Small-Angle Scattering Analyses of Nanoporous Materials

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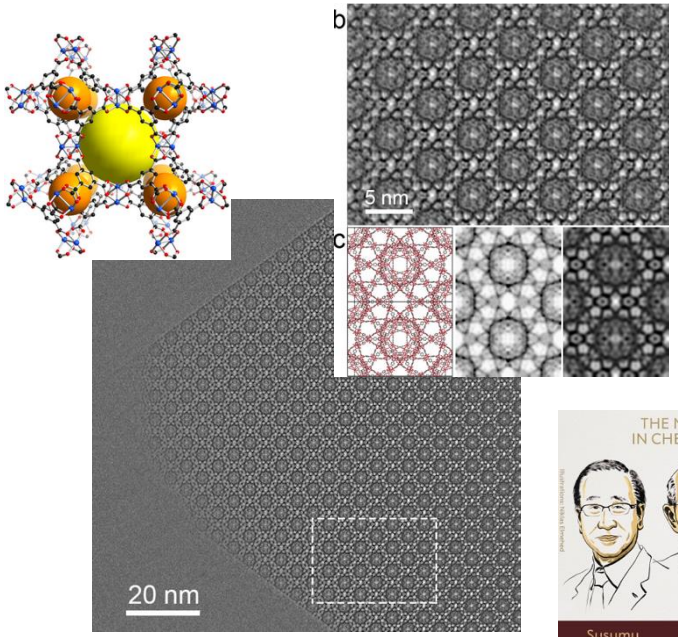
Outline

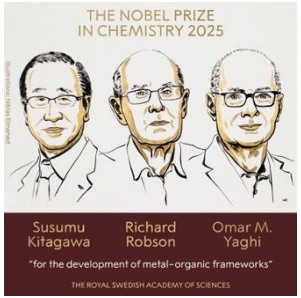
- Generalities about nanoporous materials (6 slides)
- Small-angle scattering (SAS) (12 slides)
- SAS of ordered porous materials (7 slides)
- SAS of disordered porous materials (15 slides)
- Inelastic small-angle scattering (9 slides)

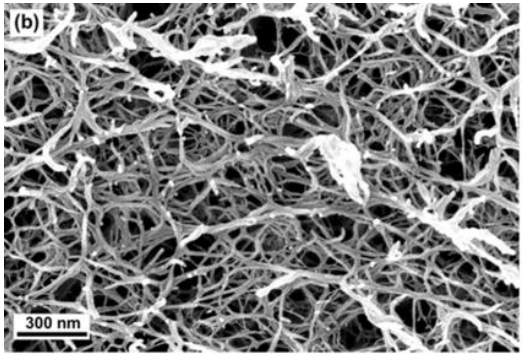
Porous materials

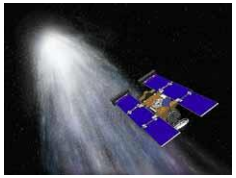
Two randoms examples of nanoporous materials

MOFS and aerogels (ordered vs disordered)





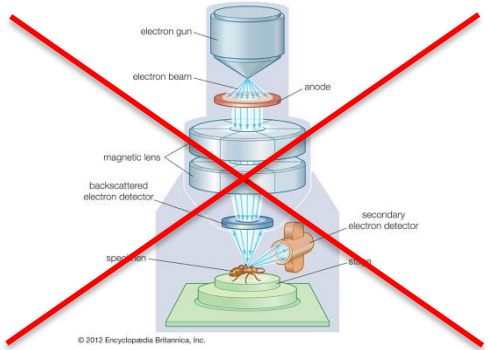




Stardust mission
(1999-2006)

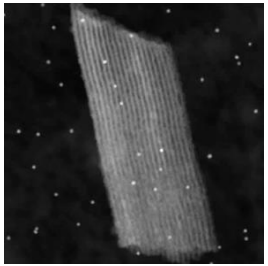
Two limits of electron microscopy

- Mostly ex-situ characterization



Even water at room temperature rules out electron microscopy

- Very poor sampling

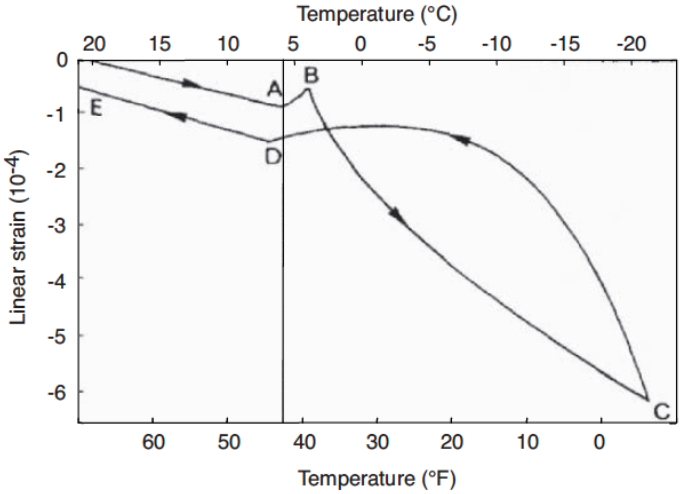


Femtograms to tons
21 orders of magnitude

The strange physical chemistry of confined matter

Water in a glass bottle

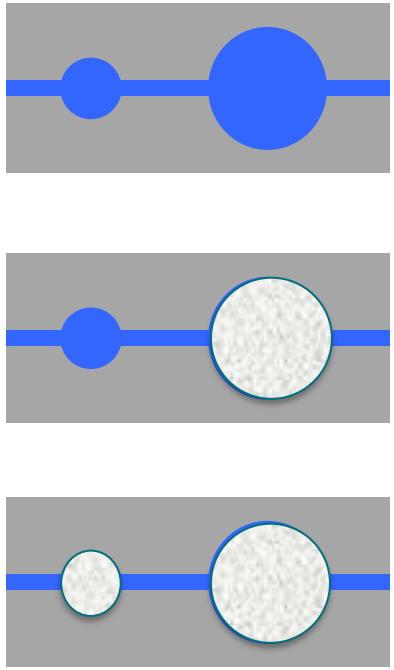
Benzene in cement paste*



*From O Coussy, Mechanics and Physics of Porous Solids, Wiley, 2010.

Cryosuction in nanopores

Cooling



T1

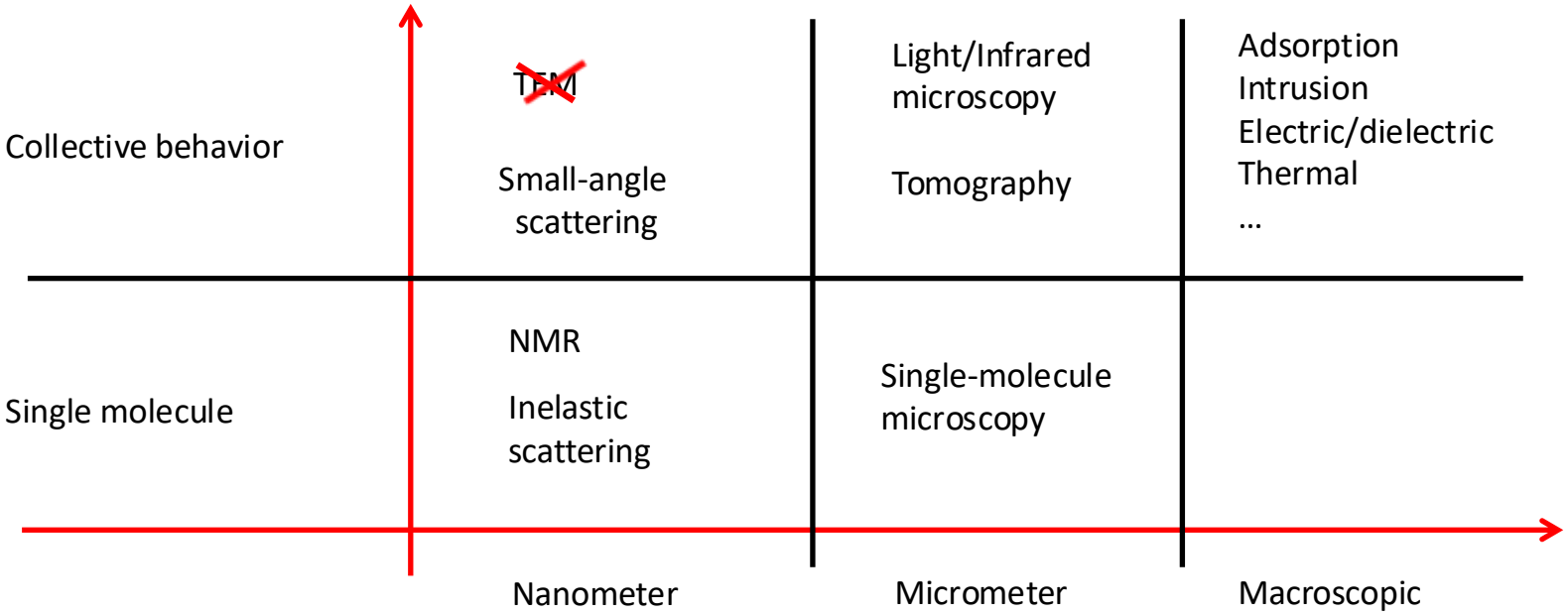
T2 < T1

T3 < T2

The smaller the pore, the lower the freezing temperature.

At intermediate temperature, the liquid is sucked into the larger (frozen) pores. Pressure builds up in those pores.

In-situ studies in porous materials

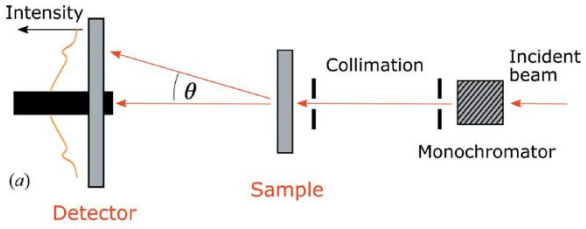


A poor man’s scattering experiment

Why is ice opaque and liquid water transparent?

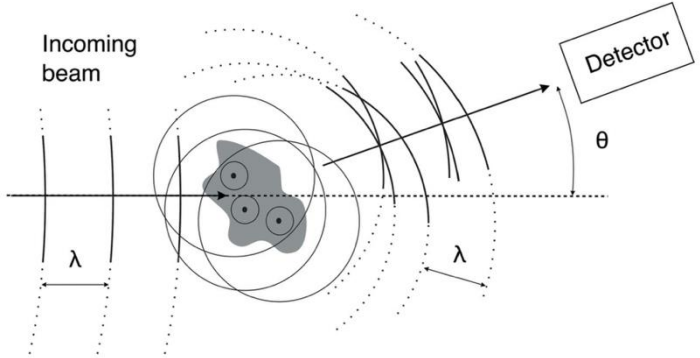
Why does Pastis/Ouzo become turbid when water is added?
Etc. etc. etc.

Small-angle scattering : SAXS, SANS, SALS,...



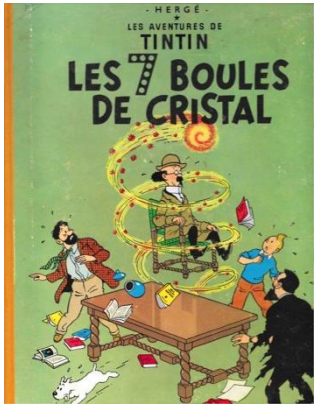
KWS-1
(MLZ)

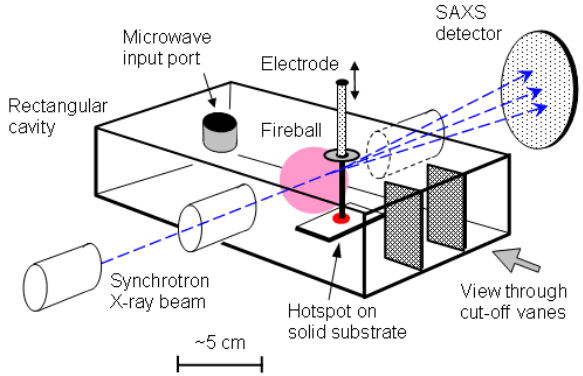
BM26
(ESRF)

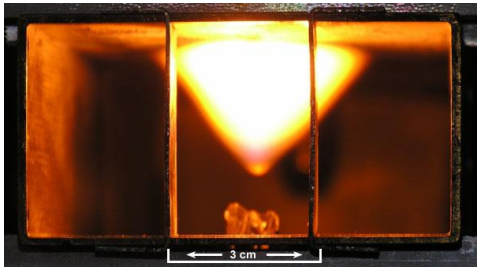


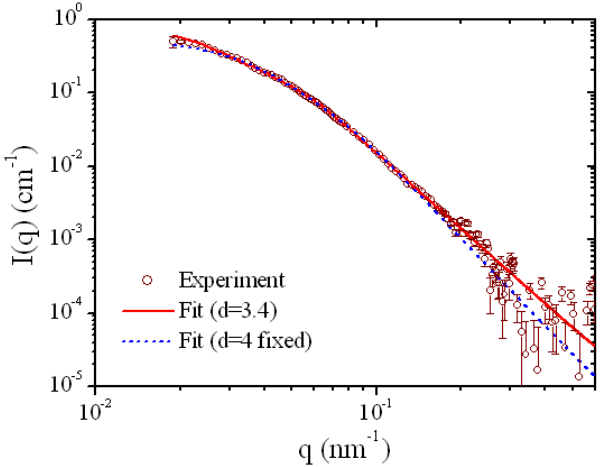
J. Appl. Crystallogr. 54 (**2021**) 1832

SAS is experimentally very versatile









PRL 100, 065001 (2008) PHYSICAL REVIEW LETTERS week ending 15 FEBRUARY 2008

Evidence for Nanoparticles in Microwave-Generated Fireballs Observed by Synchrotron X-Ray Scattering

