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Small-angle Neutron Scattering (SANS) for Structure, Composition and Thermodynamics of Energy Materials

Alisyn Nedoma
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Help Transform Tomorrow.

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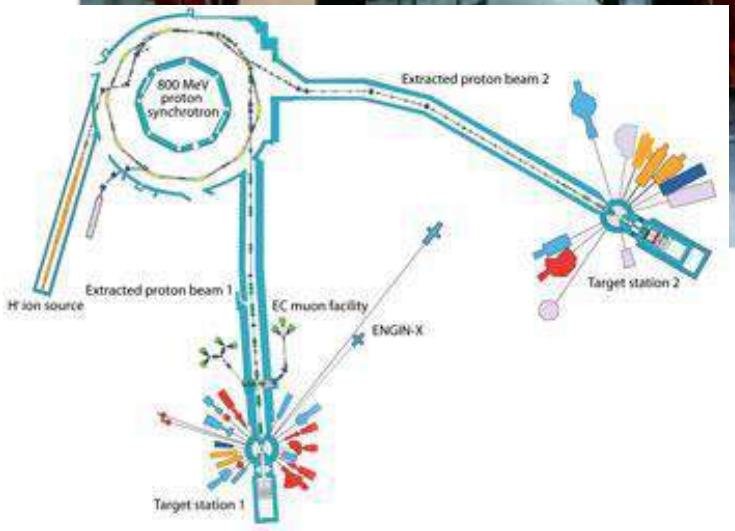
SANS spectra are information-rich

- Shape of dilute nanoparticle
- Structure
- Composition
- Thermodynamic parameters



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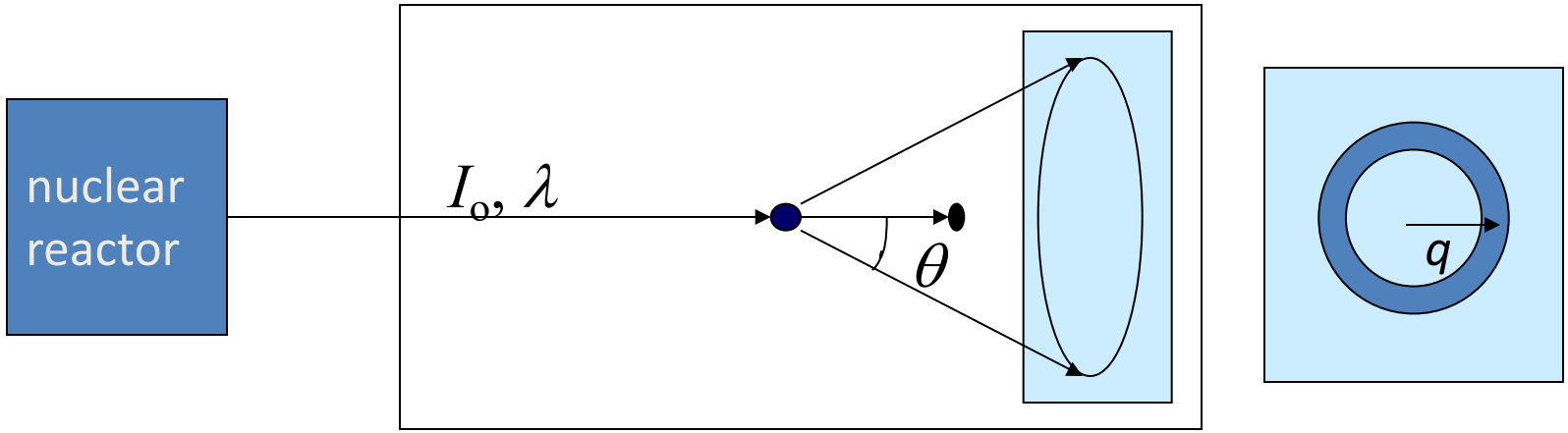
Small-angle Neutron Scattering (SANS)



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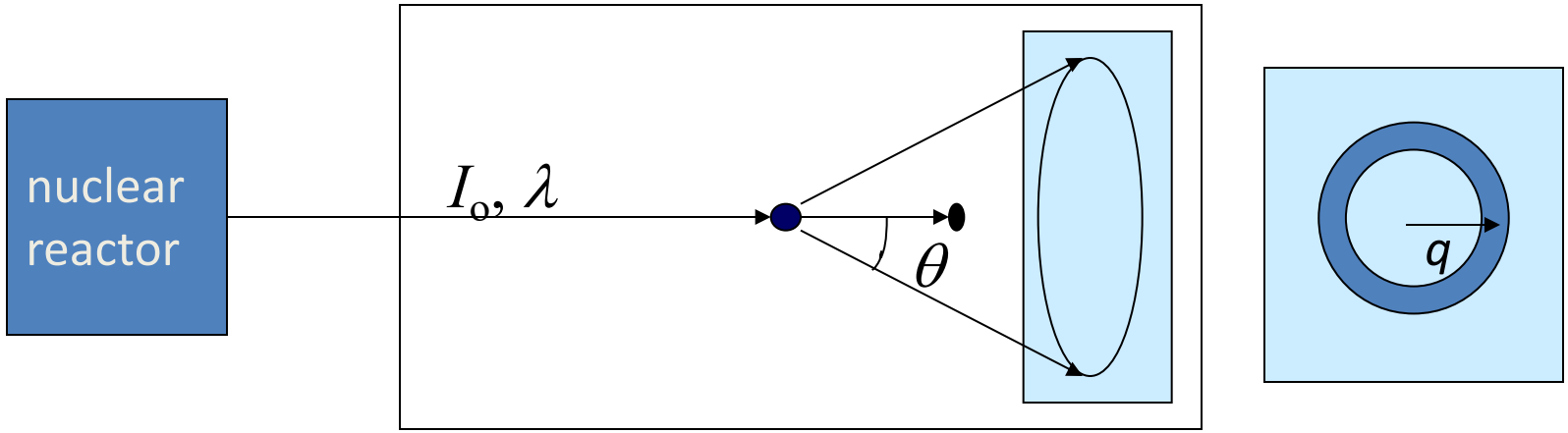
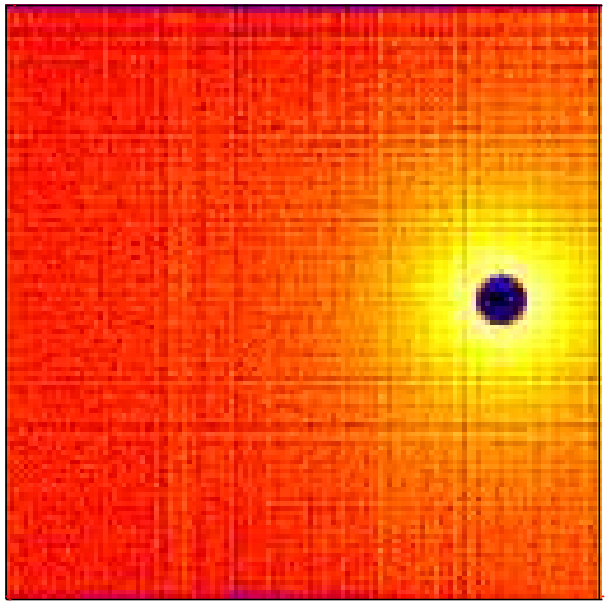
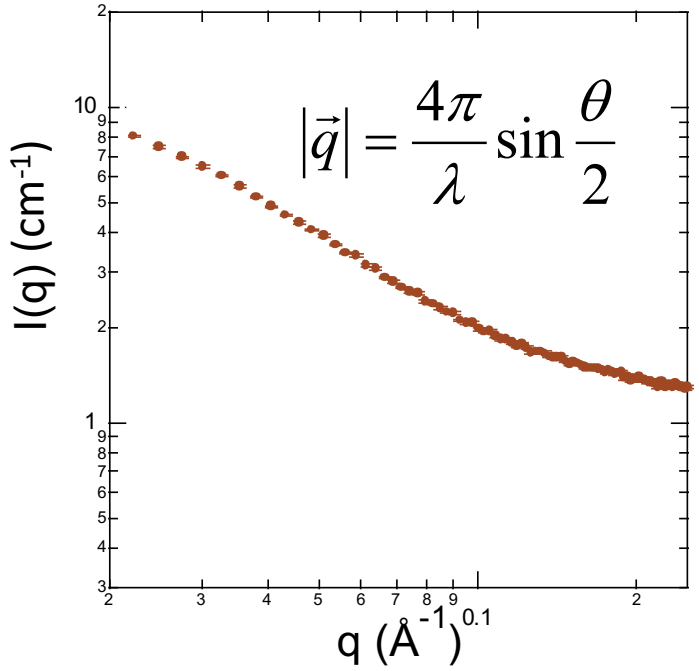
Small-angle Neutron Scattering (SANS)

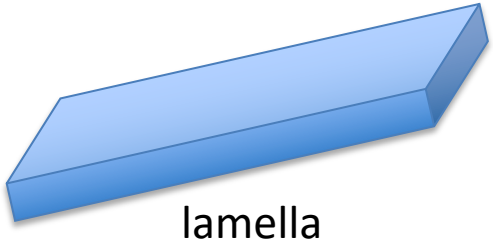




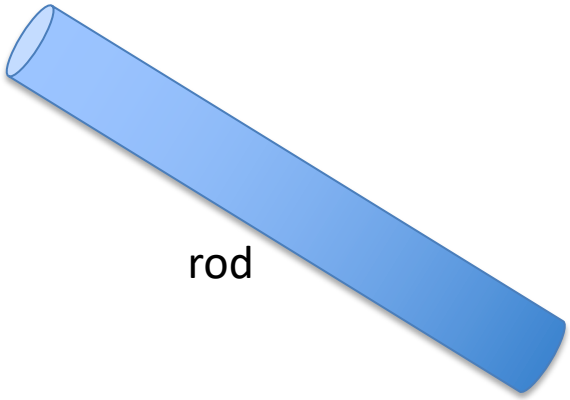


Characterizing the **shape** of a nanostructure (form factor)

