Stochastic Models of Disordered Porous Materials

for small-angle scattering analysis and more

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Leoben, July 3rd 2018

Outline

- Why models? in general and for small-angle scattering in particular

- Some stochastic models
  - Boolean models
  - Dead leaves models
  - Gaussian random field models

- Examples of SAXS data analysis
  - Supported nanoparticles
  - Confined liquids

- And more…
  - Predicting adsorption in disordered mesopores

Why use models?

- The engineer: To make inferences from incomplete data;
- The scientist: As a reality check, because models are falsifiable;
- The philosopher: Isn’t the very purpose of science to produce useful models of reality?

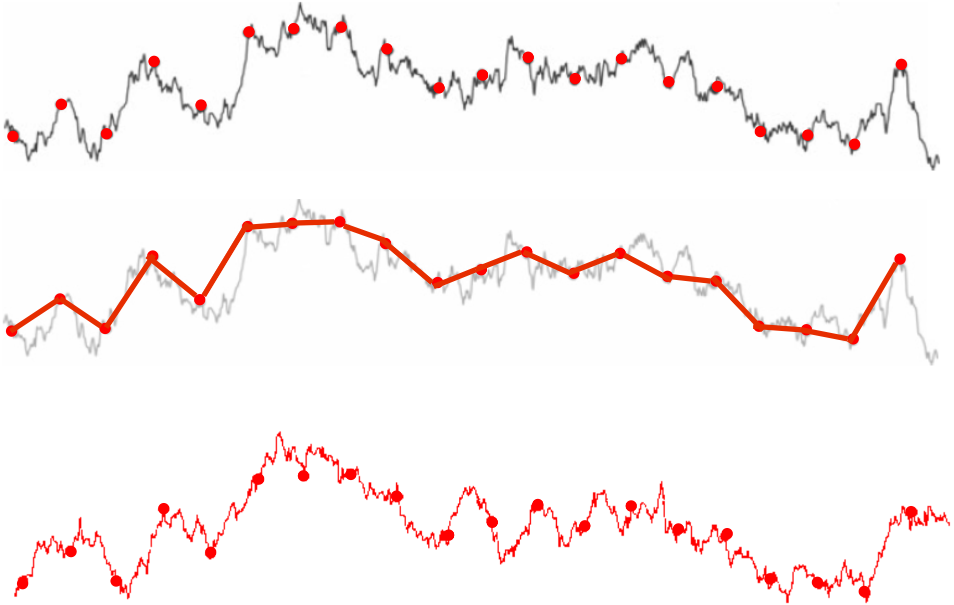
Inferences about porous materials

- Characterization data: adsorption/desorption,
  mercury intrusion,
  microscopy,
  small-angle scattering, etc.

- Inferences: Surface areas, pore volumes,
  pore size distribution, solid size distribution,
  connectivity, tortuosity, etc.
  Or even predict useful macroscopic properties

An example of inference

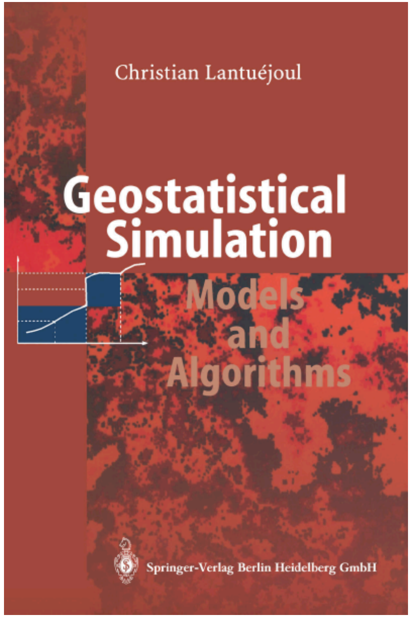
the length of an undersea cable



Data

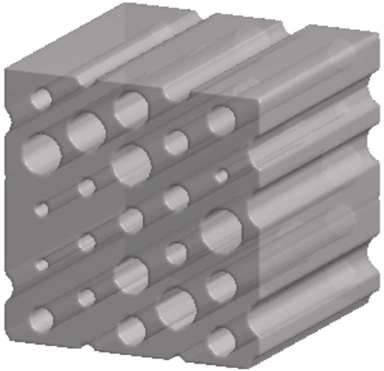
Interpolation

Model

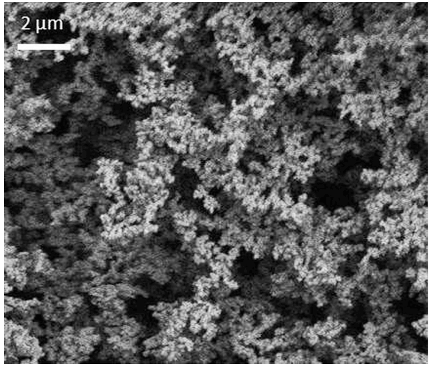


Often, “no model” = crude model

Implicit model in many data analysis procedures



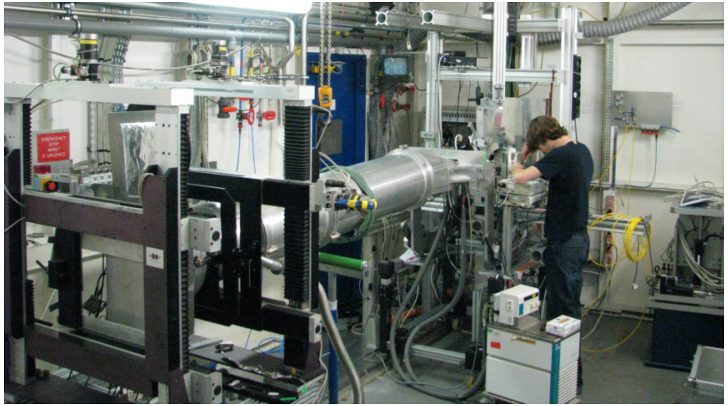
What the materials microstructure may look like*



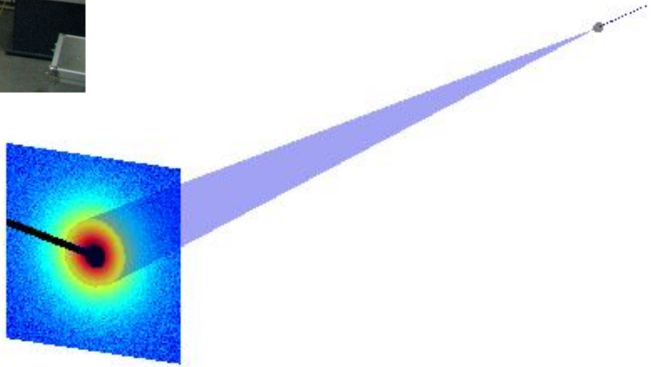
*The Journal of Supercritical Fluids 107 (2016) 201

Small-Angle Scattering (SAXS or SANS)

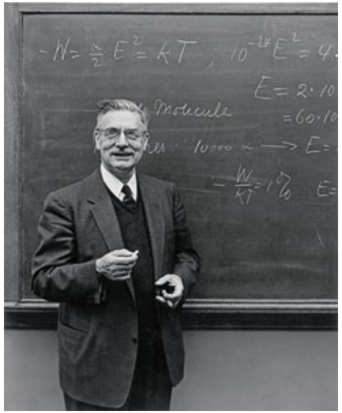
BM26@ESRF



Typically, length scales
from 1 nm to 100 nm are probed.



The mathematics of SAXS



Peter Debye 1884-1966

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

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

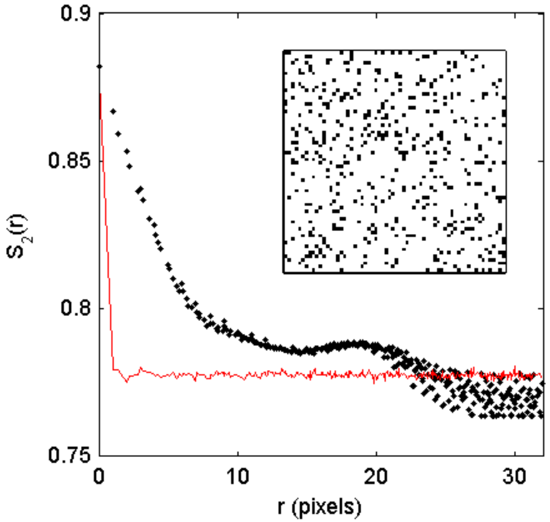
P. DEBYE, H. R. ANDERSON, JR.,† AND H. BRUMBERGER
Baker Laboratory of Chemistry, Cornell University, Ithaca, New York
(Received January 2, 1957)

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

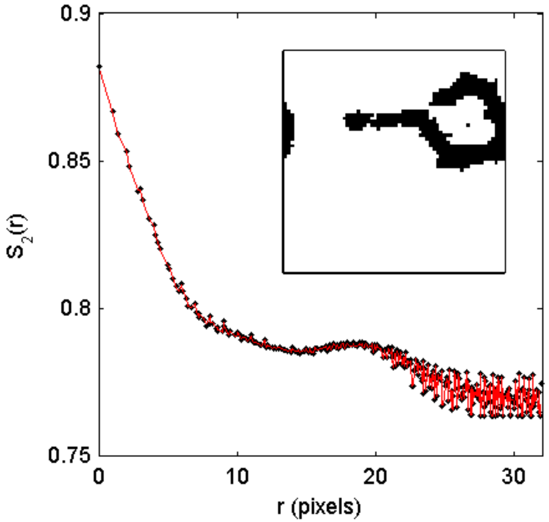
$$i=4\pi\langle\eta^2\rangle_{\mathrm{Av}}V\int_0^\infty\gamma(r)r^2\frac{\sin ksr}{ksr}dr. \tag{4}$$