J. B. A. Mitchell,[1] J. L. LeGarrec,[1] M. Sztucki,[2] T. Narayanan,[2] V. Dikhtyar,[3] and E. Jerby[3,*]

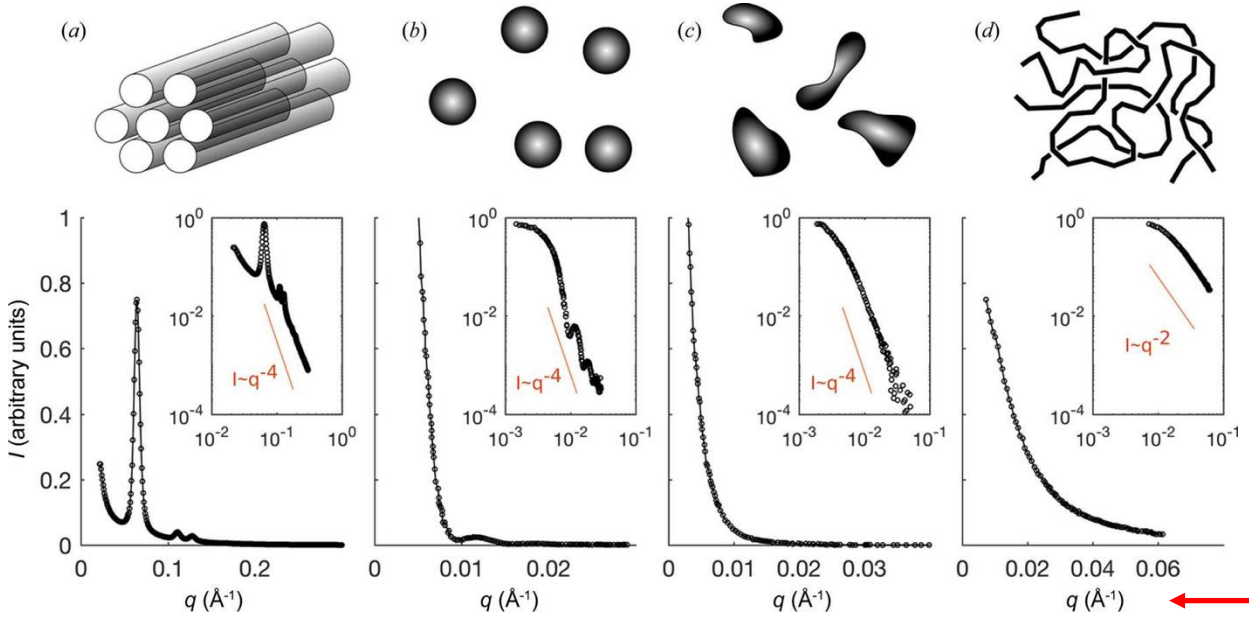
Examples of SANS/SAXS patterns

Ordered mesoporous silica

Latex nanoparticles

Soot nanoparticles

Polystyrene chains



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

Experimental break

Part 1

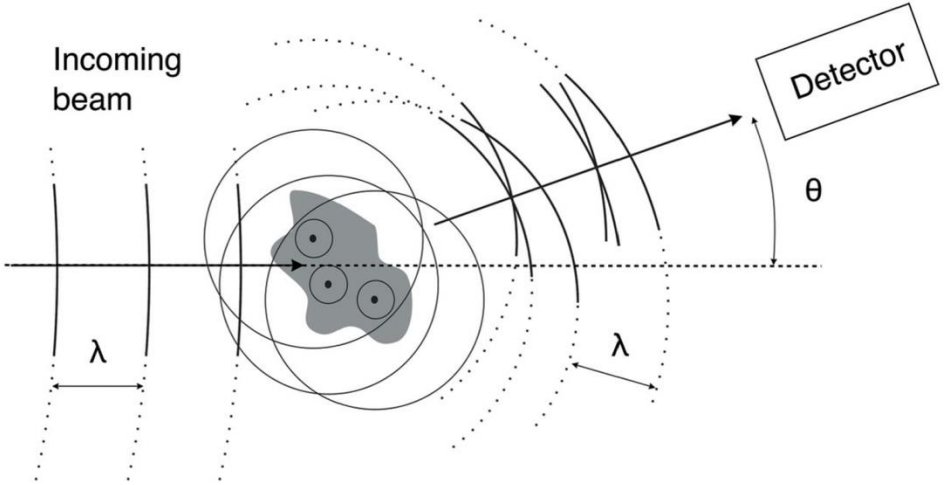
Interferences

Two pointwise sources

From Derek Muller's Veritasium, *The original double slit experiment*, Youtube, Feb **2013**

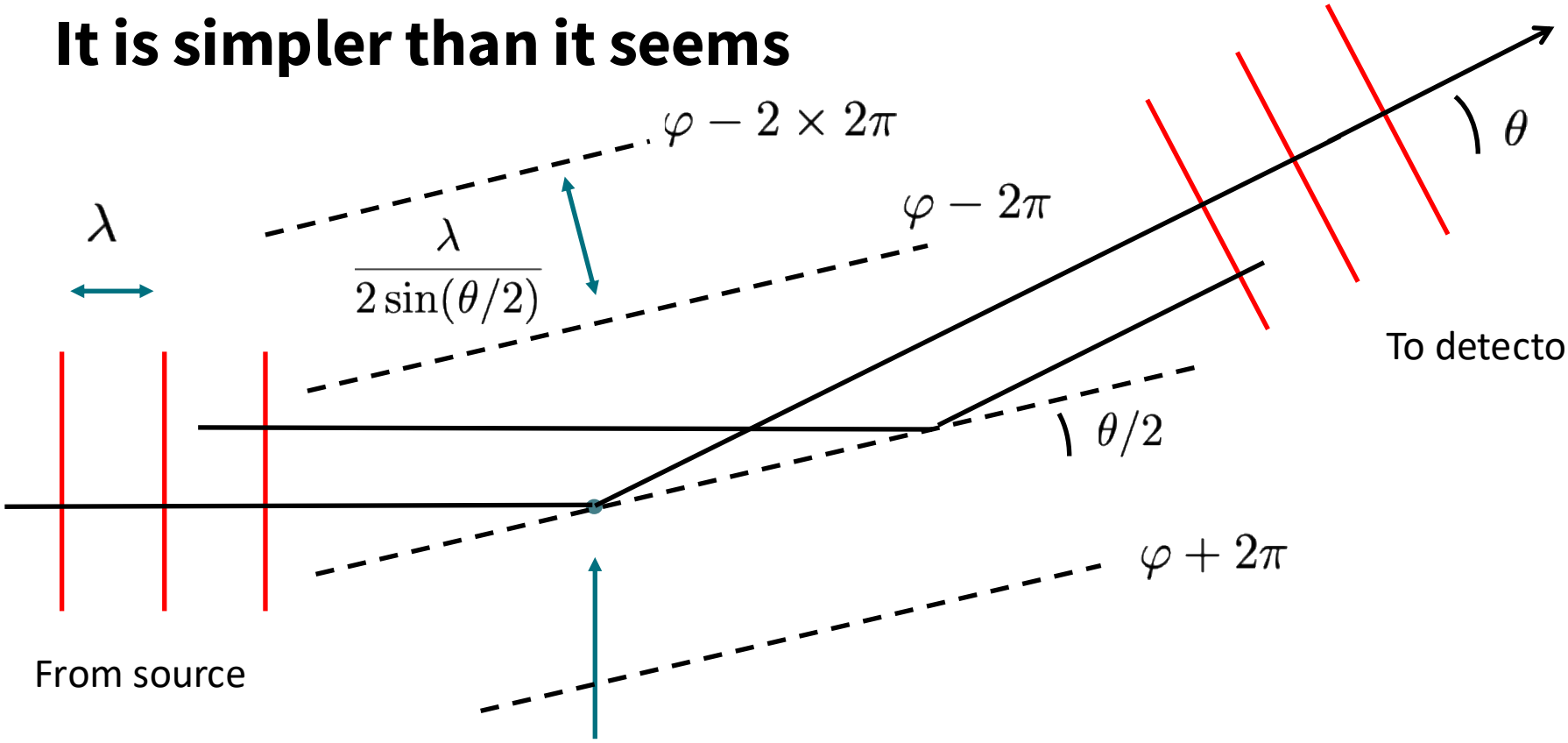
Interferences again

with infinitely many pointwise sources… (?!!!?)



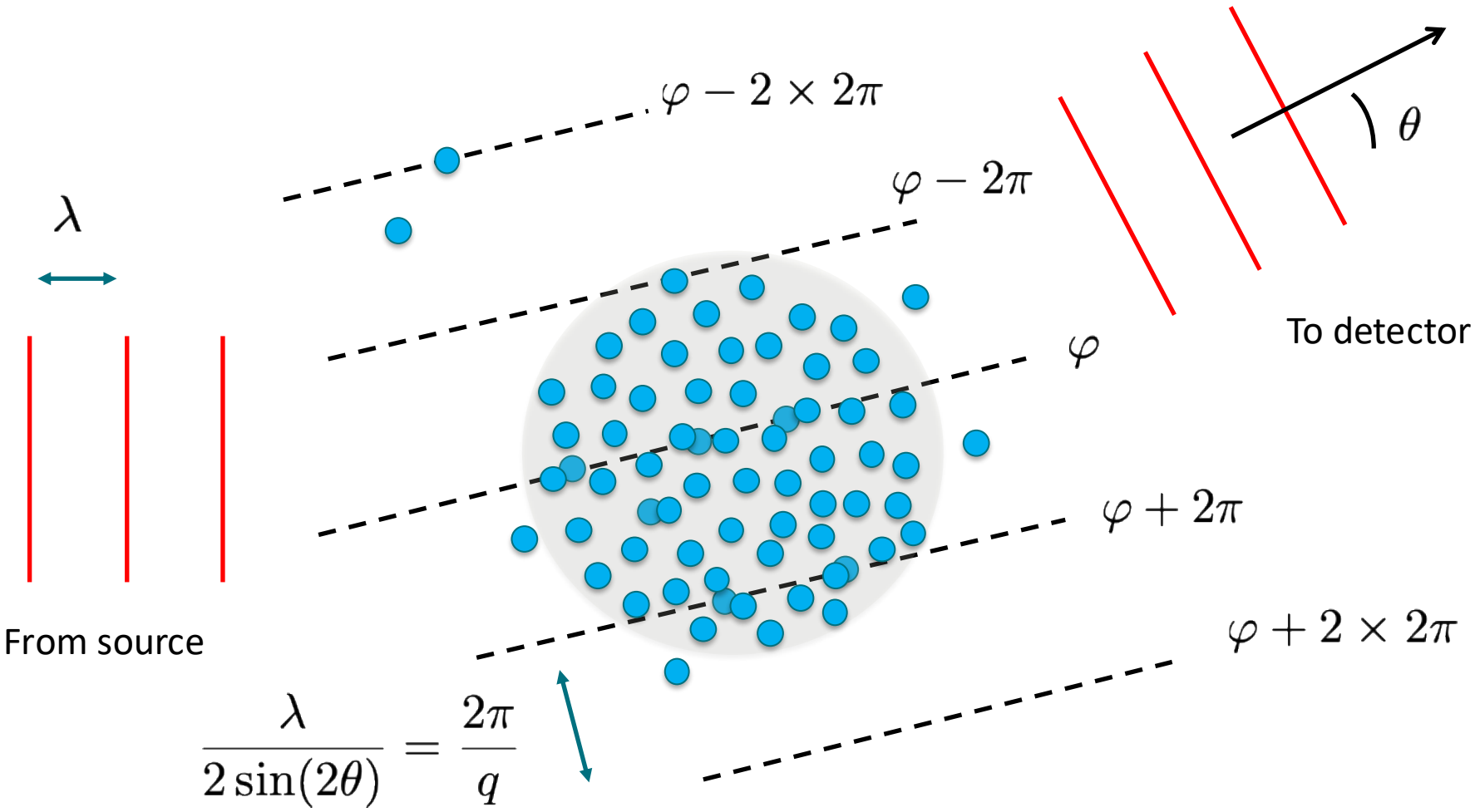
Every electron of the sample acts as a point source for a secondary wave

It is simpler than it seems

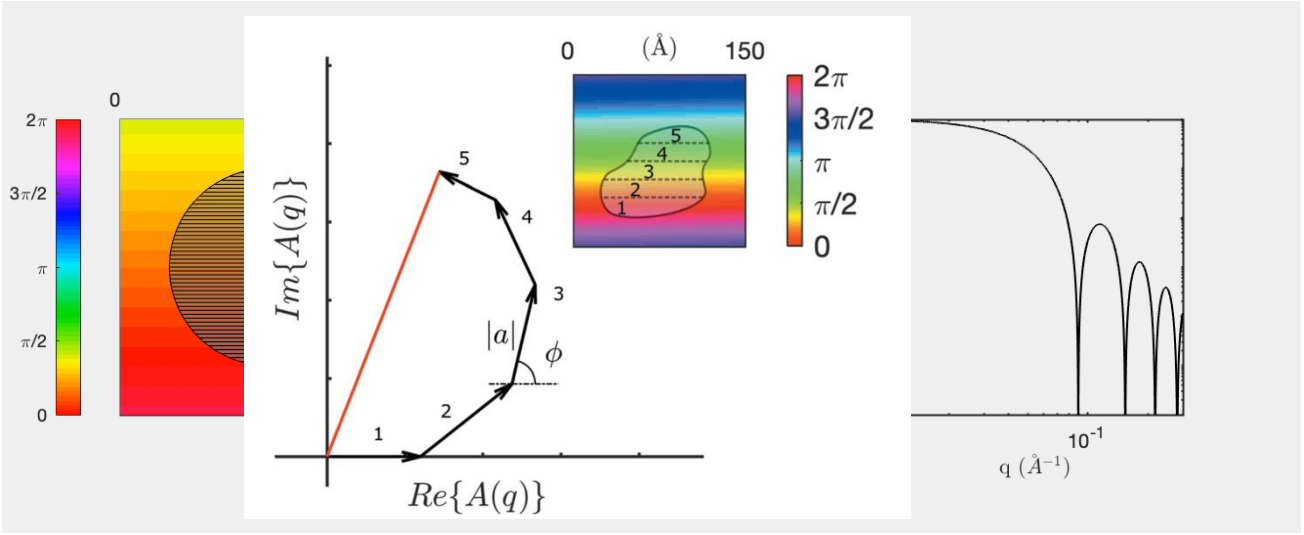


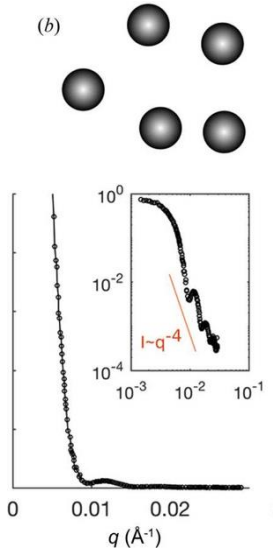
If there was an electron here, what phase would it yield?