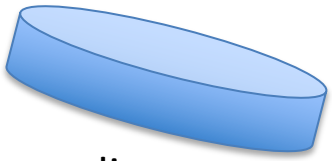
sphere



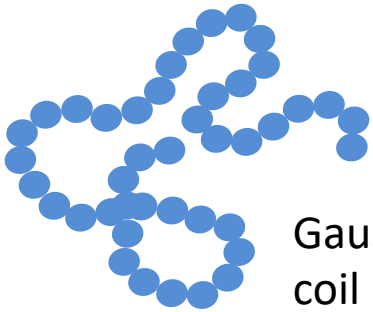
lamella



rod



disc



Gaussian coil

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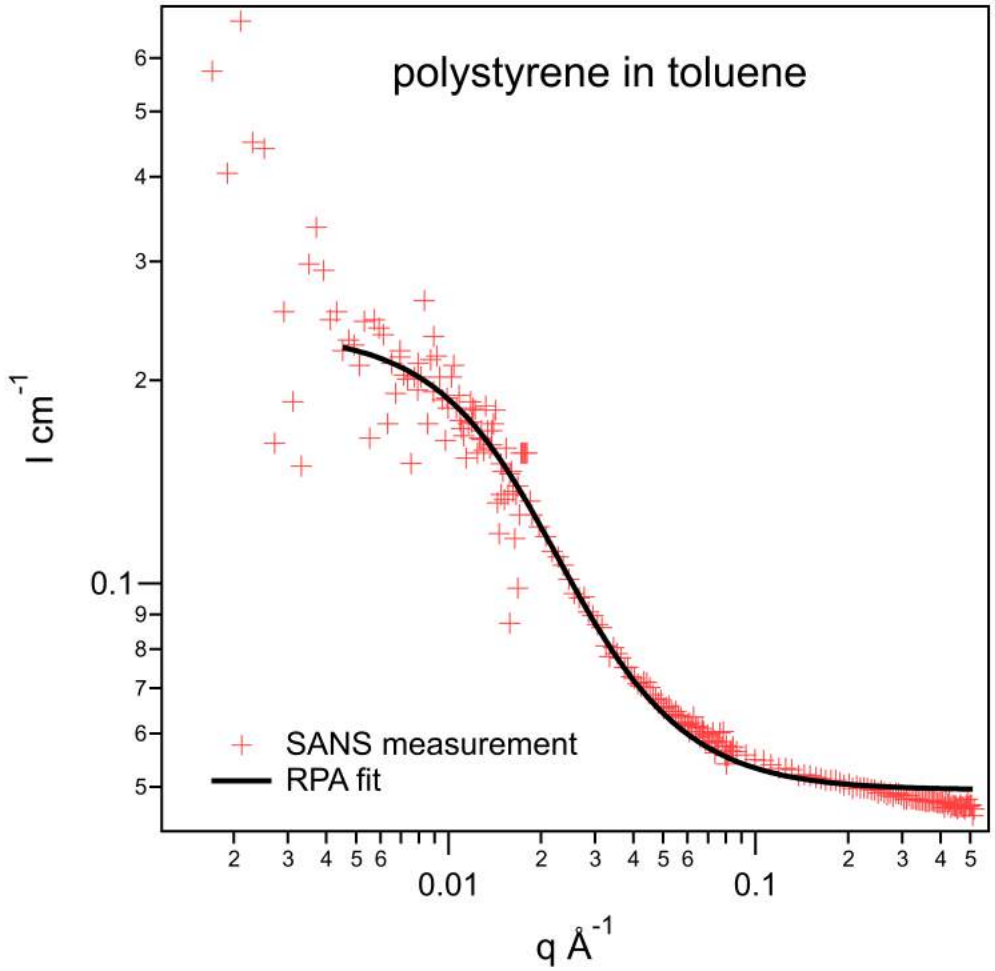
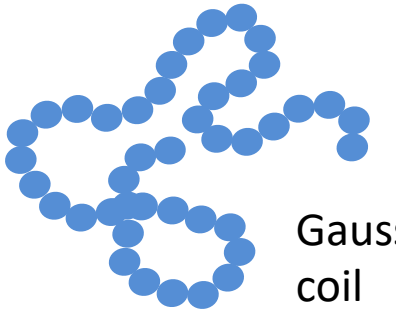
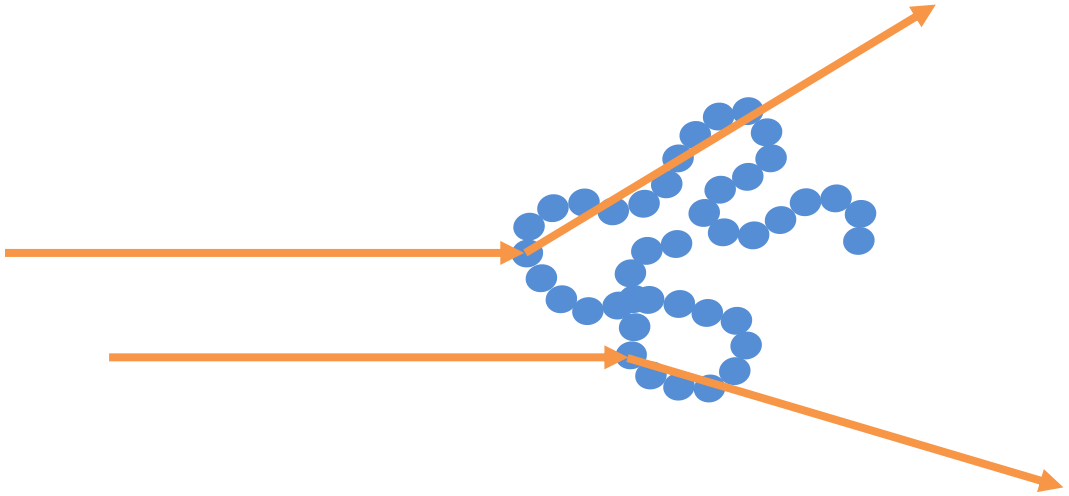
How can we use the scattering intensity to determine particle shape?





Gaussian coil

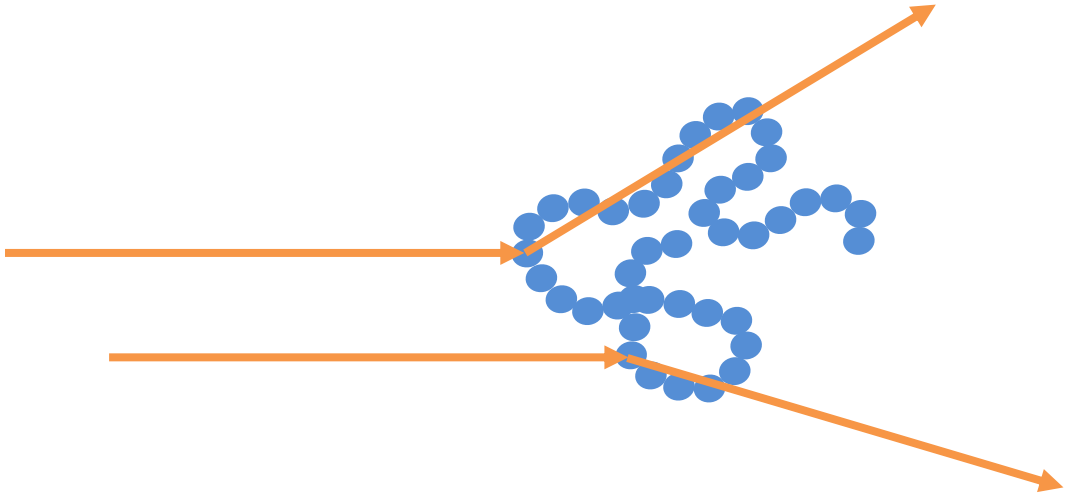
Find the real-space location of scattering bodies, $\rho(r)$



$$g^2(r) = \frac{\langle \rho(r)\rho(r') \rangle}{\langle \rho \rangle^2}$$

Autocorrelation function

Find the real-space location of scattering bodies, $\rho(r)$

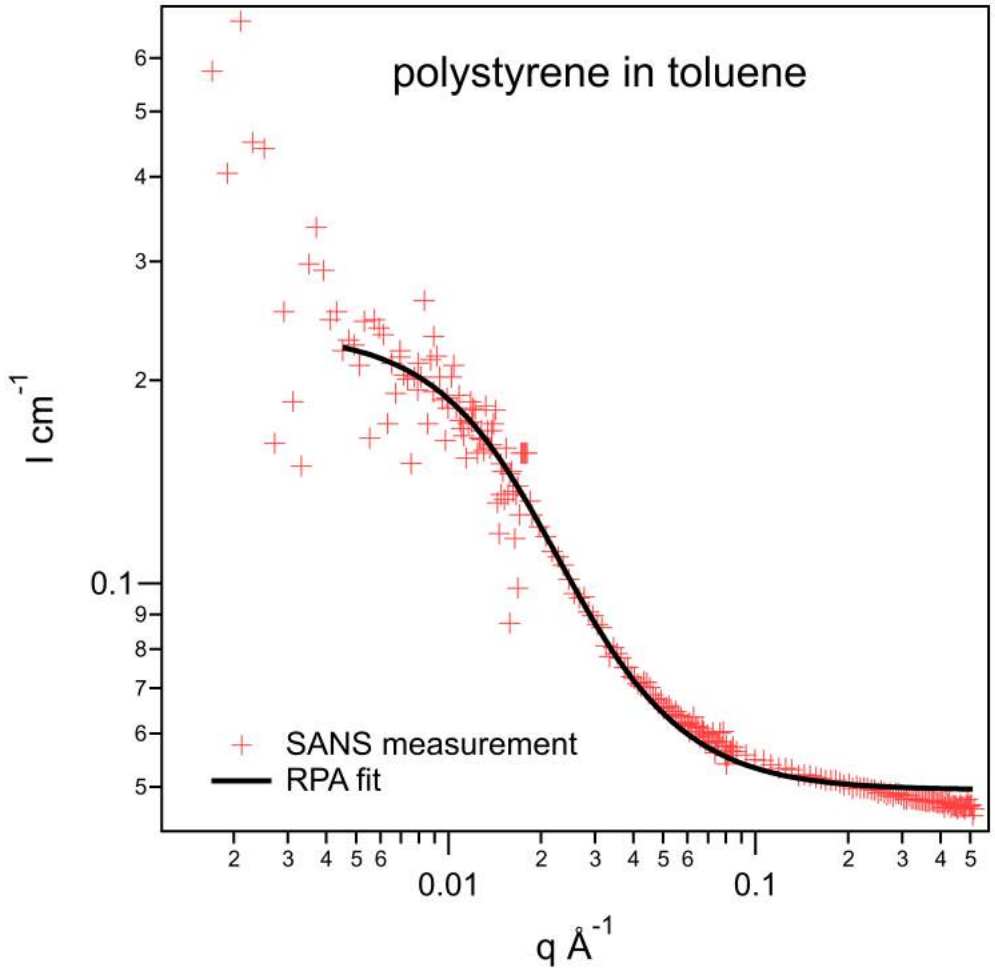


$$g^2(r) = \frac{\langle \rho(r)\rho(r') \rangle}{\langle \rho \rangle^2} \rightarrow P(q) = \int dr \int dr'\, g^2(r) \exp[iq \cdot (r' - r)]$$

Autocorrelation function

Form factor in Fourier space

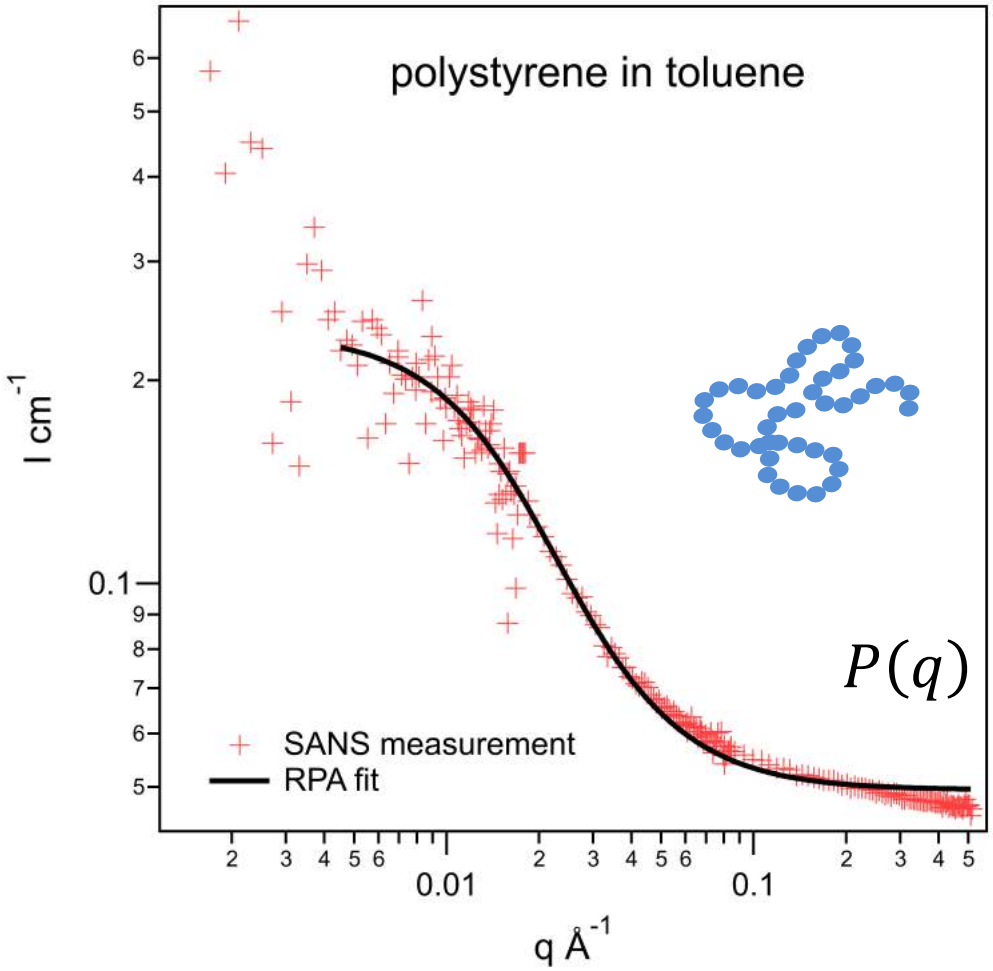
Form factor, $P(q)$ is measured by scattering



