SANS from Concentrated Dispersions

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NCNR Summer School

Neutron Small Angle Scattering and
Reflectometry from Submicron Structures
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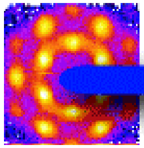
Outline

- How dilute is “dilute”?
  - Effect of concentration on Rg determination
- The structure factor and the radial distribution function
- What information is in S(q) and how do I get it?
  - Data fitting
- The real world of polydispersity
  - Approximations
  - Exact methods
- Example I: Colloidal silica
  - Size polydispersity
- Example II: Surfactant micelles
  - Charge interactions
- Summary



SANS from Dilute Systems

$$I(q) = n_p P(q)$$

n_p = number density of particles

P(q) = Form factor (<u>Intra</u>particle structure)

- <u>Guinier Approximation:</u>

  If the scatterers are "**sufficiently dilute**":

$$I(q) \approx I(0)\exp\left(-q^2R_g^2/3\right)$$

Linear Plot:

$$\ln I(q) = \ln I(0) - q^2R_g^2/3$$

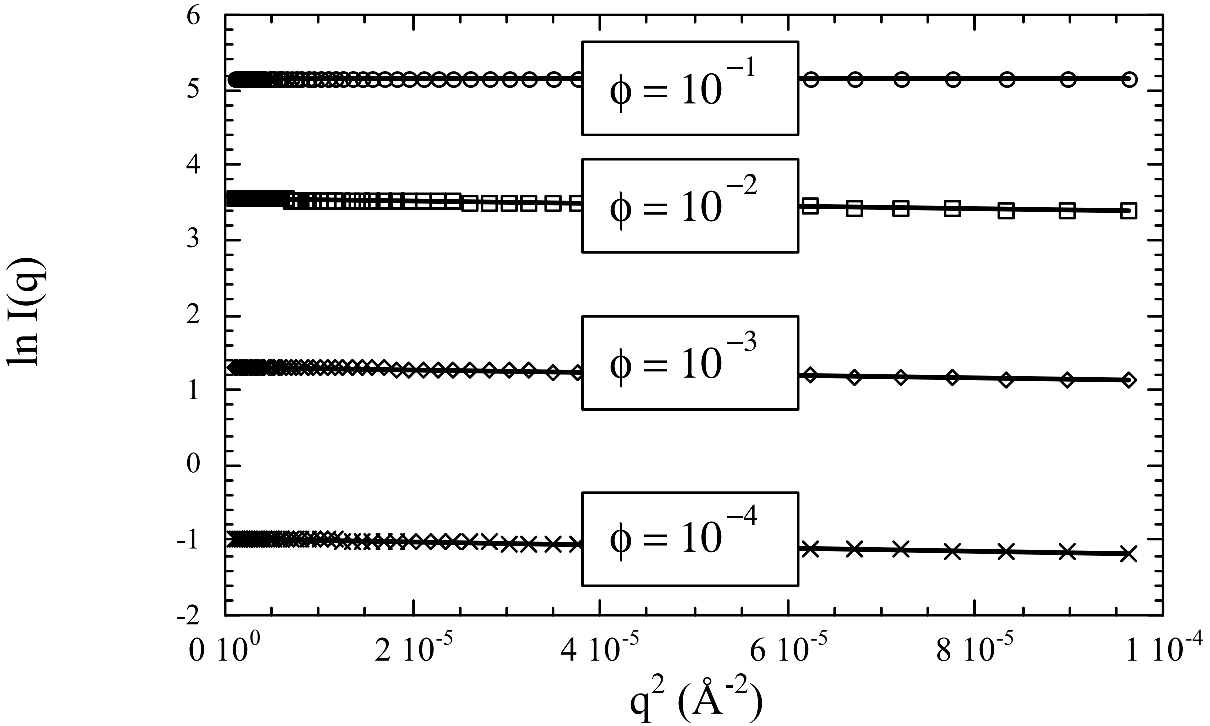
For a uniform sphere:

$$R_g^2 = \frac{3}{5}R^2$$

How dilute is “sufficiently dilute”?

- Guinier Plot for Hard Spheres

R = 100 Å



How dilute is “sufficiently dilute”?