$$\varphi = 2\pi \times \frac{L}{\lambda}$$


$\varphi - 2 \times 2\pi$
$\varphi - 2\pi$
φ
$\varphi + 2\pi$
$\varphi + 2 \times 2\pi$
λ
θ
To detector
From source
$\frac{\lambda}{2\sin(2\theta)} = \frac{2\pi}{q}$

Small-angle scattering by particles

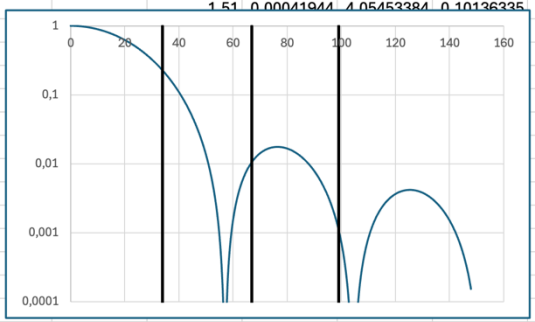




Experimental break

Part 2: data analysis

d (mm)	3600	x (mm)	angle (rad)	q (1/mm)	qR (-)	bessel^2
		0,01	2,7778E-06	0,02685122	0,00067128	0,99999989
lambda (nm)	650	0,51	0,00014167	1,36941217	0,0342353	0,99970702
(mm)	0,00065	1,01	0,00028056	2,71197307	0,06779933	0,99885136
		1,51	0,00041944	4,05453384	0,10136335	0,99743412
R (mm)	0,025					0,99545727
						0,99292362
						0,98983671
						0,98620088
						0,98202123
						0,97730362
						0,97205464
						0,96628162
						0,95999259
						0,95319632
						0,94590222
						0,93812039
						0,92986156
		8,51	0,00236388	22,8503397	0,57125849	0,9211371
		9,01	0,00250277	24,1928917	0,60482229	0,91195896
		9,51	0,00264166	25,5354427	0,63838607	0,9023397
		10,01	0,00278055	26,8779926	0,67194981	0,89229241
		10,51	0,00291944	28,2205412	0,70551353	0,88183072



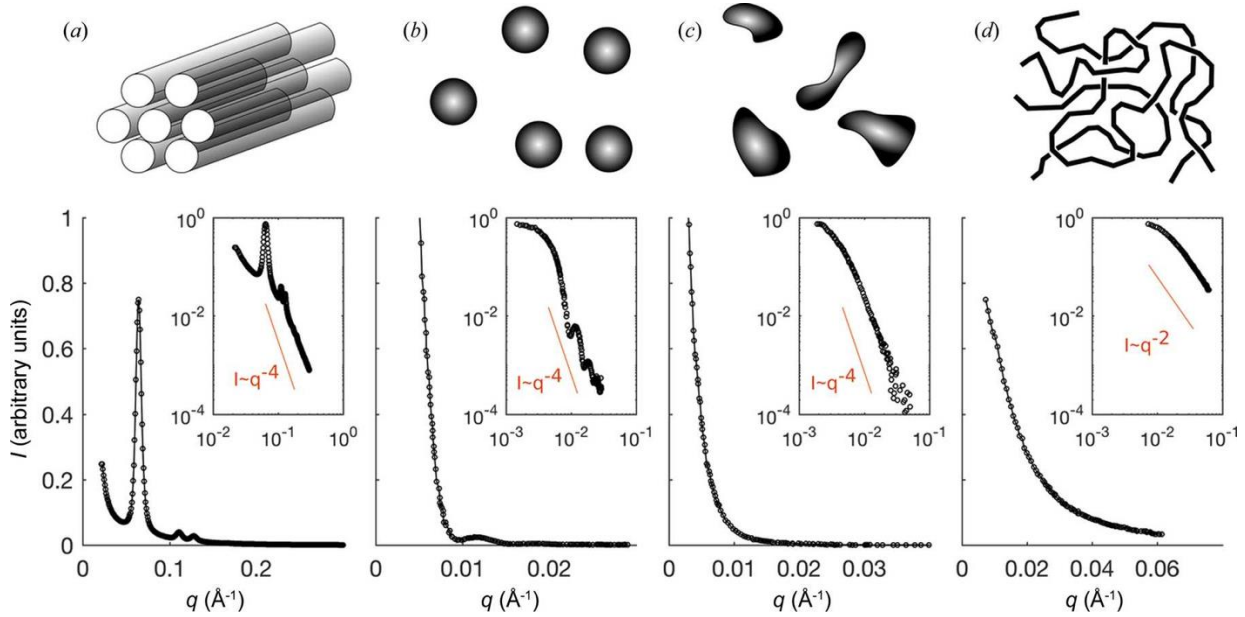
Back to the typical SANS/SAXS patterns

Ordered mesoporous silica

Latex nanoparticles

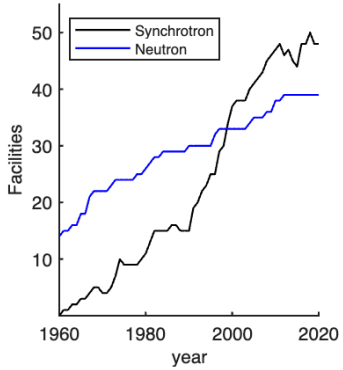
Soot nanoparticles

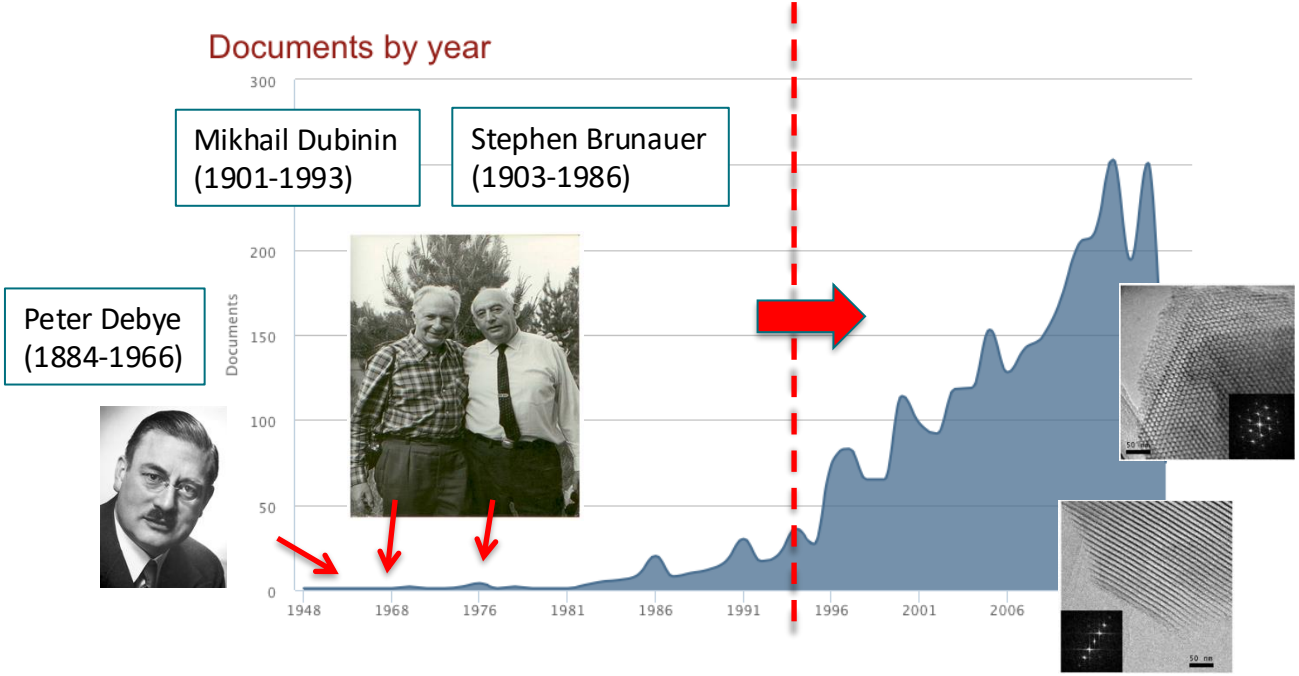
Polystyrene chains



« SAXS & Porous Materials »

A bibliographic glimpse



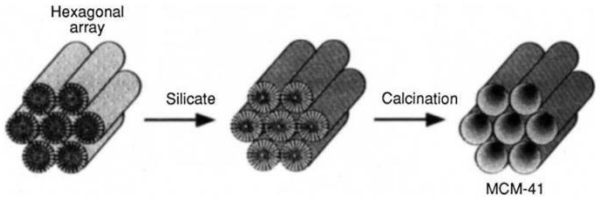


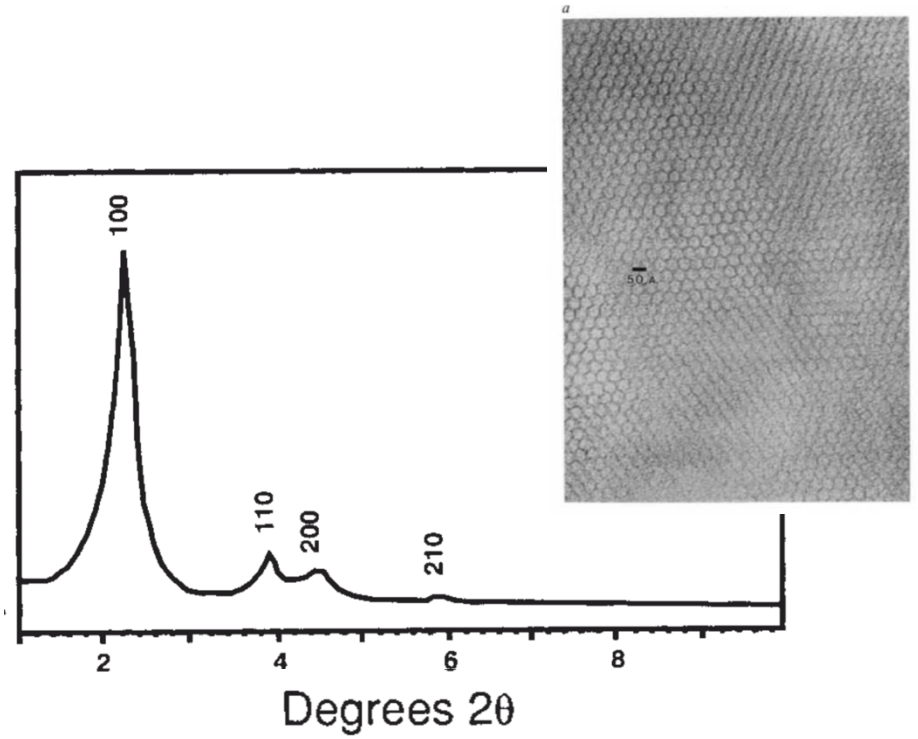
Ordered mesoporous materials (OMM)

LETTERS TO NATURE

Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism

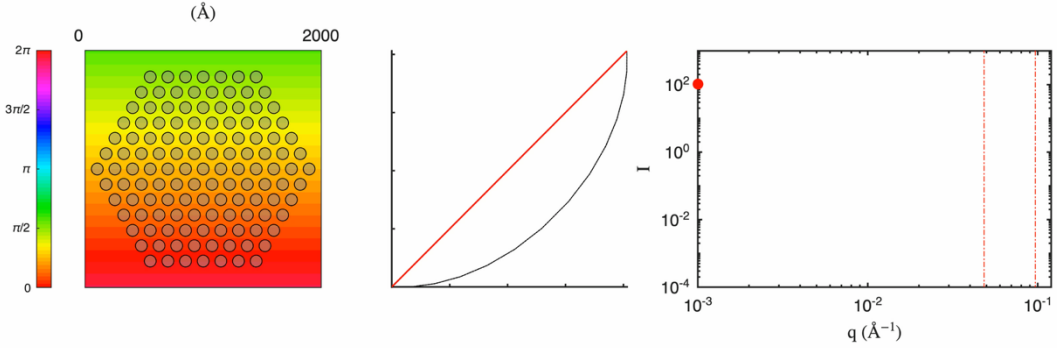
C. T. Kresge*, M. E. Leonowicz*, W. J. Roth*,
J. C. Vartuli* & J. S. Beck†