$$I(q) = \Delta\rho_{SLD}^2 P(q)$$

Scattering length density is contrast between particle and matrix

Form factor, $P(q)$ is measured by scattering



$$I(q) = \Delta\rho_{SLD}^2 P(q)$$

Scattering length density is contrast between particle and matrix

$$P(q) = \frac{1}{q^2 R_g^2}\left[\exp\left(-qR_g\right) + qR_g - 1\right]$$

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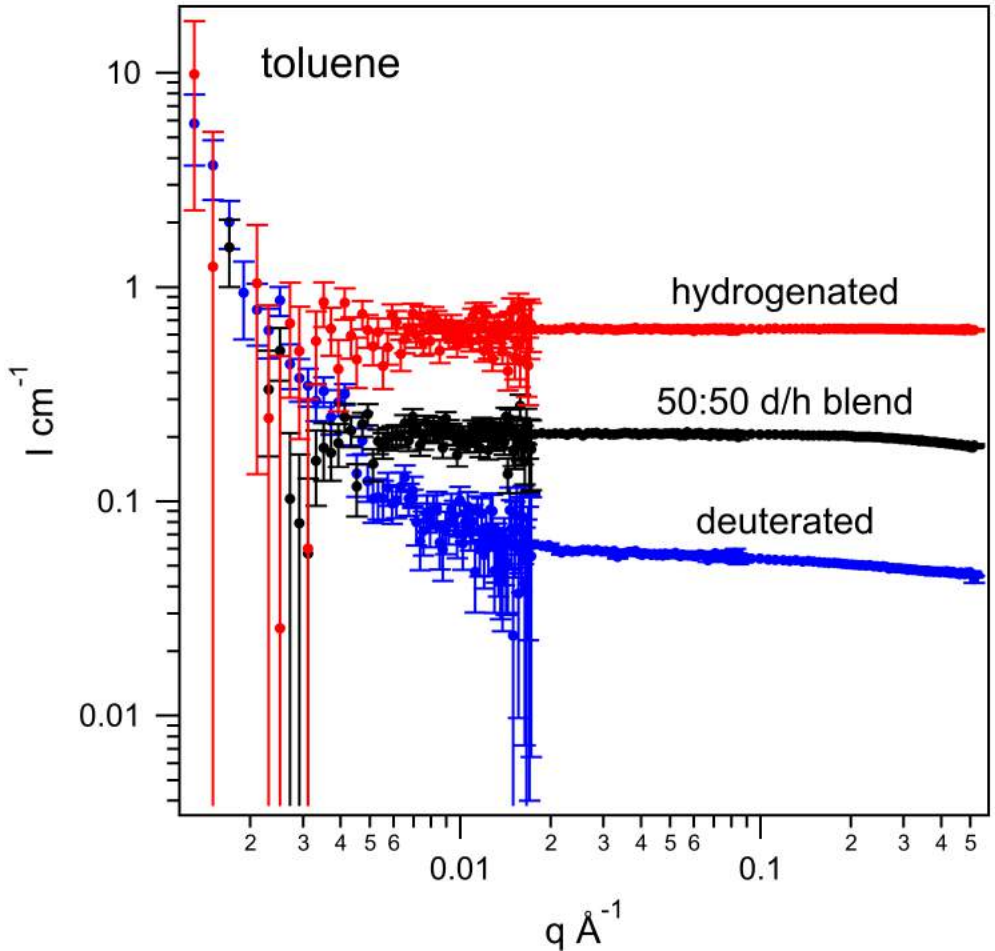
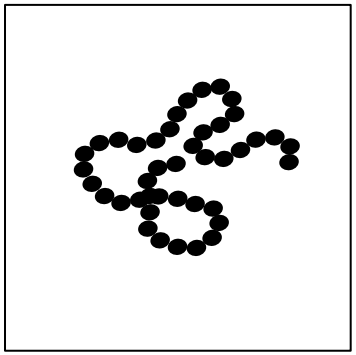
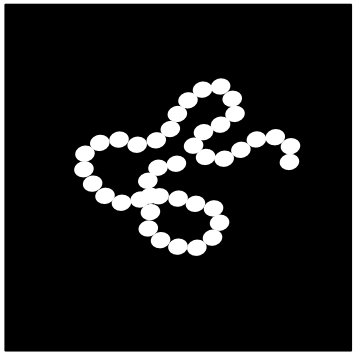
Tune the contrast using deuterium (d) and hydrogen (h)





d-polystyrene
h-toluene



h-polystyrene
d-toluene

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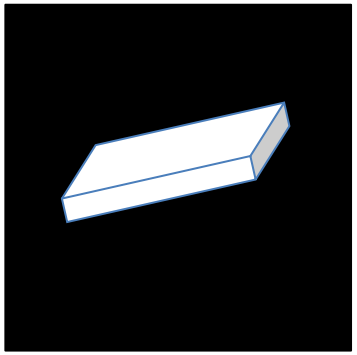
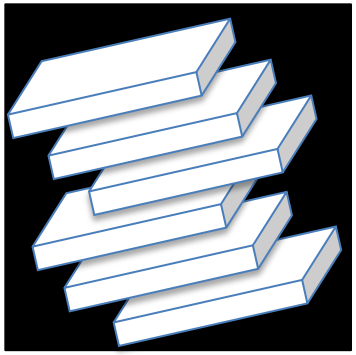
Characterizing nano**structures** using SANS



shape



structure

Repeated shapes give rise to structure

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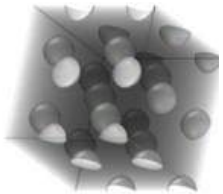
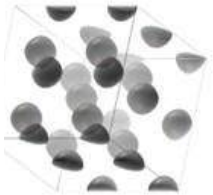
Characterizing nano**structures** using SANS

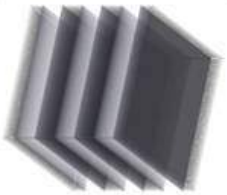




BCC spheres

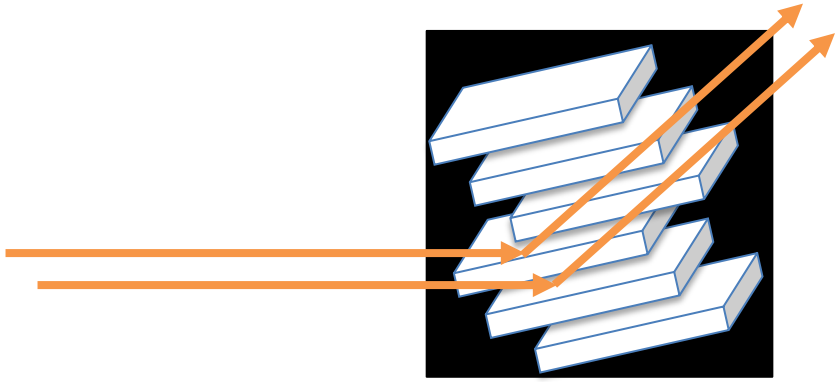
Hexagonally packed cylinders

Bicontinuous gyroid

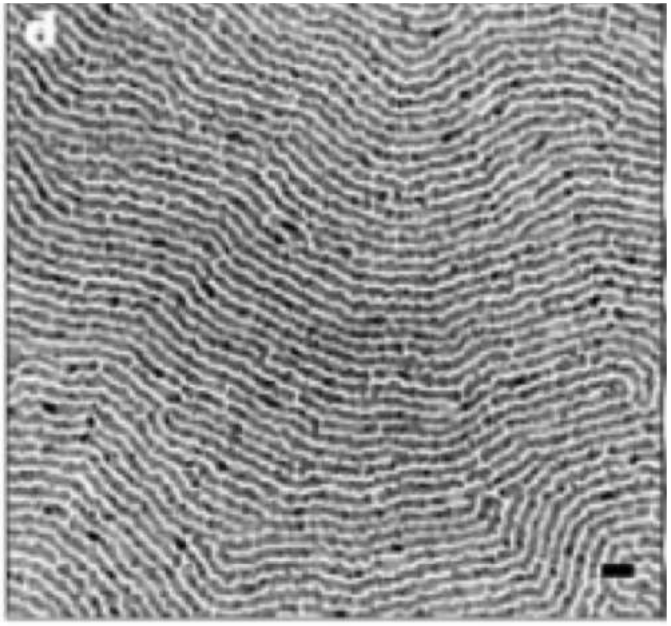


Lamellae

Characteristic spacing between 'particles' gives rise to structure factor $S(q)$

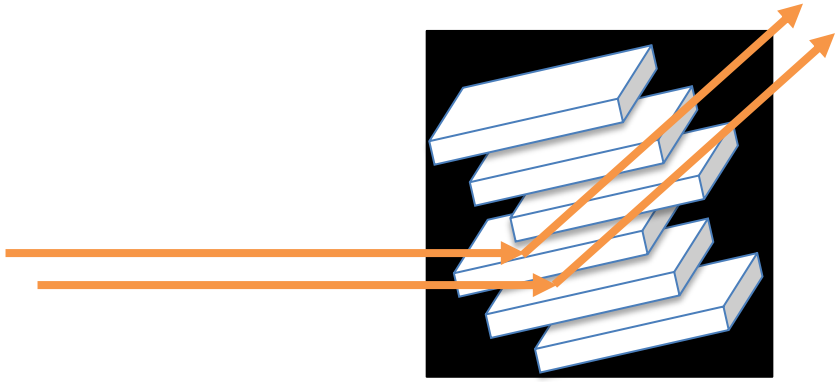


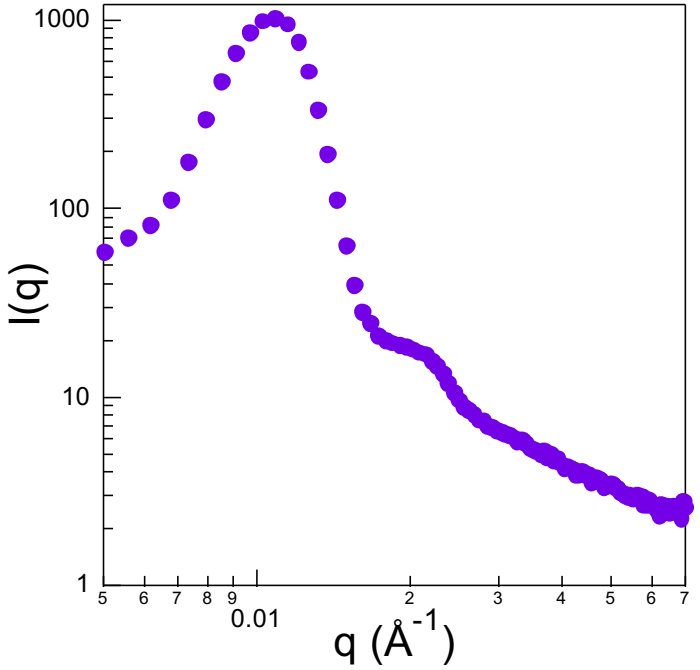
$$I(q) = (\Delta\rho_{SLD})^2 S(q) P(q)$$



Surmeet Jain and Frank S. Bates. *Science*. **2003**, 300, 460-464.

Characteristic spacing between ‘particles’ gives rise to structure factor $S(q)$





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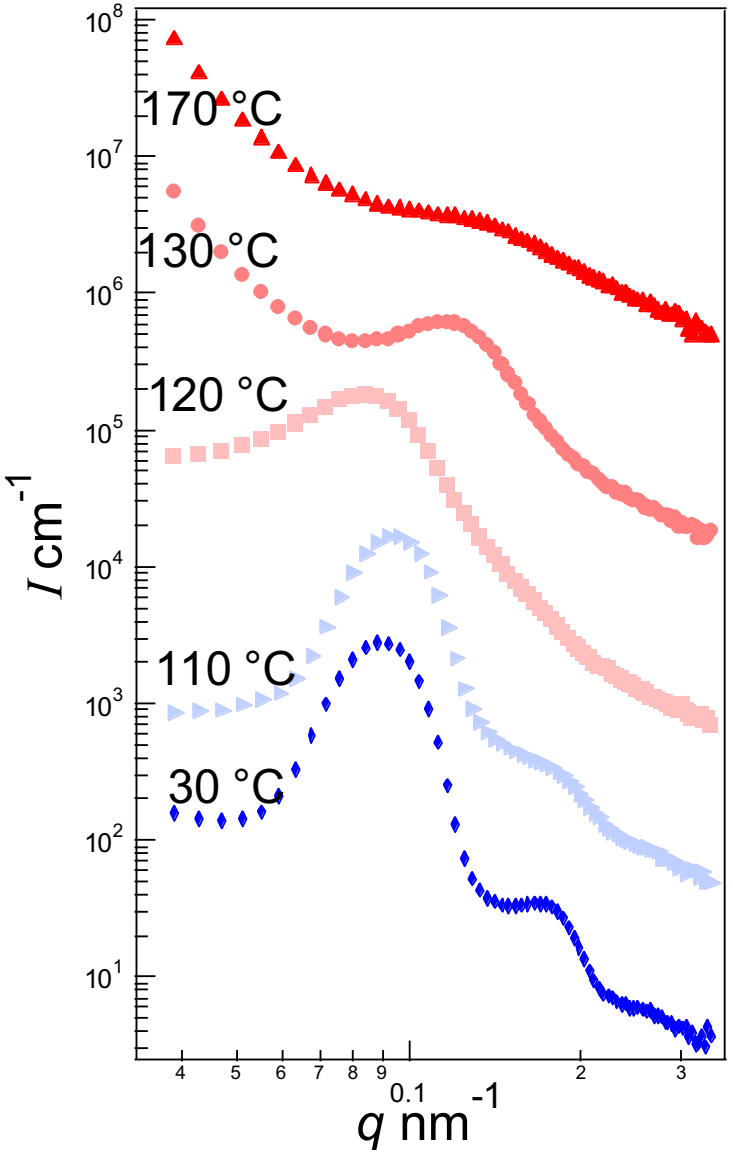
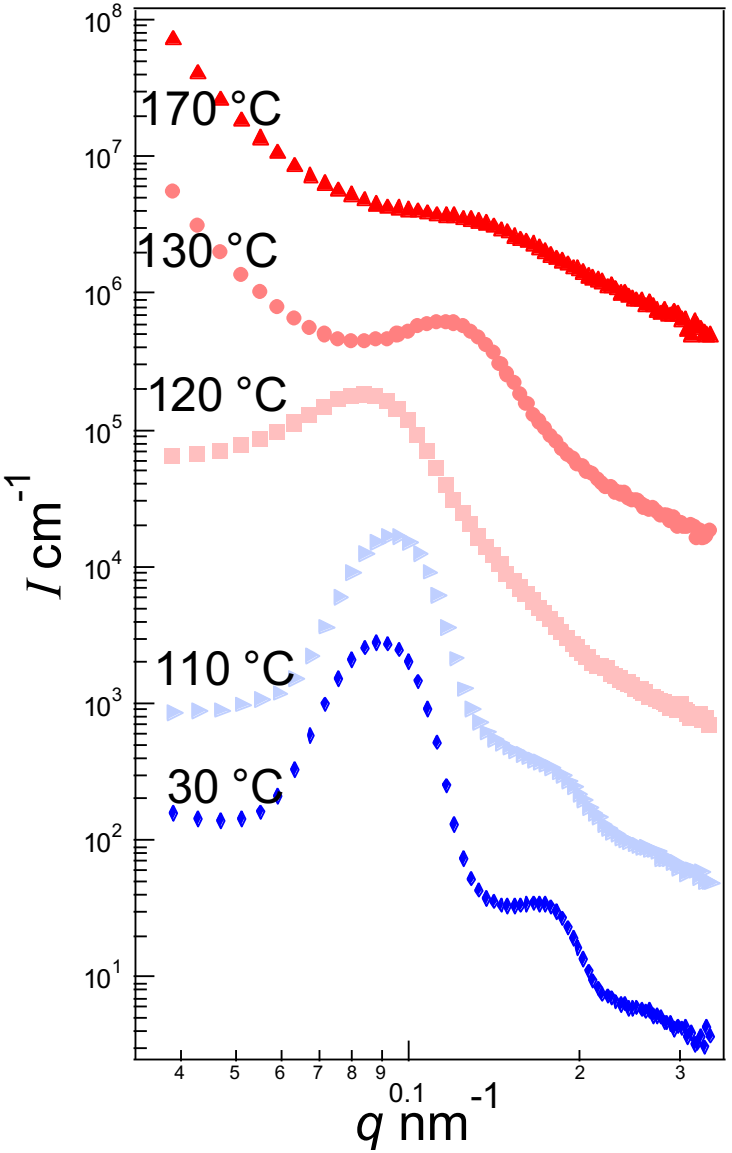