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

SAS data analysis for children



SAS data analysis for children



The missing information can be compensated with structural models

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

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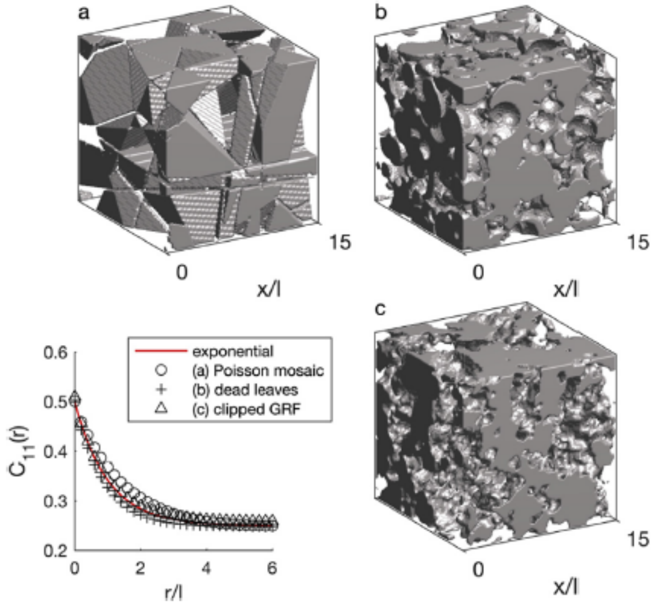
Microporous and Mesoporous Materials 257 (2018) 62–78



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Boolean models

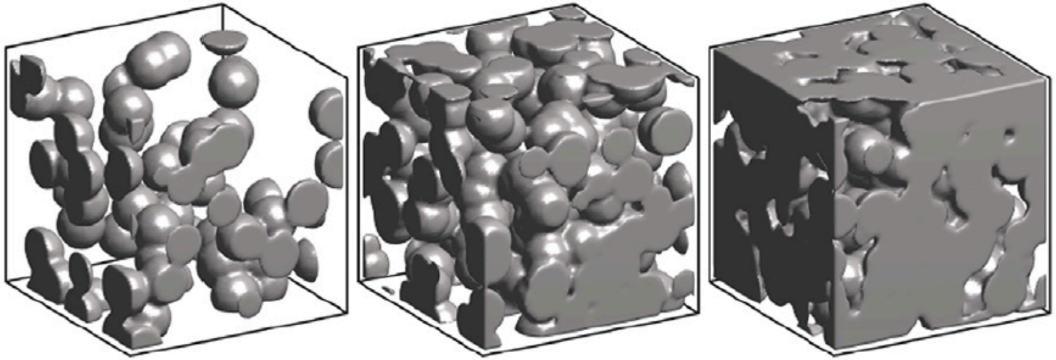
Porosity

$$\phi_0 = \exp[-\theta V]$$

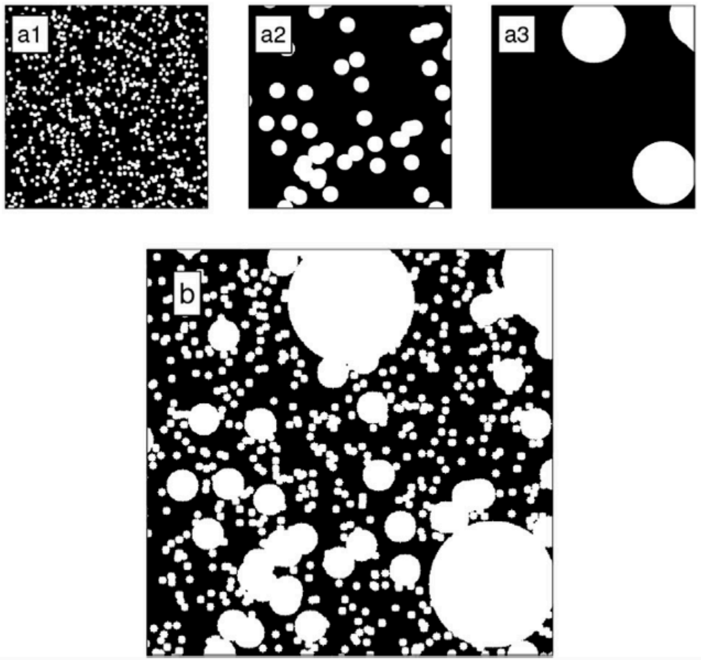
Correlation function

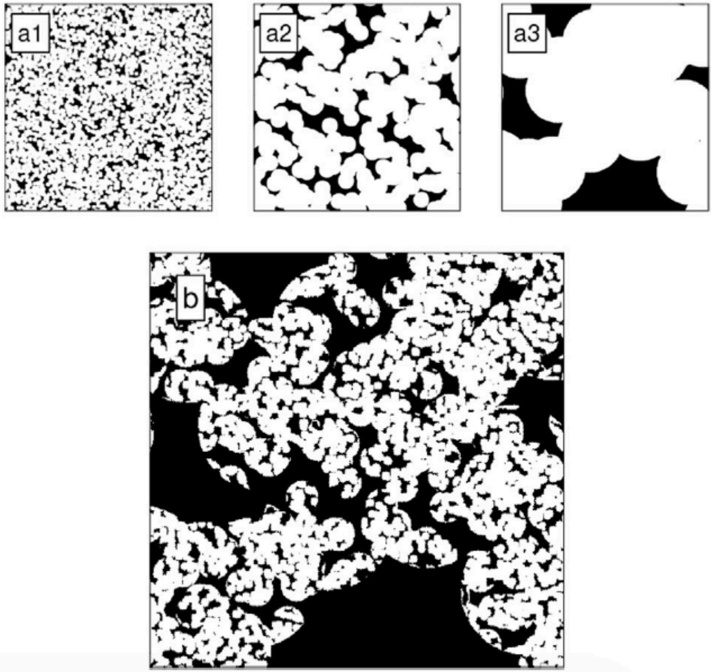
$$C_{00}(r) = \phi_0^2 \exp[\theta K(r)]$$

$$K_R(r) = \frac{4\pi}{3} R^3 \left(1 - \frac{r}{2R}\right)^2 \left(1 + \frac{r}{4R}\right)$$

