Neutron study of multilevel structures of diamond gels

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Nanodiamonds
Functionalisation, Suspensions, First Prepared DND-Gels

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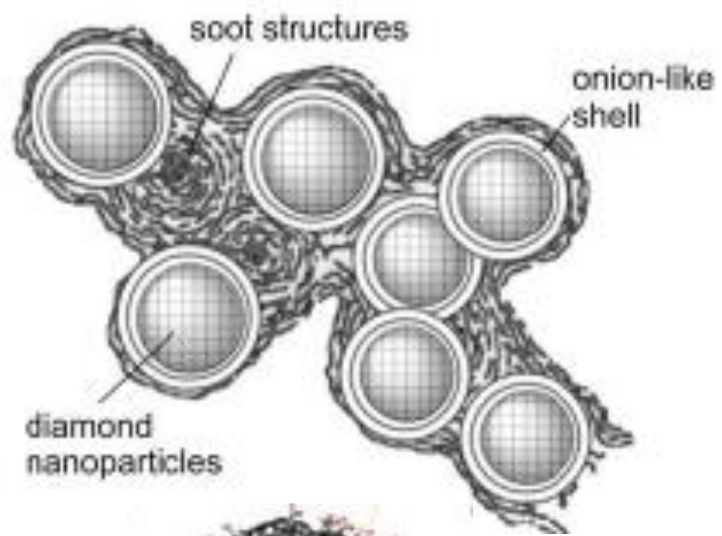
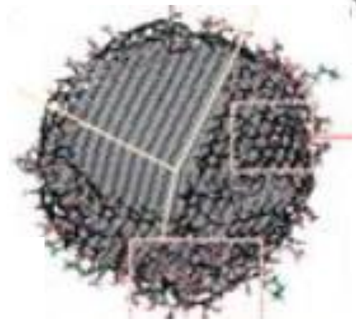
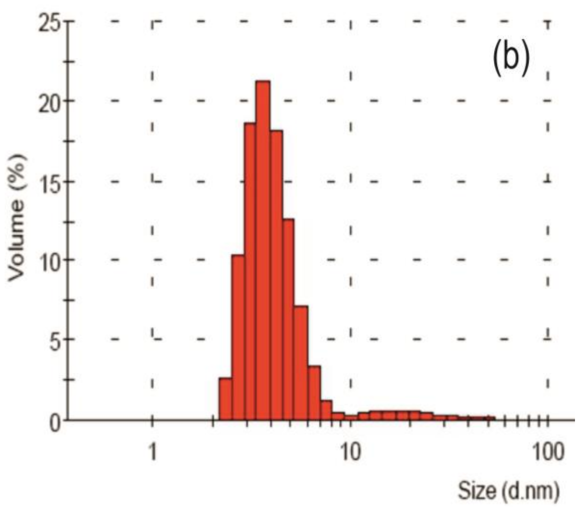
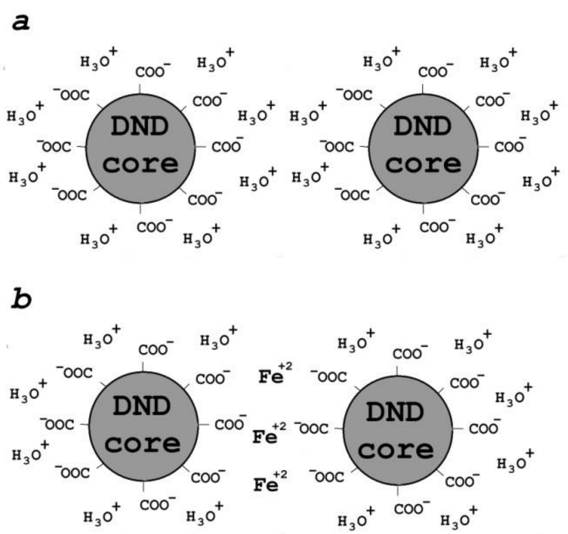


Fine techniques developed at PTI for disaggregation of diamonds materials, surface treatment (Hydrogen, Rare Earth Elements)







DND-Suspensions
Formation of double electric layer around particles by dissociation of carboxyl groups (a),
coagulation of DND via a formation of bridges in the presence of Fe ions (b)

High Lights

SANS - studies of first prepared hydrogels of diamonds with charged surface

Short-range order in the ensembles of carbon particles (size **D ~ 6 nm**) associated into fractal clusters interpenetrating and forming a network at scales ~ **100 nm**

Structures are stable in the concentration range, **C ~ 1-5 wt. %,** at ambient temperature

Cross sections $\sigma(q)$ for gels demonstrate a kink at $q \sim q^* = 2\pi/D \approx 1\ \mathrm{nm}^{-1}$ which corresponds to characteristic size of diamond particle

At $q > q^*$ dominates the scattering from single particles, $\sigma(q) \sim 1/q^4$ where the exponent indicates slightly diffusive borders of particles

At $q < q^*$ the cross sections $\sigma(q) \sim 1/q^{d_f}$ indicate the interference in scattering from the particles integrated into large clusters, fractal dimension $d_f \sim 2$

Solutions' structuring

Hydrogels of detonation nanodiamonds
Ioffe Physycal & Thechnical Institute, St.Petersburg

Particles: diamond, diameter ***~ 5 nm,*** with attached carboxyl groups or other oxygen containing groups

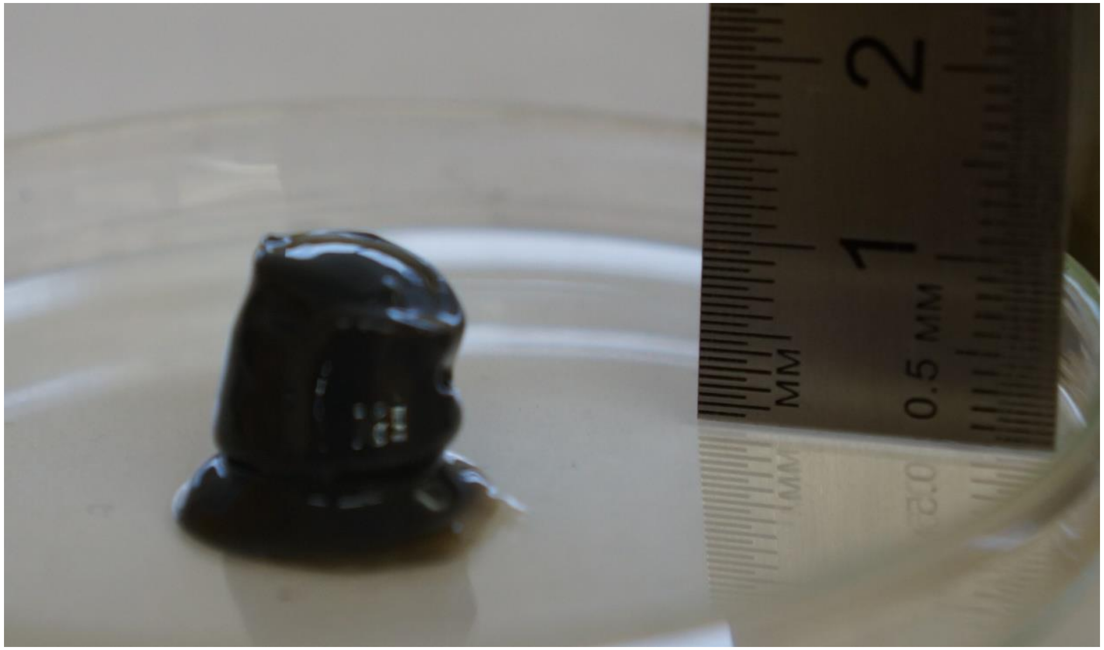
Gel: ***Stable hydrosol of*** diamonds with positive (negative) potential
$\zeta \cong$ ***0.04-0.05 V***) to prevent aggregation → ***Water Evaporation***
Sonication, Separation in Centrifuge

