Diffraction
– Small Angle Neutron Scattering

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Measurements calibrated to absolute units of scattering

Unlike crystallography, measurements of liquid and amorphous materials—wide and small angles—must be conducted to yield scattering data in absolute units.

- ✧ The macroscopic density of the samples needs to be determined so that its average scattering cross section can be calculated.
- ✧ The neutron incident spectrum and detector efficiency should be maintained as stable as possible over a long period, covering data collection of the sample, background, and calibrations runs.
- ✧ Intensities as a function of the neutron wavelength over thousands of detector pixels must be properly normalized.

$$S(Q)_{\mathrm{exp}} \sim \frac{\left[\mathrm{S}(v)-\mathrm{C}(v)\right]/\left(N_{\mathrm{S}}\sigma_{\mathrm{S}}\right)}{\left[\mathrm{V}(v)-\mathrm{B}(v)\right]/\left(N_{\mathrm{V}}\sigma_{\mathrm{V}}\right)}$$

For liquids & glasses

S, C, V, B = sample, empty container, vanadium, background of vanadium, respectively

$$I_{norm}(Q) = \frac{\dfrac{I_{S+C}-I_{bkgd}}{Tr_{S+C}} - \dfrac{I_{EC}-I_{bkgd}}{Tr_{EC}}}{\dfrac{I_{H_2O}-I_{bkgd}}{Tr_{H_2O}} - \dfrac{I_{EC}-I_{bkgd}}{Tr_{EC}}},$$

For SANS

S+C = sample & cell, EC = empty cell, bkgd = no scatterer, H_2O = water standard, Tr = transmission

SANS cross section & the scattering contrast

We consider materials that contain particles, each of which is made up of hundreds or more of atoms, such as the macromolecules in a solution, clusters (or pores) in an alloy, colloids in an emulsion, and magnetic domains in a ferromagnet. Here, the primary interests are the dimensions and shapes (hence the average molecular weight) and the surface roughness of the particles and how the particles disperse or aggregate in the host matrix.

The intensity of SANS from the particles against the background matrix of scattering-length density ρ_{bkgd} for centrosymmetric systems is

$$I(Q) = \Phi V \Delta\rho^2 \left[P(Q)\right]^2 S(Q).$$

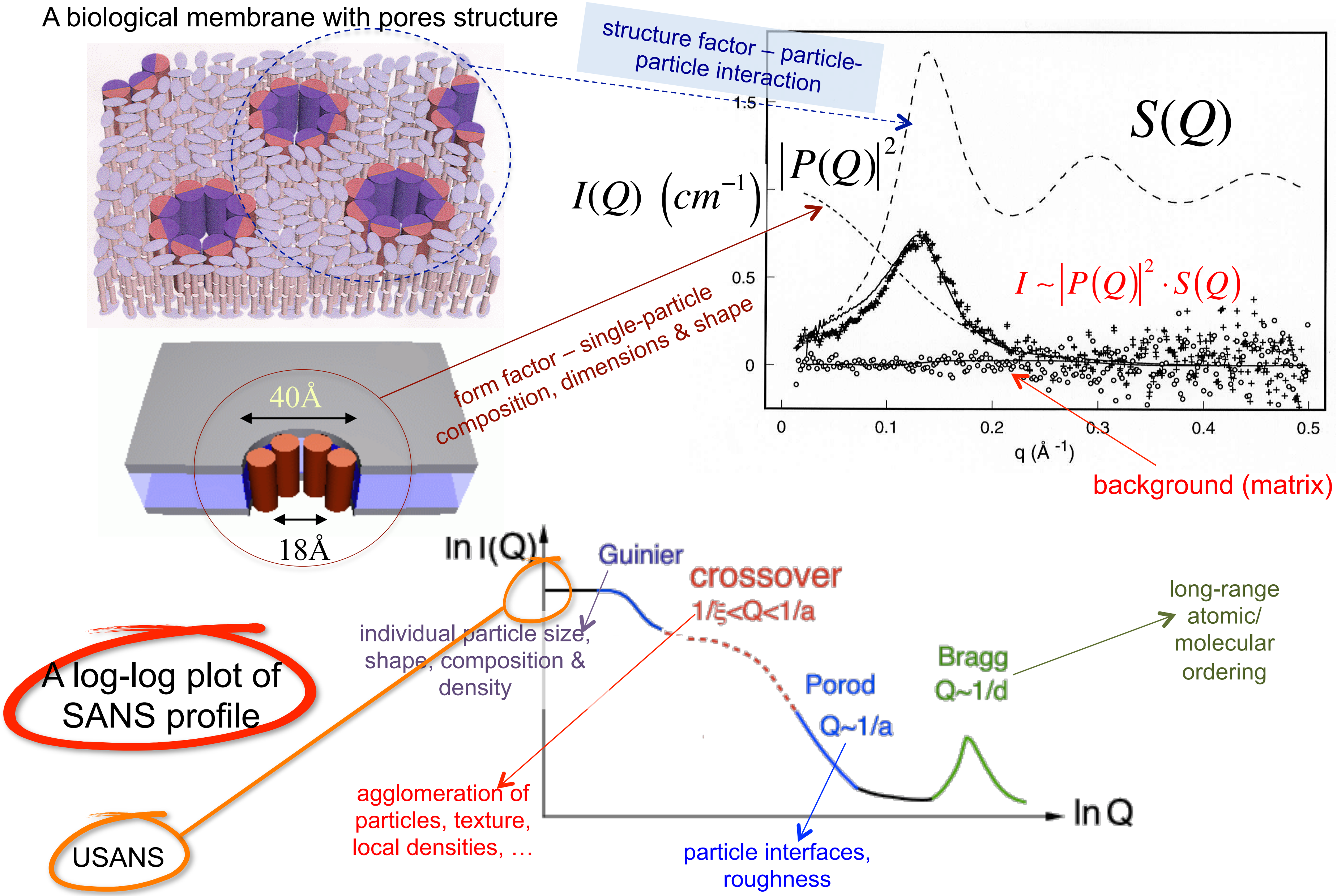
Otherwise,

$$I(Q) = \Phi V \Delta\rho^2 \frac{\left|\langle P(Q)\rangle\right|^2}{\left\langle \left|P(Q)\right|^2 \right\rangle} S(Q).$$

