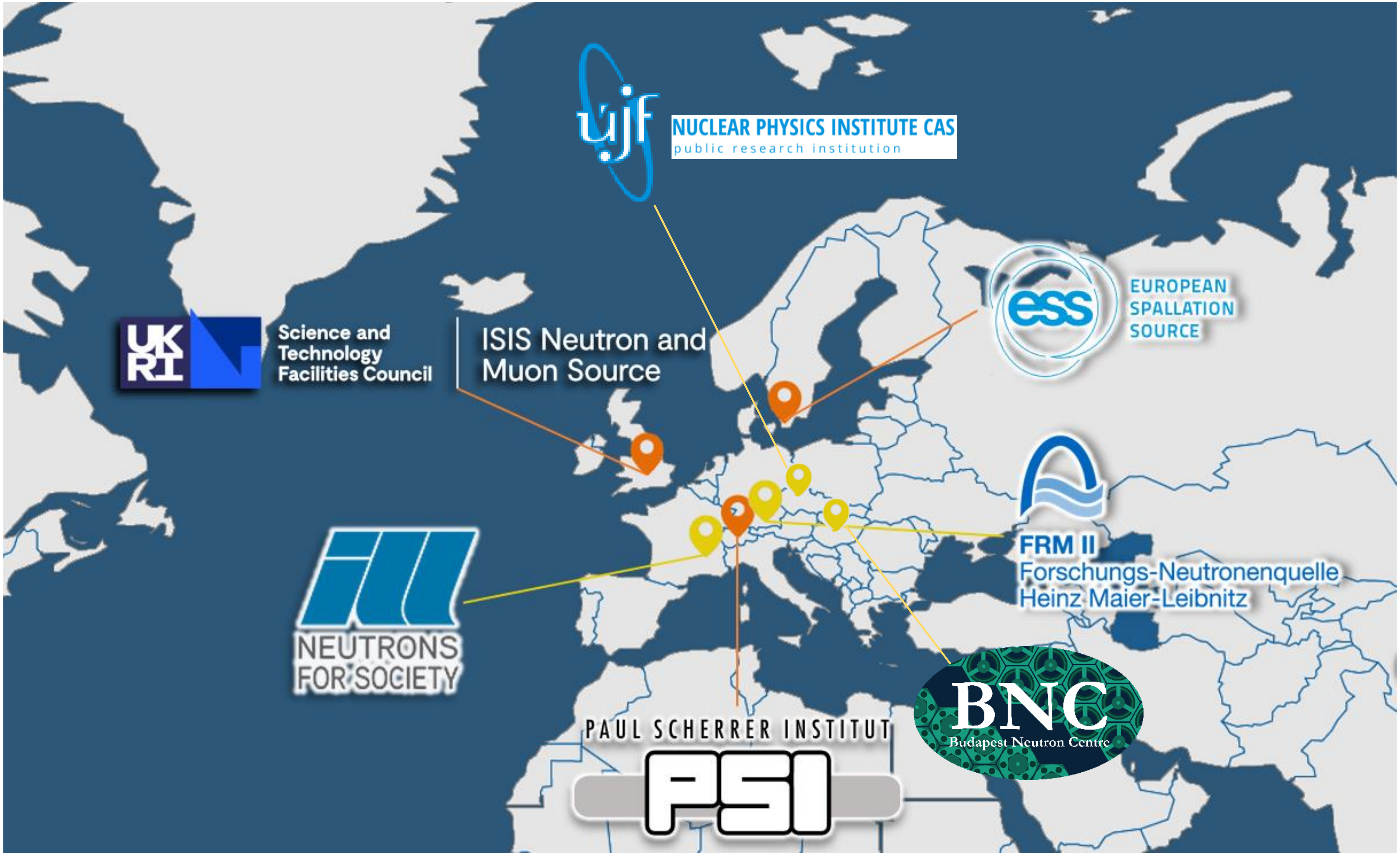
ADVANTAGES

- Well-suited for mesoscale (nm – µm)
- High penetration ability
- Noninvasivity
- Light elements sensitivity
- Isotope sensitivity
- Magnetic sensitivity