Particles' surface stabilization - annealing on the air (in hydrogen flow)

1. A.E.Aleksenskiy, E.Eydelman, A.Ya.Vul'. Deagglomeration of Detonation Nanodimonds. Nanotechnology Letters, 3, N1, 68-74 (2011)

2. A.Ya.Vul', A. T. Dideikin, A.E. Aleksenskiy, M. V. Baidakova. Detonation Nanodiamonds. Synthesis, Properties and Applications. In: "Nanodiamond", Ed O. A. Williams, Cardiff University, UK Royal Society of Chemistry "Nanoscience and Nanotechnology" (2014)

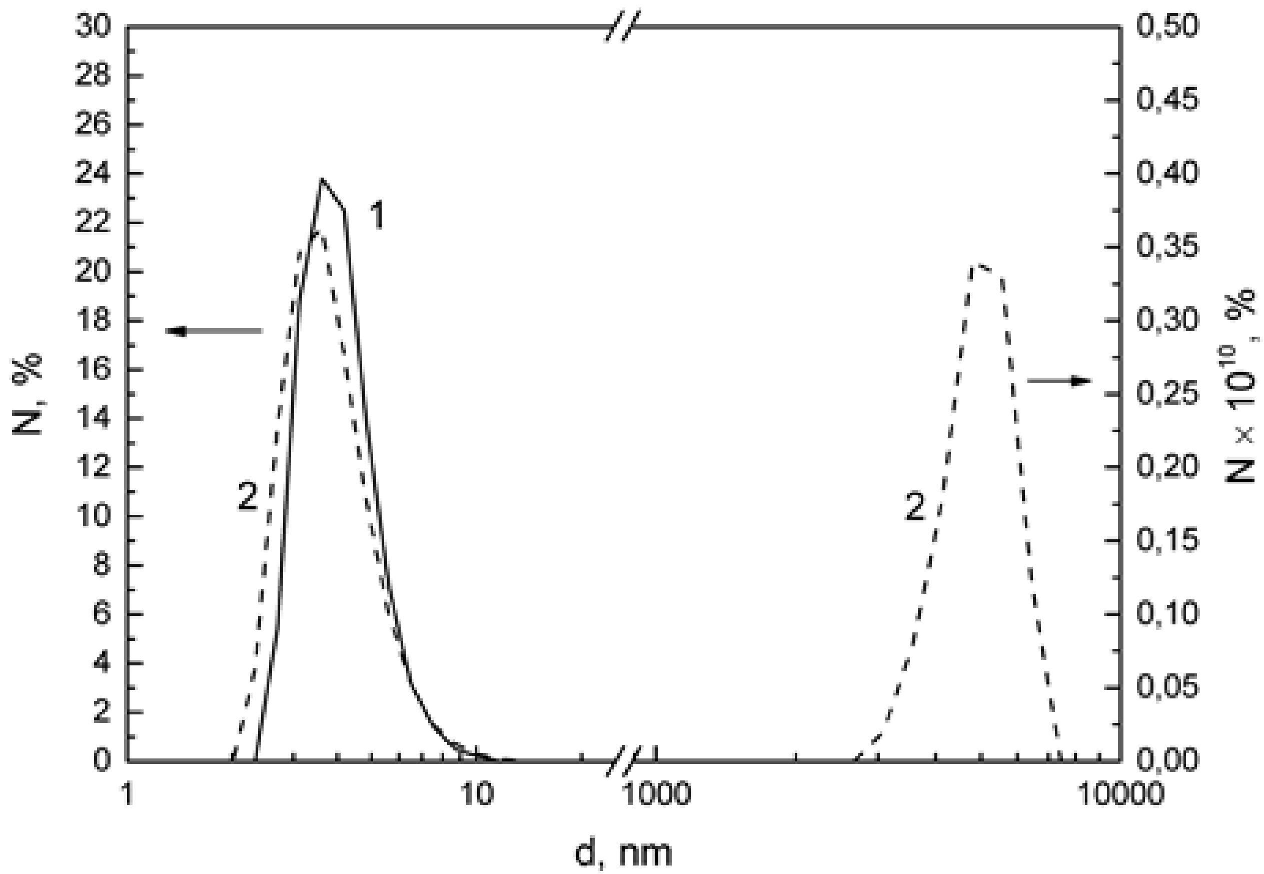
3. A.Ya. Vul' and E. D. Eydelman, M Inakuma, E.Ōsawa. Correlation between Viscosity and Absorption of Electromagnetic Waves in an Aqueous UNCD Suspension. Diamond and Related Materials, v.16, 2035-2038 (2007).



Diamgel with DND-particles' content 8 wt.% at 23°C.
Maximum height of columns ~ 2 cm

Suspensions studied

[1] M.V.Avdeev, N.N.Rozhkova, V.L.Aksenov, V.M.Garamus, R.Willumeit, E.Osawa, *J.Phys. Chem.* C, (2009) 113, 9473.
[2] O.V.Tomchuk, L.A.Bulavin, V.L.Aksenov, V.M.Garamus, O.I.Ivankov, A.Ya.Vul', A.T.Dideikin, M.V.Avdeev, *J. Appl. Cryst.* (2014) 47, 642.
[3] O.V.Tomchuk, D.S.Volkov, L.A.Bulavin, A.V.Rogachev, M.A.Proskurnin, M.V.Korobov, M.V.Avdeev, *J. Phys. Chem.* C (2015) 119, 794.

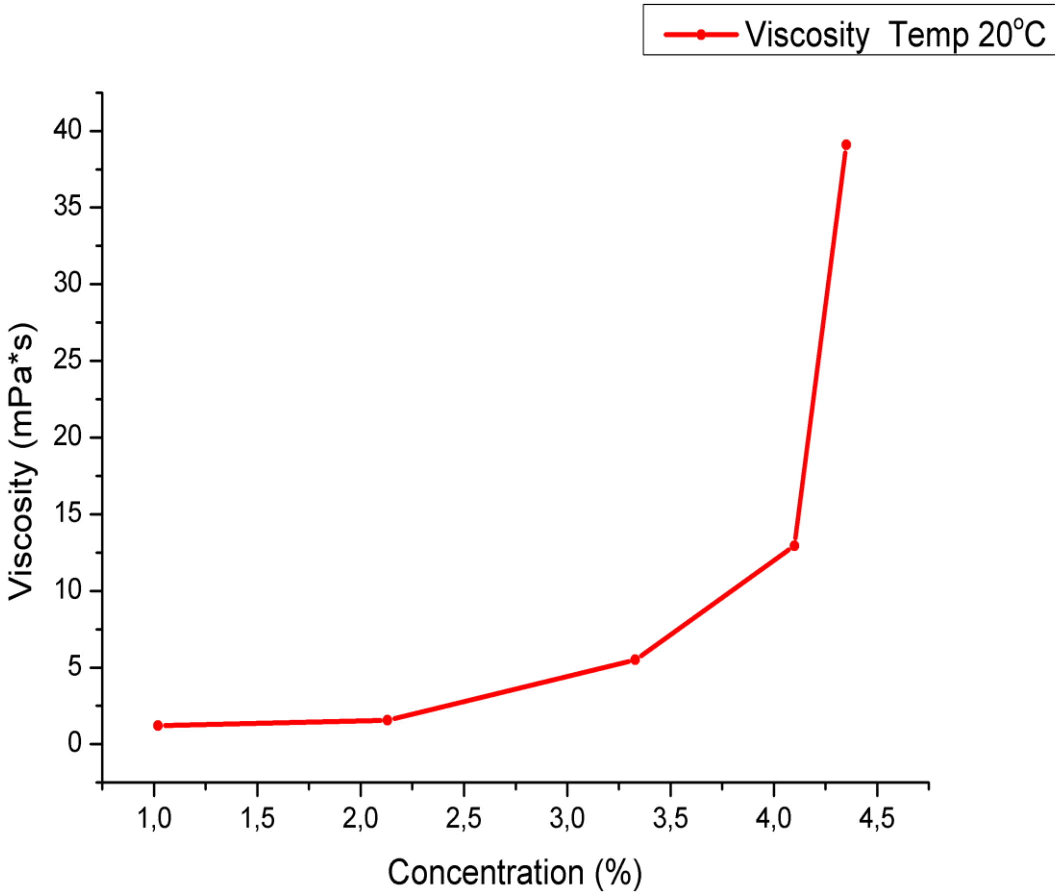


Particles' fractions over size in Hydrosol (1) and Diamgel (2) prepared from this Hydrosol