- Guinier Plot for Hard Spheres

$R = 100$ Å

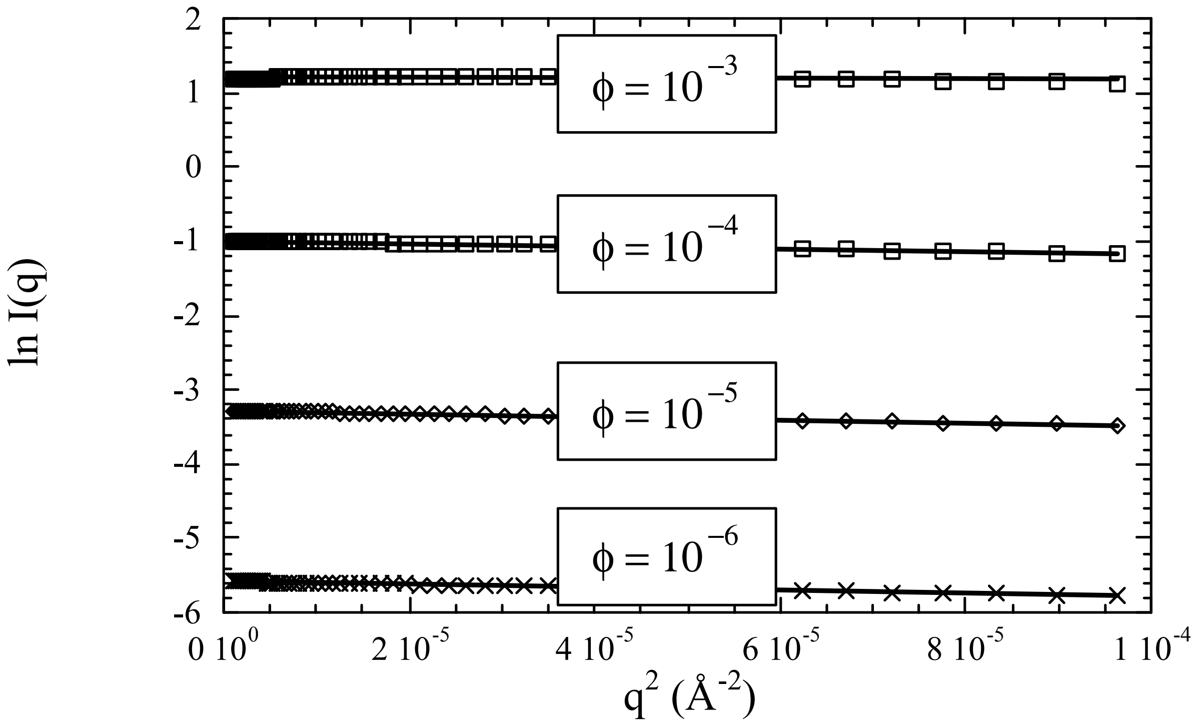
Volume Fraction	R_{sphere} (Å)	Average Separation (Å)
10^{-1}	5.4	350
10^{-2}	93.3	750
10^{-3}	99.7	1600
10^{-4}	100.0	3500

$\phi \leq 10^{-3}$ is “dilute” for spheres with hard sphere interactions

How dilute is “sufficiently dilute”?

- <u>Guinier Plot for Charged Spheres</u>

$R = 100$ Å, $Z = 50$, [salt] $= 10^{-3}$, $\kappa^{-1} = 100$ Å



How dilute is “sufficiently dilute”?

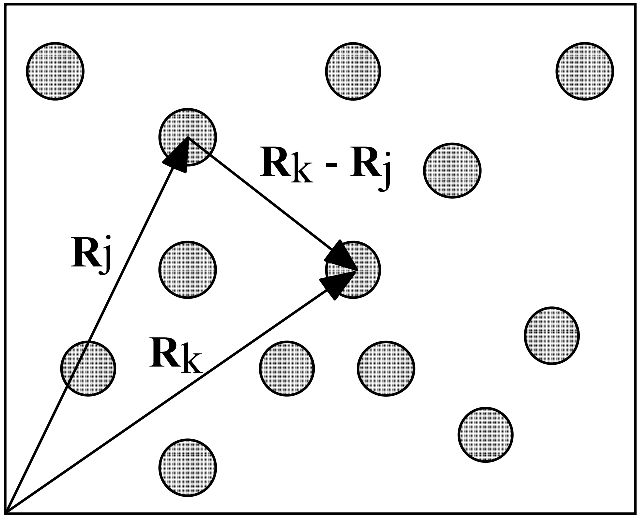
- Guinier Plot for Charged Spheres

$R = 100$ Å, $Z = 50$, [salt] $= 10^{-3}$, $\kappa^{-1} = 100$ Å

Volume Fraction	R_{sphere} (Å)	Average Separation (Å)
10^{-3}	41.2	1600
10^{-4}	96.2	3500
10^{-5}	100.0	7500
10^{-6}	100.0	16000

$\phi \leq 10^{-3}$ is “dilute” for spheres with screened Coulomb interactions

Interparticle Interference Effects



- Scattered Intensity:

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{1}{V}\sum_{k=1}^{N_p}\left\langle \left| f_k(\vec{q}) \right|^2 \right\rangle + \frac{1}{V}\left\langle \sum_{k=1}^{N_p} \sum_{\substack{j=1 \\ j\neq k}}^{N_p} f_k(\vec{q}) f_j^*(\vec{q}) e^{i\vec{q}\cdot\left(\vec{r}_k - \vec{r}_j\right)} \right\rangle$$