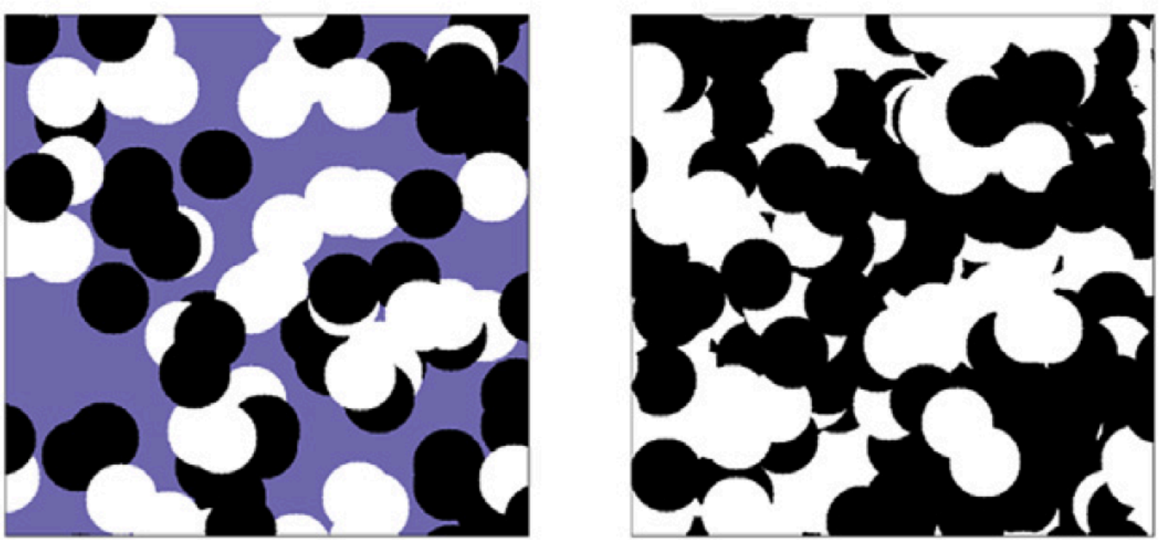


Variations of the Boolean model

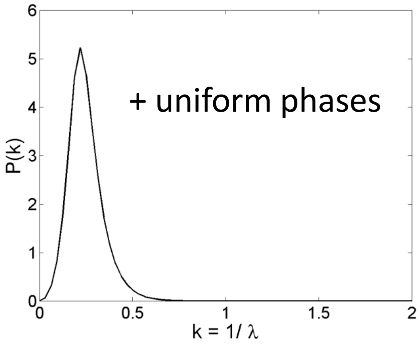




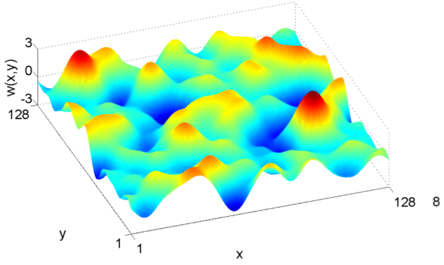
Dead-leave model

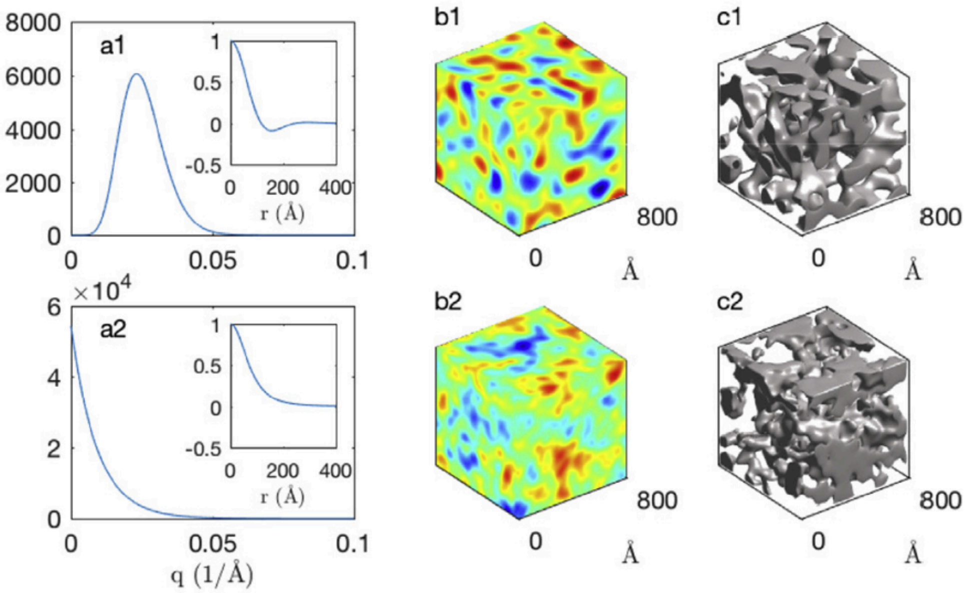


Gaussian random field models

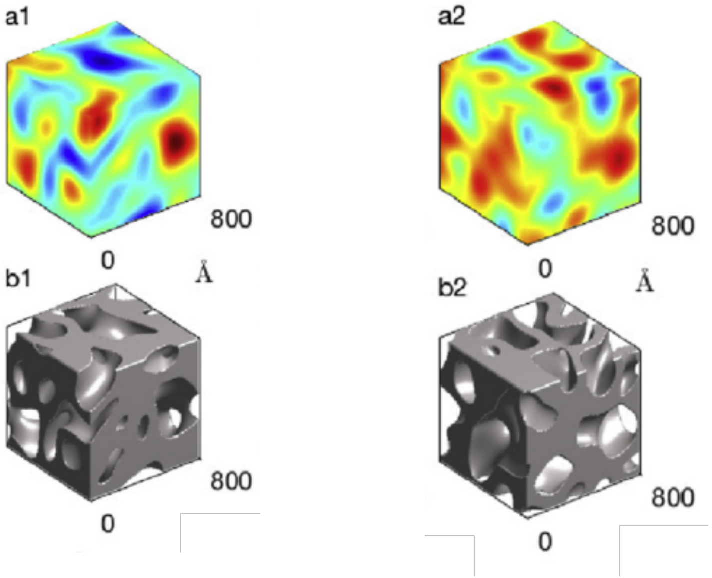


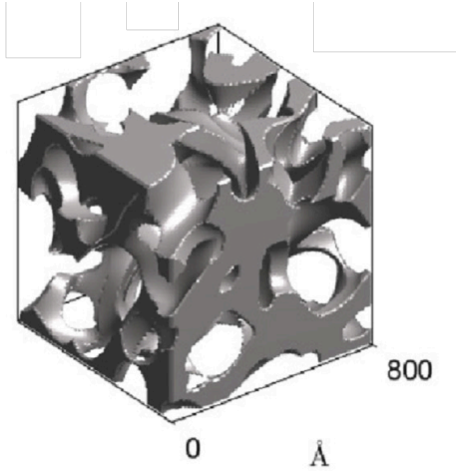
Distribution of wavevectors





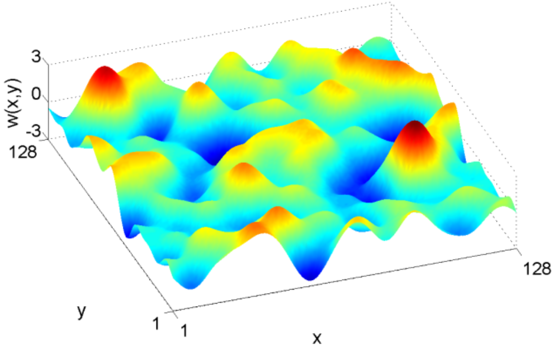
Tuning the connectivity of GRF models

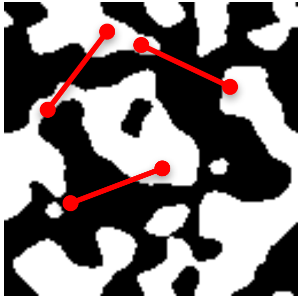


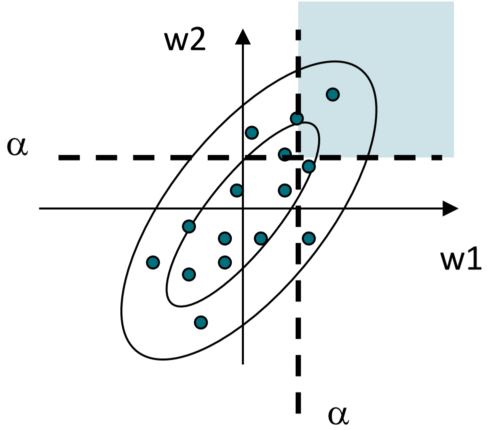


The type of mathematics in Gaussian-field models

The correlation function $P_{SS}(r)$

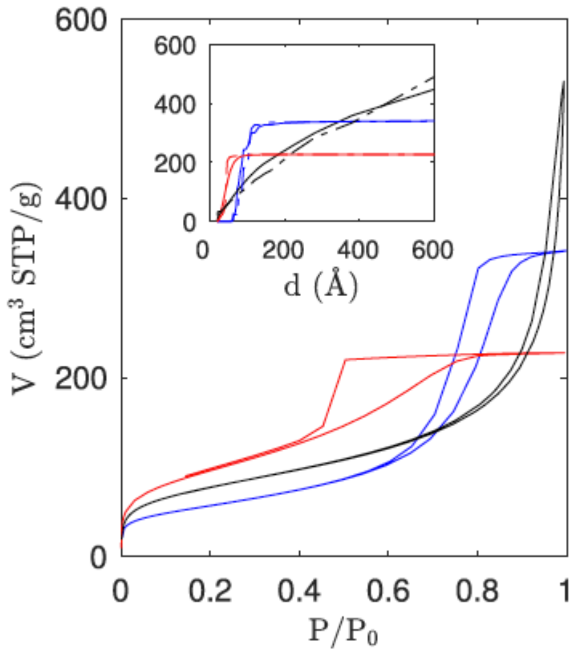




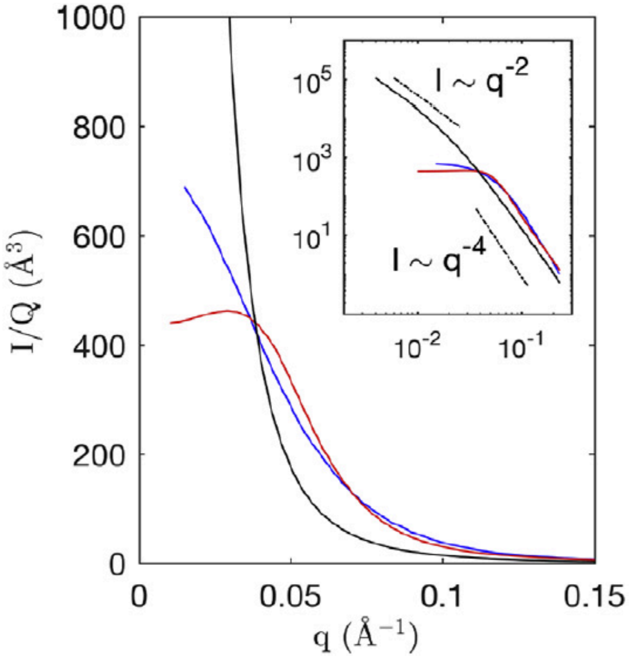


Three disordered mesoporous materials

N2 adsorption/desorption

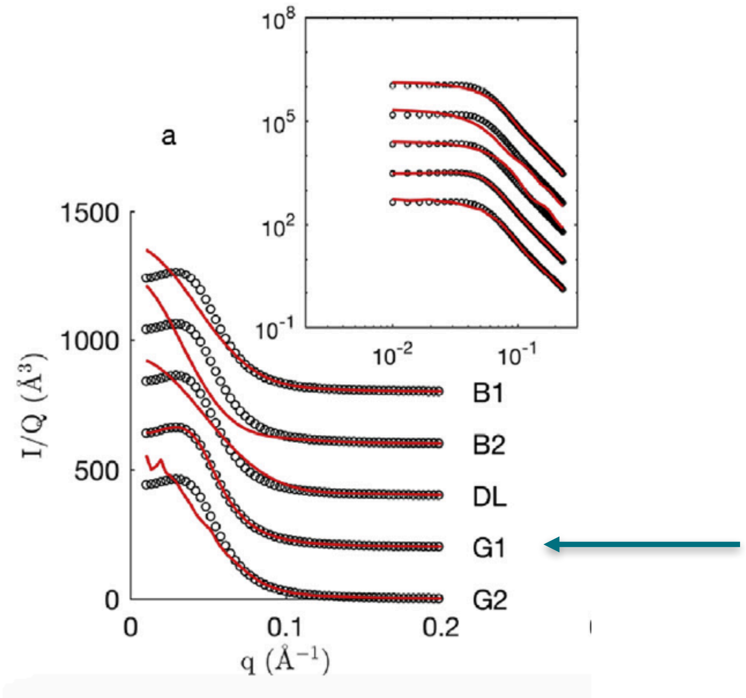


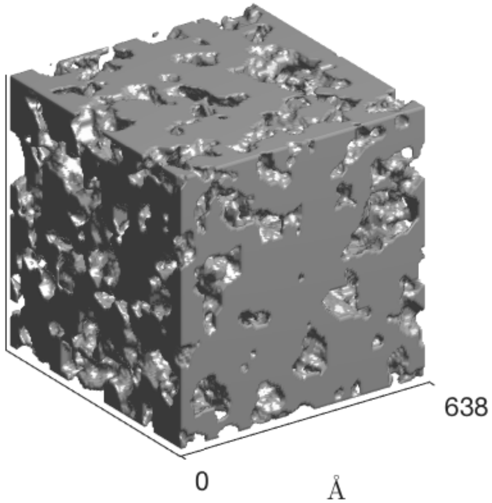
SAXS



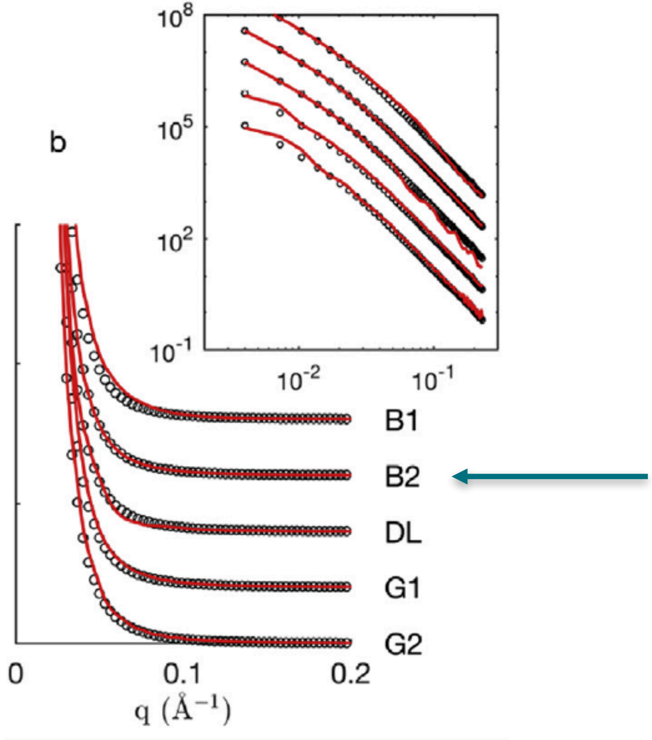
Carbon xerogel
Mesoporous alumina
Fumed silica