Dynamic light scattering at ambient temperature

Diamgel: single particles + formations of gel

Particles' concentrations: ***0.73 wt.%*** *in* ***Hydrosol; 5.29 вес. % in Diamgel***



High viscosity at low content of particles
C ~ C* ~ 3-5 wt.%

Critical concentration ***C**** depends on the sign of ζ-potential

Lower ***C**** for $\zeta > 0$

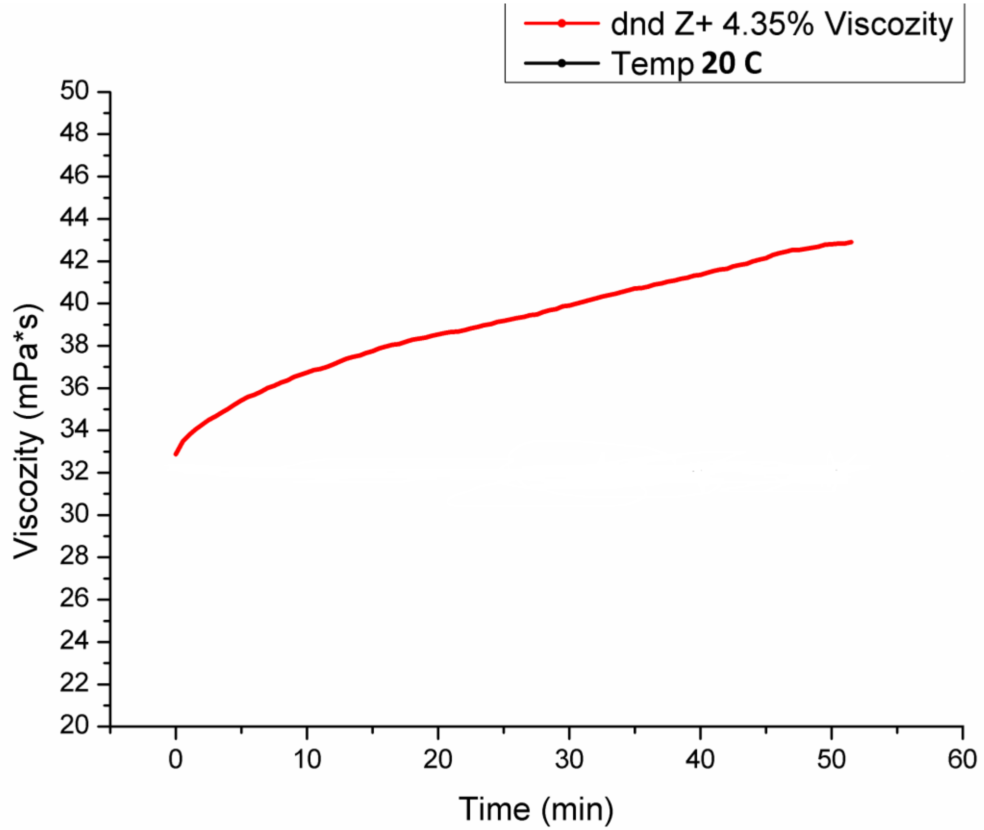
Hydrosol
pH = 7.5, C= 0,7 wt.%, $\zeta > 0$
C* = 4,2 wt.%

Negative potential, $\zeta < 0$
Threshold ***C* ~ 7 wt.%***

Gel formation, C > C*

Viscosity growth by the increase of concentration (20 °C)

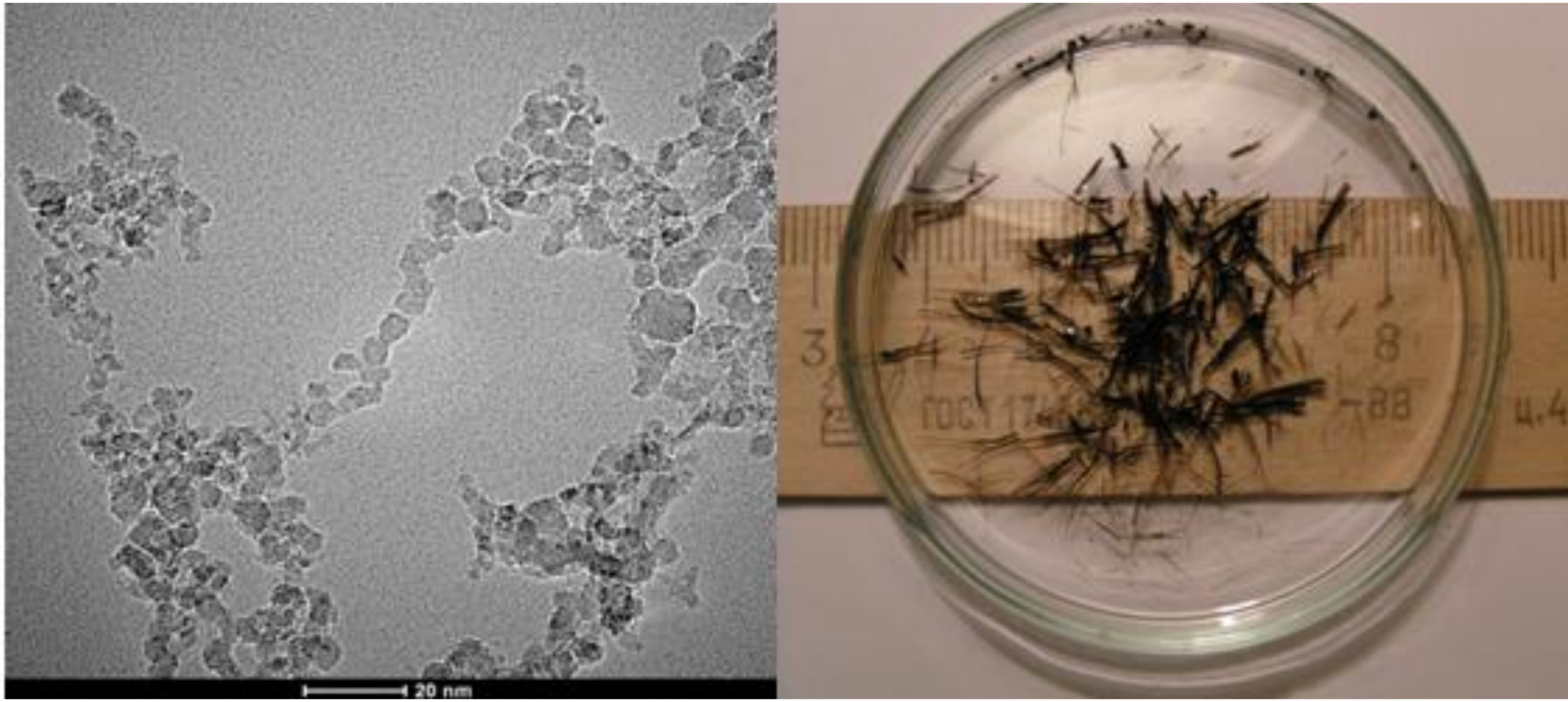
At critical concentration C* ~ 4 wt.% a giant growth of viscosity is observed