Interparticle Interference Effects

- Scattering Amplitude (Intraparticle):

$$f_k(\vec{q}) = \int_{\text{particle k}} [\rho_k(\vec{r}) - \rho_{solv}] e^{i\vec{q}\cdot\vec{r}} d\vec{r}$$

$$P(q) = \left\langle |f_k(q)|^2 \right\rangle$$

the “Form Factor”

The Structure Factor

- For monodisperse spheres:

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = n_p \left\langle \left|f(q)\right|^2 \right\rangle \left\{ 1 + \left\langle \sum_{k=1}^{N_p} \sum_{\substack{j=1 \\ j\neq k}}^{N_p} e^{i\vec{q}\cdot(\vec{r}_k - \vec{r}_j)} \right\rangle \right\}$$

$$\frac{d\Sigma}{d\Omega}(\vec{q}) = n_p P(q) \cdot S(\vec{q})$$

If isotropic, we can average over orientation:

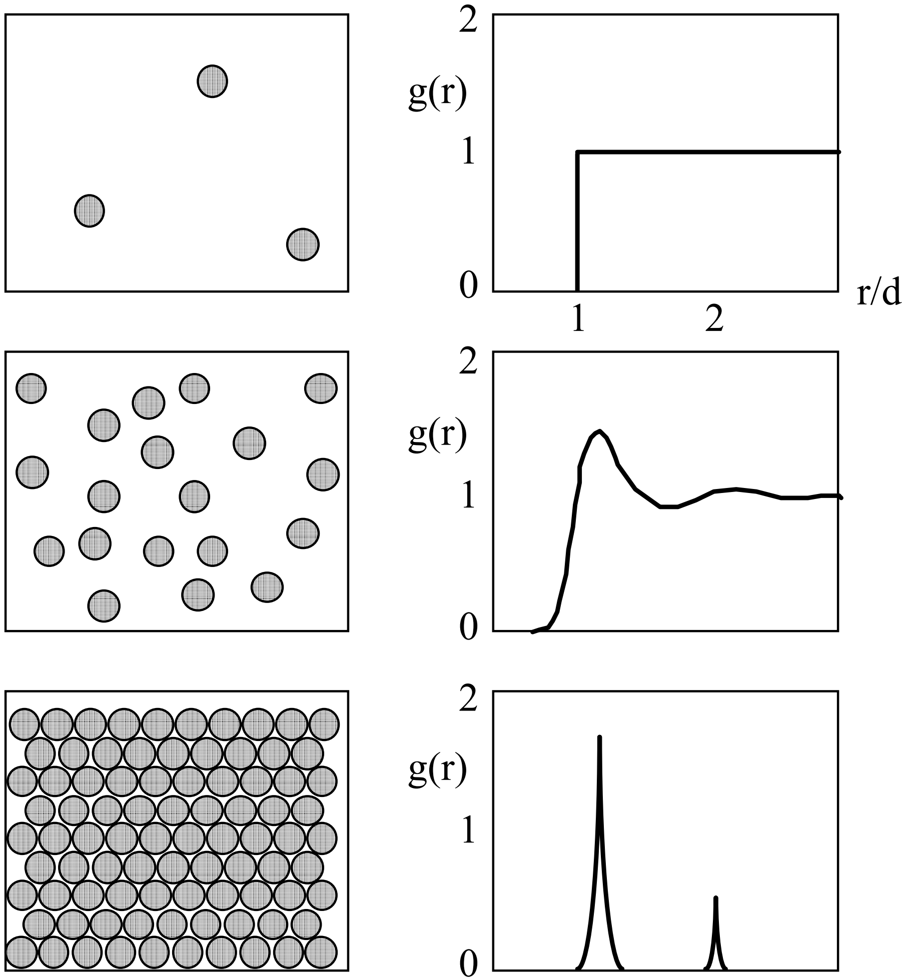
$$\left\langle S(\vec{q}) \right\rangle = S(q) = 1 + 4\pi n_p \int_0^\infty [g(r) - 1] \frac{\sin qr}{qr} r^2 dr$$

Note:

- S(q) is proportional to the number density of particles
- S(q) depends on g(r), the pair correlation function