Φ is the neutron flux and $\Delta\rho$ is the scattering contrast factor characterized by the SLD difference between the particle and the background matrix,

$$\Delta\rho \equiv \langle \rho(r) \rangle - \rho_{bkgd}.$$

Expected SANS intensity profile

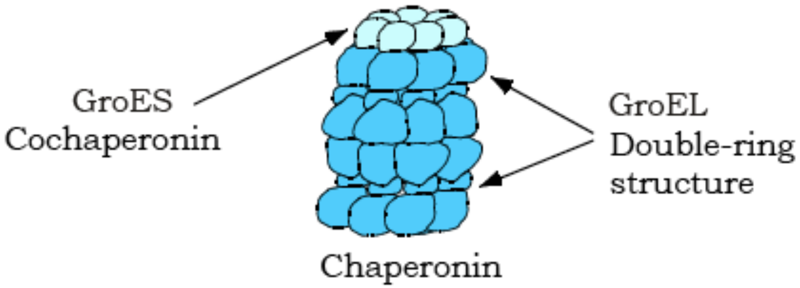


Bacterial Chaperonin Mediated Protein Folding: a SANS Study

Thiyagarajan, Henderson and Joachimiak, *Structure* (1996) 103

✧ **What are chaperonins?**

Belong to the family of hsp60s
Consists of GroEL and GroES

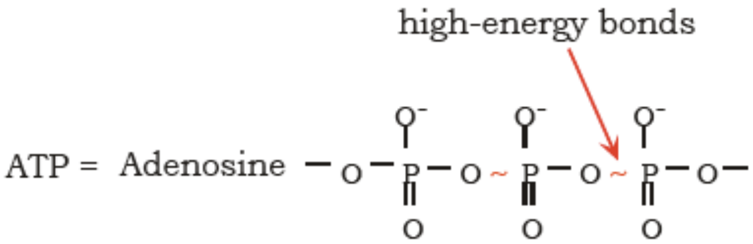


✧ **How do chaperonins assist protein folding?**

Biologically active proteins must adopt specific folded 3-D structures of the native state. Upon dilution from denaturant proteins in cells may misfold and lead to irreversible aggregation. Chaperonins assist in the correct folding by preventing aggregation.

✧ **How does ATP come into play?**

GroEL is the host facilitator, GroES is a cooperator, ATP is the energy supplier



ATP ⟶ ADP + P_i (ΔG = 30.5 kJ/mol)

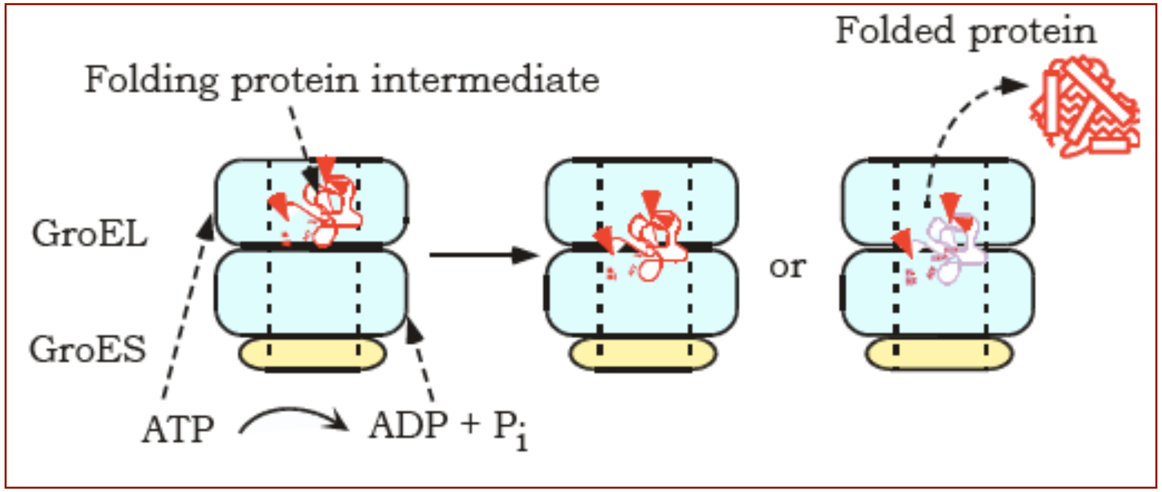
A Model for GroEL/GroES Action

✧ ***What are known?***

GroES binds asymmetrically to the GroEL cylinder, sitting like a cap on one end-surface

ATP-bound GroEL has low affinity for unfolded substrate (enzyme)

ADP-bound GroES has high affinity for unfolded substrate



✧ ***What is the structure of GroEL/ES in solution?***

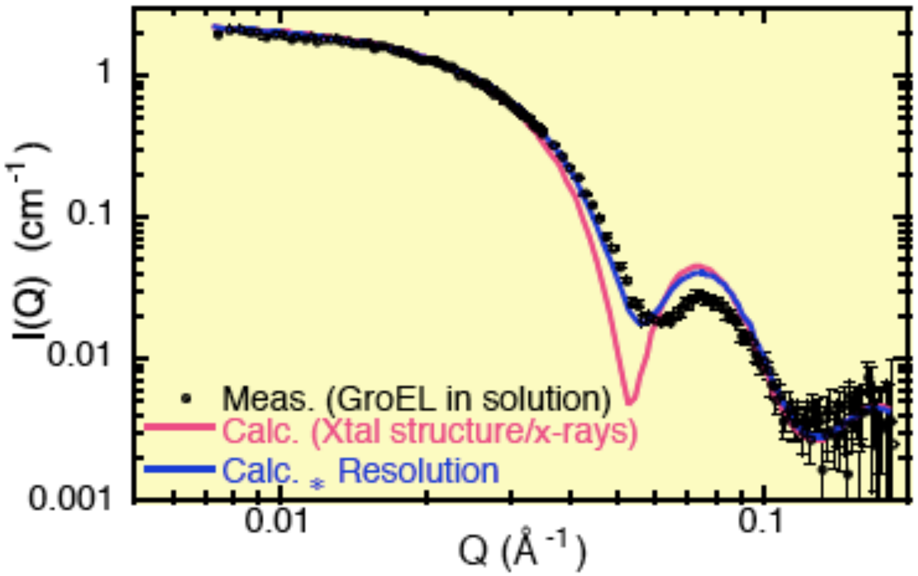
cavity, apical domains...