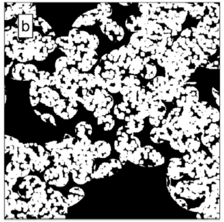
Carbon xerogel

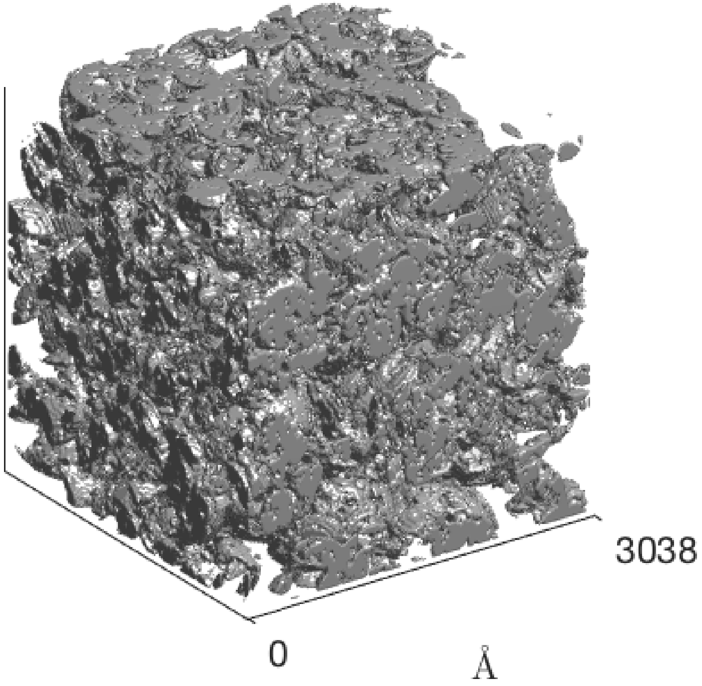




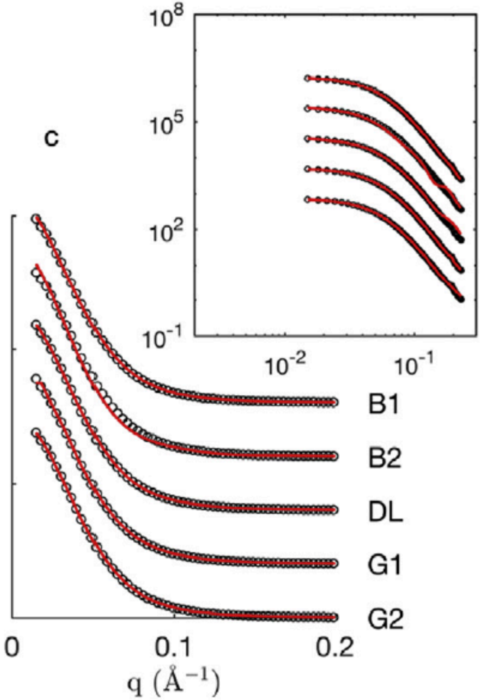
Fumed silica

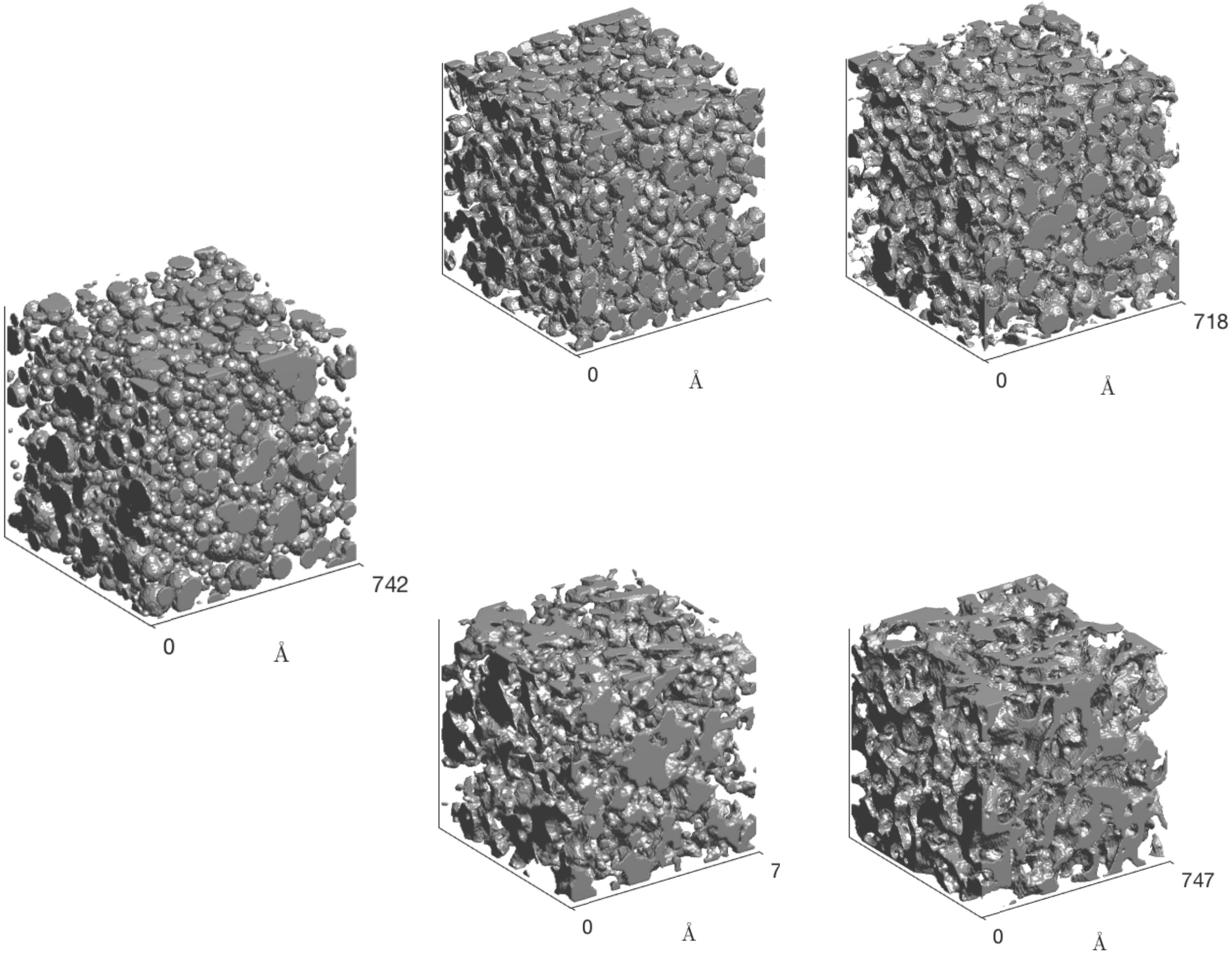




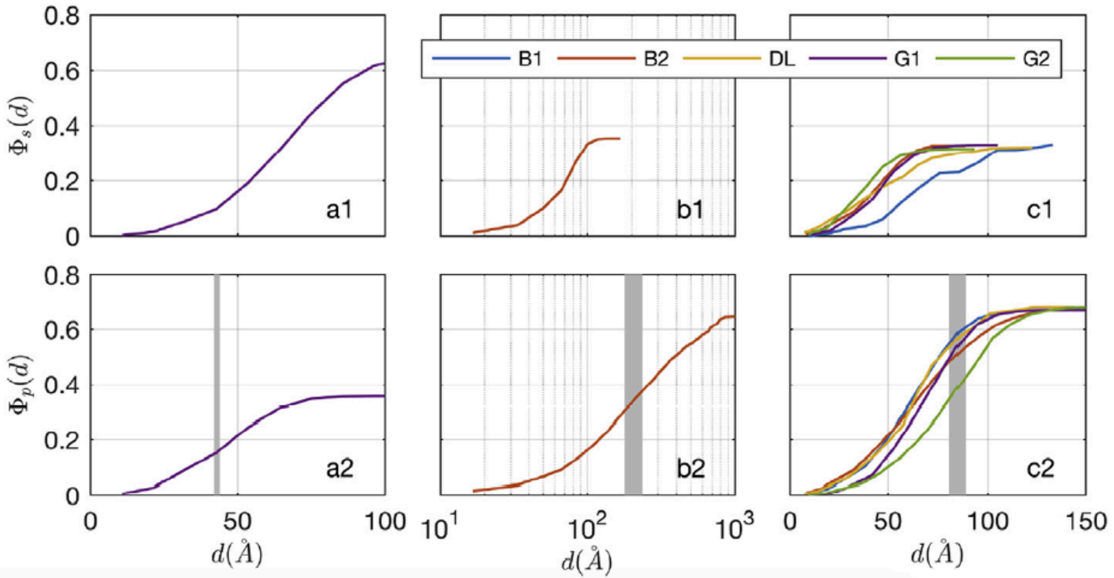


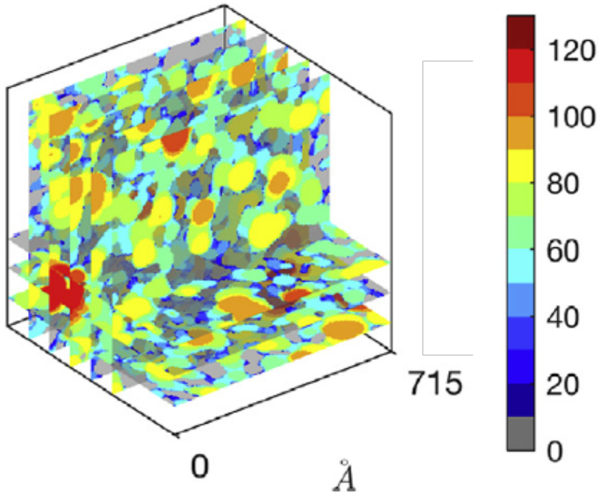
Alumina


c
10^8
10^5
10^2
10^-1
10^-2
10^-1
B1
B2
DL
G1
G2
0
0.1
0.2
q (Å^-1)


742
0
Å
0
Å
718
0
Å
7
0
Å
747
0
Å

Reality check: size distributions





Inferences: connectivity, tortuosity

Material Model	A_V [m^2 cm^{-3}]	$l_p^{(c)}$ [Å]	$l_s^{(c)}$ [Å]	A_3 [10^3 Å^3]	ϕ_s [%]	$\phi_s^{(d)}$ [%]	$\phi_p^{(d)}$ [%]	τ_p [-]	τ_s [-]	$d_p^{(m)}$ [Å]	$d_s^{(m)}$ [Å]
Xerogel											
G1	261	54	100	113	65±0.5	$\sim 10^{-3}$	$\sim$ 10–4	1.4 ± 0.0	1.1 ± 0.0	55 ± 5	75 ± 5