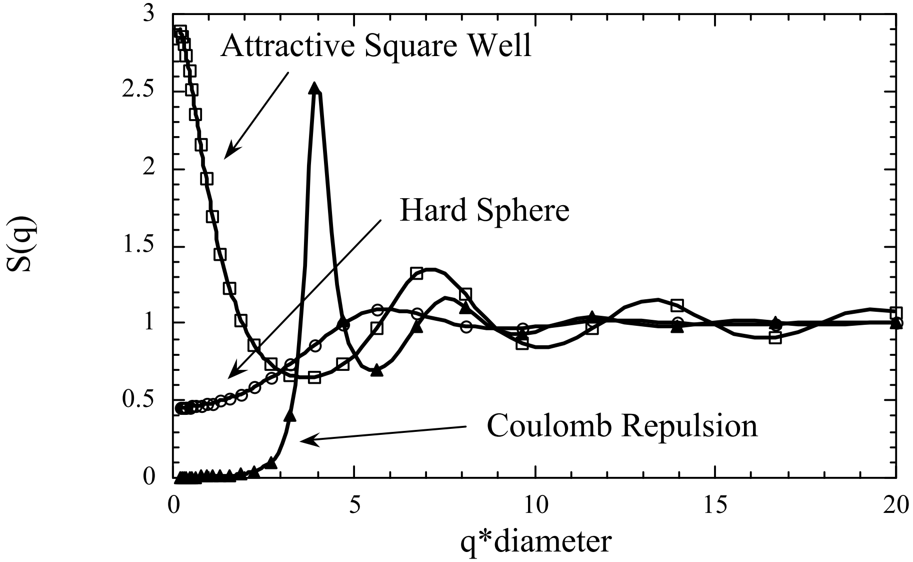
The Pair Correlation Function

- ➢ $n_p g(r)$ is a “local” density of particles
- ➢ Spatial arrangement set by interparticle interactions and indirect interactions



S(q) and Statistical Thermodynamics

- The form of the interparticle potential has a great effect on the low q value of S(q)



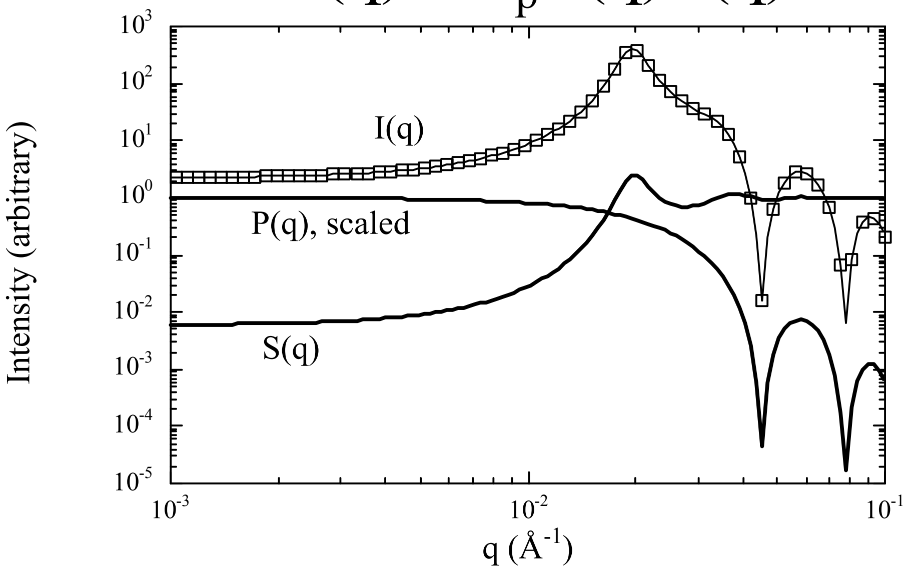
- The low q limit is proportional to the osmotic compressibility

$$S(q=0)=kT\left(\frac{\partial n}{\partial \pi}\right)$$

  - Attractive interactions ⇒ more compressible
  - Repulsive interactions ⇒ less compressible

S(q) Reflected in the Low-q Intensity

$$I(q) = n_p P(q) S(q)$$



- ➢ The form of the interparticle potential has a great effect on the low q value of S(q)
- ➢ Example of charged spheres:
  - development of "interaction peak"
  - change in low-q slope and I(0)
- ➢ Must fit model to data
  - know P(q)
  - ?calculate S(q)?

Calculation of S(q)

- Ornstein Zernicke Equation:

$$h(r) = g(r) - 1 = c(r) + n \int c\left(\left|\vec{r} - \vec{x}\right|\right) h(x) d\vec{x}$$

  - c(r) = direct correlation function
  - Integral = all indirect interactions
- A second relation is necessary to relate c(r) and g(r)
- Percus-Yevick Closure - an approximation

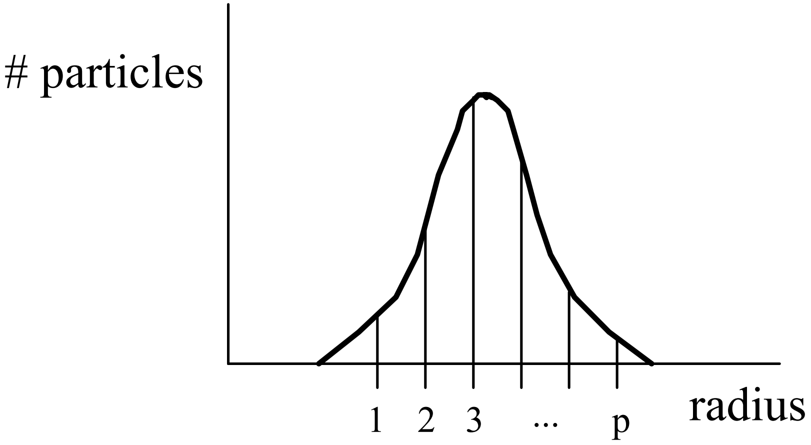
$$c(r) = g(r)\left[1 - e^{\beta u(r)}\right]$$