✧ ***How is aggregation prevented in the presence of ATP hydrolysis?***

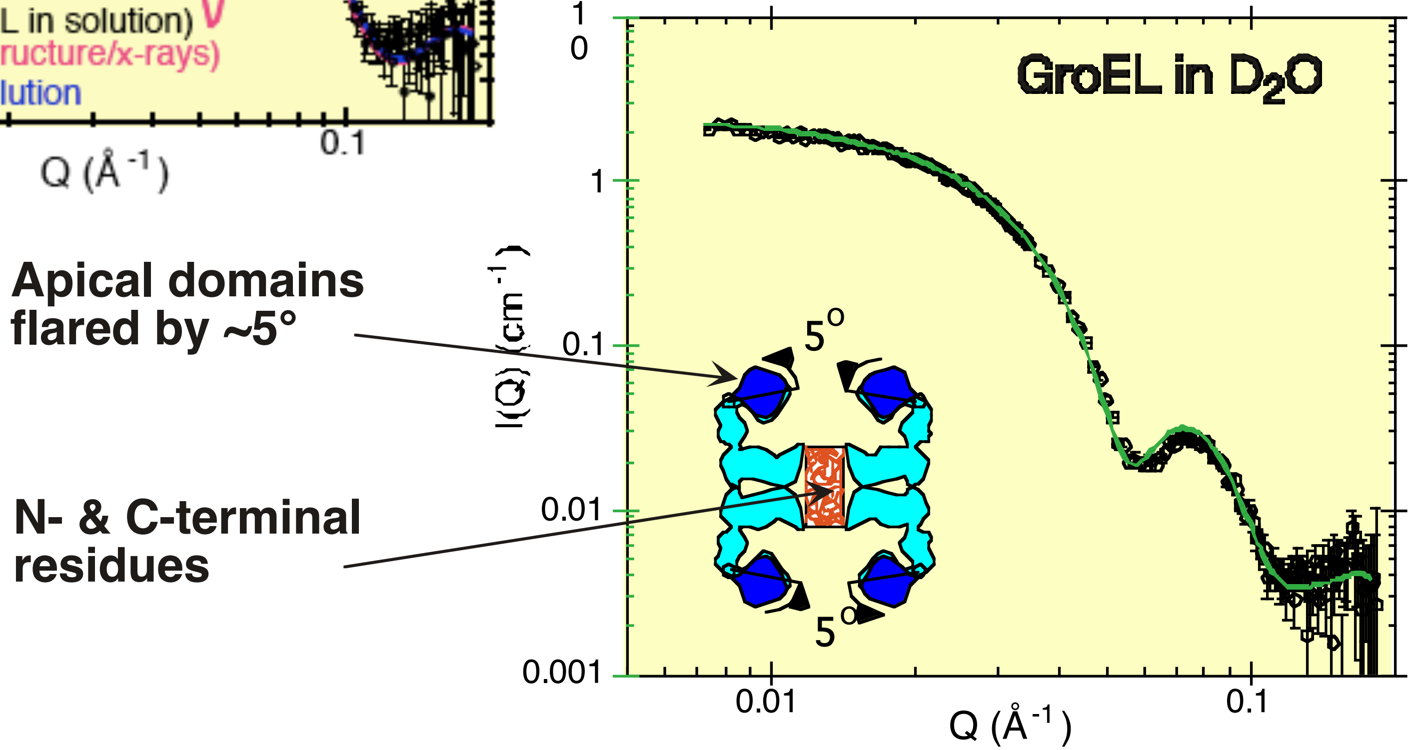
The Role of Small-Angle Neutron Scattering

- ✧ Single-crystal diffraction provides crystal structure in atomic scale only for proteins under conditions that crystallization is possible
- ✧ Small-angle scattering provides low resolution structural information, can study assemblies and their interactions in solution under relevant physiological conditions

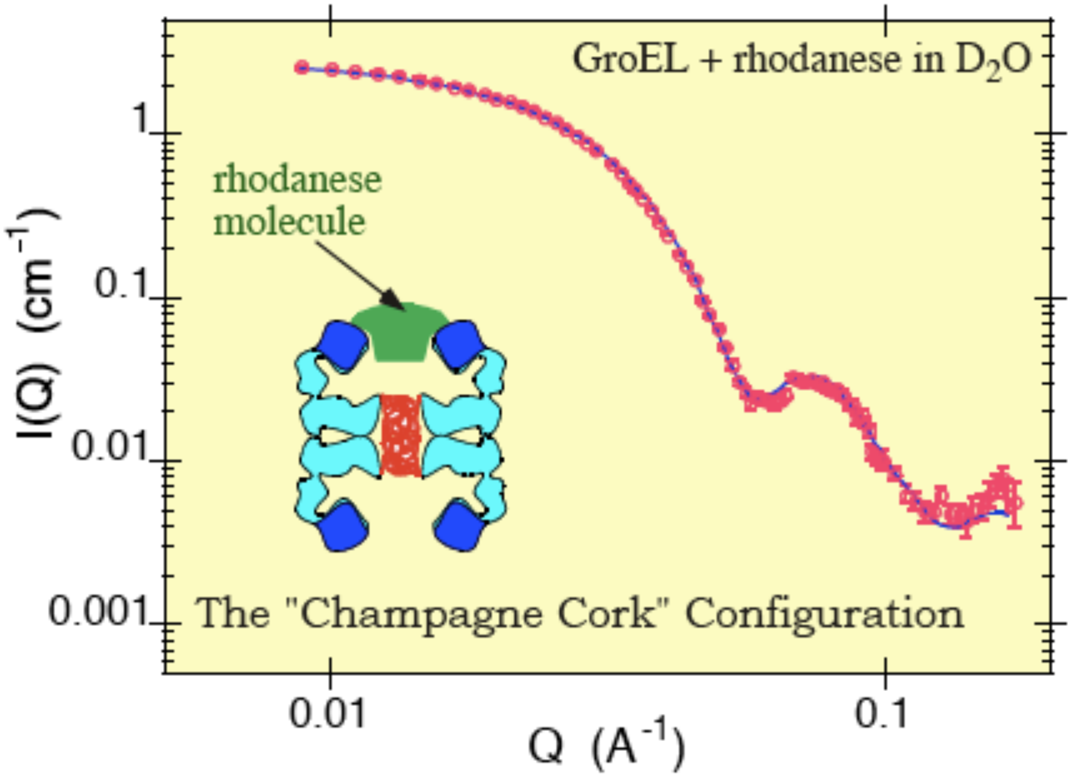
The Architecture of GroEL in solutions: The Apical domains and N- & C-Terminal Residues



Identifying the missing residues by a Monte Carlo Method



A look into the binding of protein intermediate with GroEL: the GroEL-rhodanese complex