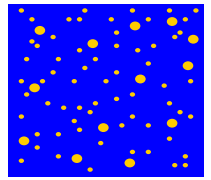
Phase characterization using structure

Phase characterization using structure

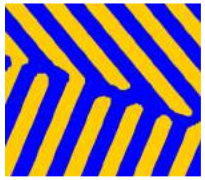


phase separated

Lamellae or microemulsions?



lamellae



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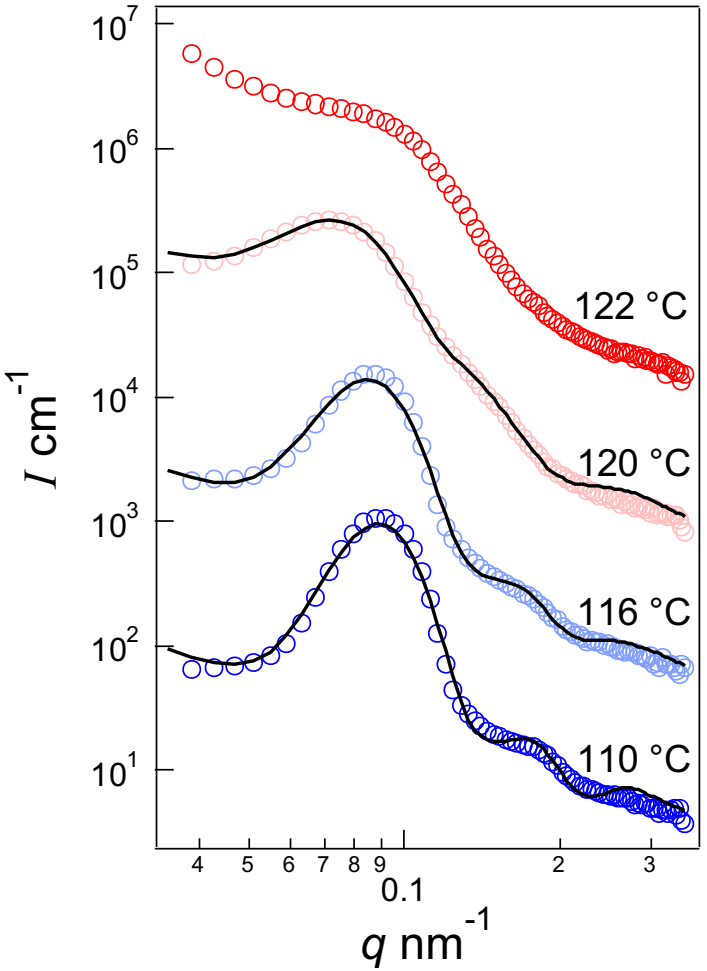
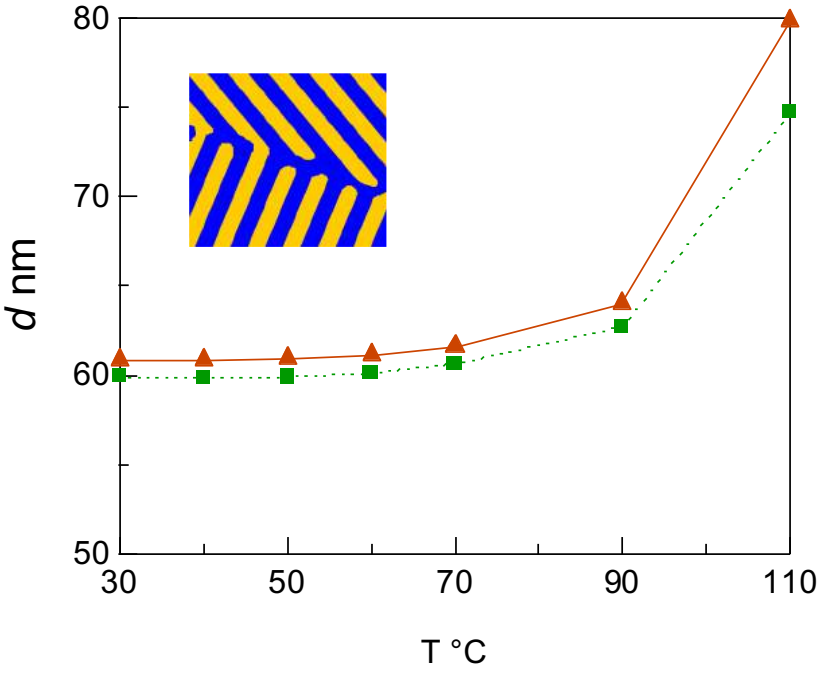
Characteristic "*d*" spacing between lamellae





Lamellar fits to SANS

SCFT theory

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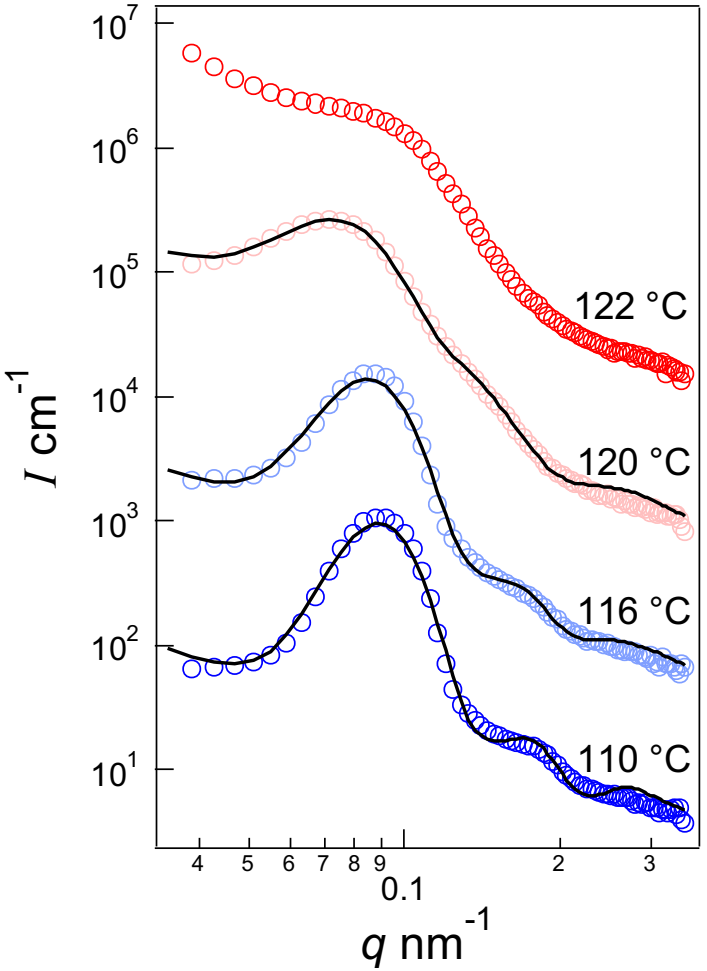
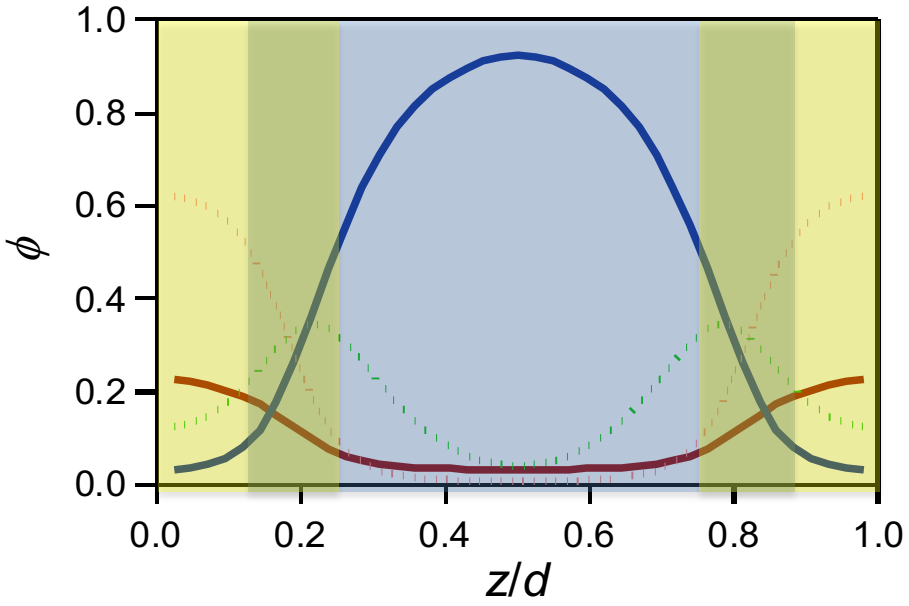
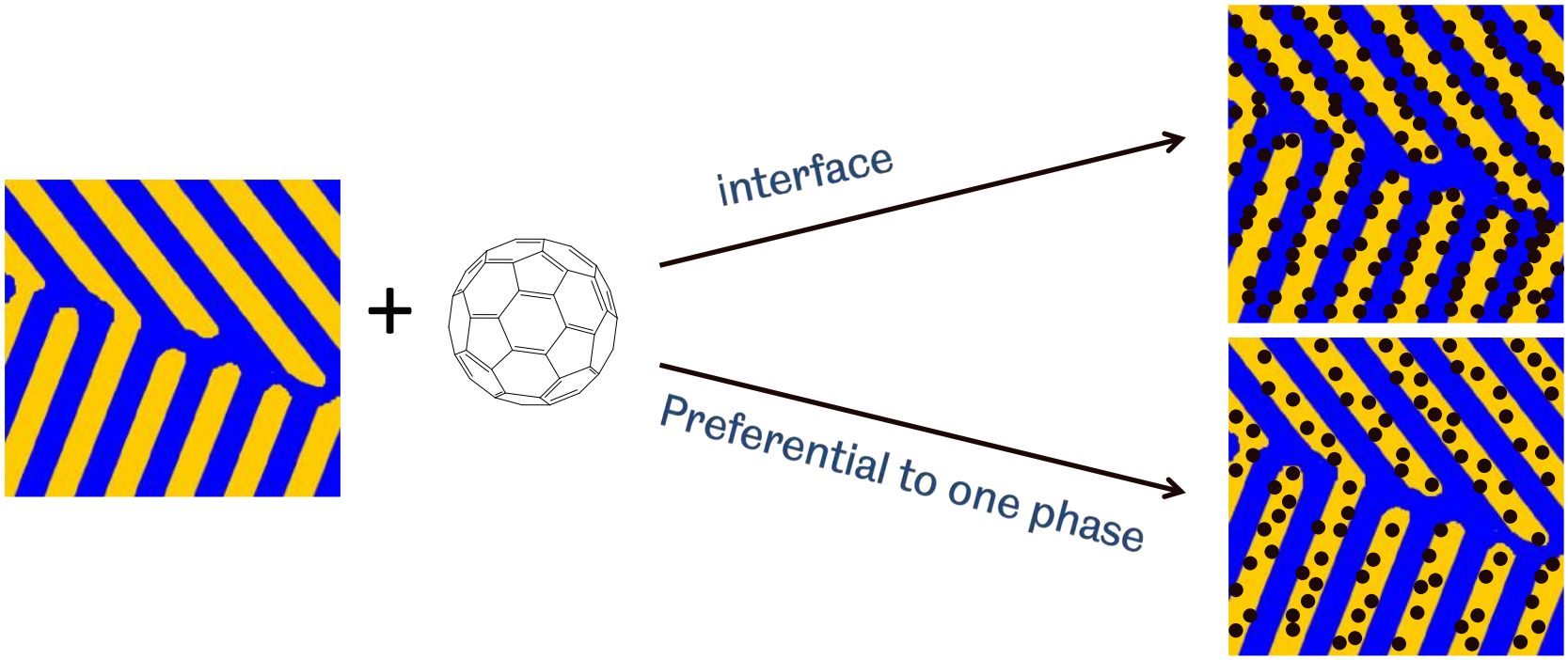
Fitting parameters can contain a wealth of information





Where does the fullerene go in lamellae?