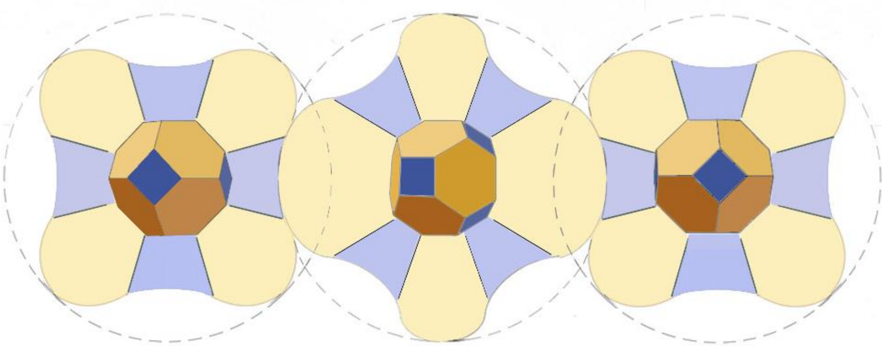


Thixotropic effect

Fast decay of gel by mechanical loading (shift)

Following very slow formation of gel structure



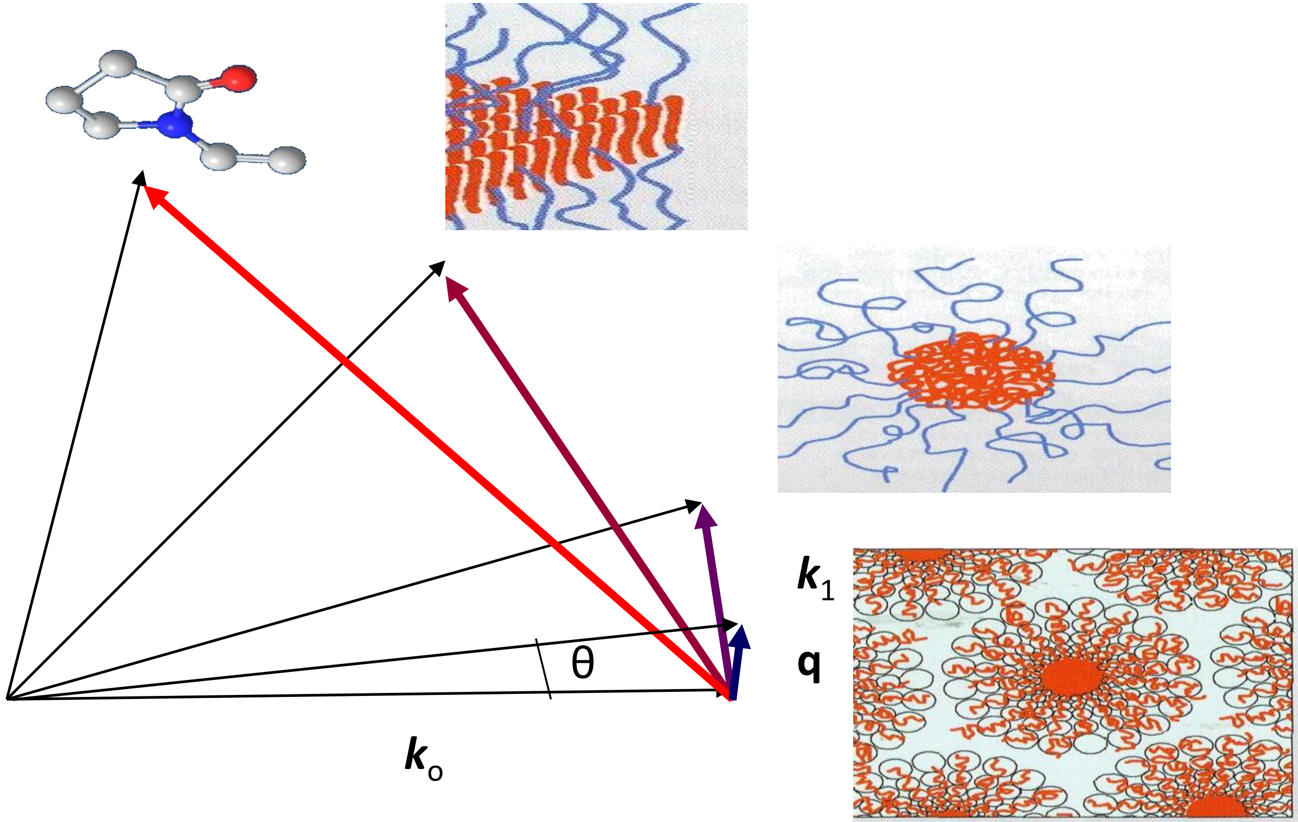


Gel dried: Chains of diamond nanoparticles (TEM, left)
Needle-like structures (right)

Schematic view of non symmetric potential of particles and formation of their chains

Particles covered by water shells (thickness ~ 5 nm)

Shells' contacts → creation of chains → gel formation



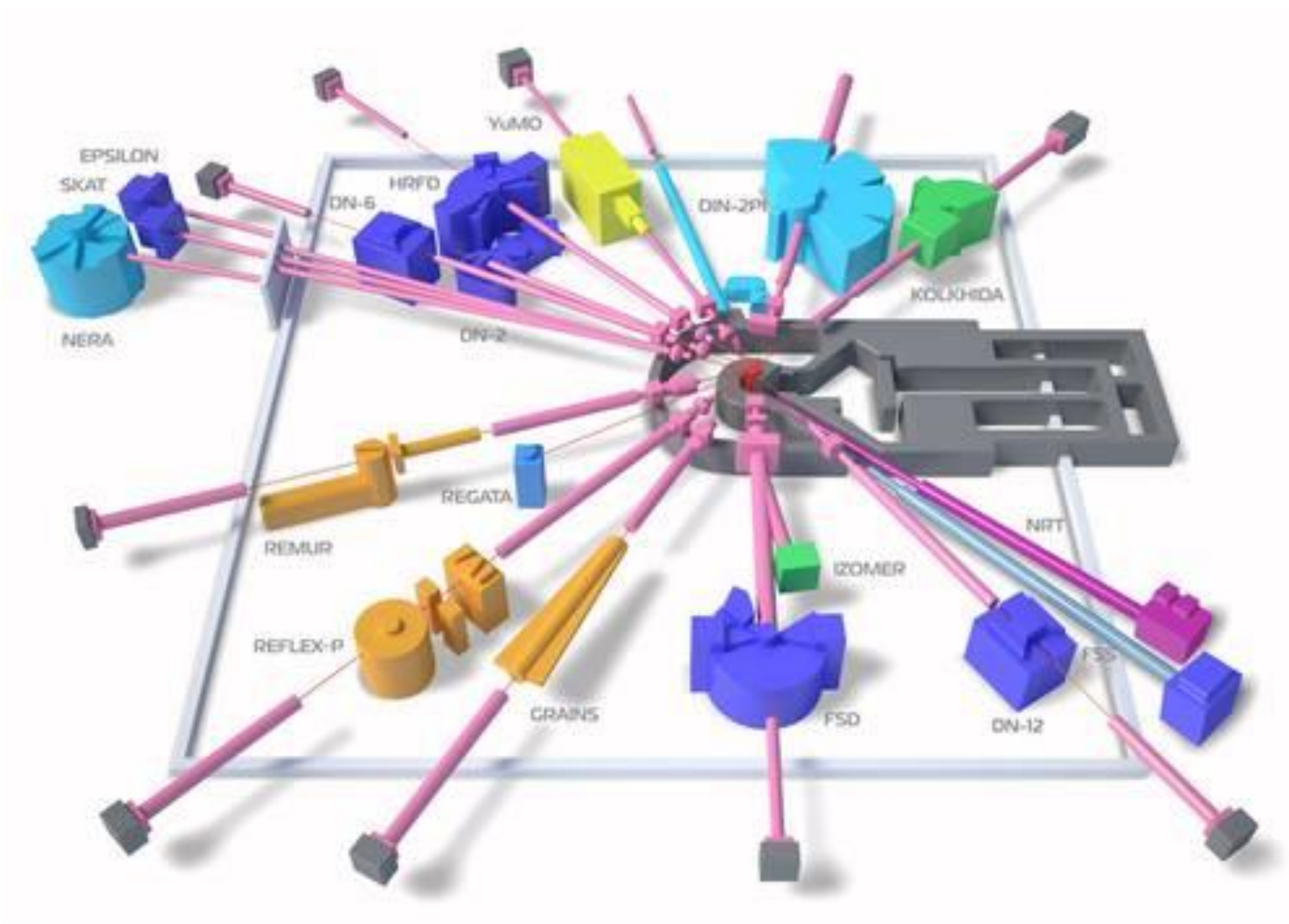
Elastic and inelastic neutron scattering