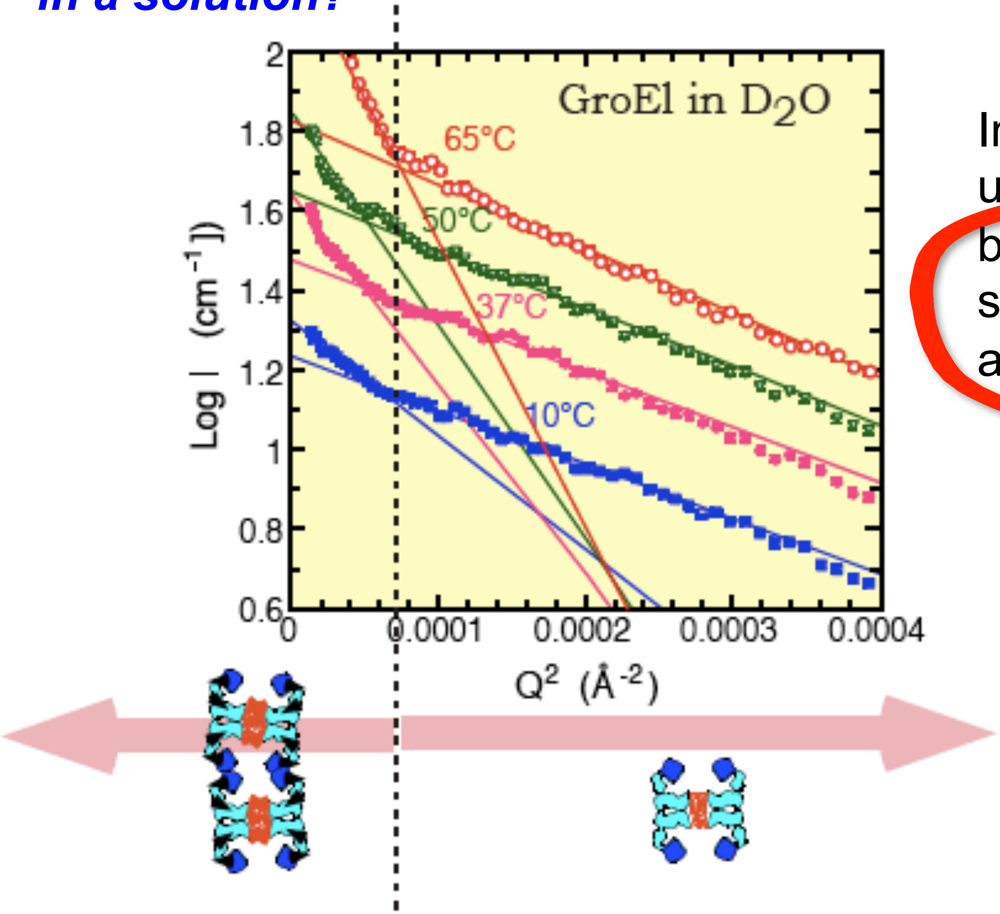


The SANS data indicate that a rhodanese molecule binds across the opening to the GroEL cavity, rather than within it. The radius of gyration of the complex increases only slightly from 63.2 Å to 64.3 Å.

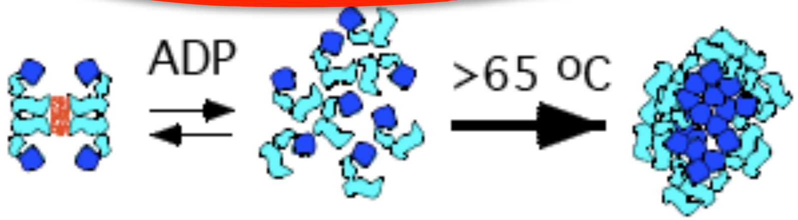
Structural Response of GroELs to Heating

When bacteria are exposed to high temperature, an enhanced synthesis of heat-shock proteins (HSP) is observed. In the case of hsp60, the response mechanism is regulated by the interplay of GroEL/GroES with ATP hydrolysis.

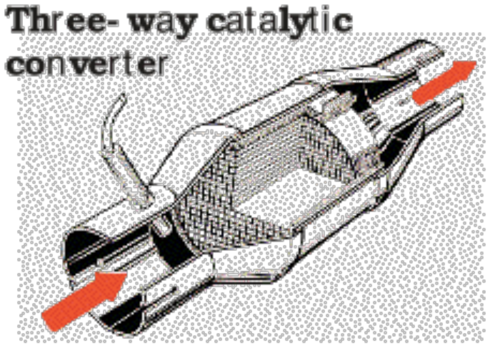
What is the structural response to upshift of temperature with only GroEL in a solution?



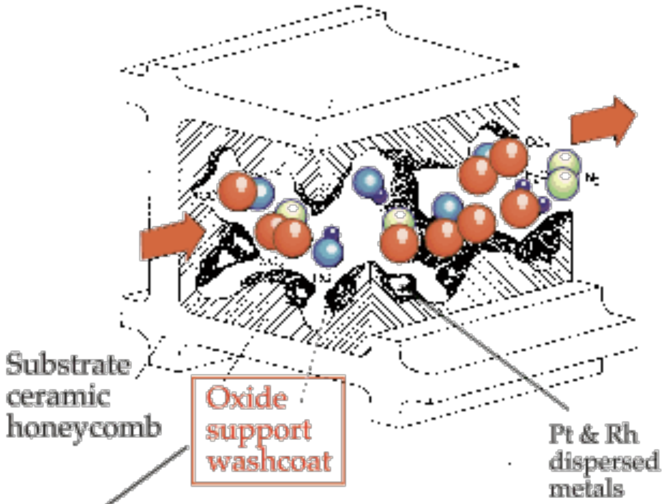
In the presence of ADP, individual units of GroEL persist up to 65°C. A breakdown of the double-ring structure forming an aggregate occurs at higher temperatures.