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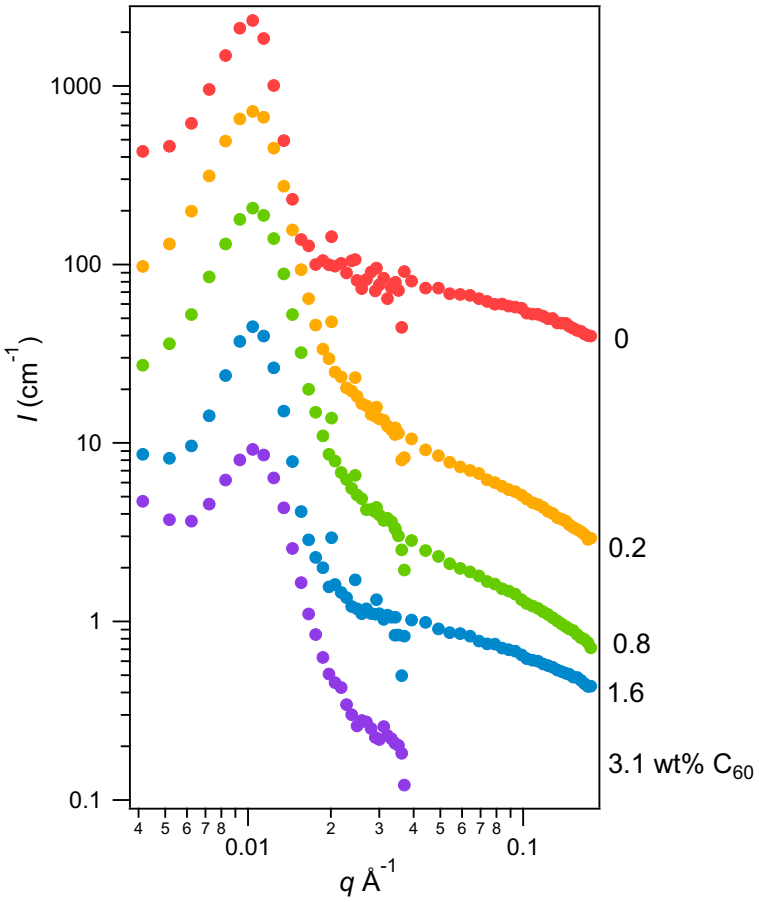
Characterizing the composition of a nanostructure



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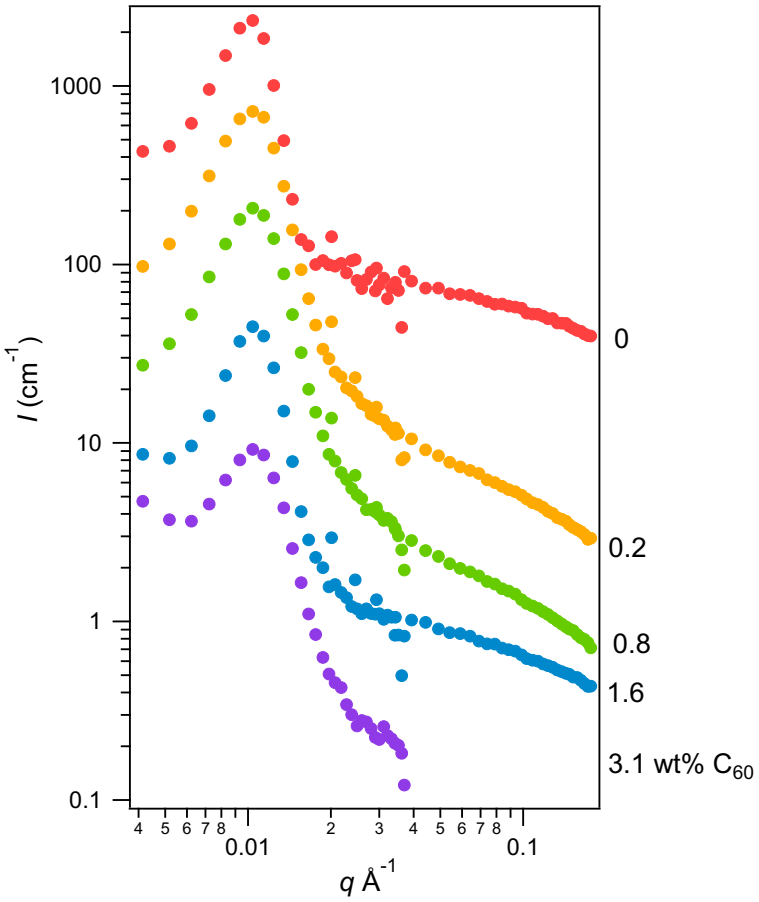
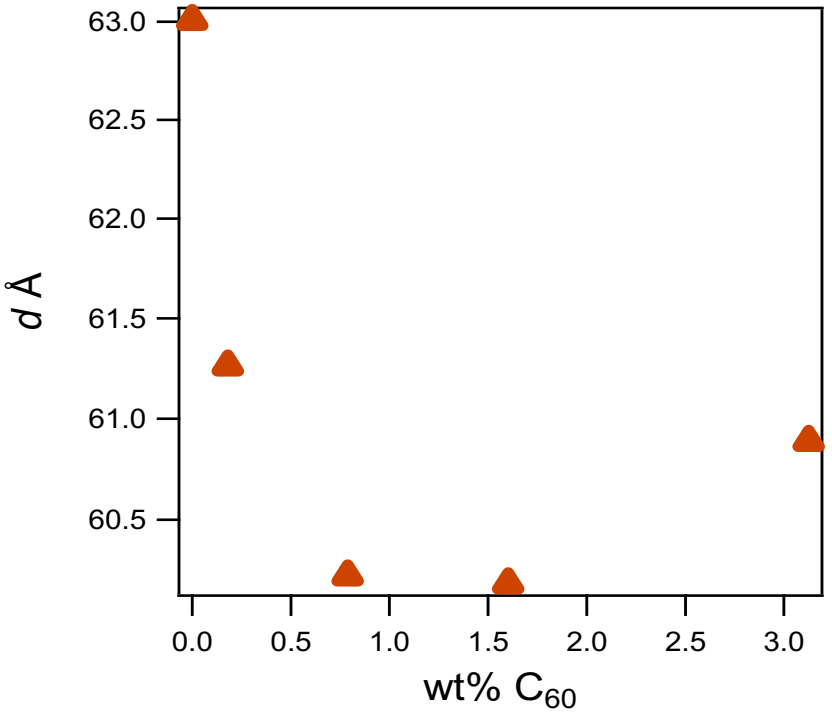
Domain spacing does not change much with C_{60}

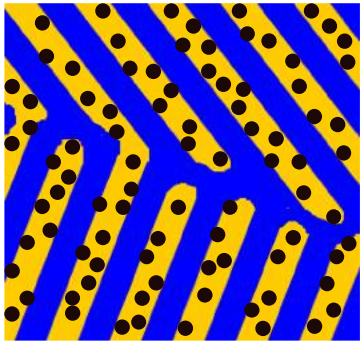




Contrast-matching can probe composition

$$I(q) = (\Delta\rho_{SLD})^2 S(q) P(q)$$

hypothesized structure



Component	ρ_{SLD} (cm^{-2})
C_{60}	5.7×10^{10}
(Yellow) polystyrene	1.4×10^{10}
(Blue) perspex	1.1×10^{10}

Contrast-matching can probe composition

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hypothesized structure

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(Blue) perspex	1.1×10^{10}
Deuterated perspex	6.9×10^{10}

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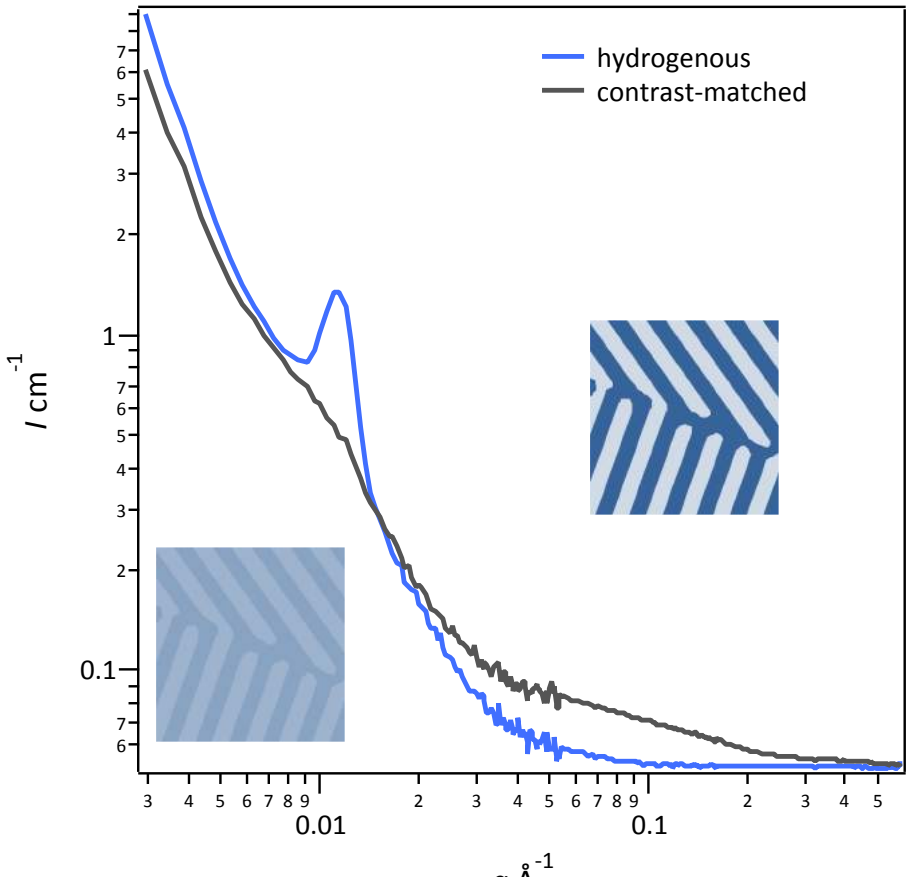
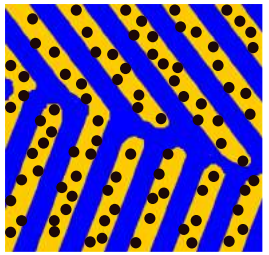
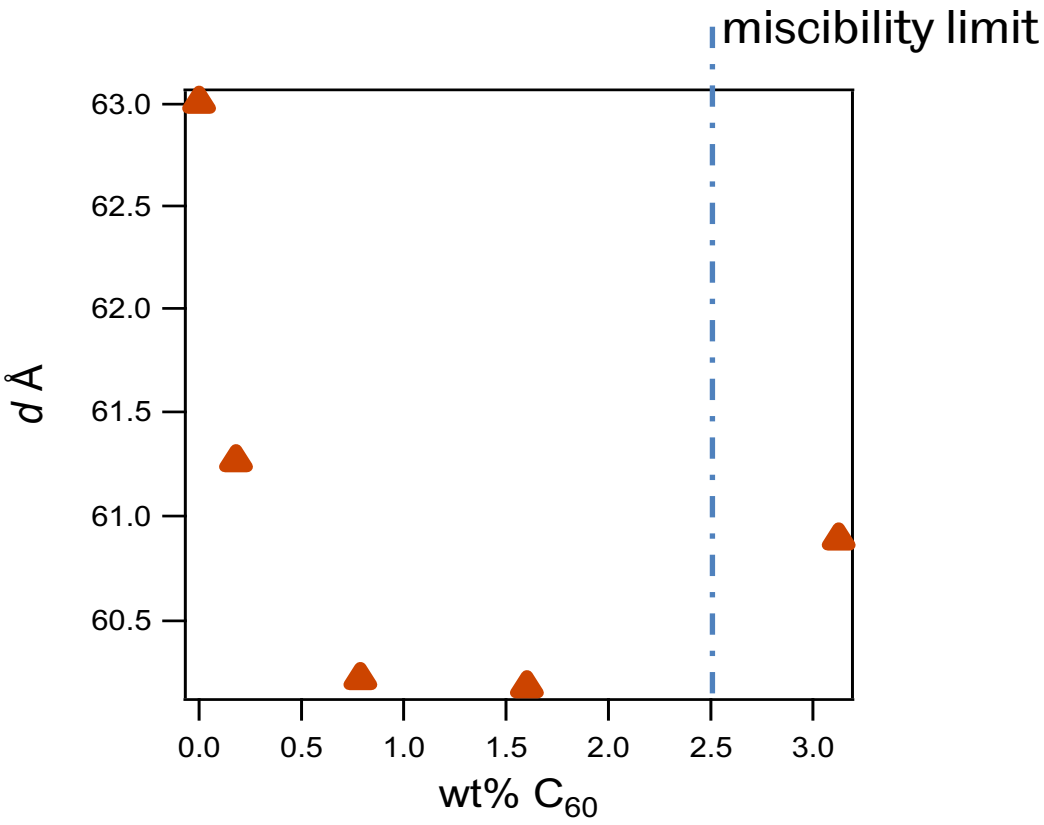


Contrast-matching 'hides' correlation peak

C_{60} segregates into the PS phase



Why did C_{60} cause the lamellae to compress?