DISADVANTAGES

- High operational cost
- Low fluxes
- Relatively large sample (mm^3 – cm^3)

Available neutron sources



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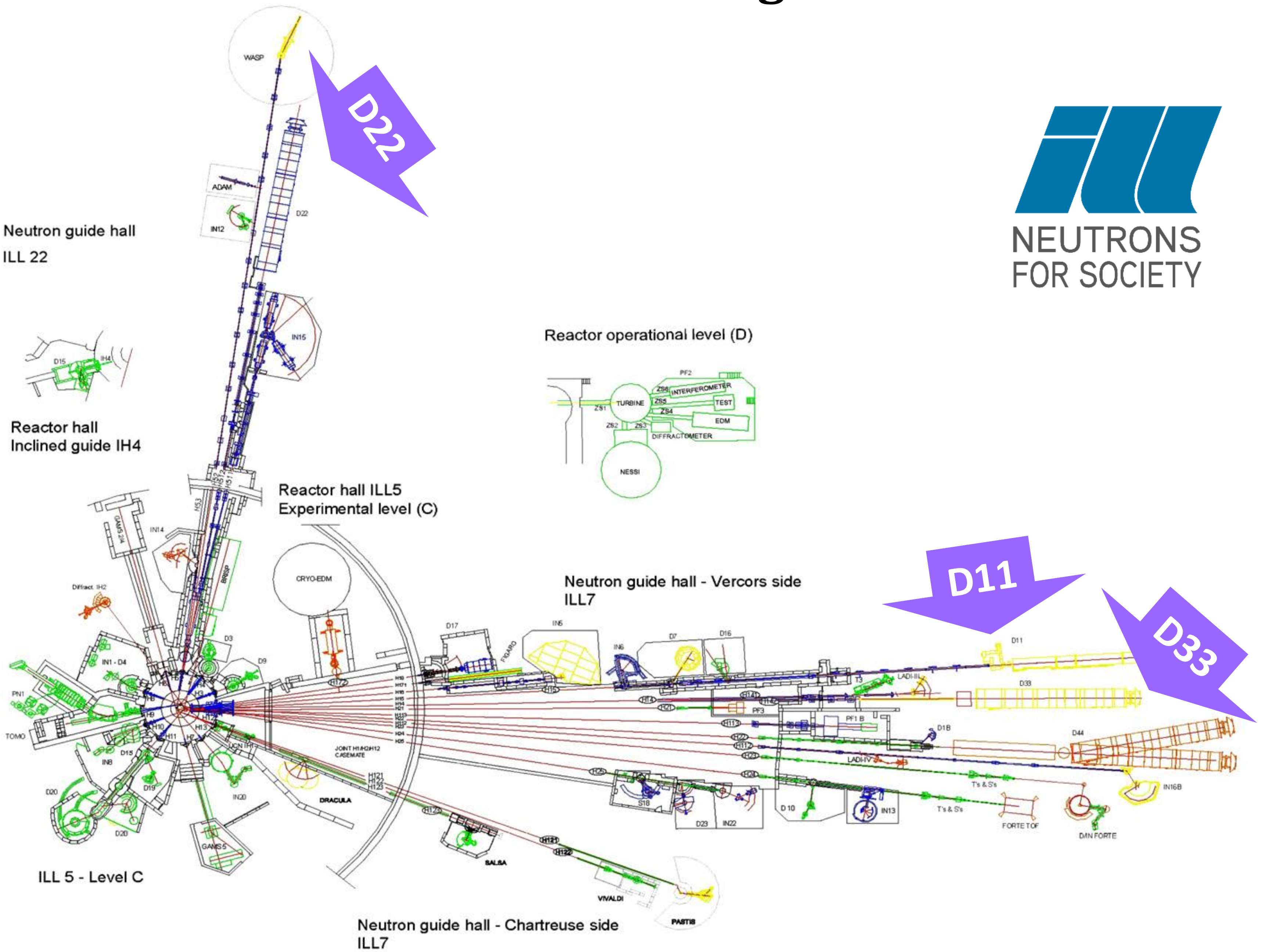