Better automobile emission-control catalysts



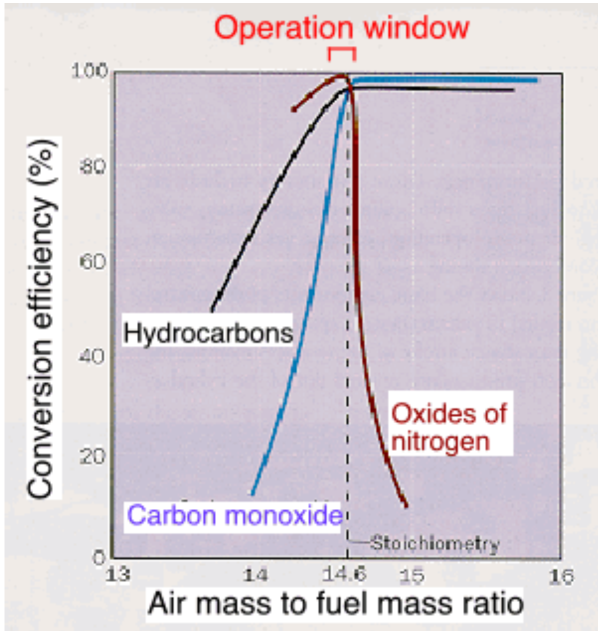
CO, HC & NOx conversion



Contained high-surface-area Al_2O_3, ZrO_2, & CeO_2

Rare-earth doping in zirconia enhances thermal stability

Ceria solute provides oxygen storage/release capability



Three-way catalytic converter

Noble metals (Pt, Pd, Rh) dispersed on a porous (surface area ~100 m^2/g) metal-oxide (Ce-ZrO_2, Al_2O_3)

Main reactions:

- Reduction of NO_x

$2NO + 2CO \rightarrow N_2 + 2CO_2$

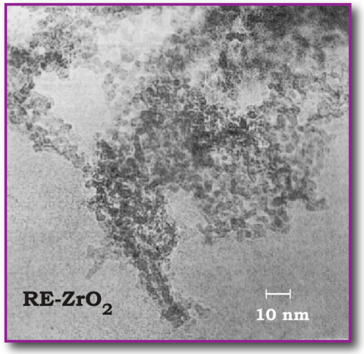
$2NO + 2H_2 \rightarrow N_2 + 2H_2O$

- Oxidation of CO and hydrocarbons: e.g.,

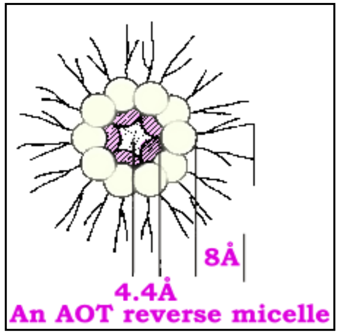
$2CO + O_2 \rightarrow 2CO_2$ (water-gas shift reaction)

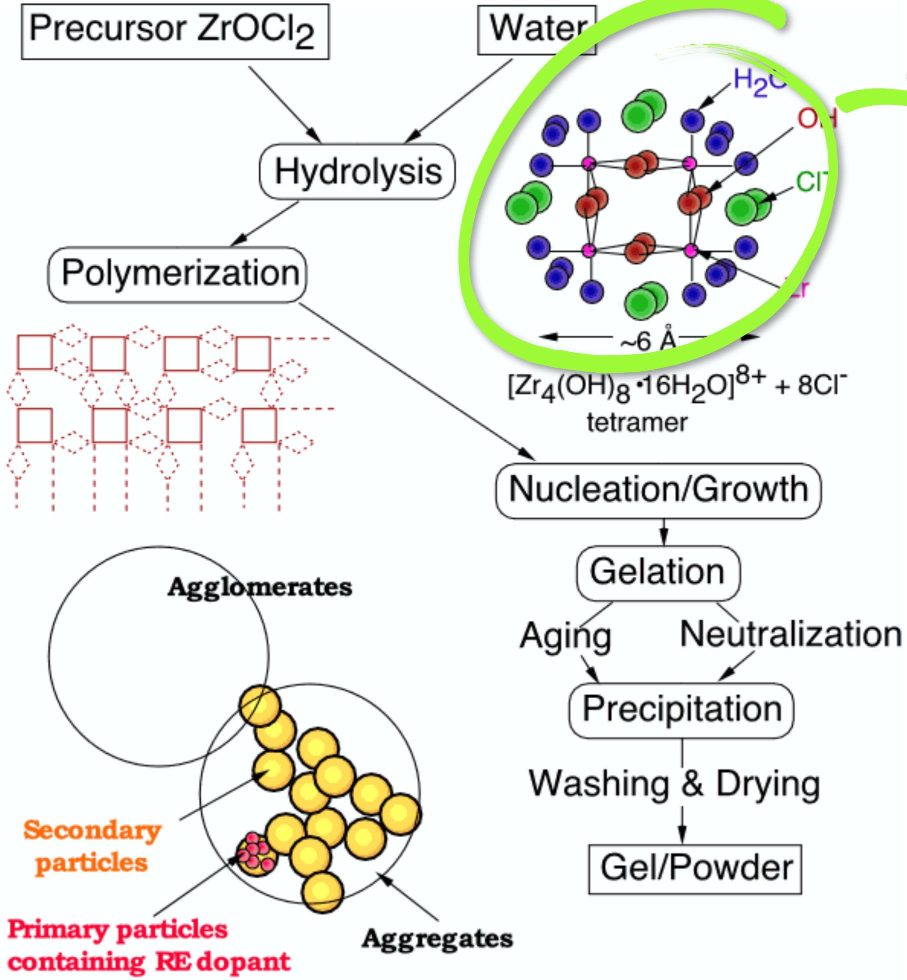
$HC + O_2 \rightarrow CO_2 + H_2O$

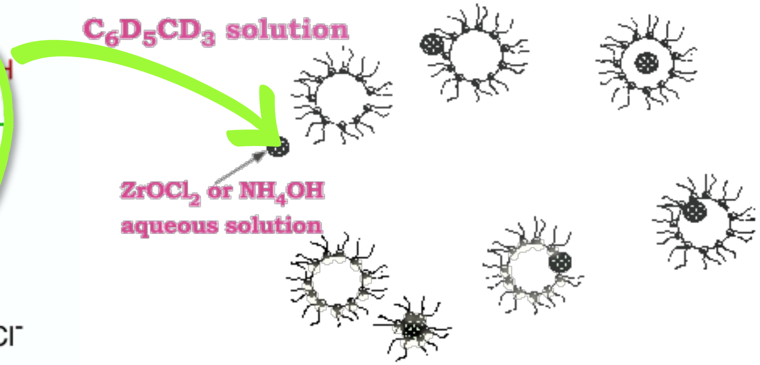
Microemulsion, colloids and aggregate of nanoparticles