Silica											
B2	173	148	83	48 397	36±1.4	$\sim 10^{-3}$	$\sim 10^{-3}$	1.1 ± 0.0	1.4 ± 0.0	200 ± 17	83 ± 8
Alumina											
B1	269	101	48	186	33±1.3	1.4 ± 0.3	$\sim 10^{-6}$	1.1±0.0	2.1±0.1	67±5	67±5
B2	318	86	40	204	32±1.0	$\sim 10^{-1}$	$\sim 10^{-4}$	1.1±0.0	1.8±0.1	69±4	48±4
DL	355	77	36	168	32±1.3	$\sim 10^{-3}$	$\sim 10^{-2}$	1.1±0.0	1.5±0.0	65±5	46±5
G1	244	112	53	166	33±1.7	$\sim 10^{-2}$	$\sim 10^{-5}$	1.1±0.0	1.4±0.0	74±5	53±5
G2	274	99	47	190	32±0.5	$\sim 10^{-1}$	$\sim 10^{-3}$	1.2±0.0	1.3±0.0	84±5	39±4

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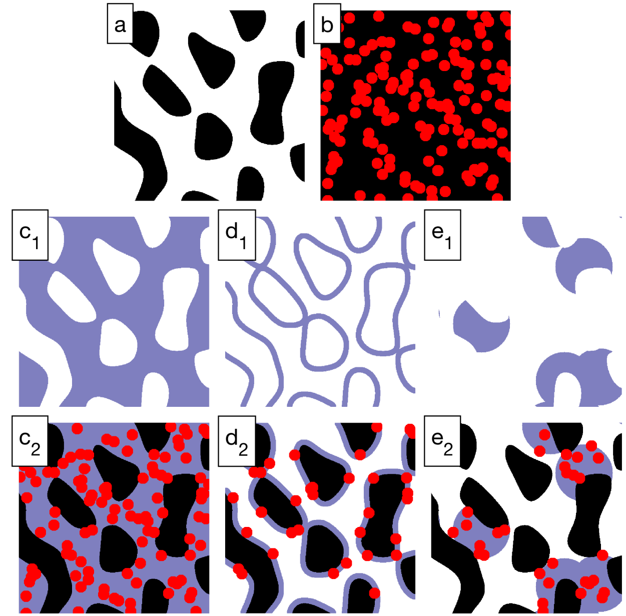
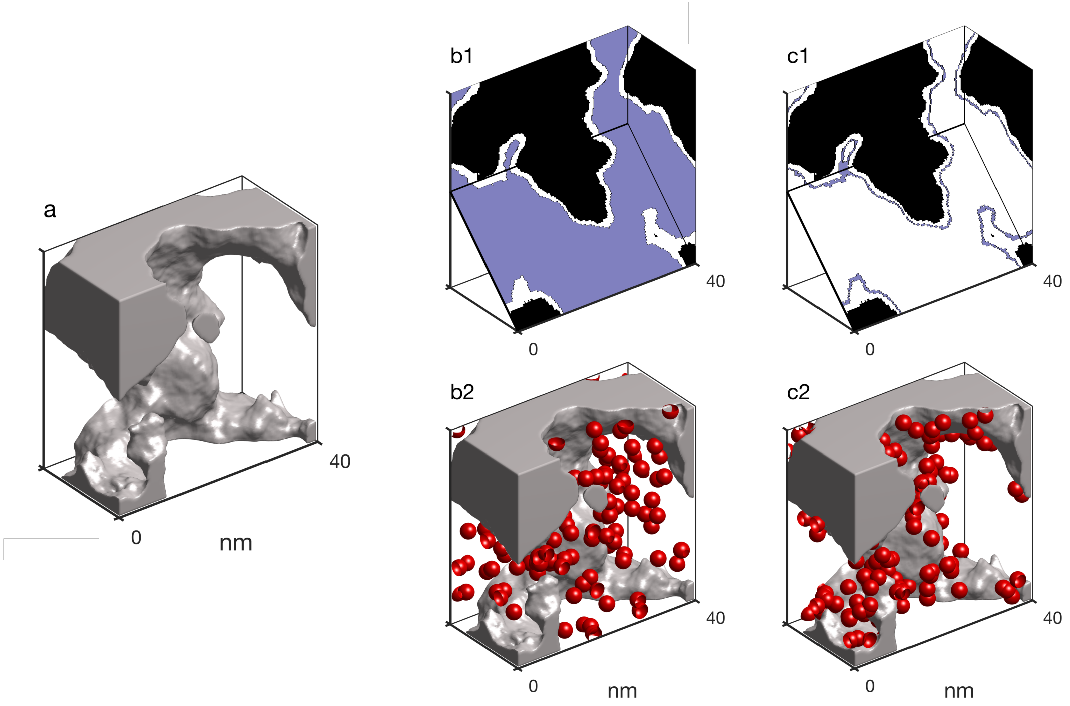
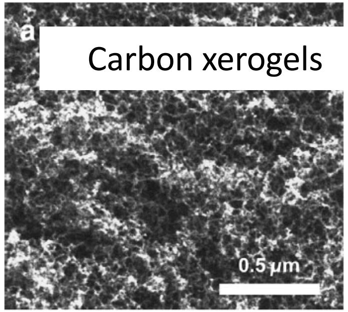
- And more…
  - Predicting adsorption in disordered mesopores