Elastic momentum transfer ***q =(4π/λ)sin(ϑ/2),*** *Spatial scale* ***R ~ 1/q***

Relaxation at molecular scales by Neutron Spin Echo

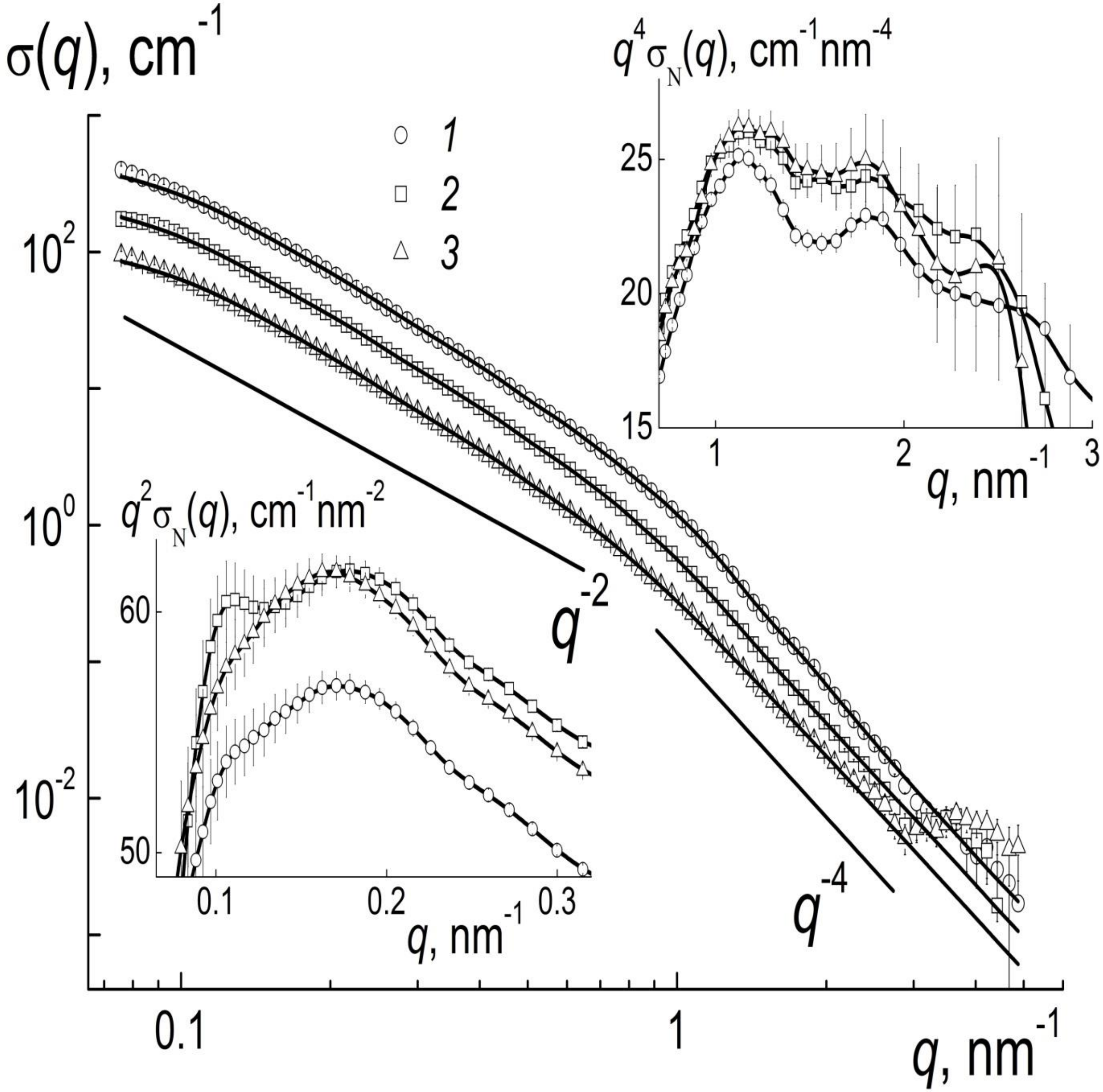
– FAST RHEOLOGY at nanoseconds and picoseconds

ОИЯИ - Реактор ИБР-2



JINR, YuMO-facility - SANS from gels

Hydrogel of diamonds with charged surface → *Dilution* ***C < C* ~ 4.2 % wt.***



Concentrations:
5.05; 2.25;1.13 % wt.
Dilution below critical

q < 1 nm⁻¹, particles correlations
q > nm⁻¹, atomic correlations in particles

Kink at ***q ~ q* ~ 1 nm⁻¹***
Reciprocal size of particle, $q^* \sim 2\pi/d_S$

Porod's law $\sigma(q) \sim 1/q^4$
Sharp borders of particles

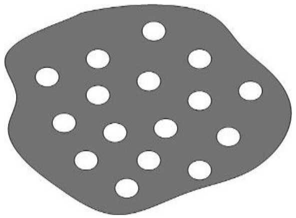
$\sigma(q) \sim 1/q^2$ - Chain structures
Polymers

Scales ≤ 100 nm

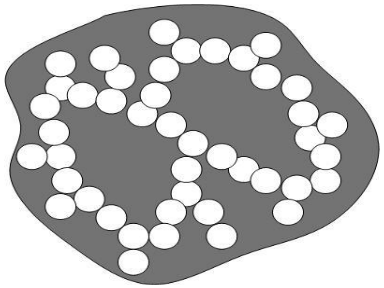
Short-range order
***Stable at* C ~ 1-5 % wt.**

States of binary system Diamonds + water

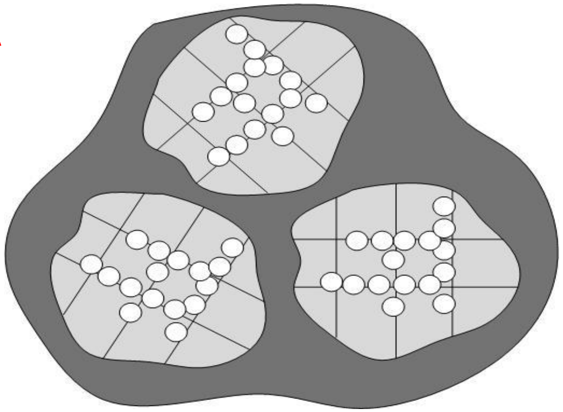
Suspension **C < C***



Gel ***C > C****



Microgel **C*/4 ≤ C ≤ C***



C < C*
Original gel
Disintegration into large domains in water

Size ≥ $2\pi/q_{min}$ ~ 10^2 nm

$\sigma(q) \sim 1 / q^{D1,2}$

D_1 ~ 4 ; D_2 ~ 2
q ≥ q* ; q ≤ q* ~ 1 nm^{-1}

Compensation of q-dependencies

Peculiarities of structure factor

Spacing of particles d_{int} in gels' networks
Debye scattering function, ***q ≥ q****