  - correct closure gives correct results
  - in general a difficult problem

$$\langle S(\vec{q}) \rangle = S(q) = 1 + 4\pi n_p \int_0^\infty [g(r) - 1] \frac{\sin qr}{qr} r^2 dr$$

Real Life Complications: Polydispersity

- Real colloidal systems are not monodisperse



- For p-components:

$$\frac{d\Sigma}{d\Omega}(q)=\sum_{i}^{p}\sum_{j}^{p}\left(n_i n_j\right)^{1/2} f_i(q) f_j(q) S_{ij}(q)$$

Real Life Complications: Polydispersity

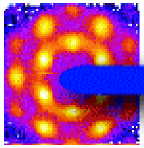
- Partial structure factors

$$S_{ij}(q) = \delta_{ij} + 4\pi\left(n_i n_j\right)^{1/2} \int \left[g_{ij}(r) - 1\right] \frac{\sin qr}{qr} r^2 dr$$

- Set of O-Z equations

$$h_{ij}(r) = c_{ij}(r) + \sum_{k}^{p} n_k \int c_{ik}\left(\left|\vec{r} - \vec{x}\right|\right) h_{kj}(x) d\vec{x}$$

Would really like $\frac{d\Sigma}{d\Omega}(q) = n_p P(q) S'(q)$



Two Approximations:

1. Average Structure Factor

$$\frac{d\Sigma}{d\Omega}(q) = n_p \overline{f^2(q)} \cdot \overline{S}(q)$$

Good for moderate polydispersity

2. “Beta” Decoupling

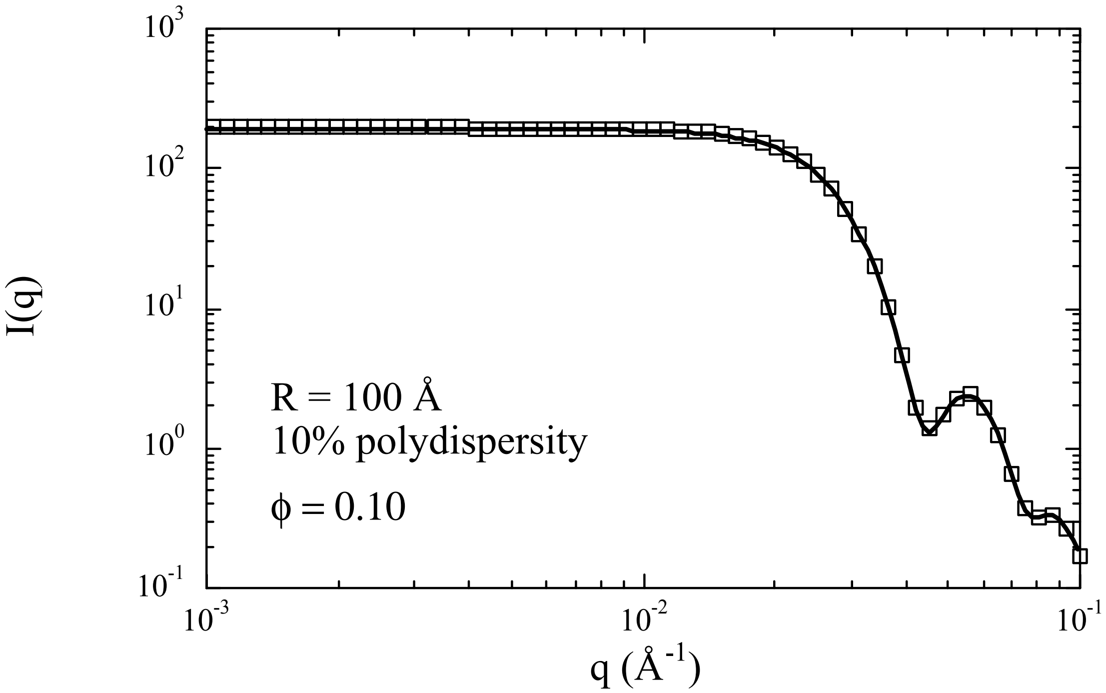
$$\frac{d\Sigma}{d\Omega}(q) = n_p \overline{f^2(q)}\, S'(q)$$

$$S'(q) = 1 + \left(\overline{f(q)}^2 \middle/ \overline{f^2(q)} \right) [S(q) - 1] = 1 + \beta(q)[S(q) - 1]$$