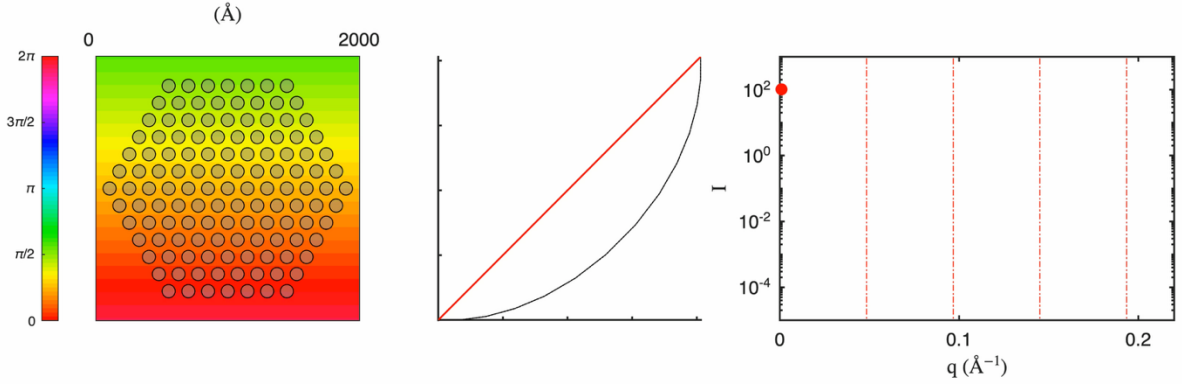




NATURE · VOL 359 · 22 OCTOBER 1992

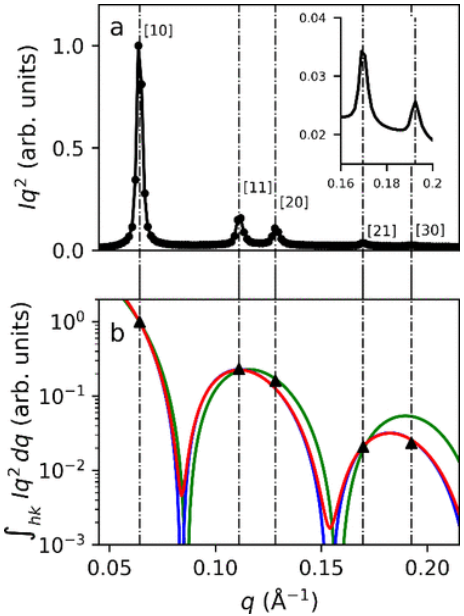
Small-angle Scattering by OMMs



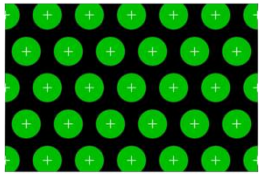


Pore Sizes from Small-Angle Scattering

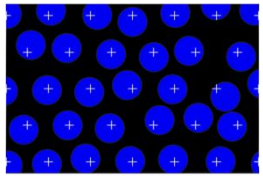
SAXS of SBA-15



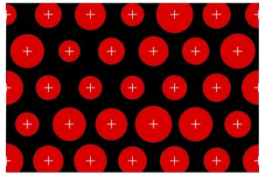
Ideal lattice

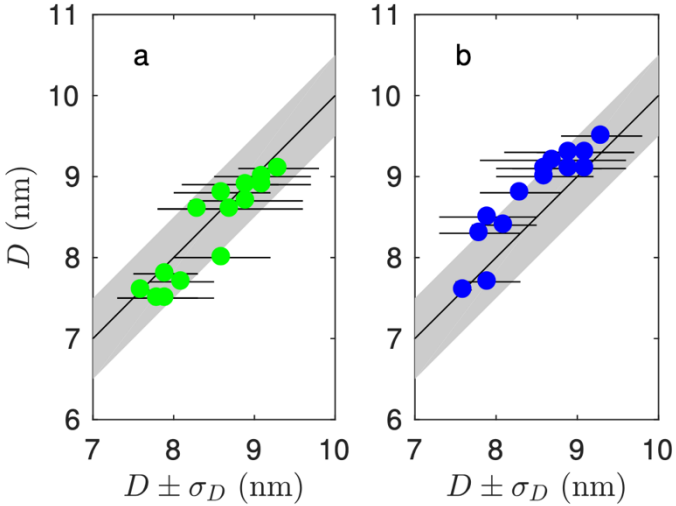


Positional disorder



Size disorder

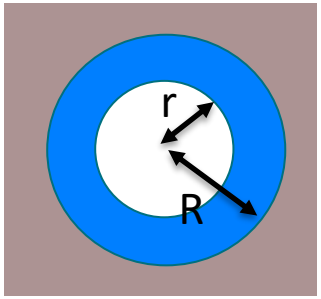


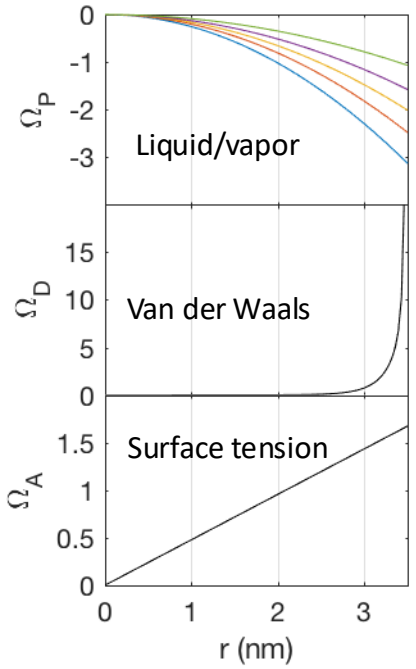


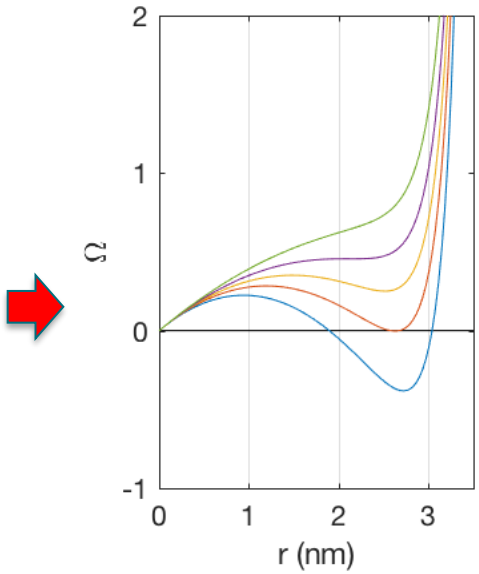
https://doi.org/10.1021/acs.langmuir.4c01609
Langmuir 2024, 40, 17444−17453

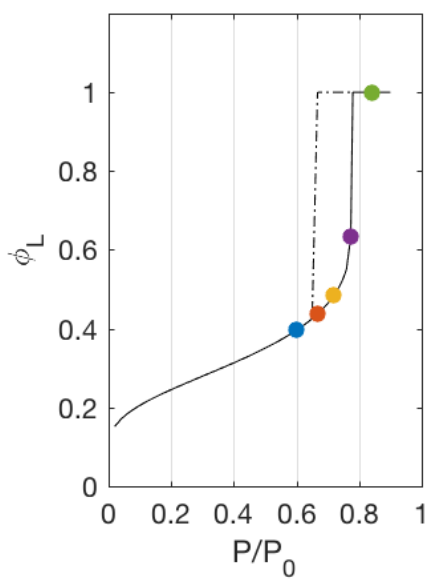
Capillary condensation/evaporation

The Derjaguin-Broekhoff- de Boer picture



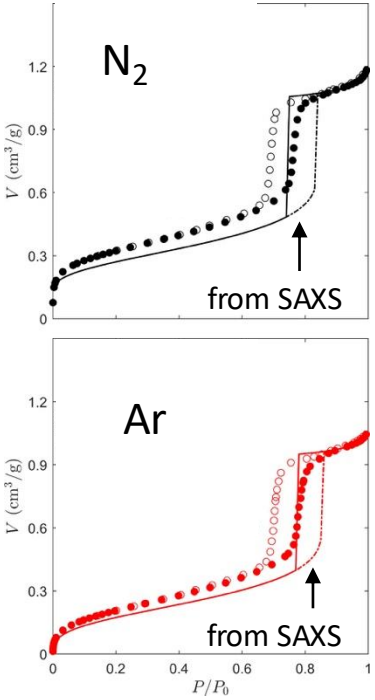




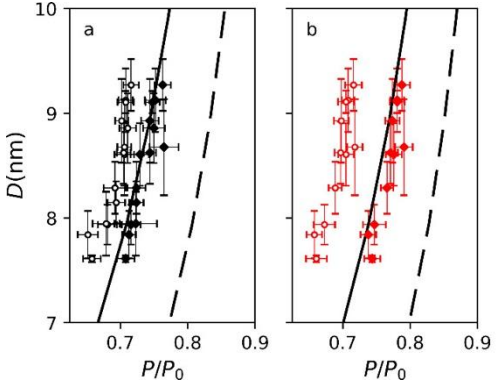


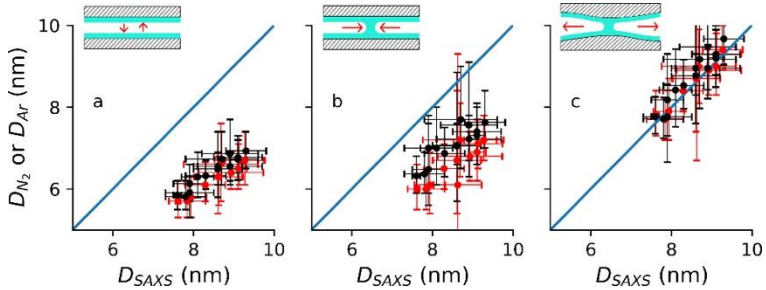
Phys. Chem. Chem. Phys., 2018, **20**, 13646–13659

SAXS versus Sorption Pore Sizes



Capillary condensation seems to occur at thermodynamic equilibrium



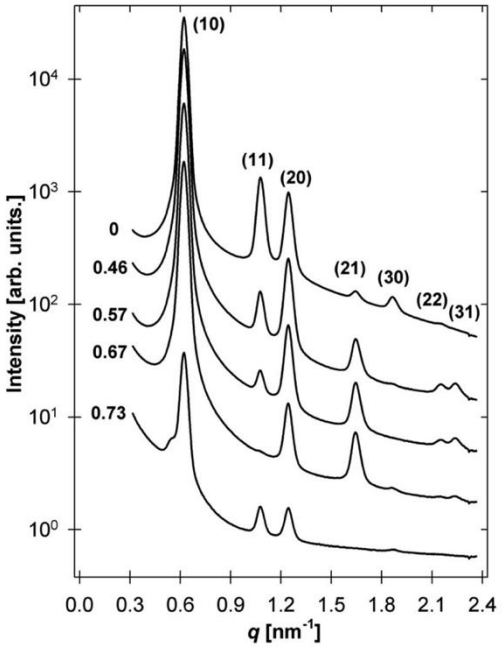


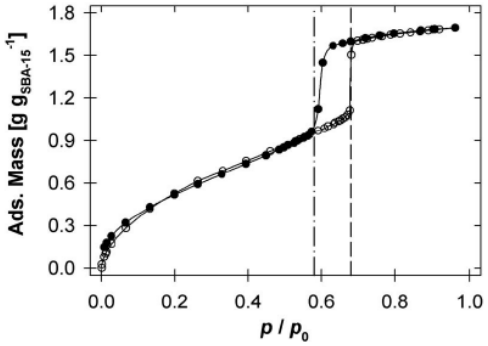
Langmuir 2024, 40, 17444–17453

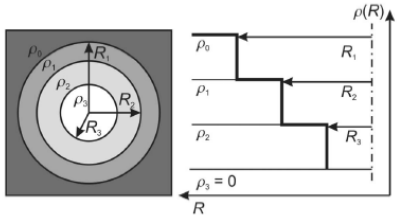
PHYSICAL REVIEW B **73**, 184109 (2006)

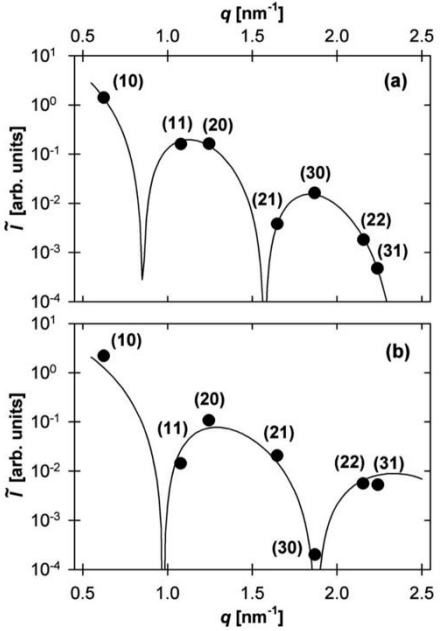
Physisorbed films in periodic mesoporous silica studied by *in situ* synchrotron small-angle diffraction

Gerald A. Zickler,[1] Susanne Jähnert,[2] Wolfgang Wagermaier,[1] Sérgio S. Funari,[3] Gerhard H. Findenegg,[2] and Oskar Paris[1,*]









Outline

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- Inelastic small-angle scattering (9 slides)

Two-point correlation functions

Strictly equivalent to the interference approach

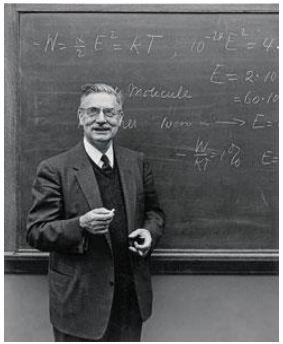
JOURNAL OF APPLIED PHYSICS VOLUME 28, NUMBER 6 JUNE, 1957

Scattering by an Inhomogeneous Solid. II. The Correlation Function and Its Application*

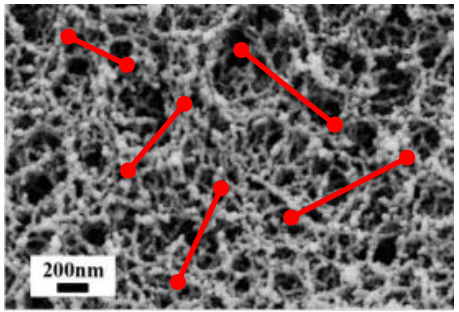
P. DEBYE, H. R. ANDERSON, JR.,† AND H. BRUMBERGER
Baker Laboratory of Chemistry, Cornell University, Ithaca, New York
(Received January 2, 1957)

$$\gamma(r)\langle\eta^2\rangle_{Av} = \langle\eta_A\eta_B\rangle_{Av}, \qquad (1)$$

$$i = 4\pi\langle\eta^2\rangle_{Av} V \int_0^\infty \gamma(r) r^2 \frac{\sin ksr}{ksr} dr. \qquad (4)$$



Peter Debye 1884-1966



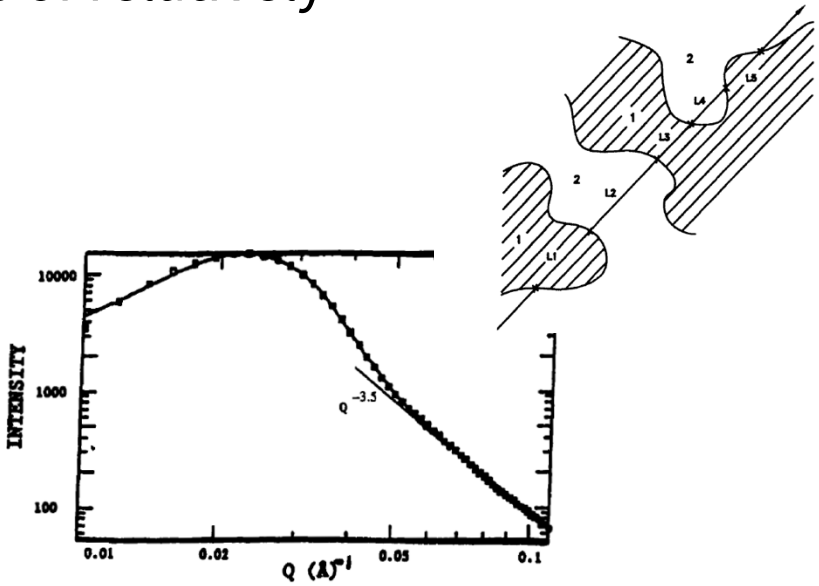
$$C(r) = \text{Prob}\left\{\begin{array}{l} x \text{ in the Solid} \\ x + r \text{ in the Solid} \end{array}\right\}$$

* This research was supported by the Esso Research and Engineering Company, Elizabeth, New Jersey.