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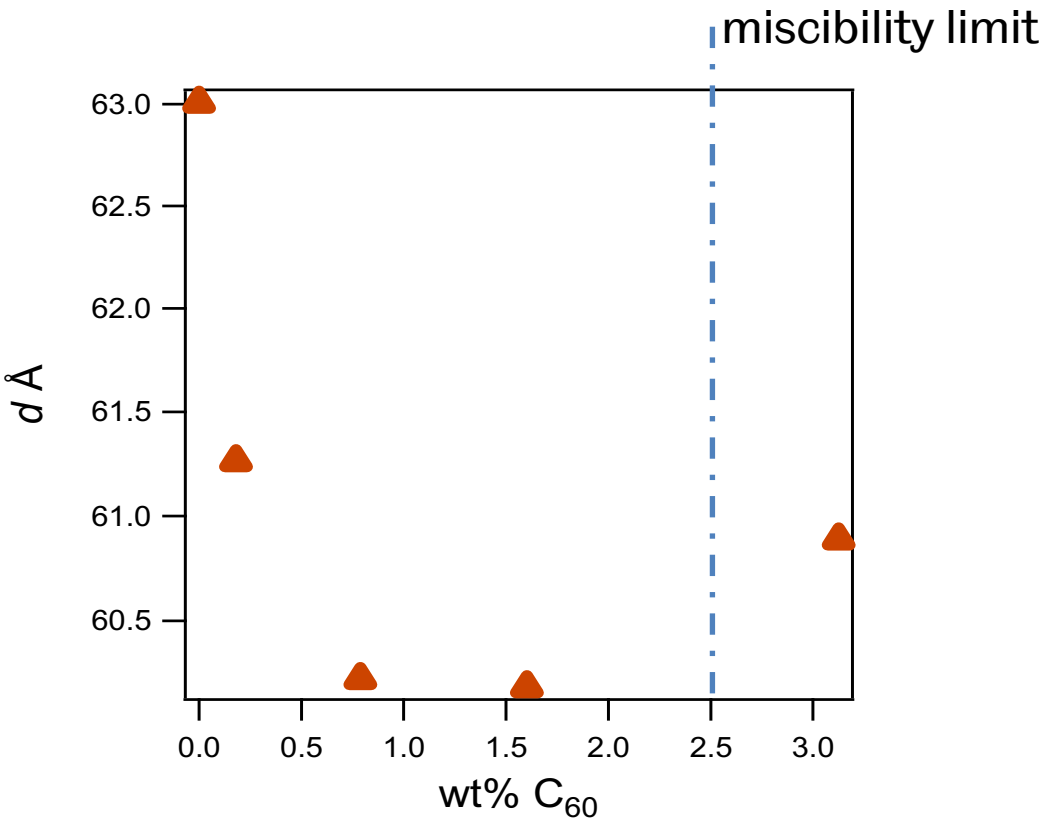
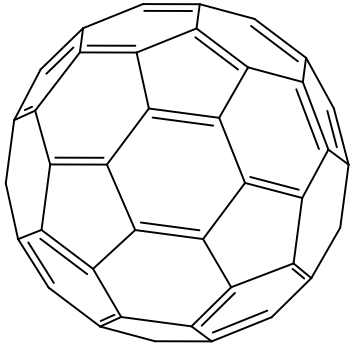
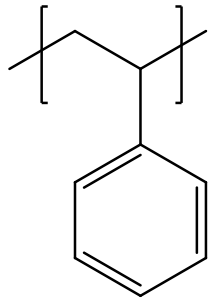


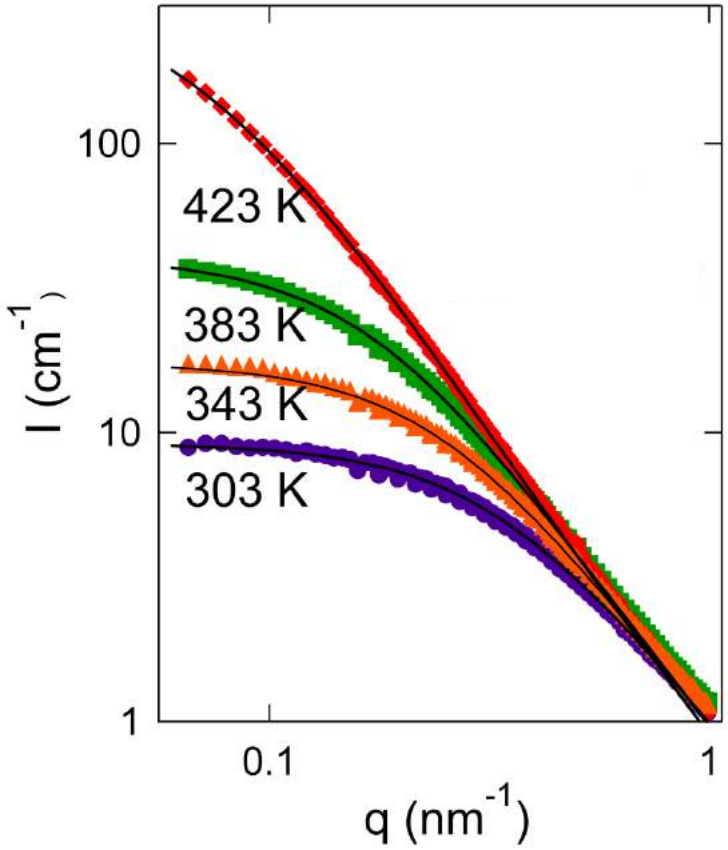


C_{60}



polystyrene

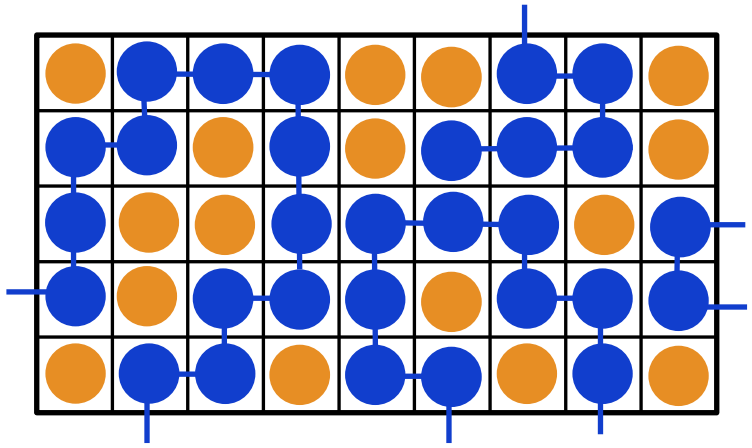
SANS measures thermodynamic parameters at low-q