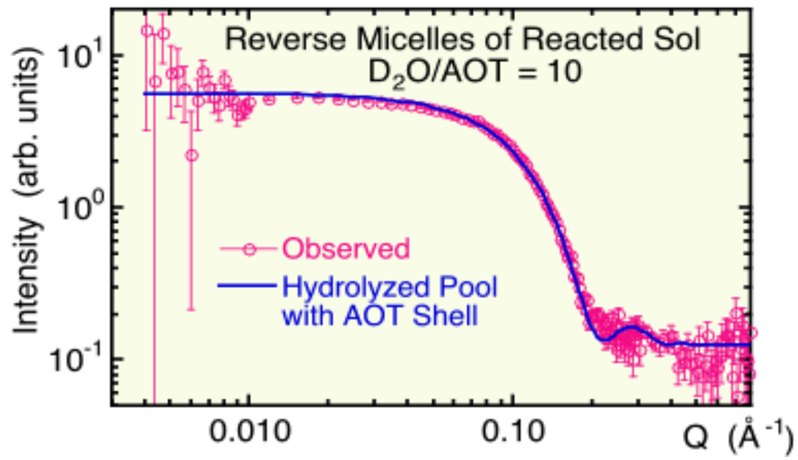


SANS study of a tetramer in reverse micelle



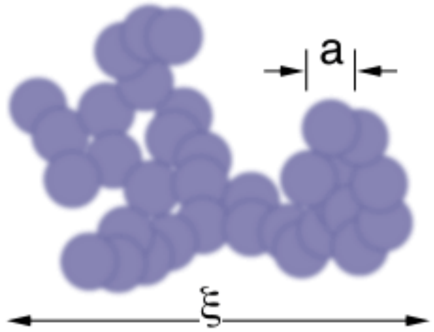




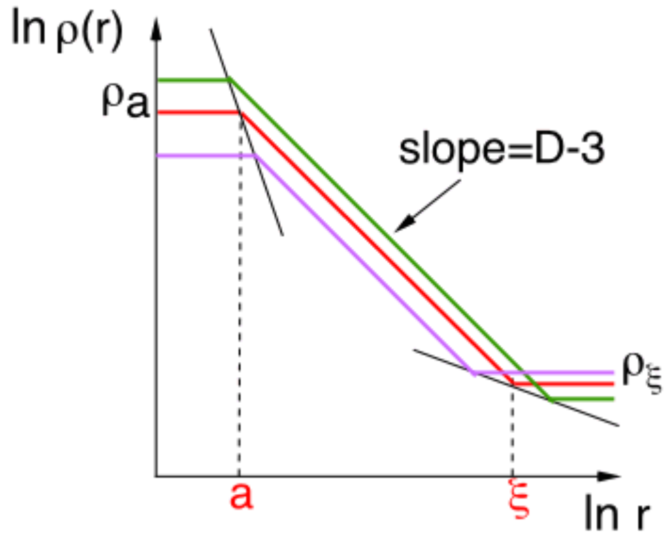


Scaling behavior of local densities & Fractals

Local Density



symmetry in the local density

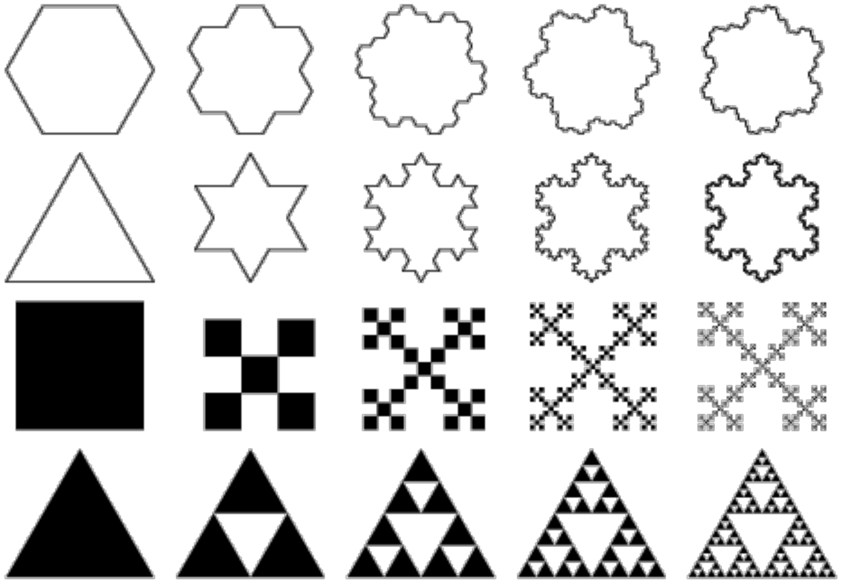


If samples show: $\frac{\rho_a}{\rho_\xi} = \left(\frac{\xi}{a}\right)^{D-3}$ for a given D,

then they are mutually self-similar.

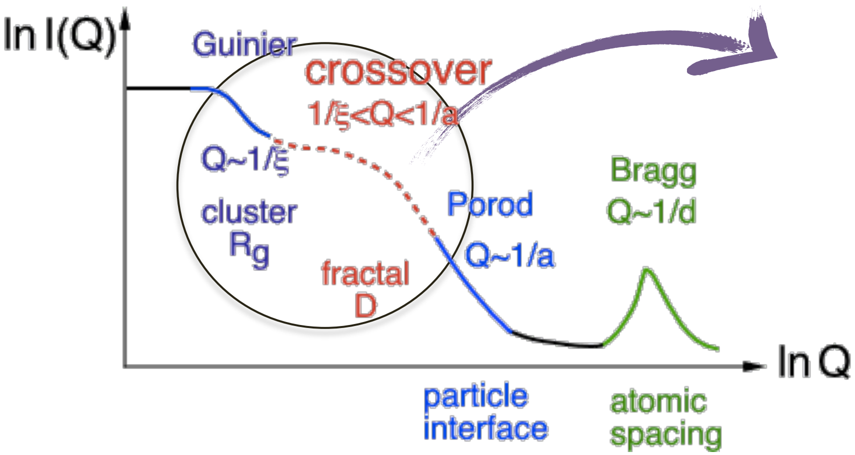
fractal dimension

Self-similarity & fractal objects



More on SANS profiles

SANS provides a measure of the local (scattering length) density *ρ(r)* as a function of length scale *r* (through Fourier-transformed reciprocal space).