SAXS/SANS in disordered materials

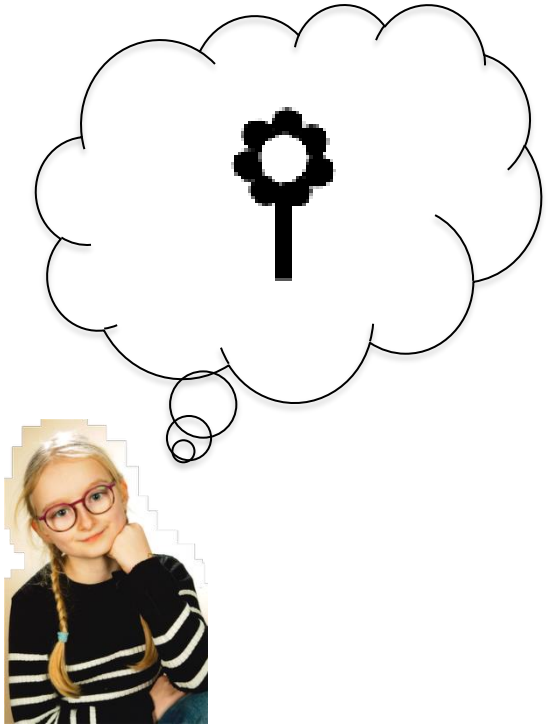
is traditionally discussed in terms of relatively unspecific geometrical concepts

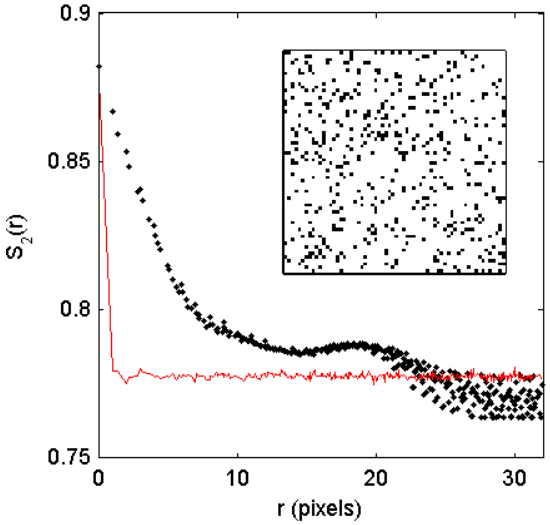
- Correlation lengths
- Fractal dimensions
- Surface areas
- Average chord lengths
- Etc.



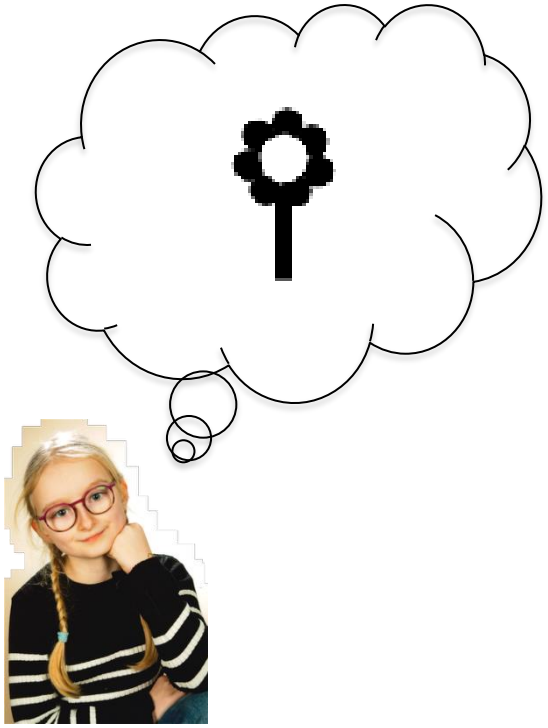
S.K. Sinha, *Small-Angle Scattering from Porous Materials*, Experimental Methods in the Physical Sciences 35 (1999) 223.

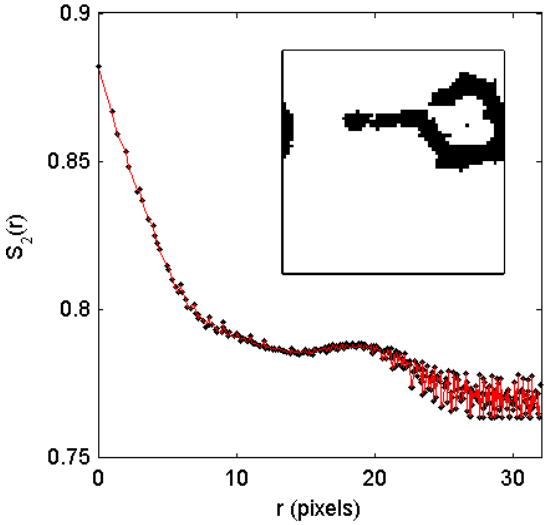
Scattering data analysis for (my) children



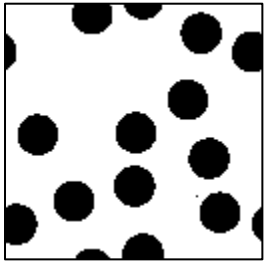


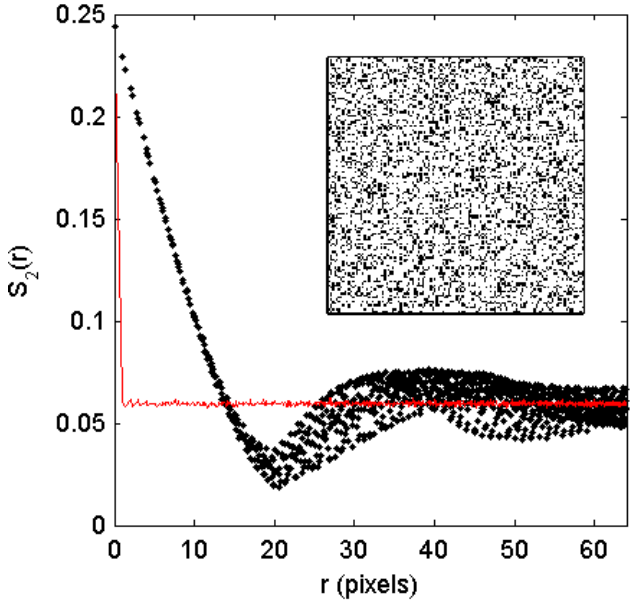
Scattering data analysis for (my) children





Direct reconstruction has a unique solution only for simple structures





In general, models are needed

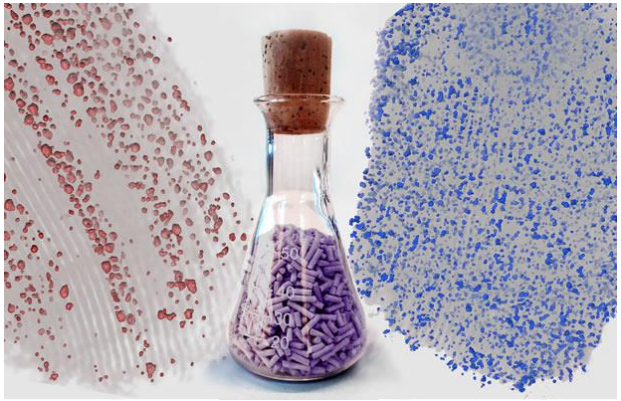
PHYSICAL REVIEW E **85**, 051140 (2012)

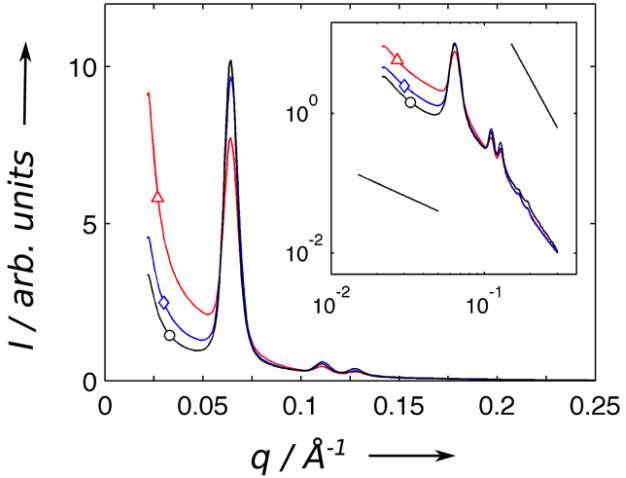
LETTERS
PUBLISHED ONLINE: 11 NOVEMBER 2012 | DOI: 10.1038/NMAT3471
nature materials

Towards stable catalysts by controlling collective properties of supported metal nanoparticles

Gonzalo Prieto[1], Jovana Zečević[1], Heiner Friedrich[2], Krijn P. de Jong[1]* and Petra E. de Jongh[1]*

(Modelling Example 1)



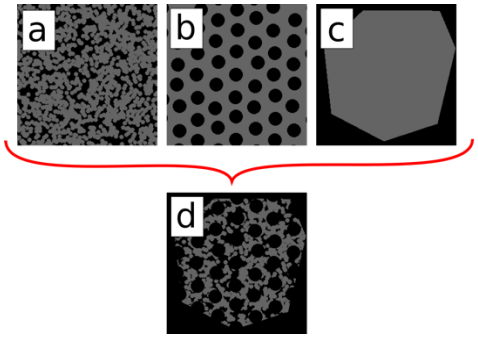


THE JOURNAL OF PHYSICAL CHEMISTRY C
DOI: 10.1021/acs.jpcc.5b09556
J. Phys. Chem. C 2016, 120, 1488−1506

Small-Angle Scattering Analysis of Empty or Loaded Hierarchical Porous Materials

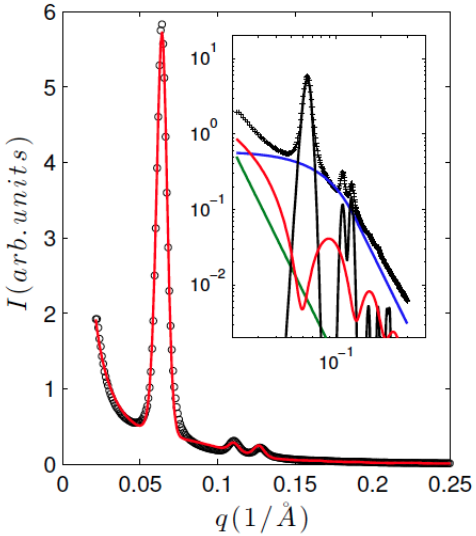
Cedric J. Gommes,*,† Gonzalo Prieto,‡,§ and Petra E. de Jongh‡

Micropores Mesopores Grain

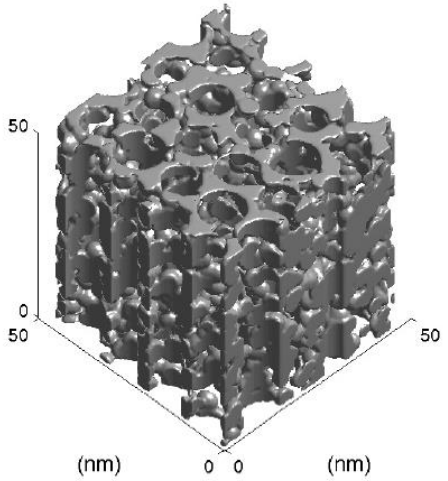


Complete model of the empty porous material

SAXS



Empty porous material



Angewandte Communications

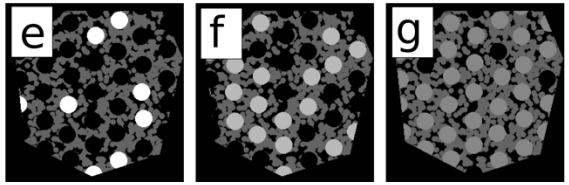
Nanoparticles

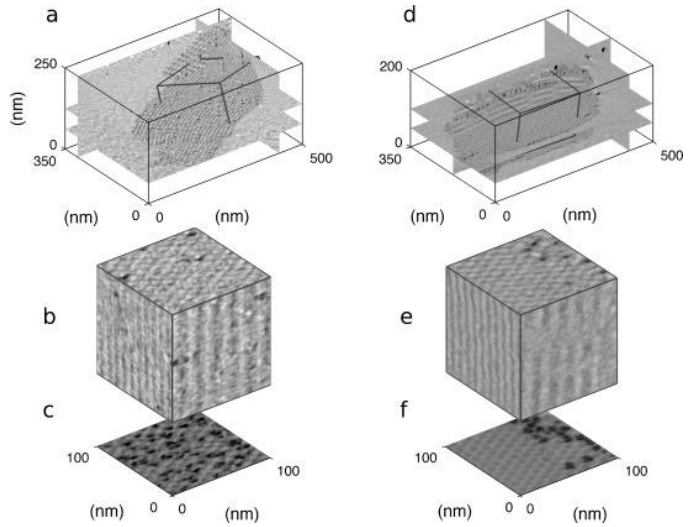
International Edition: DOI: 10.1002/anie.201505359
German Edition: DOI: 10.1002/ange.201505359

Mesoscale Characterization of Nanoparticles Distribution Using X-ray Scattering

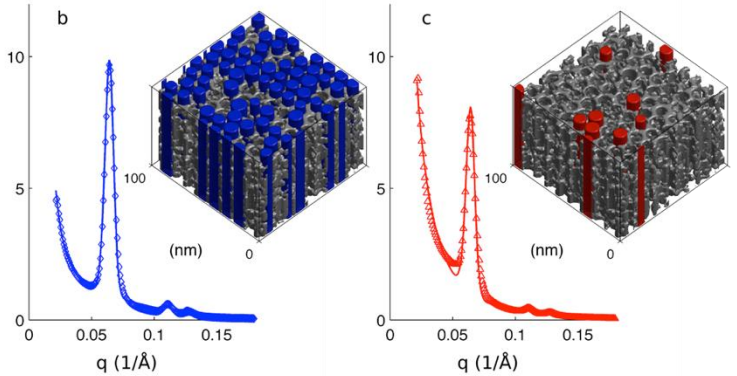
Cedric J. Gommes, Gonzalo Prieto, Jovana Zecevic, Maja Vanhalle, Bart Goderis, Krijn P. de Jong, and Petra E. de Jongh**

Model of metal loading





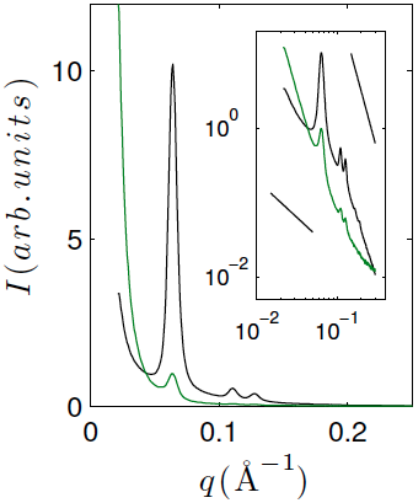
Electron tomography (3DTEM)