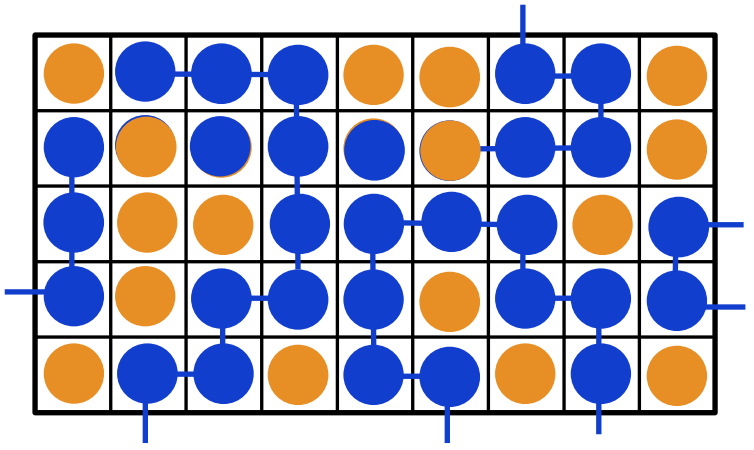
Random Phase Approximation

$$S(q)^{-1} = \frac{\partial^2(\Delta G/k T)}{\partial \phi^2}$$

Fluctuations in composition give rise to scattering

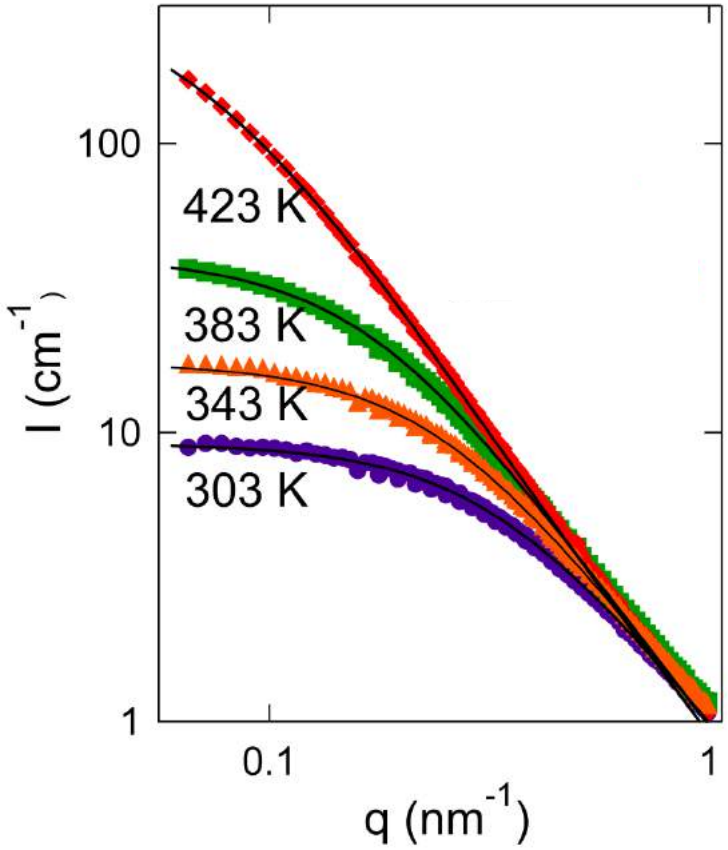


t



$t + \Delta t$

SANS measures thermodynamic parameters at low-q



Random Phase Approximation

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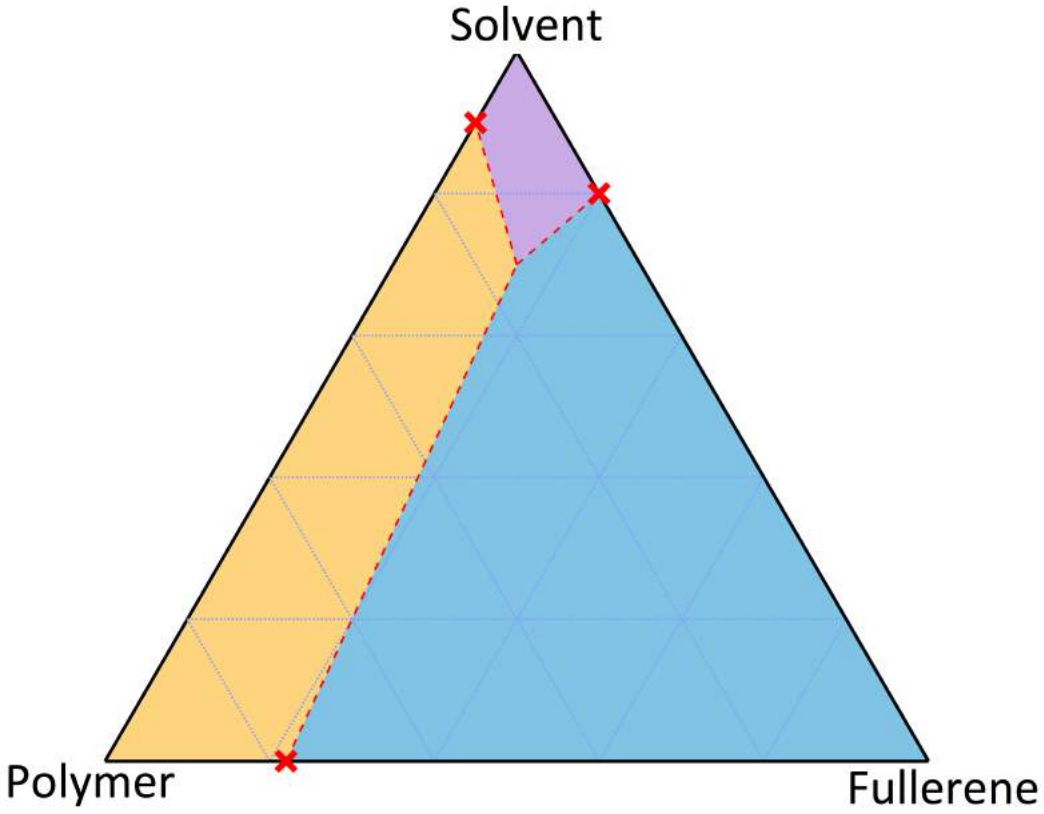
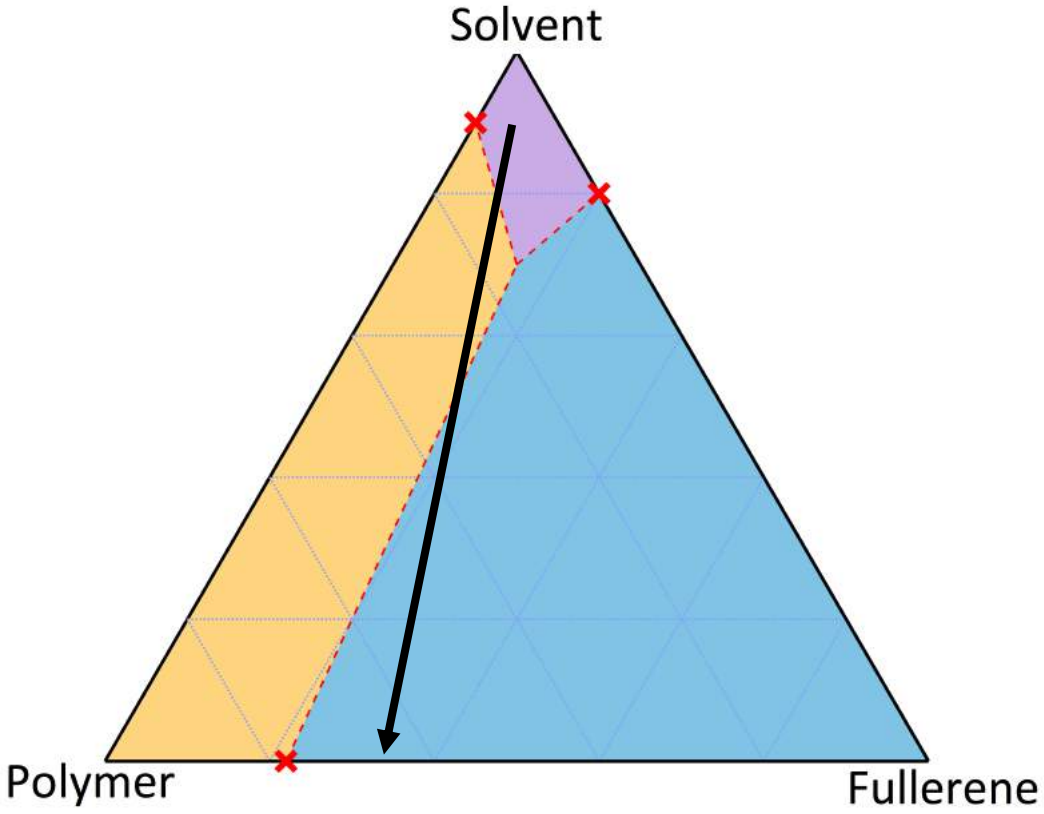
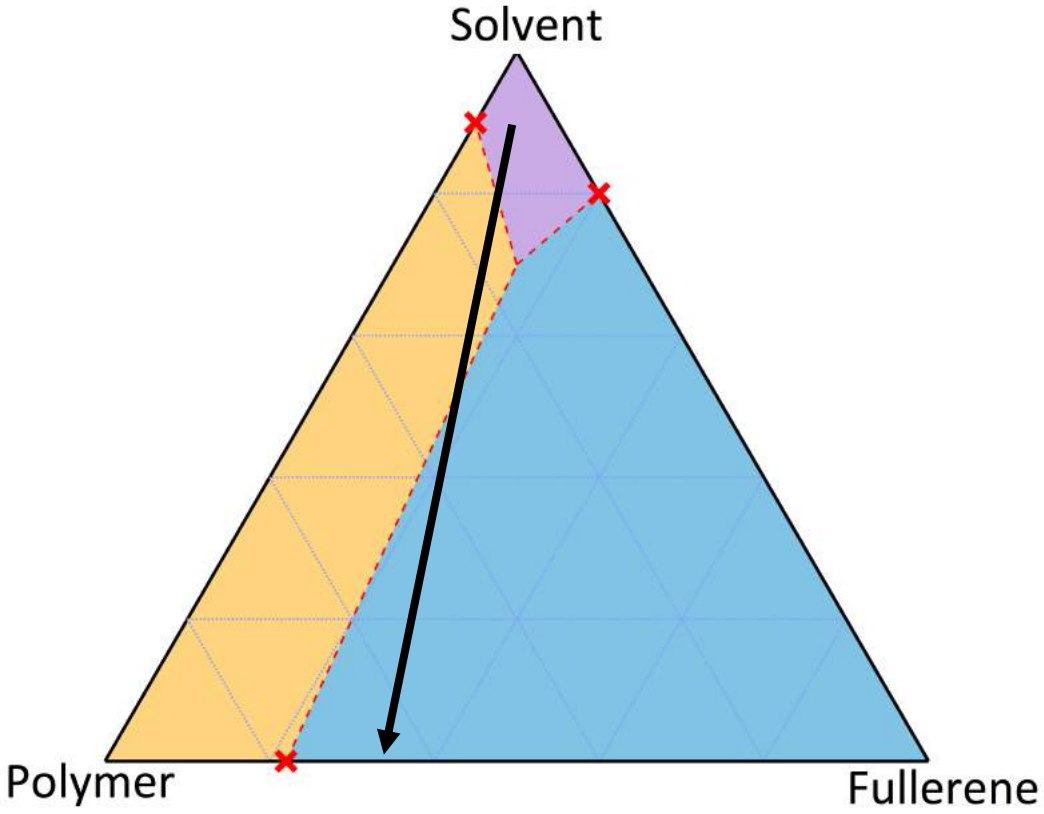
Thermodynamics affects performance through structure