- ➢ Good only at low polydispersity
- ➢ Useful for non-spherical particles

Performance of Polydisperse Approximations

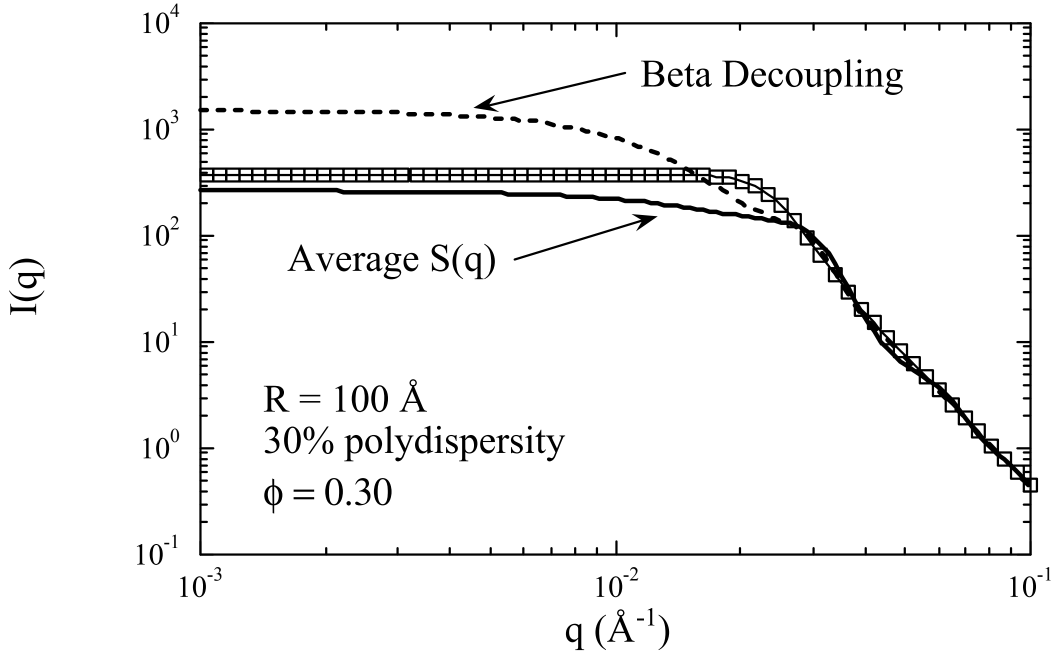
- ➢ Model calculations for polydisperse hard spheres



- ➢ Form factor oscillations are damped out
- ➢ Both approximations work well

High Polydispersity, High Concentration

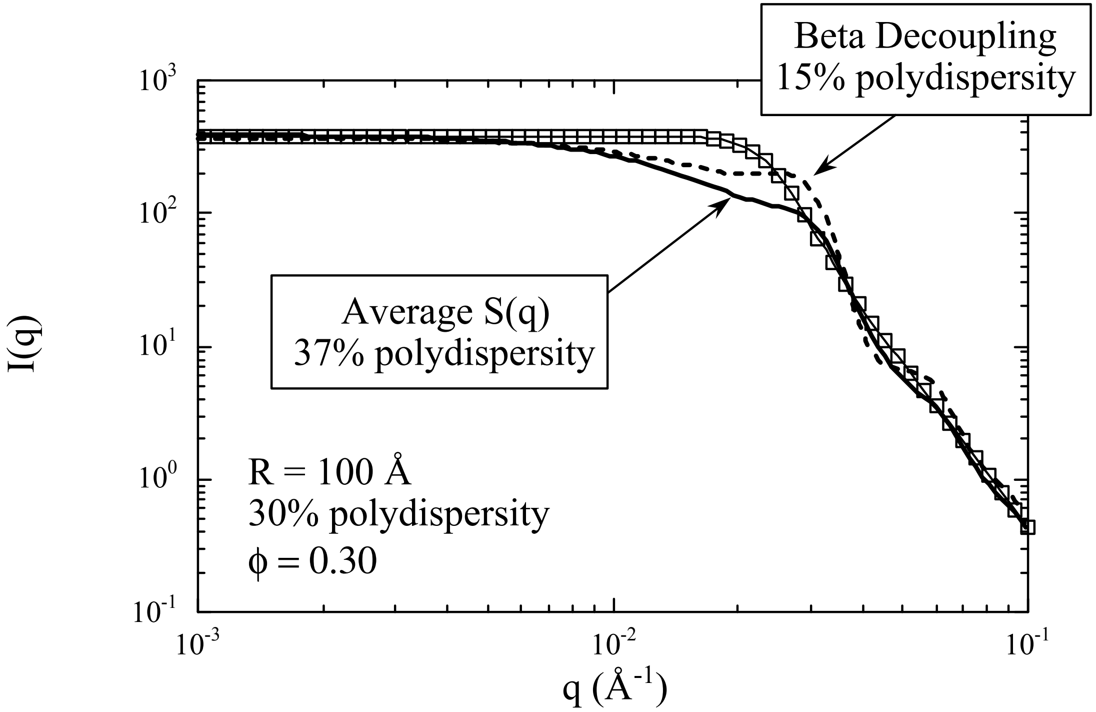
- ➢ Model calculations for polydisperse hard spheres