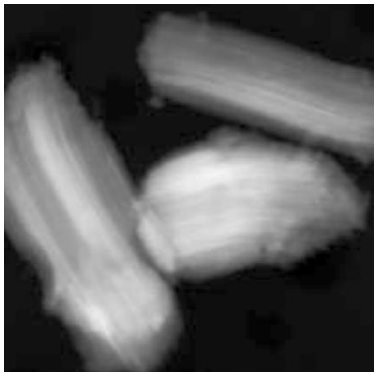


SAXS

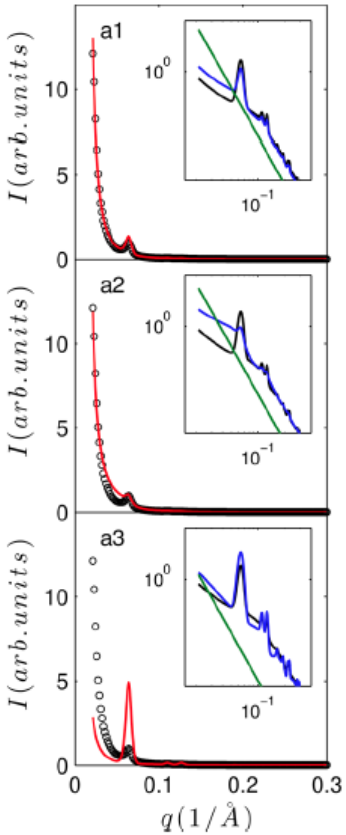
SAXS is sometimes more informative than TEM

SBA-15 impregnated with copper-nitrate





200 nm

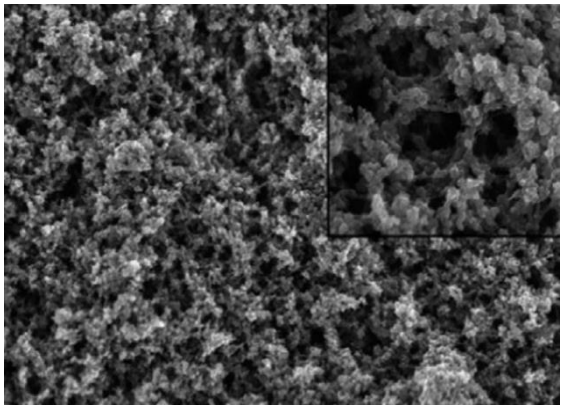


J. Phys. Chem. C 120 (2016) 1488-1506

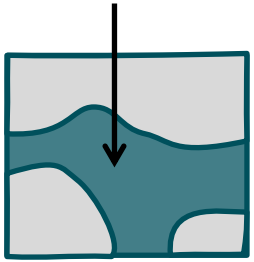
In-situ SAXS of confined liquids

(Modelling Example 2)

Carbon gels

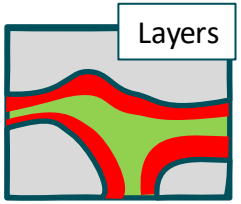


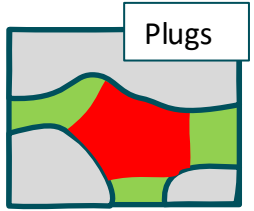
nitrobenzene/hexane
critical solution
Tc ~ 20°C

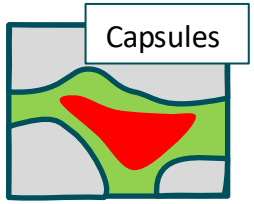


?

Cooling





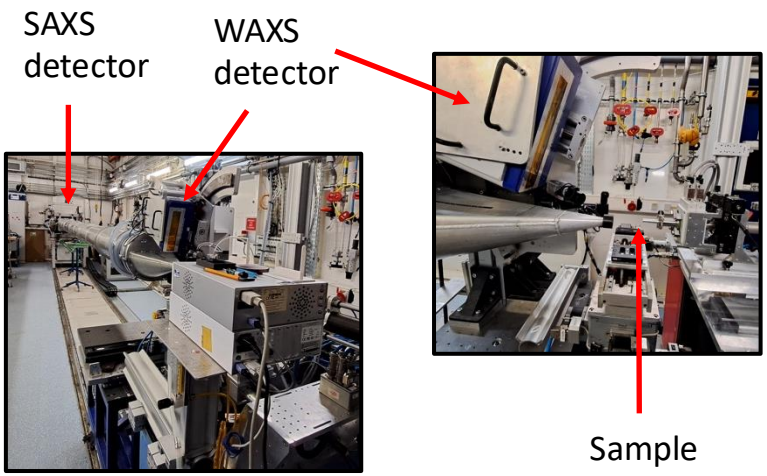


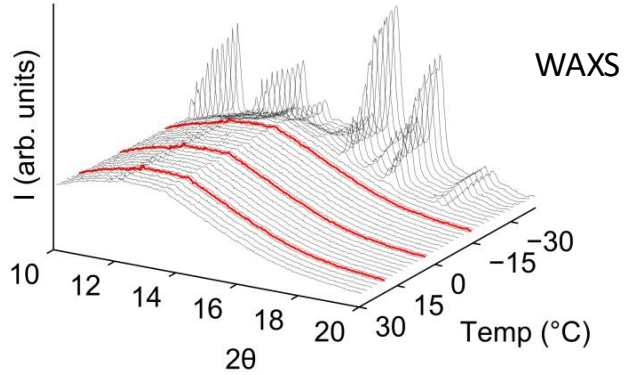
J. Appl. Cryst. (2013). **46**, 493–504

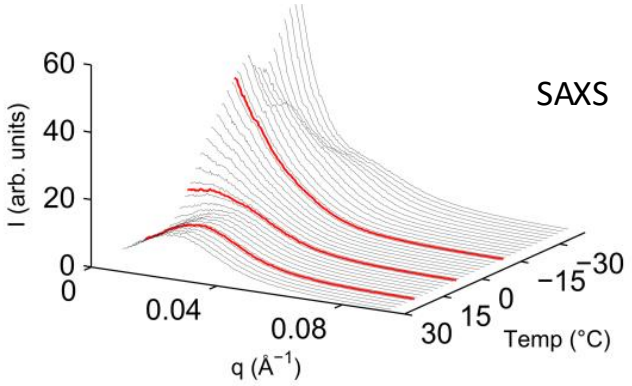
A.J. Liu et al, Phys. Rev. Lett. 65 (1990) 1897
L. Monette et al. Phys. Rev. A 46 (1992) 7664

In-situ SAXS/WAXS data

Nanometer-scale reorganization of liquids

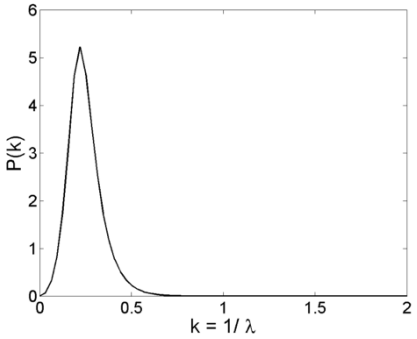




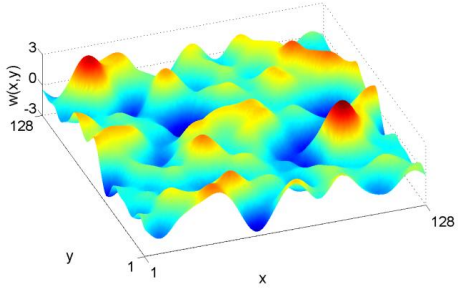


Dual Belgian Beamline (DUBBLE, BM26 @ ESRF)

Gaussian-field models of disordered porous materials

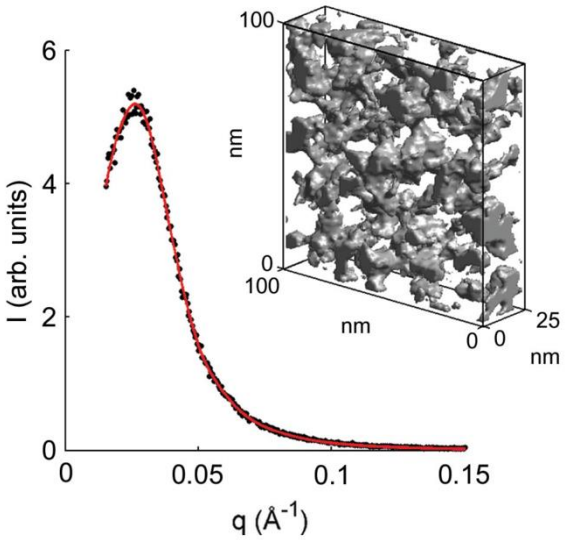


Power spectral density

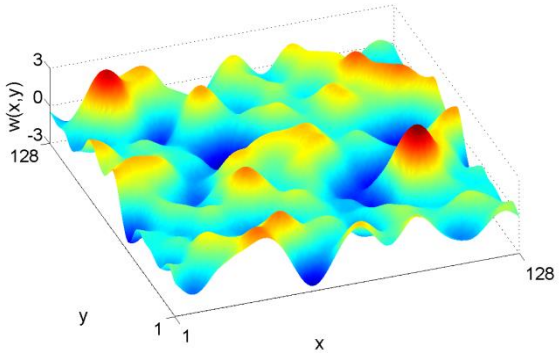


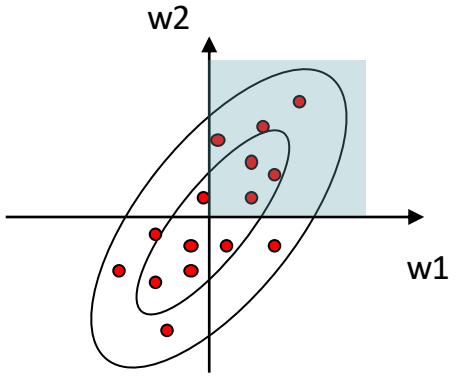
$$W(\mathbf{x}) = \sqrt{\frac{2}{N}} \sum_{n=1}^{N} \sin\left[\mathbf{q}_n \cdot \mathbf{x} - \varphi_n\right]$$

SAXS of empty carbon gel



The type of mathematics in Gaussian-field models



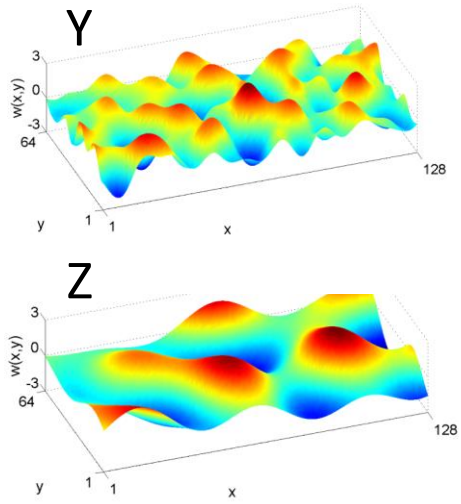


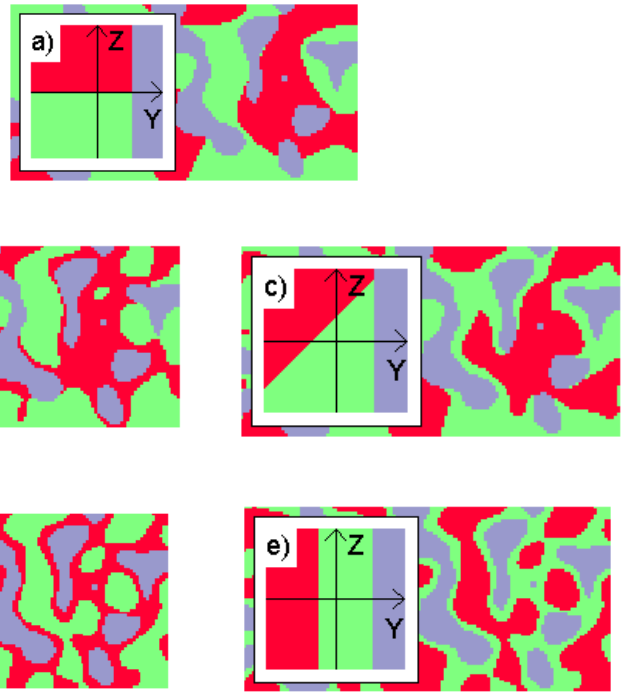
C(r) = probability for the two ends of a random stick with length r to be in the white phase

same as " to have a W > threshold "