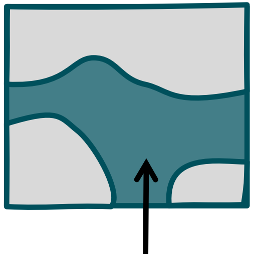
Example 1: supported nanoparticles



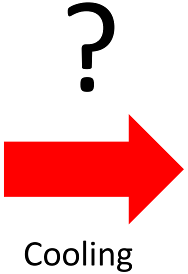


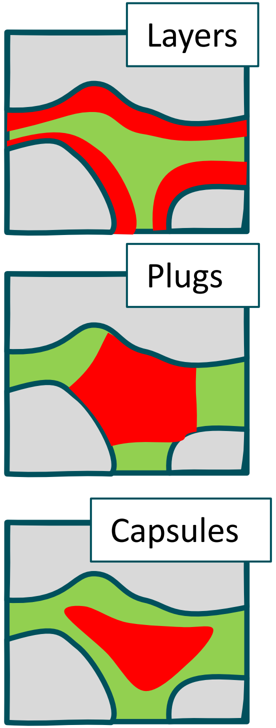
Example 2: confined liquids

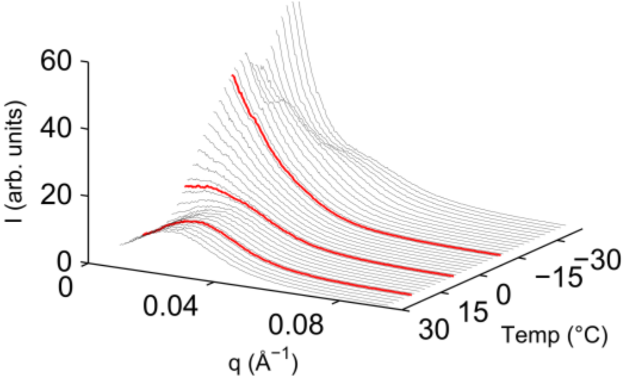


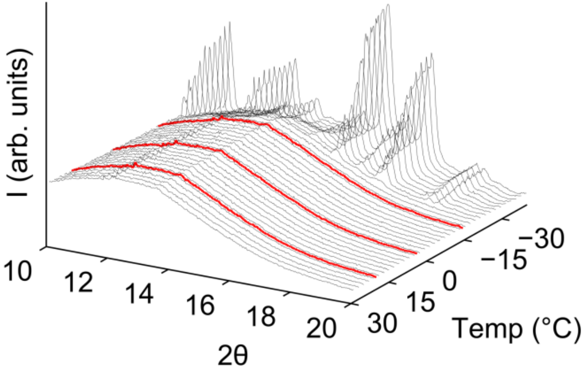


nitrobenzene/hexane
Critical solution
Tc ~ 20°C

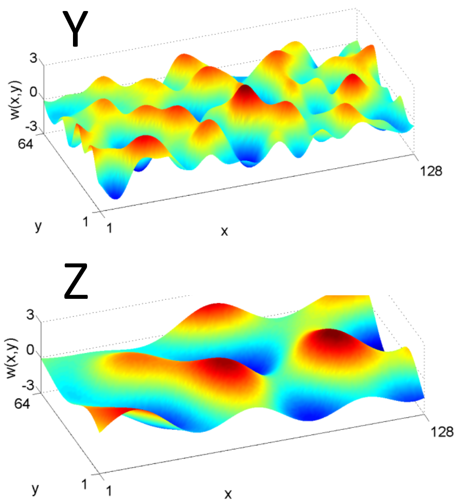


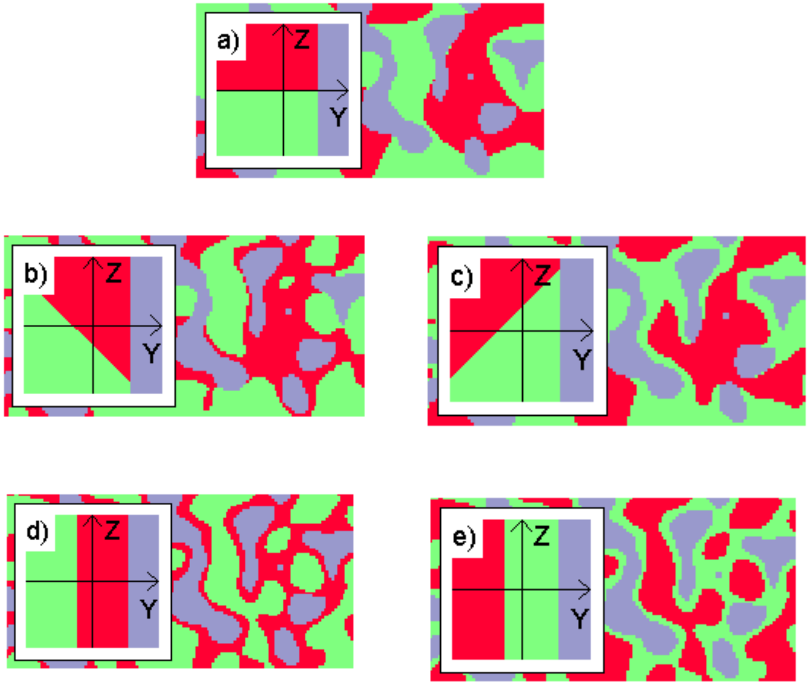






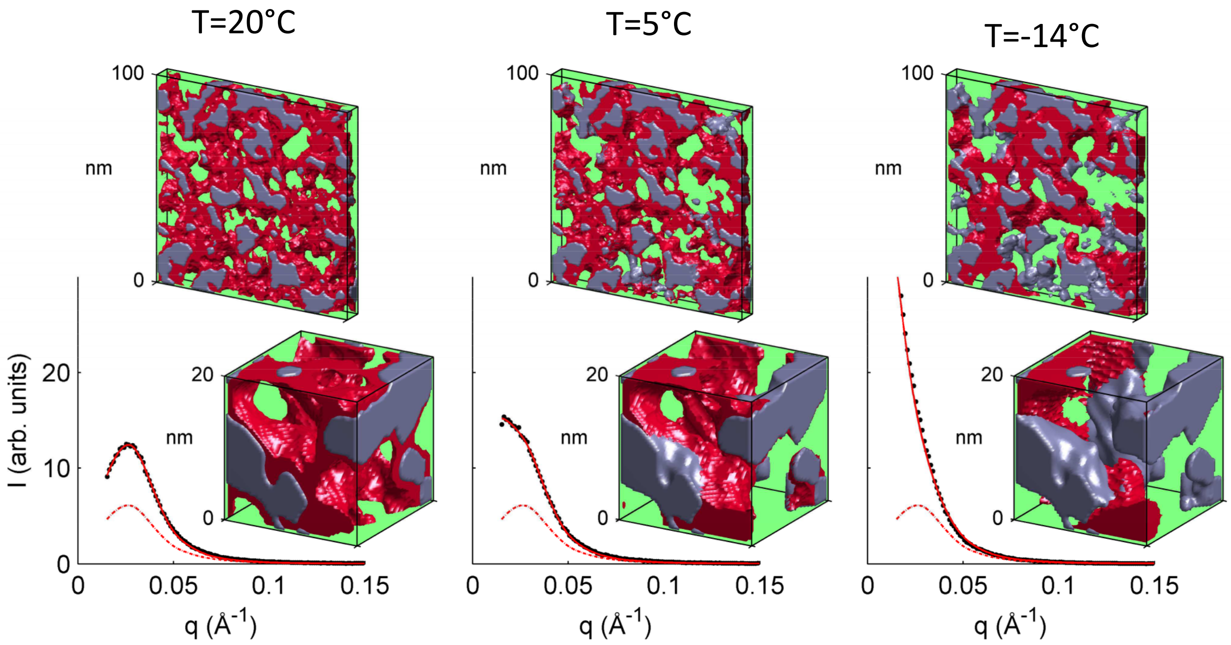
Plurigaussian models of confined liquids





C. Lantuéjoul, Geostatistical Simulations, Springer 2002

Nanometer-scale wetting transitions



C. Gommes, J. Appl. Cryst. (2013) 46, 493-504

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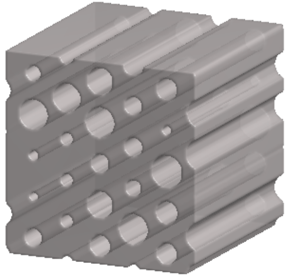
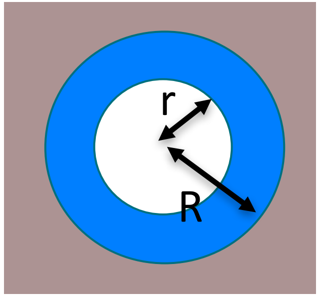
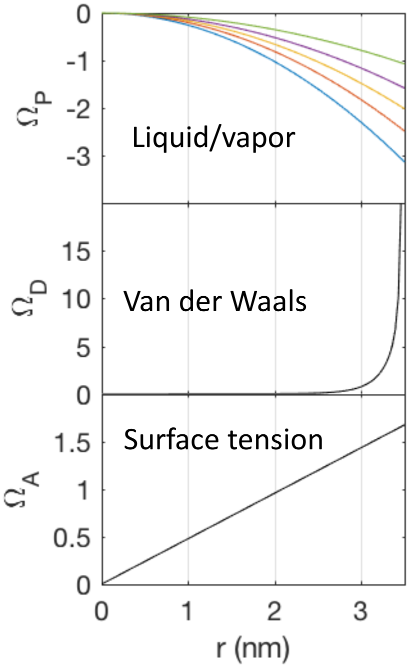
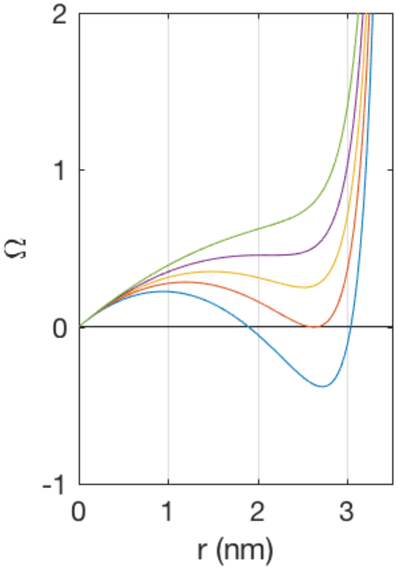
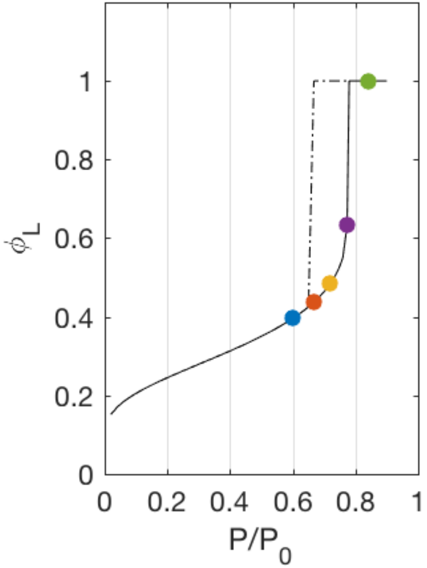
Derjaguin-Broekhoff-de Boer (D-BdB) free energy