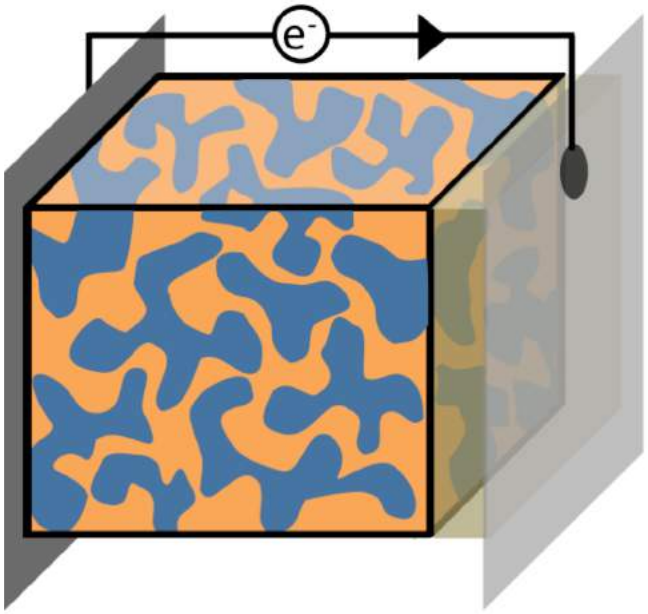


Thermodynamics affects performance through structure

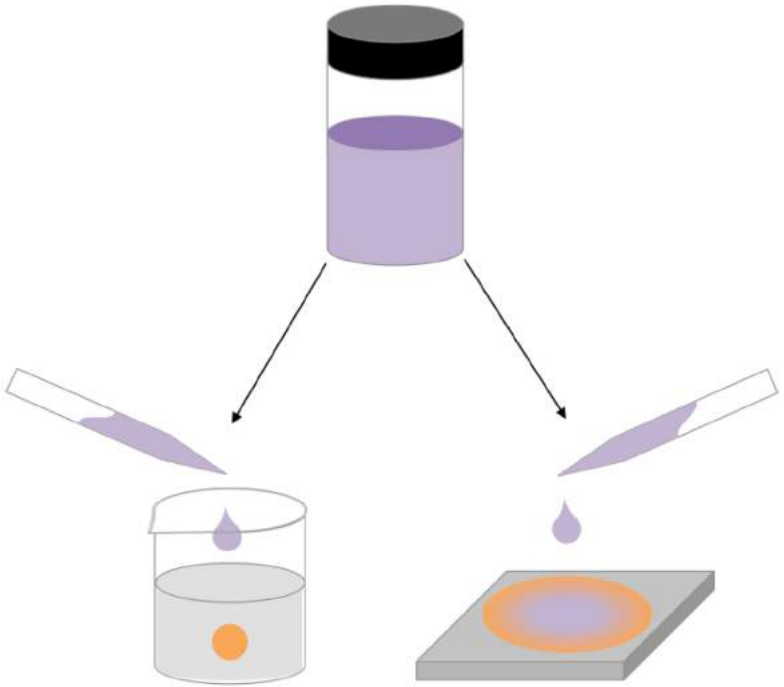


Thermodynamics affects performance through structure



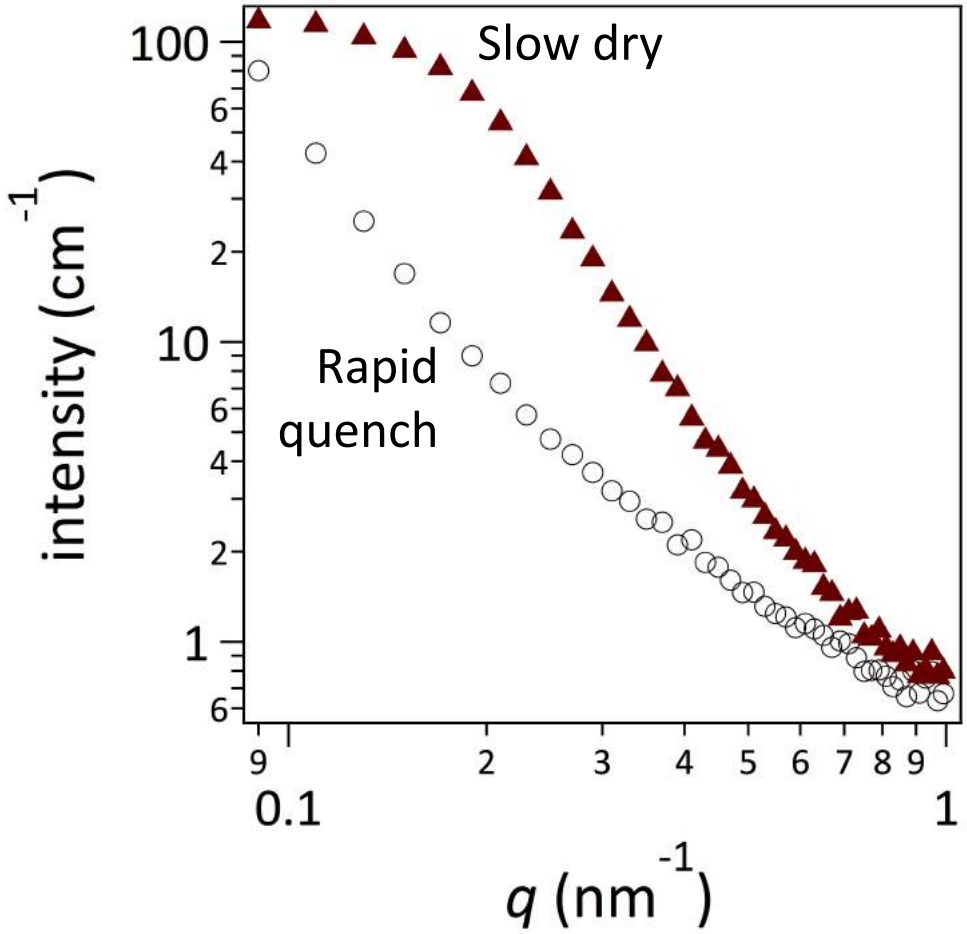


Thermodynamics affects performance through structure

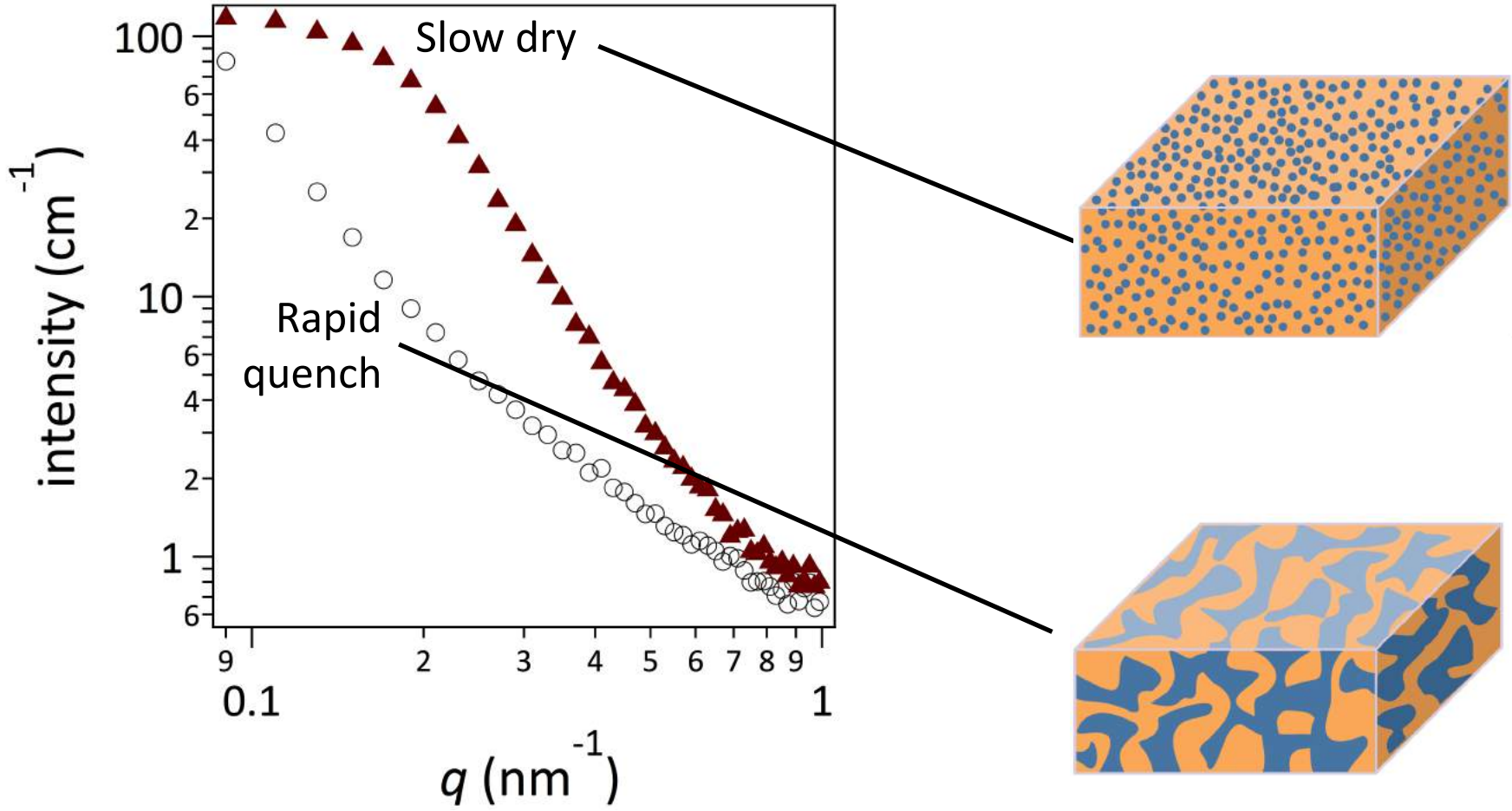


fast quench slow dry

Kinetics affects solar cell structure



Kinetics affects solar cell structure



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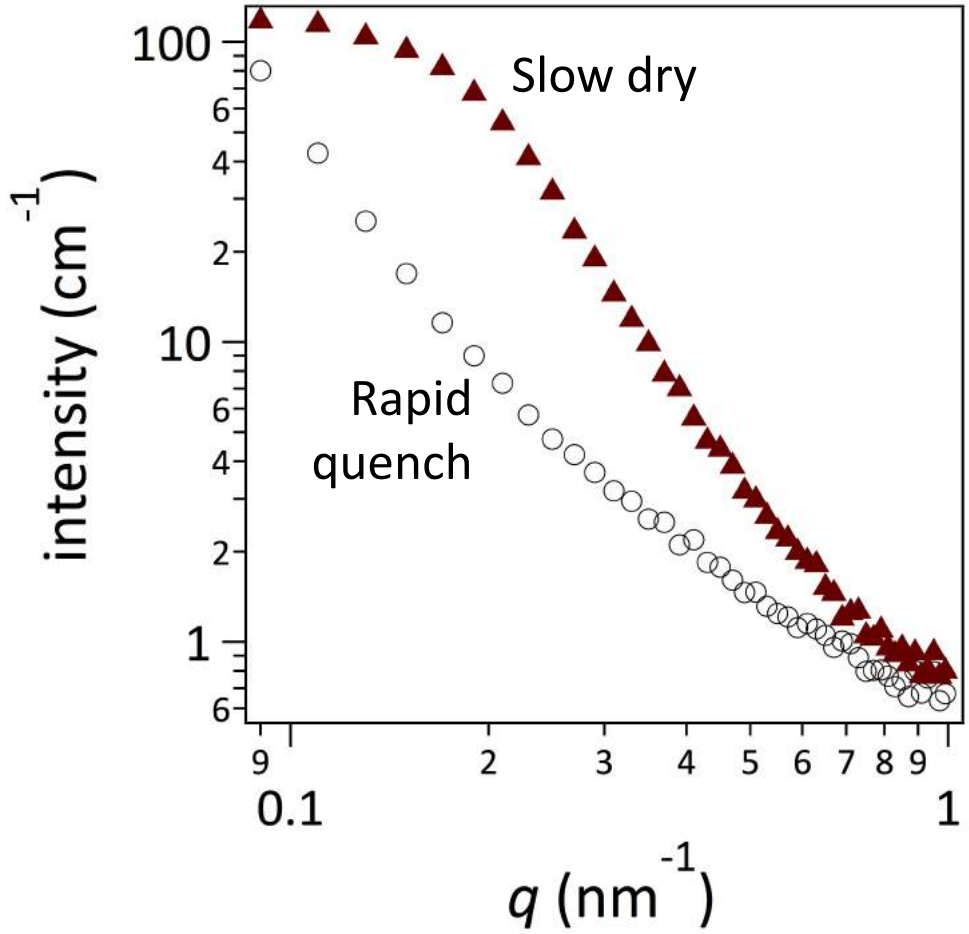
Kinetics affects solar cell structure



	Rapid quench	**Slow dry**
Polymer Crystallinity	57 wt%	38 wt%
Dissolved Fullerenes	5 vol%	44 vol%

Weighing qualities of neutron scattering

Pros	Cons
• Statistically meaningful	• Large sample volume (~50 mg)
• Particle shape	• Beamline access, long wait
• Structure	• Challenging analysis
• Composition	• Long acquisition times (~1 min)
• Thermodynamic interactions	

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Science & Technology Facilities Council
ISIS

National Institute of Standards and Technology
U.S. Department of Commerce

NEUTRONS FOR SOCIETY

PAUL SCHERRER INSTITUT
PSI

OAK RIDGE National Laboratory

Orphée Laboratoire Léon Brillouin

Thank You!

SANS (~1–500 nm)

- Shape
- Structure
- Composition
- Thermodynamic interactions

Alisyn Nedoma
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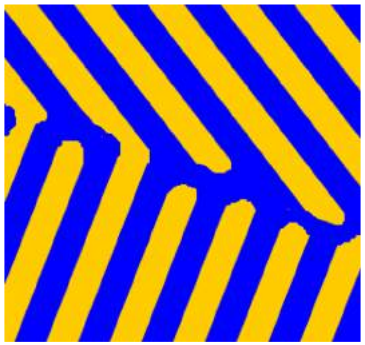
Statistically meaningful due to large measured volume

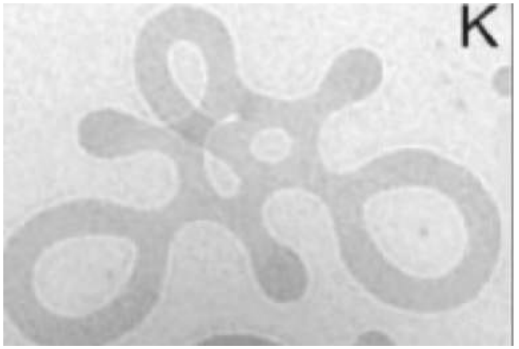
Small-angle Neutron Scattering (SANS) measures structure and composition

Can get information on composition from absolute intensity

Structure of a material
Shape of nanostructures
Composition of nanomaterials

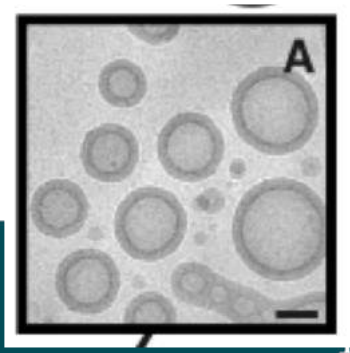


~200 nm



Micelles

Surmeet Jain and Frank S. Bates.
Science. **2003**, 300, 460-464.



Vesicles

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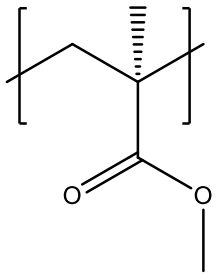
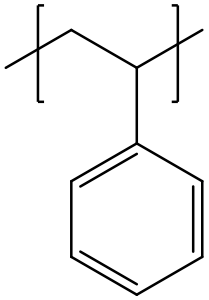


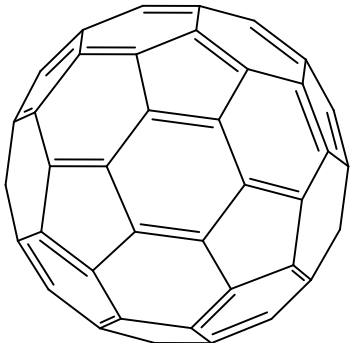
dPMMA

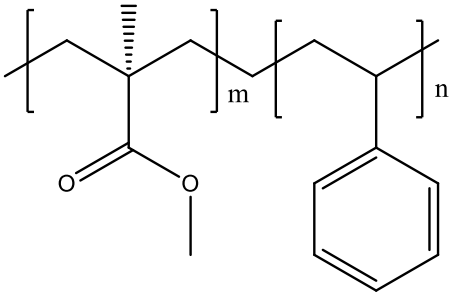
T_g = 80°C



PS

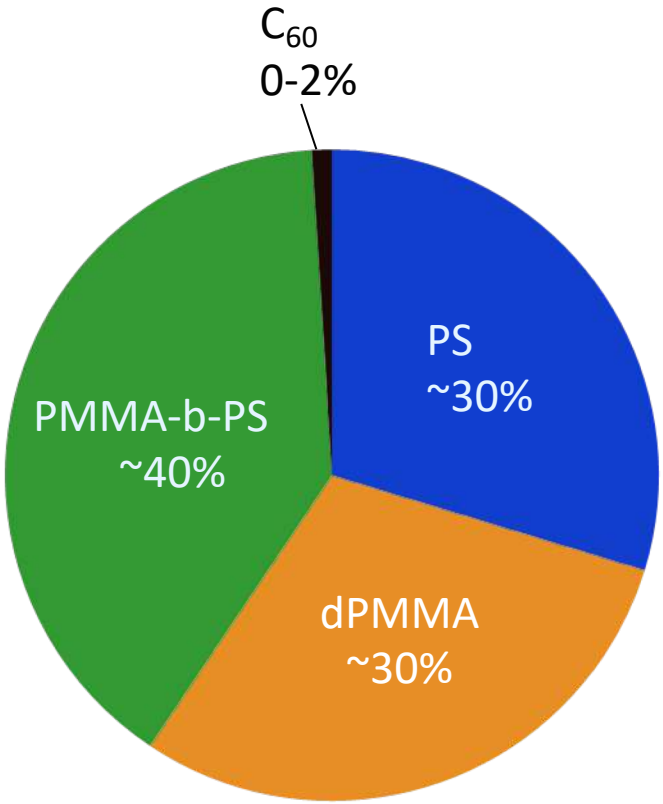
T_g = 80°C





PMMA-b- PS

T_g = 107-132°C



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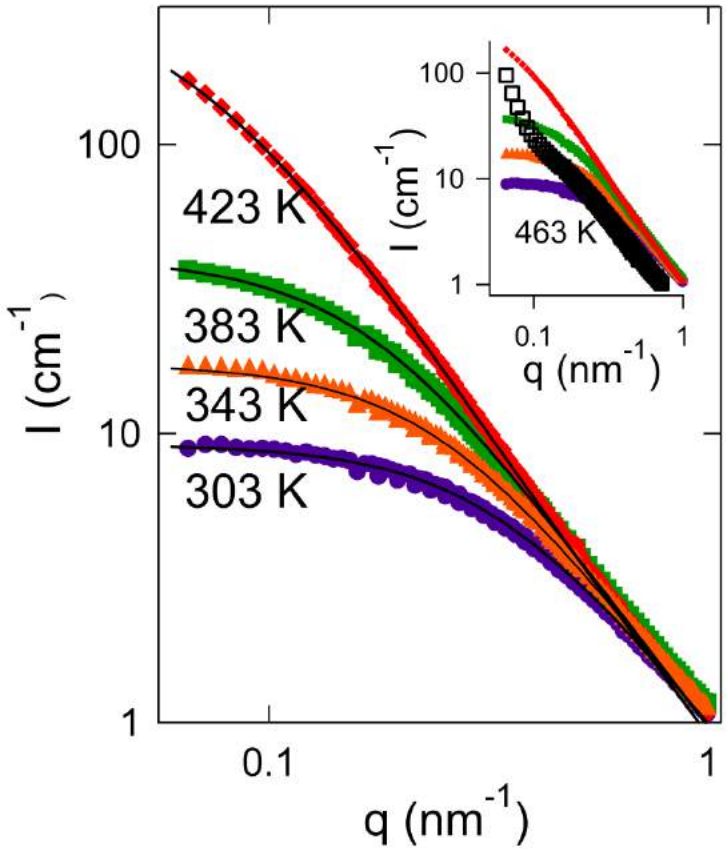
Quantifying thermodynamic interaction parameters using SANS



$$I(q) = k\left[\frac{1}{N_B^*\phi_A P_A(q)} + \frac{1}{N_B^*\phi_B P_B(q)} - 2\chi_{AB}\right]^{-1}$$

$$= \frac{1}{q^2 R_{g,i}^2}\left[\exp\left(-q^2 R_{g,i}^2\right) + q^2 R_{g,i}^2 - 1\right]$$

Locate phase boundary

Determine value for χ_{AB}

[2] De Gennes, P.G. Scaling Concepts in Polymer Physics; Cornell University Press: Ithaca, NY 1979.C