Multiphase generalization of GRF models

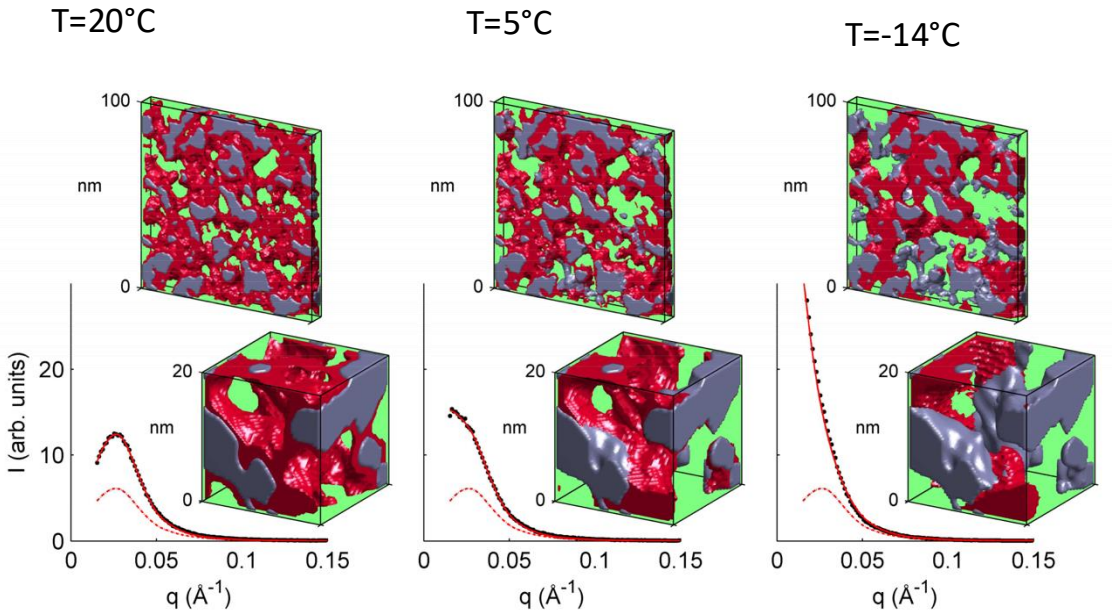
Plurigaussian models

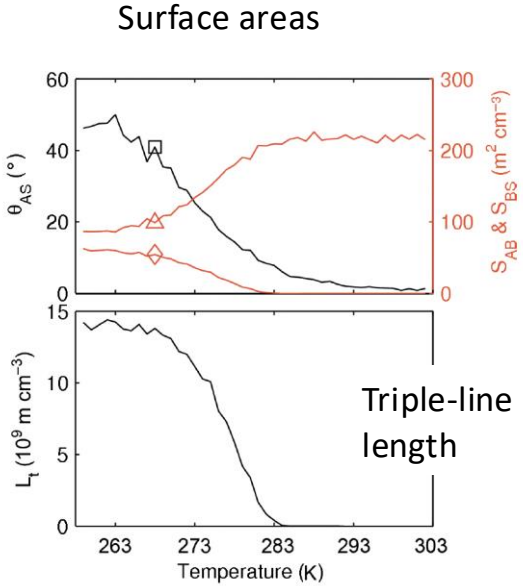




Lantuéjoul
Geostatistical Simulations,
Springer 2002

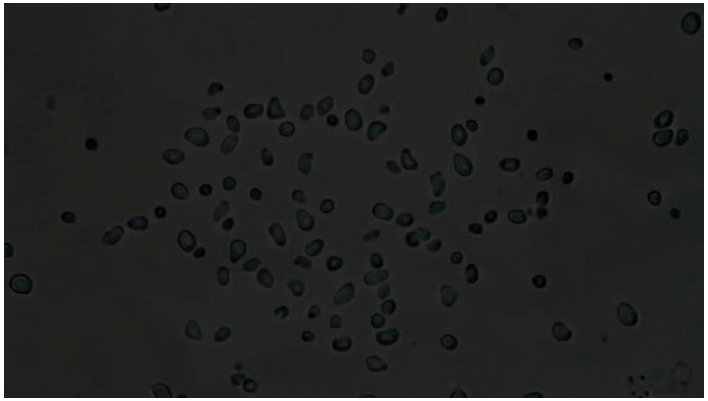
Nanometer-scale wetting transitions





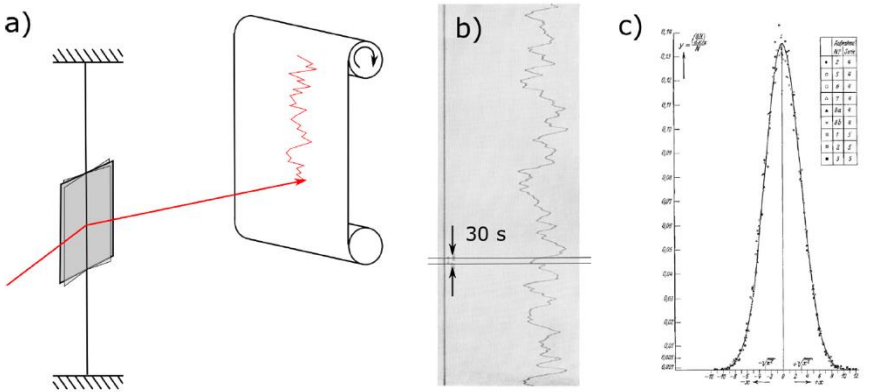
J. Appl. Cryst. (2013). **46**, 493–504

Nothing small is static



Stokes-Einstein's relation $D = \frac{k_B T}{6\pi\eta R}$

Yeo Yong Kiat, Youtube June 2014
Pollen grains in water - Brownian motion



Versuche zur Messung der Avogadro-Loschmidtschen Zahl aus der Brownschen Bewegung einer Drehwaage[1])

Von Eugen Kappler

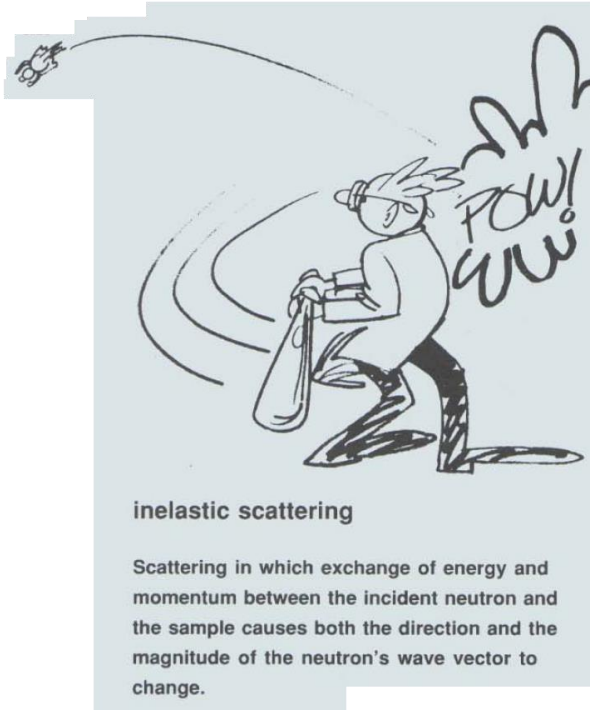
Equipartition theorem $\langle E \rangle = \frac{k_B T}{2}$

Kappler, Annalen der Physik, 1931

Inelastic neutron scattering

Neutron Spin Echo (NSE) instrument
J-NSE `PHOENIX' (Garching)
By courtesy of Dr. Olaf Holderer

JÜLICH Forschungszentrum



R. Pynn, Los Alamos Science 19 (1990)

Van-Hove correlation functions

For inelastic scattering by time-dependent structures

Leon van Hove (1924-1990)

PHYSICAL REVIEW VOLUME 95, NUMBER 1 JULY 1, 1954

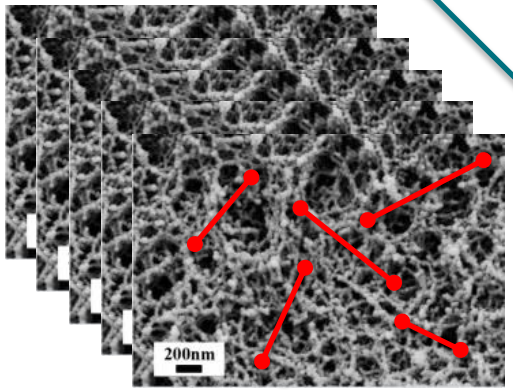
Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles

LÉON VAN HOVE
Institute for Advanced Study, Princeton, New Jersey
(Received March 16, 1954)

$$G(\mathbf{r},t)=N^{-1}\left\langle \sum_{l,j=1}^{N} \int d\mathbf{r}'\cdot\delta(\mathbf{r}+\mathbf{r}_l(0)-\mathbf{r}')\delta(\mathbf{r}'-\mathbf{r}_j(t))\right\rangle, \quad (10)$$

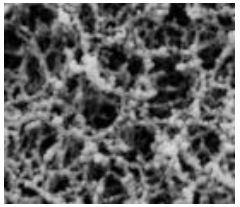
$$\frac{d^2\sigma}{d\Omega d\epsilon}=\frac{a^2N}{2\pi\hbar}\frac{k}{k_0}\int \exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]\cdot G(\mathbf{r},t)d\mathbf{r}dt. \quad (26)$$

time

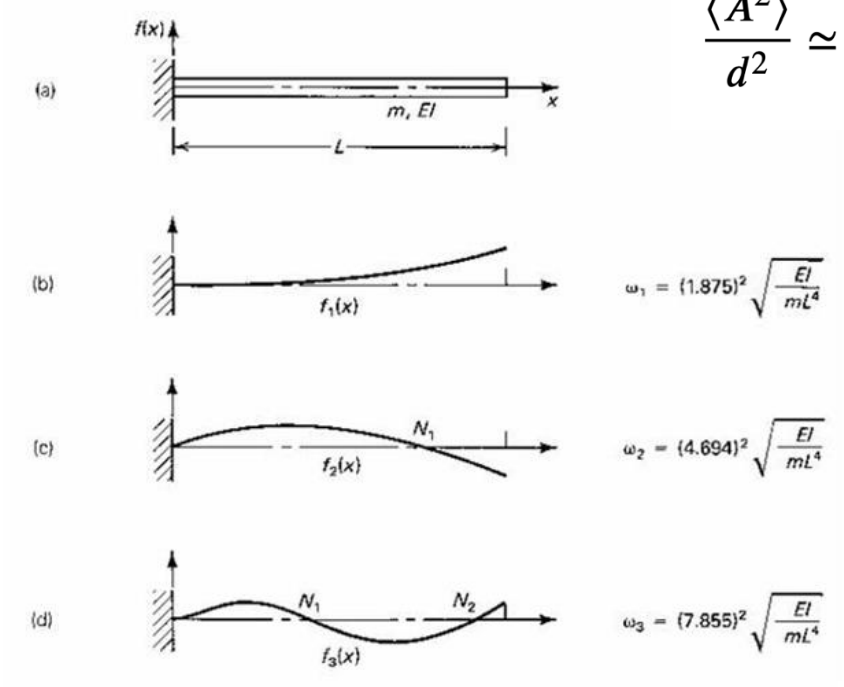


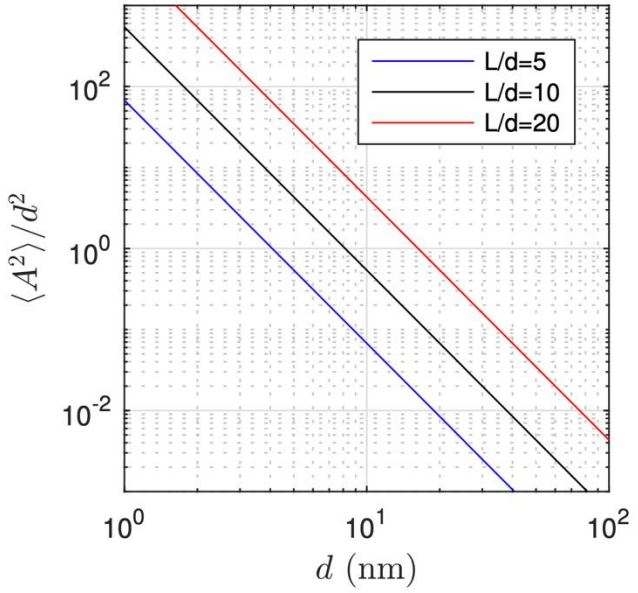
$$C(r,\tau) = \text{Prob}\left\{ \begin{array}{l} x \text{ in the Solid at time } t \\ x+r \text{ in the Solid at time } t+\tau \end{array} \right\}$$

Thermal fluctuations of a cantilever beam



$$\frac{\langle A^2 \rangle}{d^2} \simeq 6.8 \frac{k_B T}{E d^3} \left(\frac{L}{d} \right)^3$$





VOLUME 64, NUMBER 19 PHYSICAL REVIEW LETTERS 7 MAY 1990

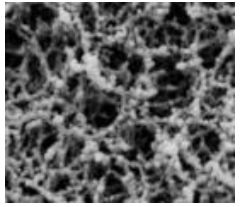
Dynamics of Weakly Connected Solids: Silica Aerogels

D. W. Schaefer and C. J. Brinker
Sandia National Laboratories, Albuquerque, New Mexico 87185

D. Richter, B. Farago, and B. Frick
Institut Laue-Langevin, 38042 Grenoble, France
(Received 13 November 1989)

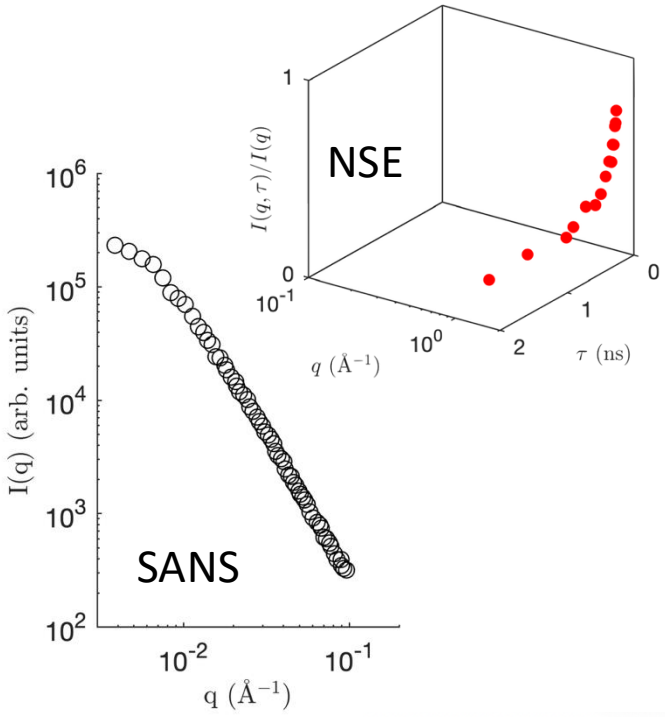
Applying neutron spin-echo spectroscopy, we investigate low-energy vibrational excitations in a series of silica aerogels of varying connectivity. Connectivity is adjusted both by precursor solution chemistry and by heat treatment. Polymeric aerogels show fractonlike densities of states, whereas colloidal materials exhibit a peak in the μeV regime. On sintering, the low-frequency excitations disappear. We conclude that neutron spin-echo spectroscopy provides a measure of the topological aspects of disordered materials.