- ➢ Form factor oscillations disappear
- ➢ Both approximations fail at low q

Stretching the Approximation Too Far

- Model calculations for polydisperse hard spheres



Beta Decoupling
15% polydispersity

Average S(q)
37% polydispersity

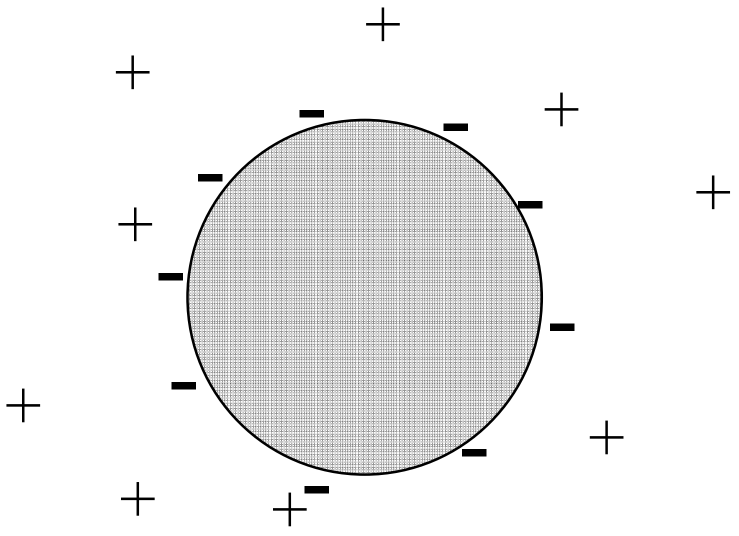
R = 100 Å
30% polydispersity
$\phi = 0.30$

- “Fitting” an approximate model gives incorrect results
- More exact calculations are necessary for high concentration or high polydispersity

Example I

Determining the Size and Polydispersity of Colloidal Silica

- Experimental system
  - Spherical SiO_2 particles in aqueous solvent
  - Charge stabilized with negative surface charge

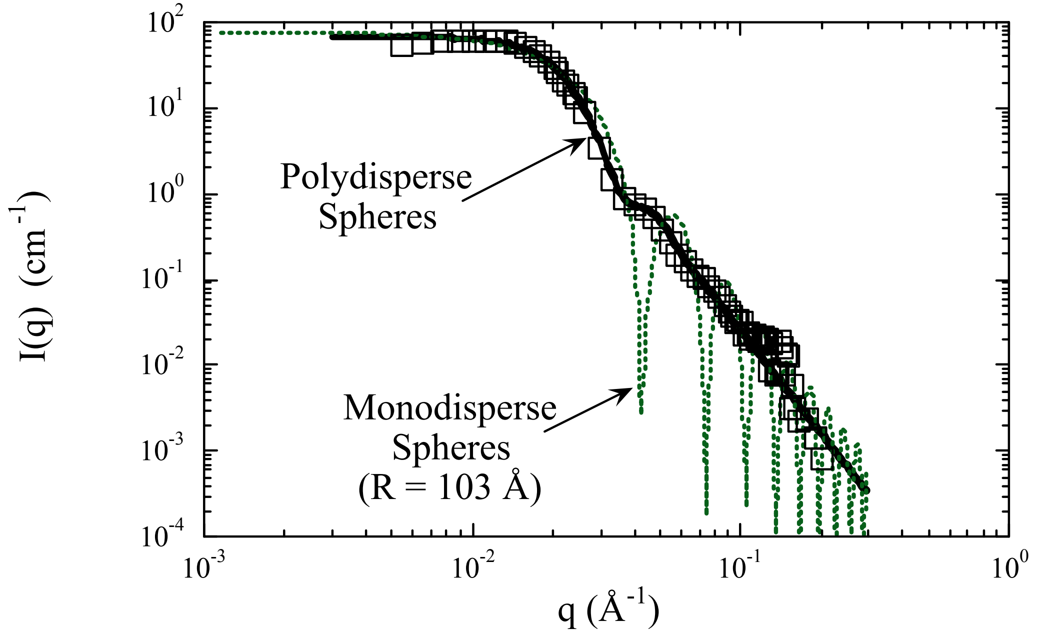


Example I

- For modeling of polydisperse charged spheres:
  - Must know ionic strength to calculate screening
  - Fit the particle charge, Z
  - Must use an approximation for P(q)S(q)
- Screen the electrostatic interactions by adding salt
- Model with the analytical solution for polydisperse hard spheres