$\sin(qd_{int})/(qd_{int})$

Maximum **$X = q_{int}d_{int}$ ≈ 7.72**

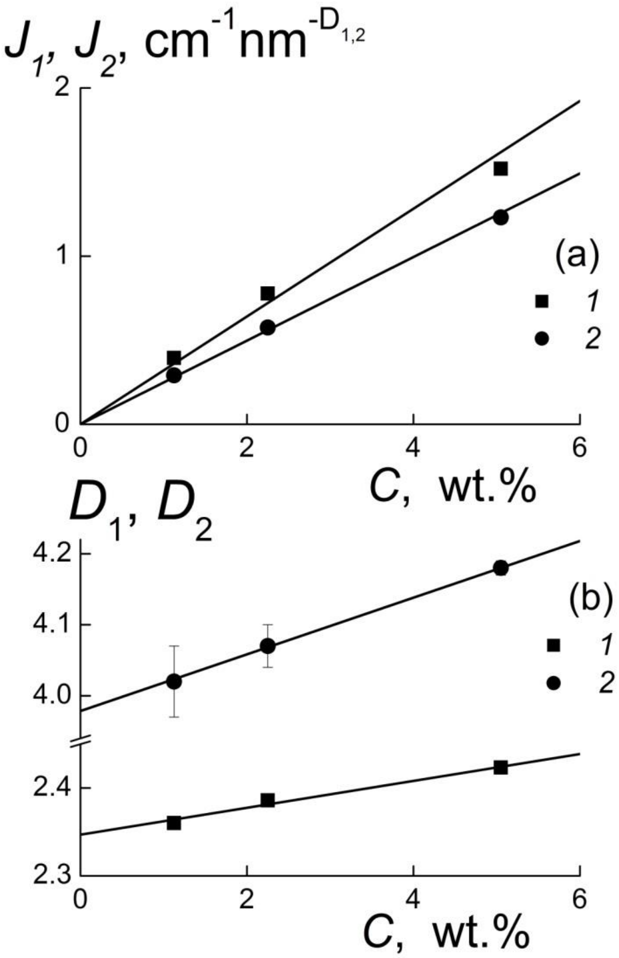
q_{int} ≈ 1.1 nm^{-1} = X/d_{int}

d_{int} ≈ 7 nm exceeds a characteristic diameter of particle, ***$d_{int} - d_S$ ≈ 1 nm***

Network, q ≤ q*
$D_w = X/q_w$ ≈ 40 nm
q_w ≈ 0.18 nm^{-1}

Parameters

$$\sigma(q) \sim 1 / q^{D1,2}$$



D_2 - geometry of particles' surface

$C \to 0,\ D_{02} = 3.98 \pm 0.04$

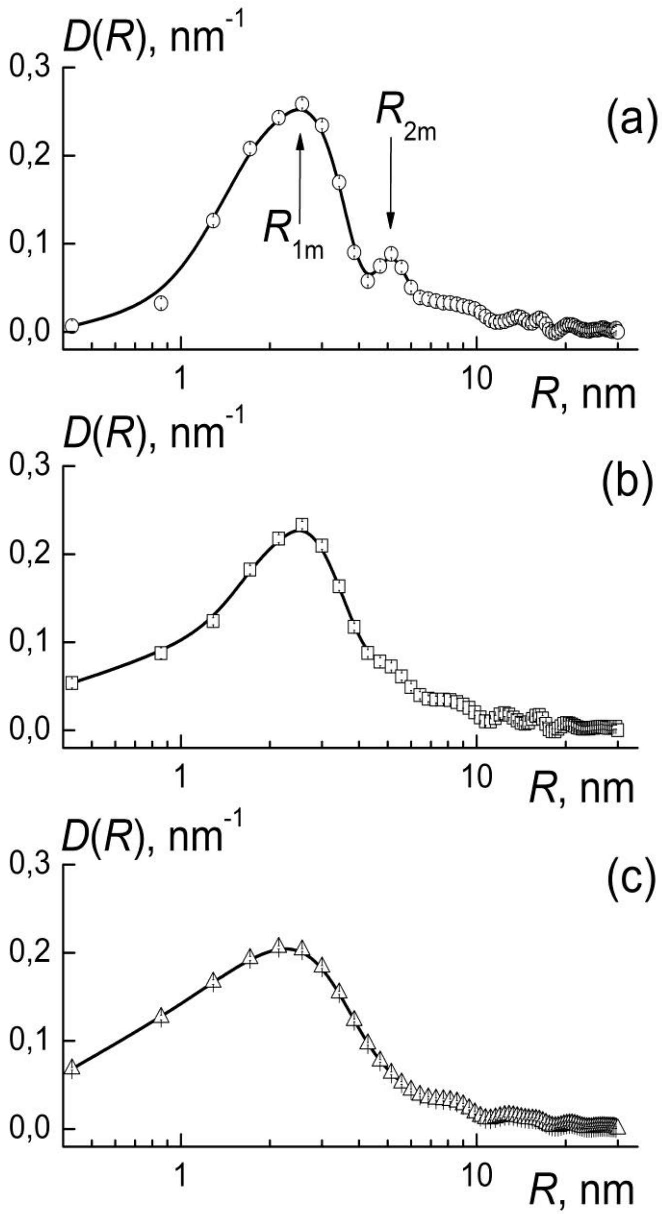
Branched structures

$3 > D_1 \sim 2.3\text{-}2.4 > 2 = D_G$ - *gaussian chain*

$C \to 0,\ D_{01} = 2.35 \pm 0.01 > 2$

Dilution $\varphi_1 = 1.44$ % → $\varphi_3 = 0.22$ % vol.

Model of uniform spheres - particles' size distribution



Volume fractions ***D(R)*** of particles vs. their radius ***R***:
Concentrations **5.05; 2.25;1.13** % wt. (a,b,c)

Maximum positions R_{1m} ~ *2.4-2.6 nm*
Dispersions
$\delta = \pm(1/2)(\Delta R/R_m) \sim 0.5\text{-}0.8\ \Delta R$ - FWHM