In the fractal regime: $I \sim Q^{-2D+D_S}$

Limiting cases:

- mass fractal: $D_S=D$, $I \sim Q^{-D}$

  $\lim Q\xi=1 \quad I \rightarrow \rho_\xi^{-\frac{2D-3}{3-D}}$

- smooth compact objects: $D=3$, $D_S=2$, $I \sim Q^{-4}$
- objects w/ rough surfaces: $D=3$, $2<D_S<3$

Mass-fractal-like aggregate

$$I \propto |P(Q)|^2 \cdot S(Q)$$

spherical particles

$$P(Q) = V(\Delta\rho)\left[3\frac{\sin(Qr_0) - Qr_0\cos(Qr_0)}{(Qr_0)^3}\right]$$

$$S(Q) = 1 - 4\pi\phi\int_0^\infty |g(r)-1| r^2 \frac{\sin(Qr)}{Qr} dr$$

fractal object

$$N(r) = \left(\frac{r}{r_0}\right)^D, \quad \Rightarrow \quad \phi|g(r)-1| = \frac{D}{4\pi}\frac{1}{r_0^D} r^{D-3} h\left(\frac{r}{\xi}\right)$$

cutoff function

(Sinha et al. 1984)

$$h\left(\frac{r}{\xi}\right) = \exp\left(-\frac{r}{\xi}\right)$$

$$S(Q) = 1 + \frac{1}{(Qr_0)^D}\frac{D\Gamma(D-1))}{\left(1+\frac{1}{Q^2\xi^2}\right)^{\frac{D-1}{2}}}\sin\left[(D-1)\tan^{-1}(Q^\xi)\right]$$

polydispersity

$$\langle P(Q)\rangle = \int P(Q,r) f(r) dr$$

$$f(r) = \frac{1}{\sqrt{2\pi}\ln\sigma_g}\exp\left\{-\left[\frac{\ln\left(\frac{r}{r_0}\right)}{\sqrt{2}\ln\sigma_g}\right]^2\right\}$$

size distribution: log-normal distribution function

$\otimes$ instrumental resolution function

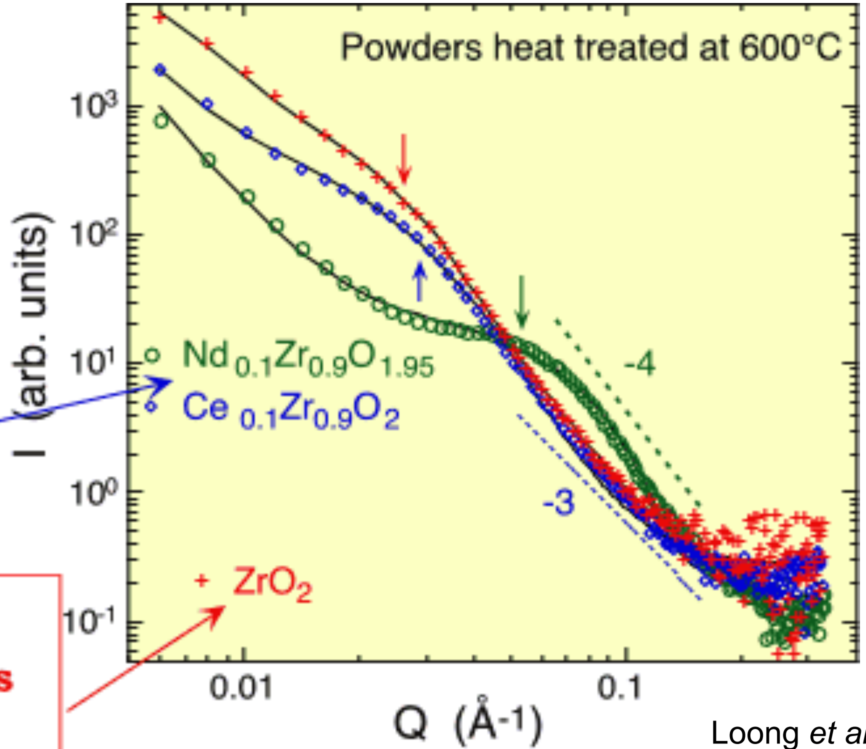
SANS (SAXS) is capable of characterization of nanoparticles - shape & size distribution and inter-particle interactions - in suspension, aggregate or composite in absolute scale.

Microstructure influenced by synthesis & rare-earth doping

The effects of heat treatments and rare-earth doping

Rare- earth doped ZrO_2:
- **Mass- fractal aggregate of rough particles**
- **mesoporous**

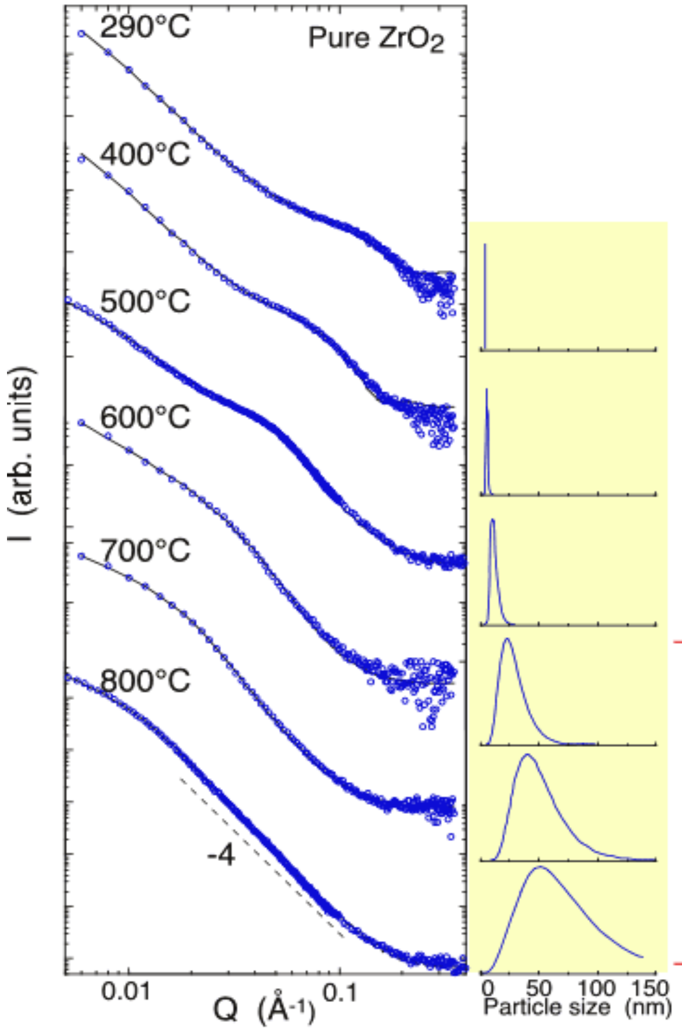
Pure ZrO_2:
- **Clusters of smooth particles**
- **macroporous**



Loong *et al.* (1997)

- ✧ The solution method enables the synthesis of nano-porous, mass-fractal-like RE-doped ZrO_2 powders with higher surface areas than pure ZrO_2
- ✧ Different RE dopants control the microstructure differently (particle size, surface smoothness, etc.)