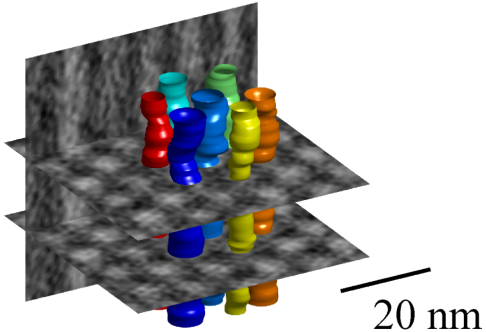






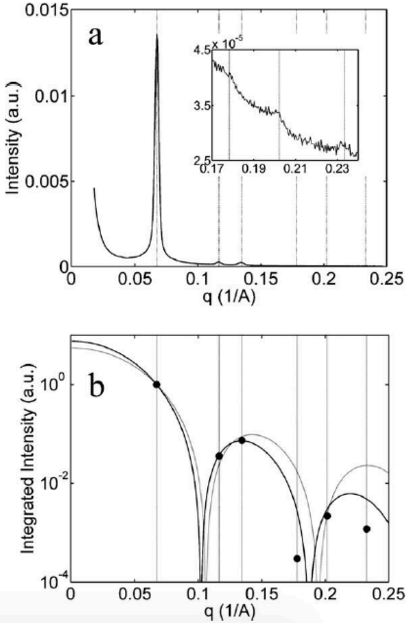
Disorder matters: SBA-15 ordered silica

- SBA-15 pore structure:
  Electron tomography

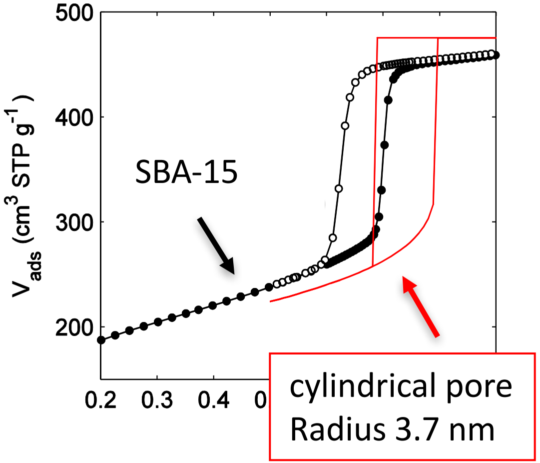


	Electron Tomography	Scattering
R_m (nm)	3.6 ± 0.2	3.7
σ_R (nm)	1.2 ± 0.2	0.6

- SBA-15 pore structure:
  Small-Angle Scattering



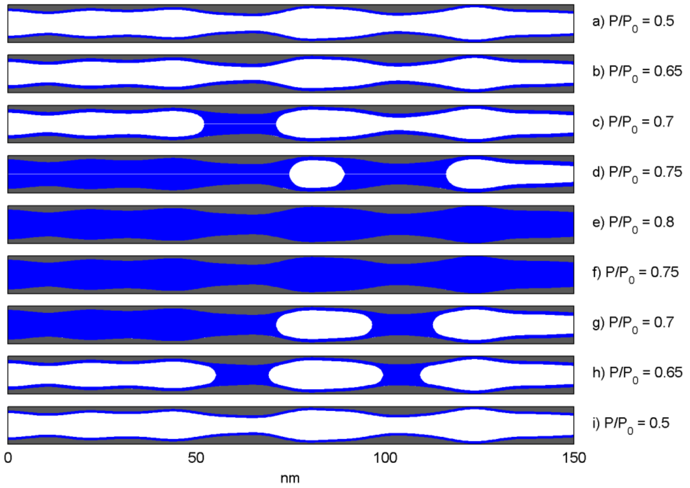
- Nitrogen adsorption isotherms



Gommes et al. Chem. Mater. **2009**

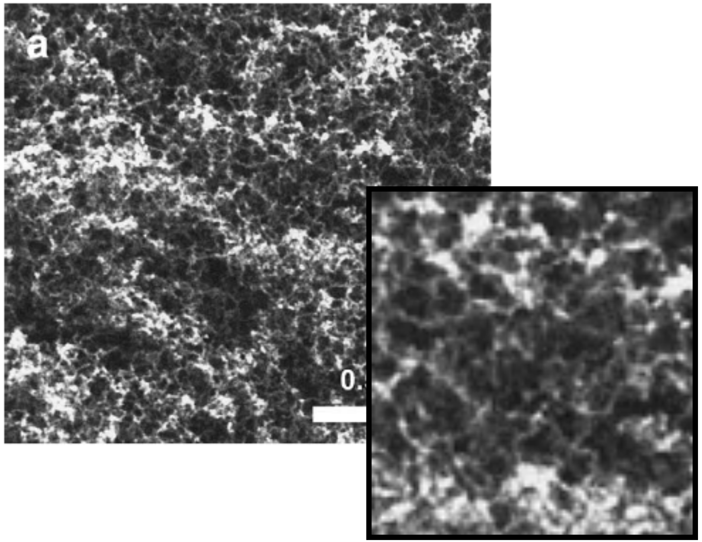
How to model disorder?

- Mild disorder: add defects

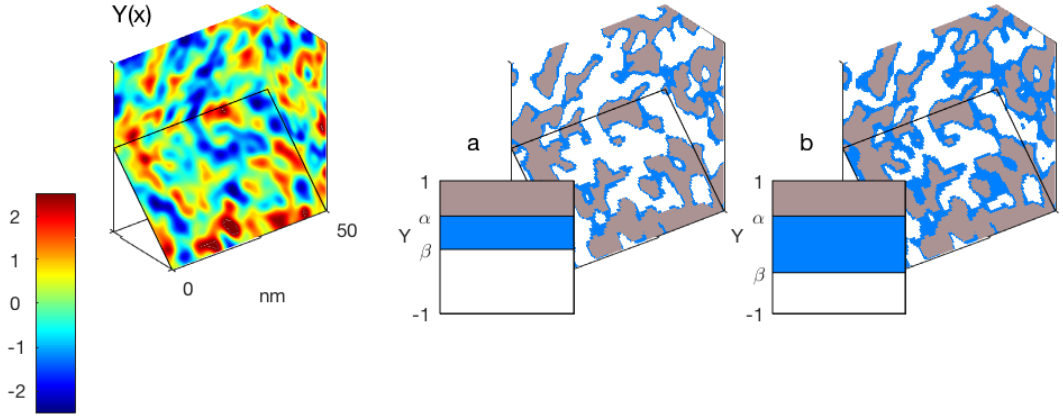


Ravikovitch & Neimark, Langmuir 22 (**2006**) 11171
Gommes, *Langmuir* 28 (**2012**) 5101
....

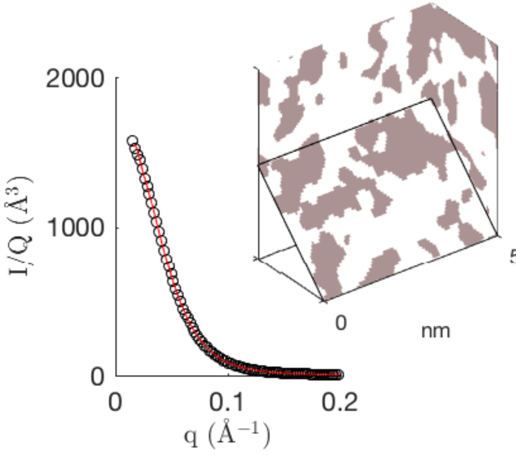
- Wild disorder?