Spectra are in agreement with ***DLS*** data

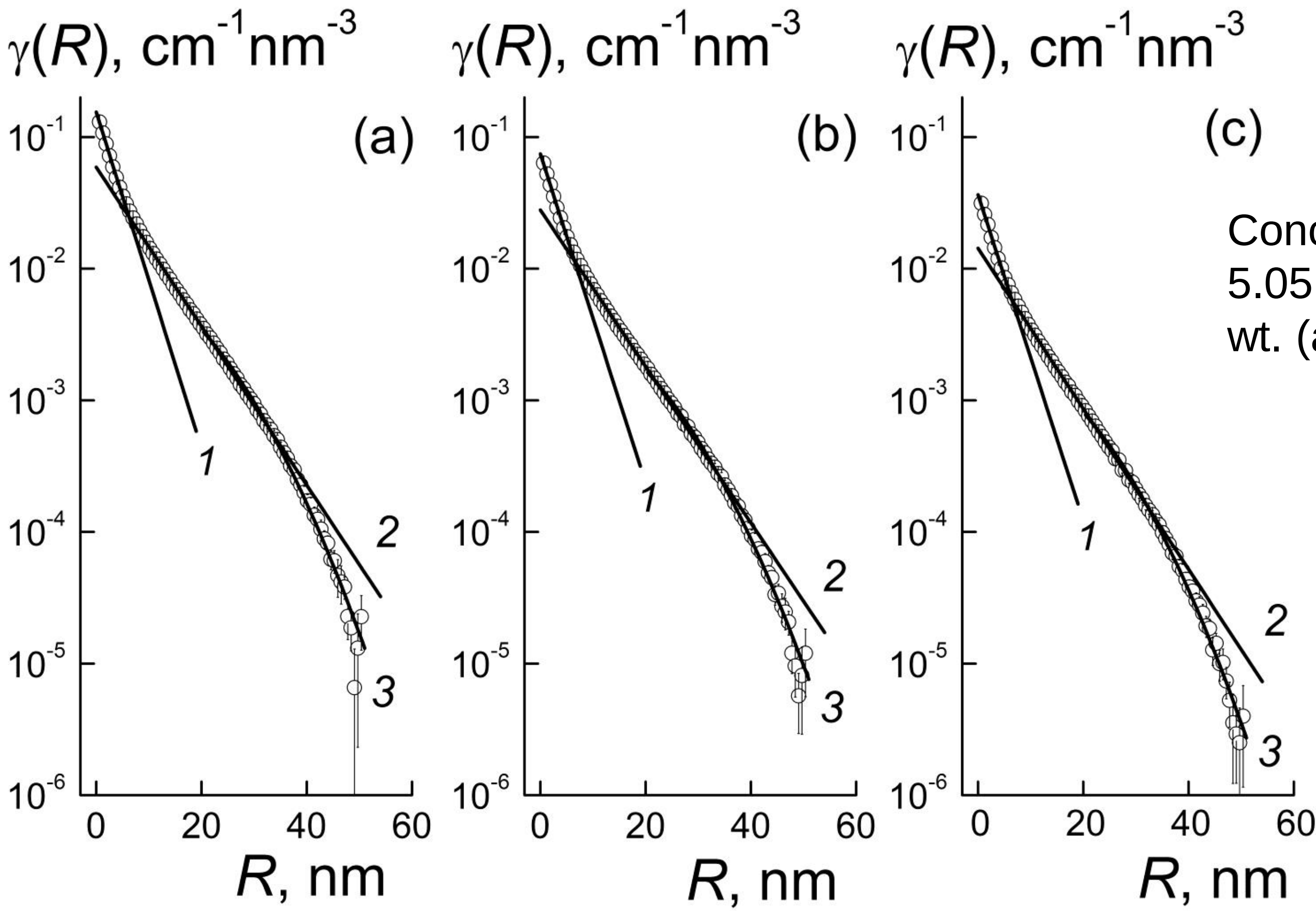
Single particle, radius R_{1m} ~ *2.6 nm*

Diameter R_{2m} **~ 5.1 nm ~ 2**R_{1m}

Double - triple diameter of particle,
R ~ 10-15 nm

Short-range order !

Correlations inside particles and between them



Concentrations
5.05; 2.25;1.13 %
wt. (a,b,c)

$$\gamma(R) = (1/2\pi)^3 \int \sigma(q)[\sin(qR)/(qR)] 4\pi q^2 dq \text{ , } \gamma(R) = \langle \Delta\rho(r)\Delta\rho(r+R) \rangle$$

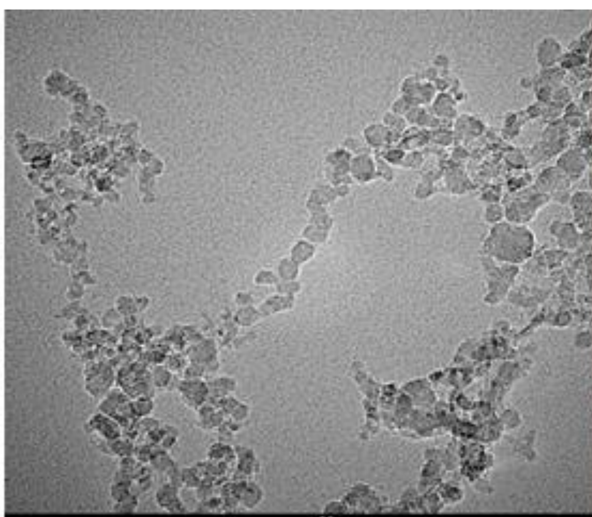
$\Delta\rho(r) = \rho(r) - \langle\rho\rangle$, $\Delta\rho(r+R) = \rho(r+R) - \langle\rho\rangle$ deviations of scattering length densities $\rho(r)$, $\rho(r + R)$ in two points, $\langle\rho\rangle = \Sigma(b_i N_i)$ – sum over nuclei lengths

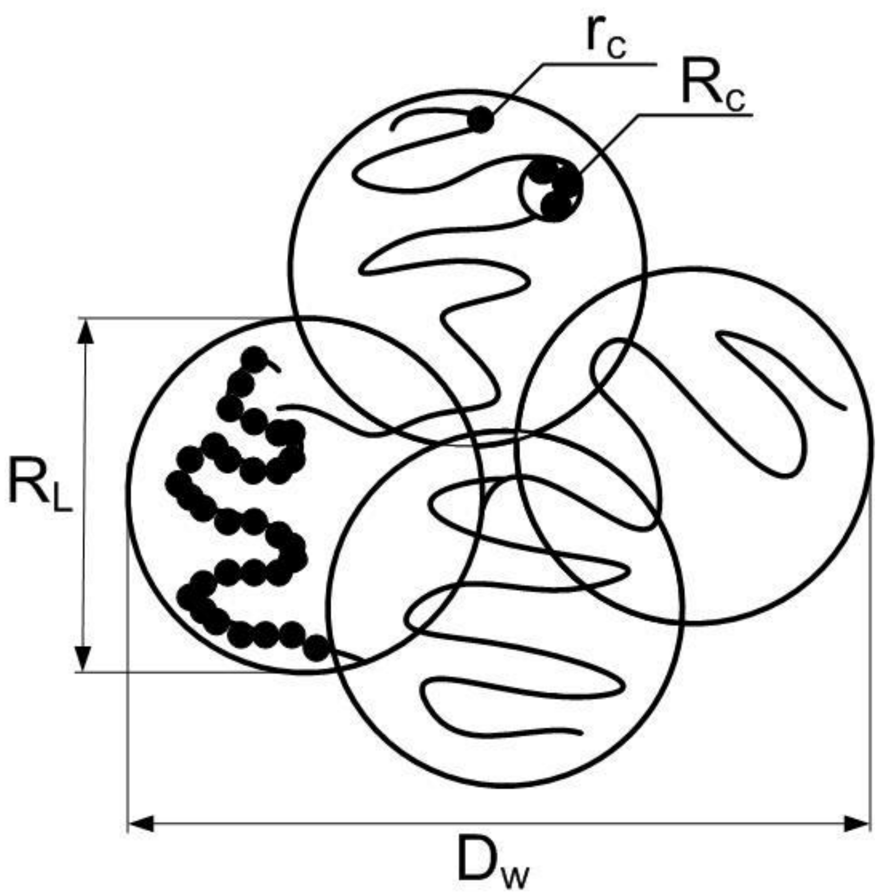
Three levels of correlations

1. Short Radii, $0 \le R \le 6$ nm (inside particles) $\gamma_1(R) = A_1 \exp(-R/r_C)$
Correlation radius r_C and geometrical radius of sphere **$r_S = (3/4) r_C \approx 2.6$ nm**
Maximum in spectrum **$D(R)$**