Re-analyzing old scattering data with a new model



10-100 nm

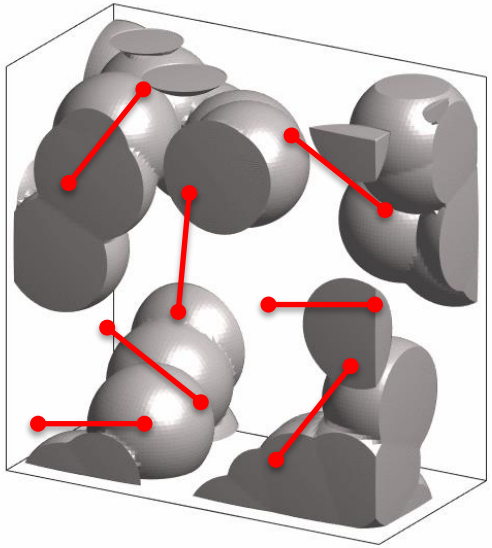
Porosity > 90%

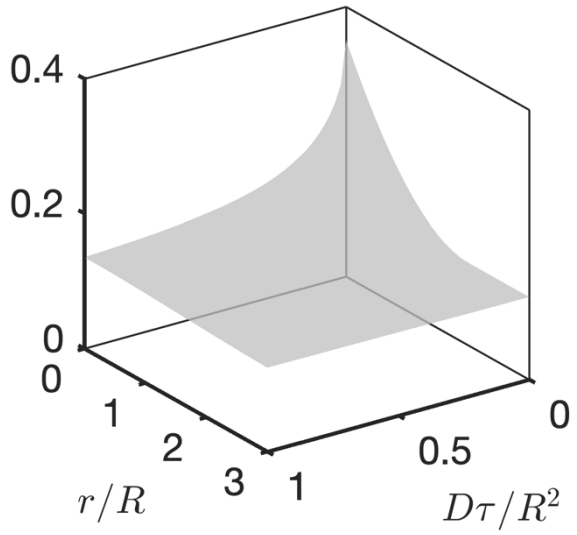


Gels **2022**, *8*, 236.

Time-dependent Boolean models

A building block for more complex models





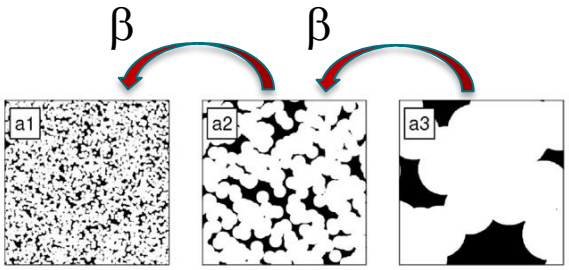
$$C_{00}(r,\tau) = \exp[-2\eta + \eta K(r,\tau))]$$

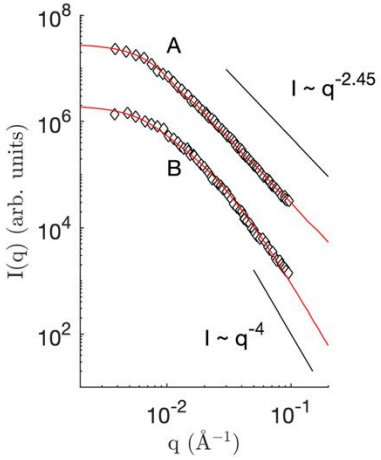
$$K(r,\tau) = \int \mathrm{d}^3 j \, K(\mathbf{r}-\mathbf{j}) f_\tau(\mathbf{j})$$

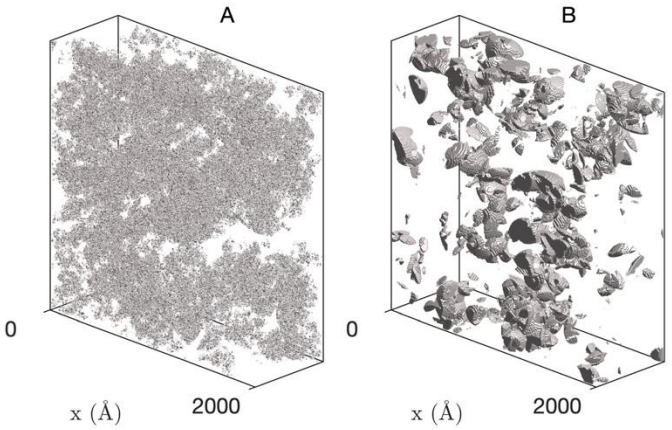
$$f_\tau(\mathbf{j}) = \frac{1}{(4\pi D\tau)^{3/2}} \exp\left[-\frac{|\mathbf{j}|^2}{4D\tau}\right]$$

Hierarchical structures from Boolean models

Low-density fractal-like structures





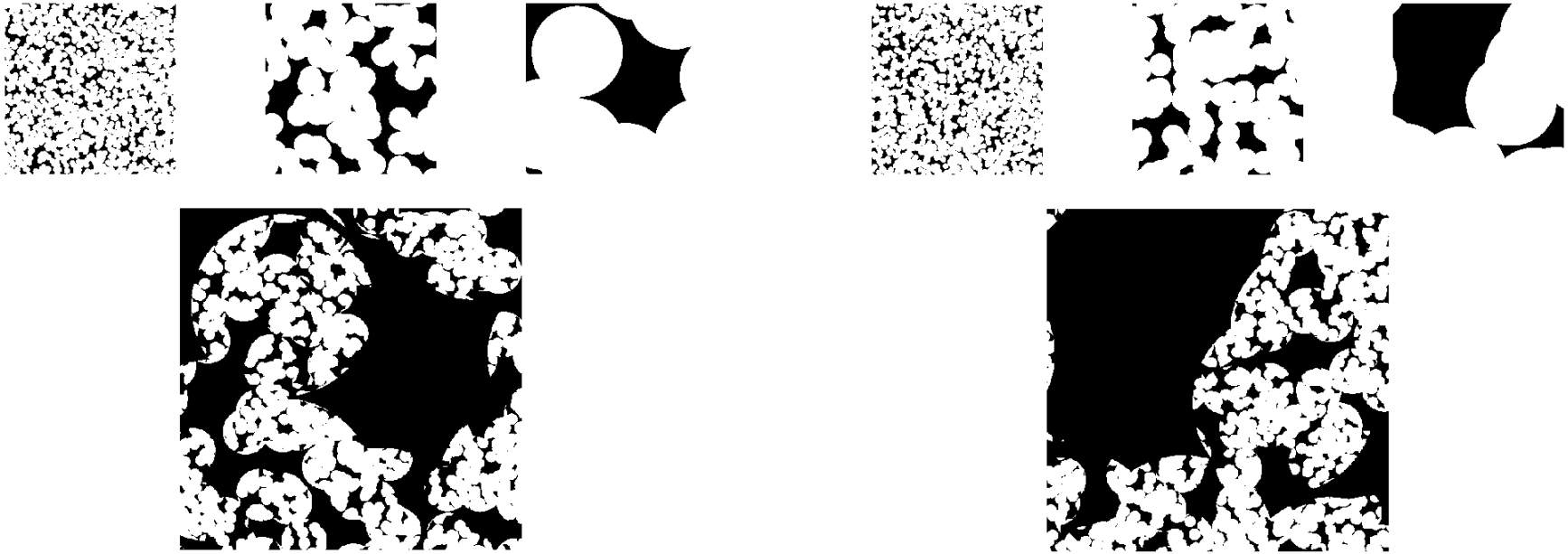


$\phi_1 = \varphi_1 \times \varphi_1 \times \ldots$

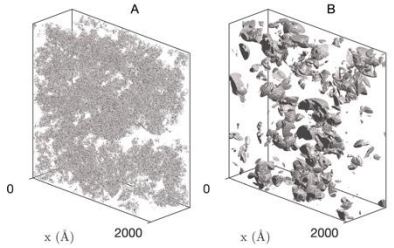
Gels **2022**, *8*, 236.

Multiscale fluctuations

With scale-dependent diffusion coefficient

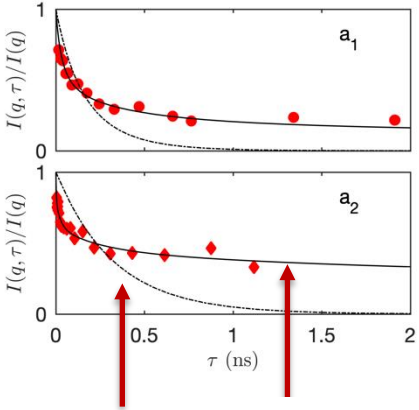


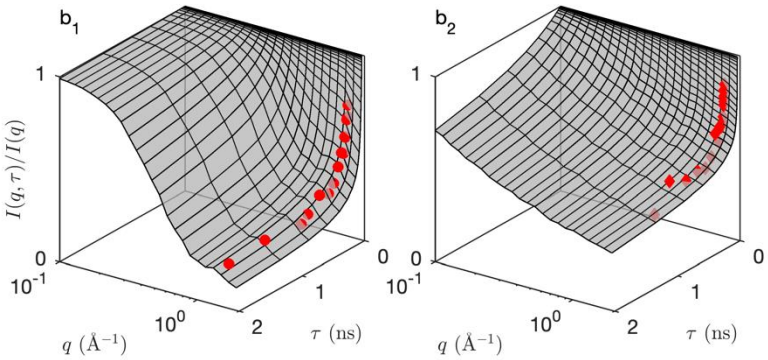
NSE data analysis in aerogels with scale-dependent diffusion coefficents

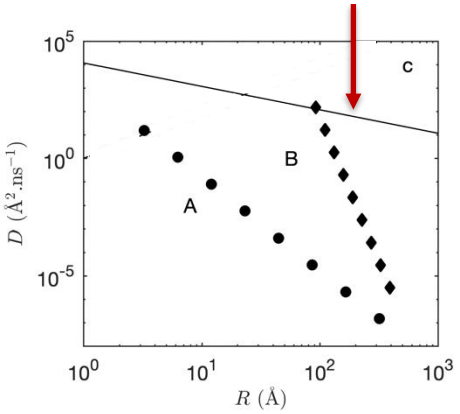


Hints of distinctly different topologies

$$D = \frac{k_B T}{6\pi\eta R}$$







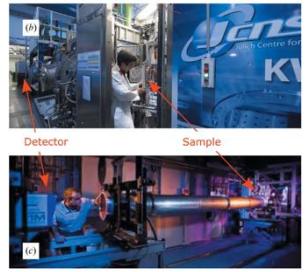
Constant D

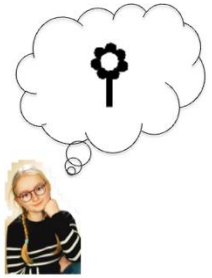
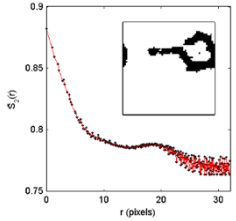
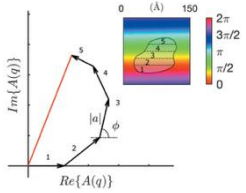
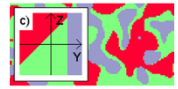
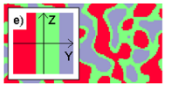
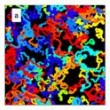
$$D = D_1 \left(\frac{R_1}{R} \right)^{\delta}$$

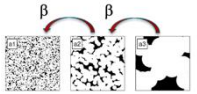
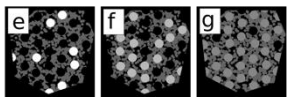
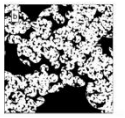
Gels **2022**, *8*, 236.

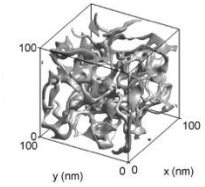
Conclusions/highlights

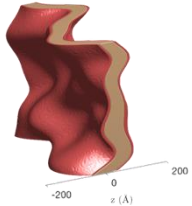
- Small-angle scattering experiments offer a unique window into nanoporous materials, also for in situ studies
- The information is very rich but indirect
  (and it is not as obscure as some people claim)
- Models offer flexible approaches to convert reciprocal-space data into real-space structure and dynamics
- Feel free to get in touch

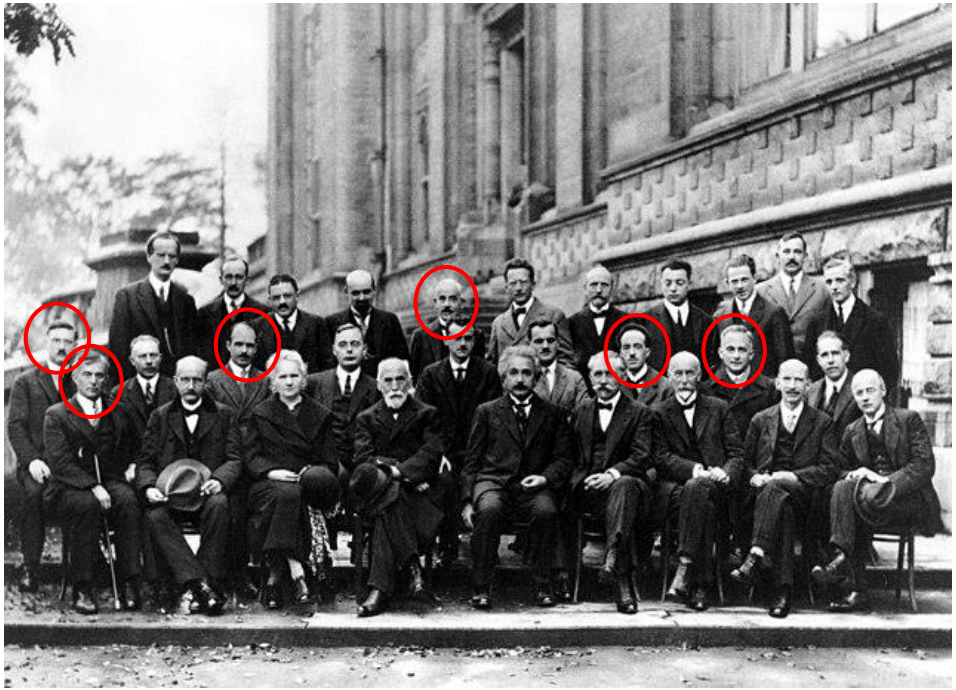









Solvay conference (1927)

P. Debye

T. De Donder

W. Bragg

L. de Broglie

M. Born

I. Langmuir

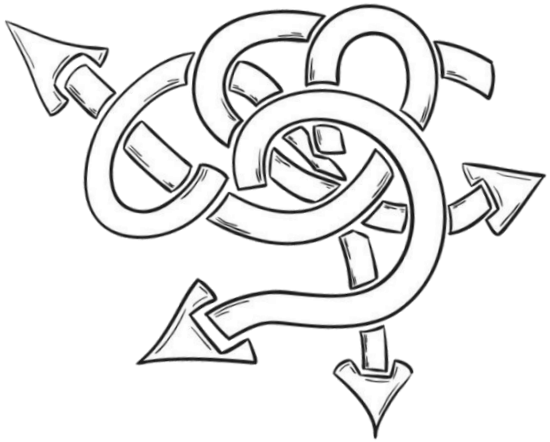
Leon van Hove (1924-1990)

Ilya Prigogine (1917-2003)

Thank you
for your attention

and for your questions

Cedric.Gommes@uliege.be



teaching and education

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Small-angle scattering for beginners

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