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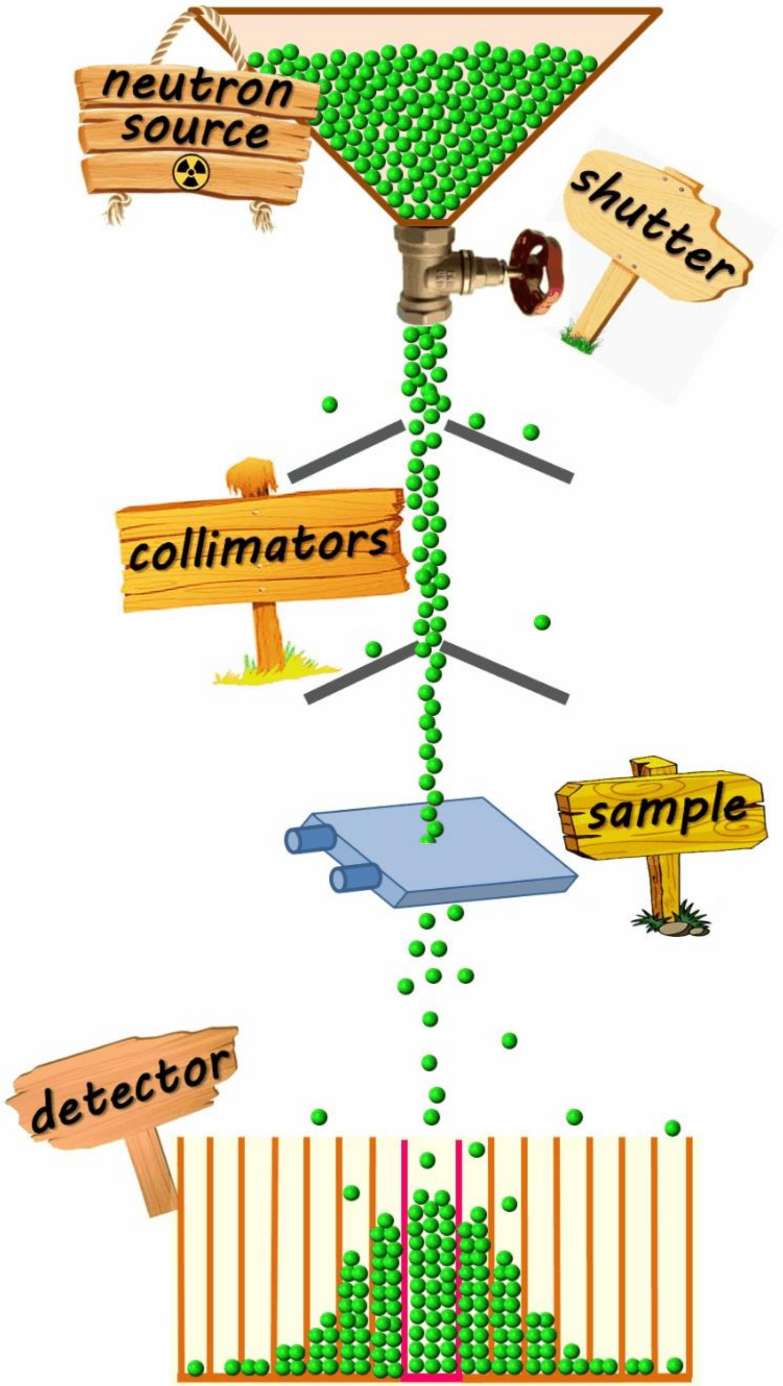

Dziękuję za uwagę!

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