2. Intermediate $R \ge 10$ nm exceeds particle's diameter
First coordination sphere around a particle, **$\gamma_2(R) = A_2 \exp(-R/R_C)$, $R_C = 7.19 \pm 0.03$ nm**
Volume **$V_C = 4\pi \int \exp(-R/R_C) R^2 dR = 8\pi R_C^3 \approx 9.3 \cdot 10^3$ nm^3 ~ $10\, V_1$**
Single particle **$V_1 = 8\pi r_C^3 \approx 990$ nm^3**
Particles inside the coordination sphere **$(A_2 V_C)/(A_1 V_1) = m = 3.6 \pm 0.1$**
Fragment of a branched chain forming a network

3. Large scale, $R \ge 20$ nm, gaussian function $\gamma_3(R) = A_3 \exp[-(R/R_L)^2]$, $R_L = 19.9 \pm 0.1$ nm
Network cell's size **~ $2R_L$ ~ 40 nm**





Model of gaussian chains

End-to-end distance $R_L^2 = nd_S^2$

Number of units (coupled particles)

$n = (R_L^2/d_S^2) = 15.0 \pm 0.2$

Volume fraction of particles $\varphi = 1.44\ \%$
Chains' concentration
$N_L = \varphi/(n\pi d_S^3/6) \approx 1.3 \cdot 10^{16}\ cm^{-3}$

Spacing $R_{int} \approx N_L^{-1/3} \approx 40\ nm \sim 2R_L$

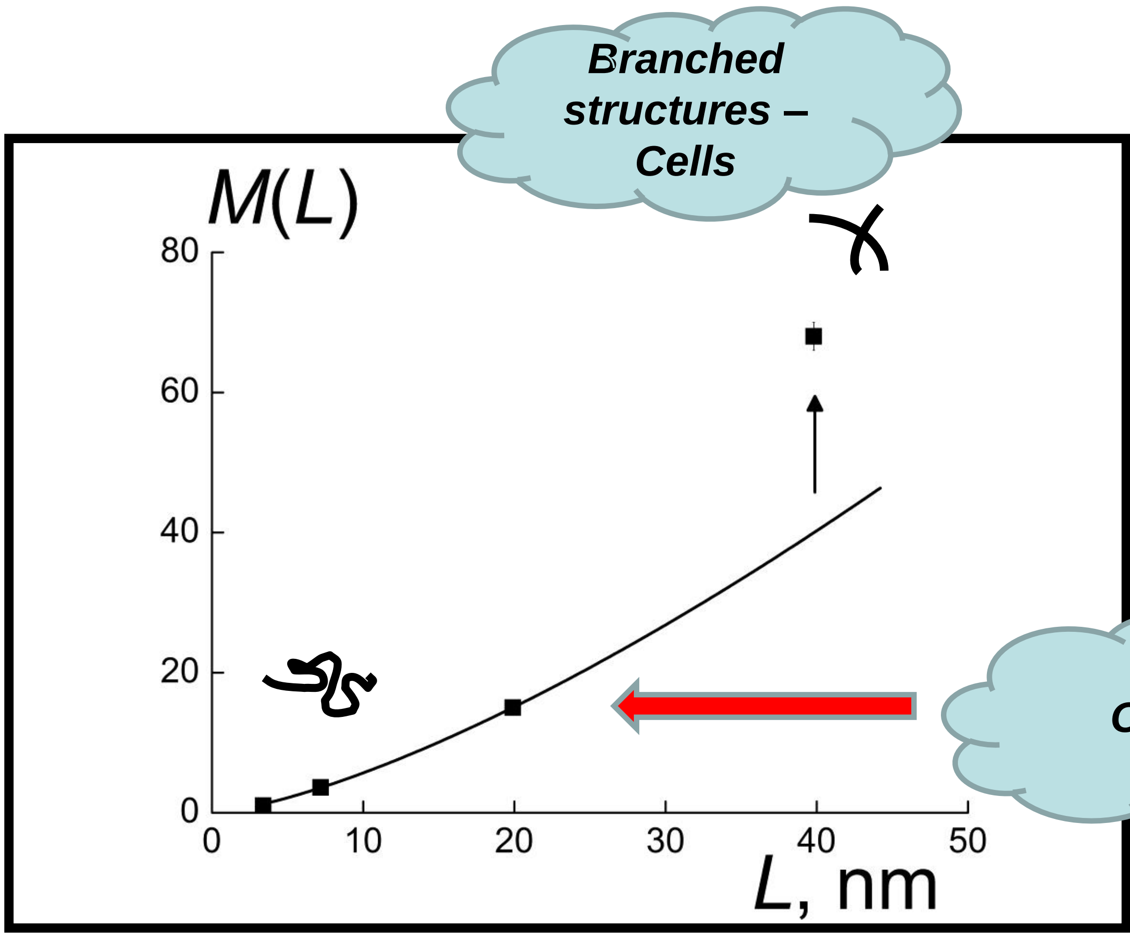
Cell diameter $D_w \sim 2R_L \sim 40\ nm$
Number of particles in a cell
$m_L \sim 70$

Chain's contour length
$L_C = nd_S \approx 80\ nm \sim 2D_w$
Overlapping - Gel Formation
Junctions' functionality
$f_C = m_L/n \approx 4$

Hierarchy of structural levels in Gel

Scales: ***$L = r_C; R_C; R_L; D_w$ ~ 3 – 40 nm,***
Growth by **1** order in magnitude
Corresponding Mass Enhancement: ***M = 1; 4; 15; 70***

Mass Factal: $M \sim L^{D_f}$, $D_f = 1.41 \pm 0.03$ **Chains with Excluded Volume**



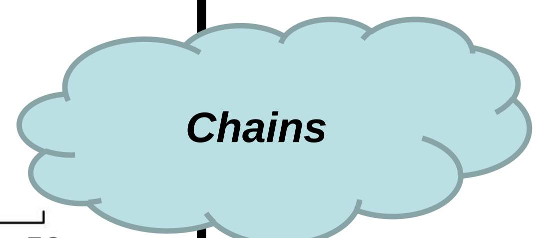
Cell Level – exponent

$D_{EF} = \ln(m_L)/\ln(D_w/r_C) \approx 1.7 > D_f$

Functionality of junctions

$\ln(f_C) = D_{EF} \cdot \ln(D_w/r_C) - \ln(n)$

$f_C \sim 4$



Diamonds - Contrast factor relatively to the surrounding medium

Pristine Gel: $\varphi = 1.44\ \%$, $A_1 = (\Delta\rho_D)^2\varphi$ ⟹ $\Delta\rho_D = (10.36 \pm 0.01)10^{10}\ cm^{-2}$

$$\Delta\rho_D = \rho_D - \langle\rho\rangle = (1-\varphi)(\rho_D-\rho_W)$$

Difference between the scattering lengths density of the **carbon material** and the average parameter for sample's volume

$$\langle\rho\rangle = \varphi\rho_D+(1-\varphi)\rho_W$$

$\rho_W = -0.56 \cdot 10^{10}\ cm^{-1}$ -- scattering length density for light water

Length density of particles $\rho_D = \Delta\rho_D/(1-\varphi)+\rho_W = (9.95 \pm 0.01)10^{10}\ cm^{-2}$

is by ***15 % lower*** than a similar parameter $\rho_{DI} = 11.7 \cdot 10^{10}\ cм^{-2}$

for crystalline diamond (density of ***3.5 g/cm³***)

Summary

SANS study of new gels of nanodiamonds has shown several levels of these systems structural organization

- ***the correlations inside single particles,***
- ***neighboring particles in the first coordination sphere,***
- ***chain-like formations and at last***
- ***the cells of gel as composed of these chains joint***

It was established a substantial stability of these forms of particles assembly even by a dilution of system from original gel with ~ 5 % wt. of carbon fraction to rare system containing ~ 1 % of diamonds only

This stability confirms a domain structure of gel observed by Dynamic Light Scattering

Thank You for attention!

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