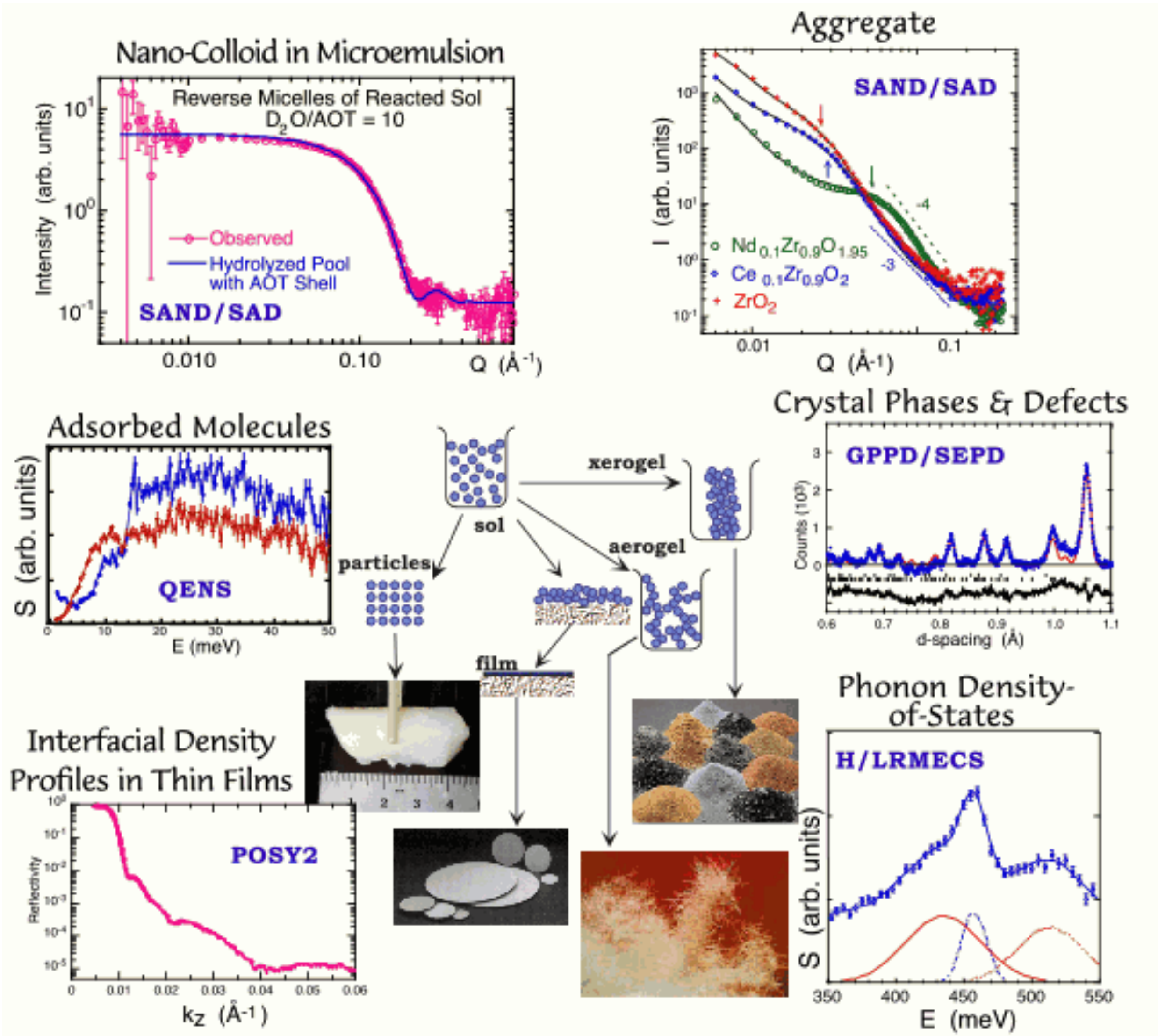
Resistance to sintering reinforced by rare-earth doping



Below ~600°C
- **Mass- fractals,**
- **Narrow particle size distribution: 3.6 to 11.2 nm,**
- **Microporous & mesoporous. (solid lines: mass- fractal model)**

Above ~600°C
- **Clusters of smooth particles,**
- **Broad size distribution 22.8 to 68.4 nm,**
- **Macroporous (solid lines: Ornstein- Zernike model)**

How to decide which neutron experiment is best for a problem?



Choose the best techniques to answer the questions concerning the relationship between structure and function of materials.

References

Cowley, J. M. (1995), *Diffraction Physics*. *Amsterdam*, Elsevier Science B. V.

Egami, T. and S. J. L. Billinge (2003), *Underneath the Bragg Peaks, Structural Analysis of Complex Materials*. *Amsterdam*, Elsevier.

Feigin, L. A. and D. I. Svergun (1987), *Structure Analysis by Small-Angle X-ray and Neutron Scattering*. *New York*, Plenum Press.

Fultz, B. and J. Howe (2008), *Transmission Electron Microscopy and Diffractometery of Materials*. *Berlin*, Springer-Verlag.

Glatter, O. and O. Kratky, Eds. (1982). *Small Angle X-ray Scattering*. *New York*, Academic Press.

Hammouda, B. "Probing Nanoscale Structures - The SANA Toolbox".

Higgins, J. S. and H. C. Benôit (1994), *Polymers and Neutron Scattering*. *Oxford*, Clarendon Press.

Neder, R. B. and T. Proffen (2008), *Diffuse Scattering and Defect Structure Simulations. A cook book using the program DISCUS*. *Oxford*, Oxford University Press.

Nield, V. M. and D. A. Keen (2001), *Diffuse Neutron Scattering from Crystalline Materials*. *Oxford*, Clarendon Press.

Schweika, W. (1998), *Disordered Alloys. Diffuse Scattering and Monte Carlo Simulations*. *Berlin*, Springer_Verlag.

Wong, J. and C. A. Angell (1976), *Glass. Structure by Spectroscopy*. *New York*, Marcel Dekker, Inc.

Thank You

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Questions?