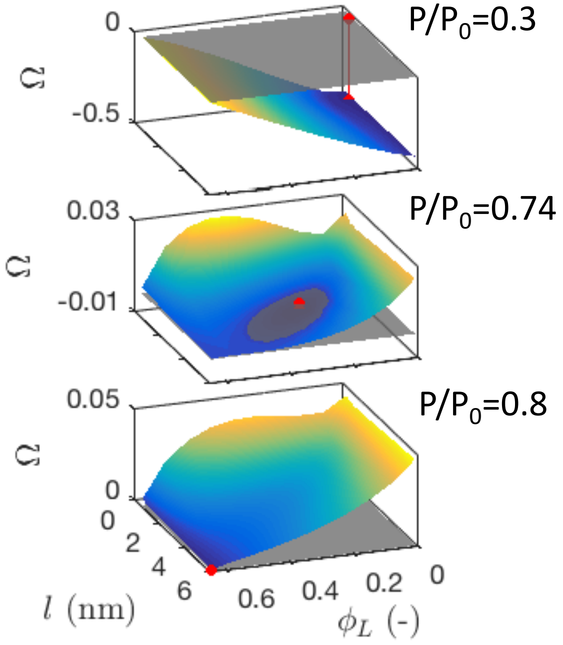


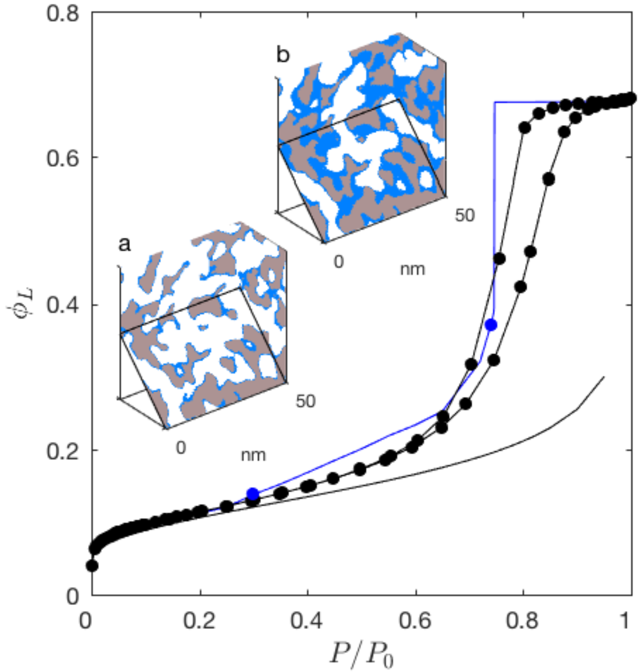
Plurigaussian model of the condensate



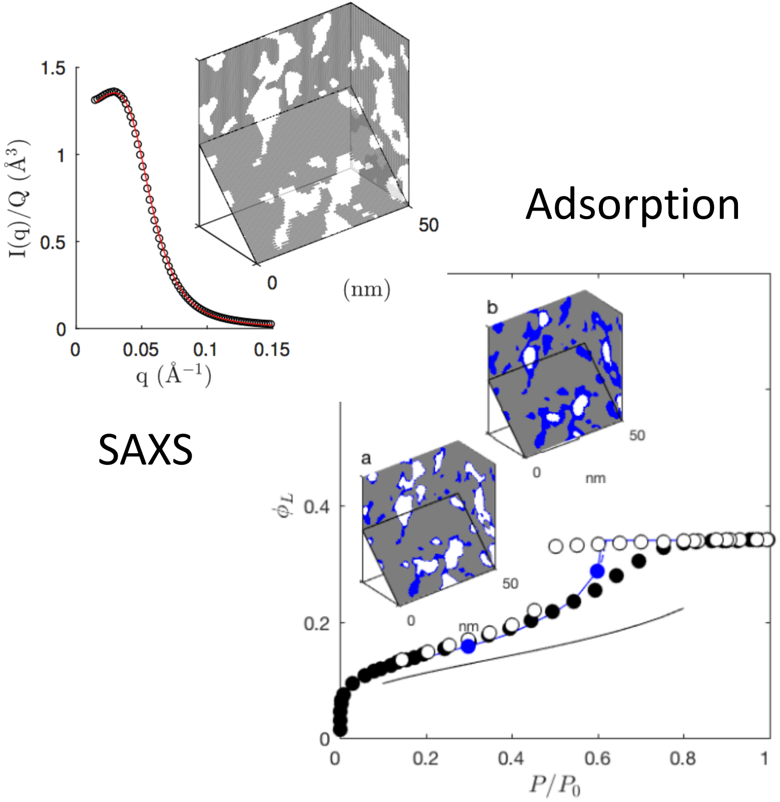
Energy landscape of a liquid condensate in mesoporous alumina

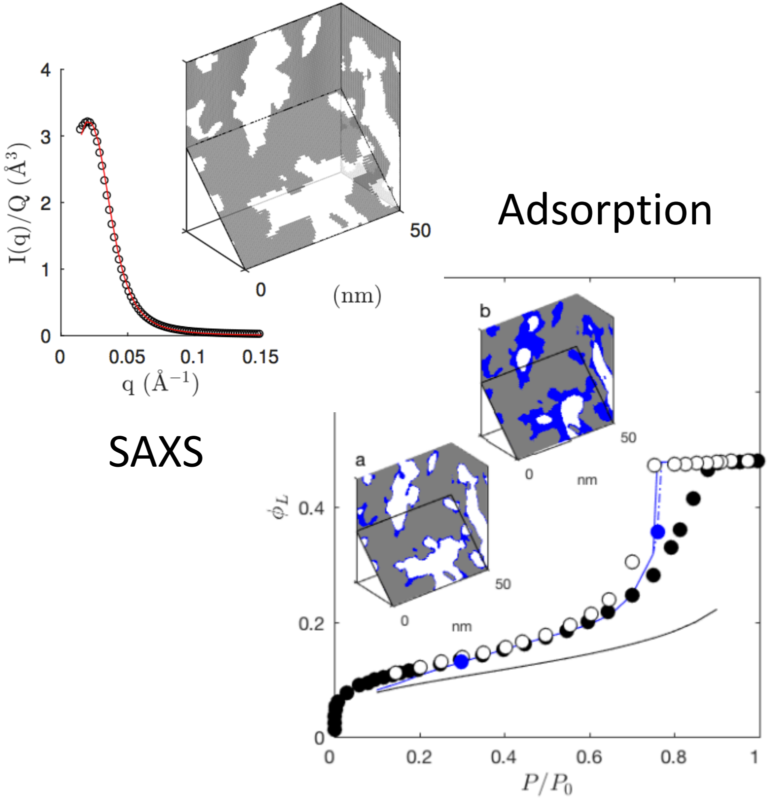




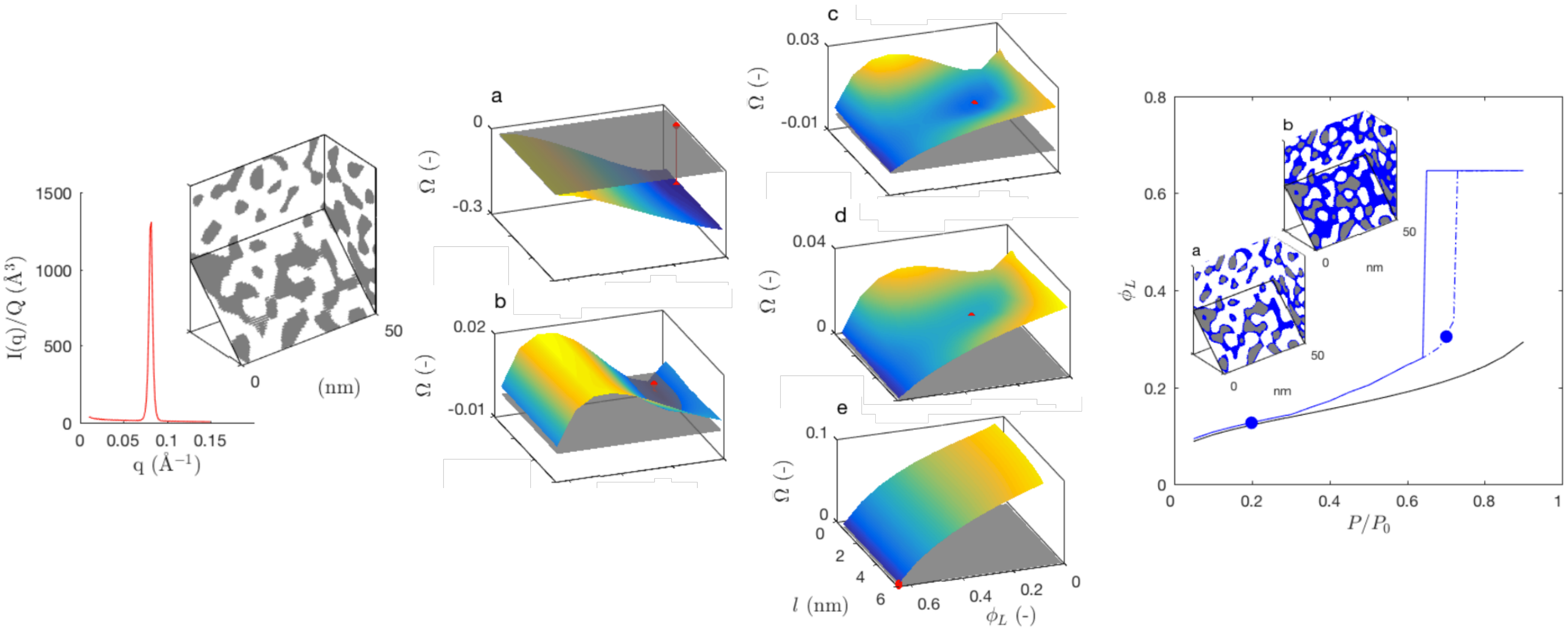


Carbon aerogels: from SAXS to adsorption

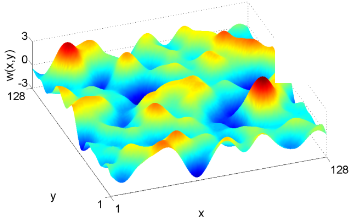


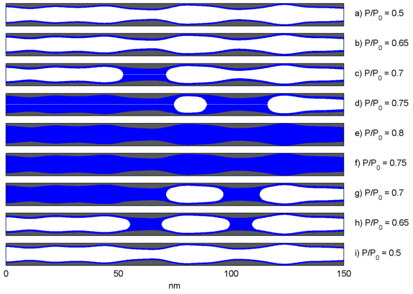


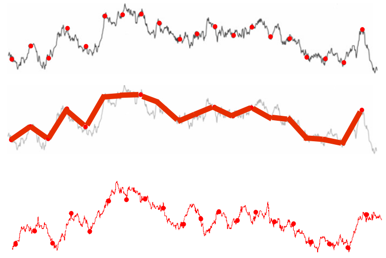
Hysteresis in monodispersed GRF models



Conclusions







- Geometrical complexity does not rule out conceptual simplicity;
- Disorder is not merely a nuisance, it changes the physics
- Many mathematical models are available from other fields (e.g. geostatistics), so let’s use them!