Example I

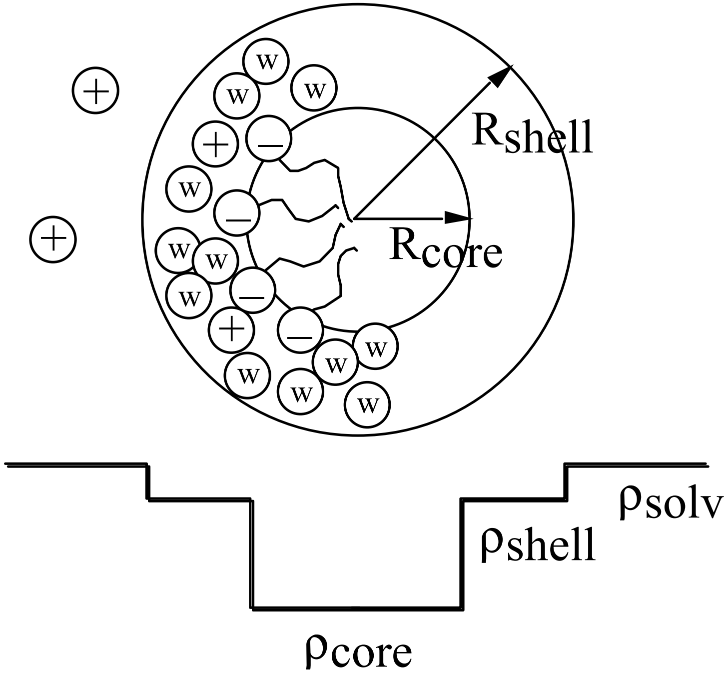
- Polydisperse hard spheres - analytic solution



- Known parameters
  - $\Delta\rho = 1.3 \times 10^{10}$ cm^{-2}
  - $\phi = 0.096$
- [NaCl] = 0.1 M (to give hard sphere interactions)
  - Fitted parameters
  - R = 115 Å
  - $\sigma_R / R = 0.17$

Example II

Aggregation and Charge of Surfactant Micelles



- Sodium dodecyl sulfate
- $CH_3(CH_2)_{11}SO_4^-$ Na^+

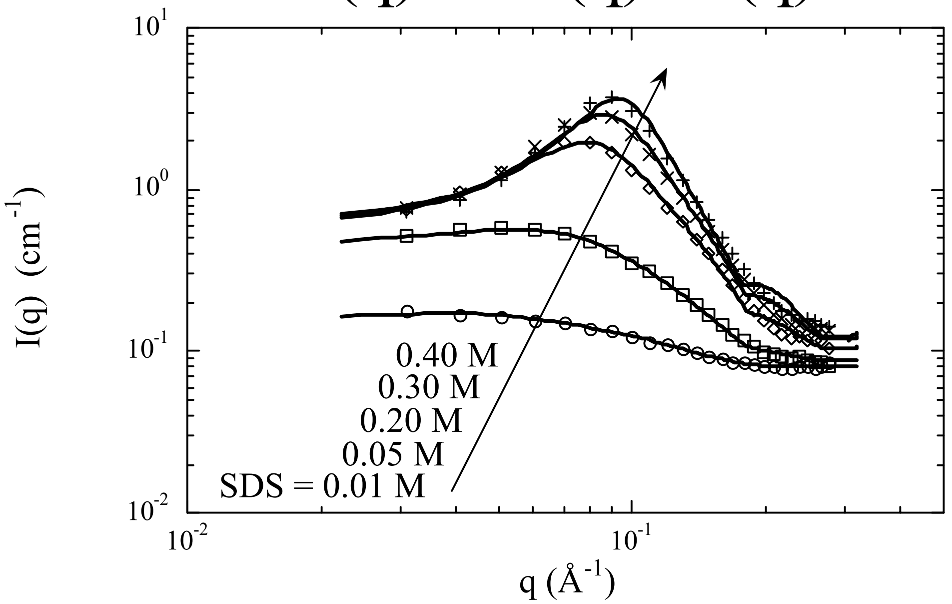
Example II

- Micelles form in solution above the CMC of the surfactant
- Try to measure the form factor:
  - can’t dilute - only monomeric surfactant upon dilution
  - can’t add salt - would change structure as well as interactions
- Must fit P(q) and S(q) simultaneously
  - $P(q) \Rightarrow$ Aggregation number
  - $S(q) \Rightarrow U(r) = f\{\delta, \kappa(\delta), r\}$

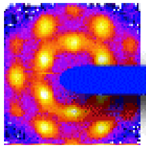
Example II

- SANS and Modeling Results

$$I(q) = nP(q) \cdot S'(q)$$



[SDS] (M)	Agg #	Ionization
0.01	86	0.20
0.05	86	0.21
0.20	91	0.25
0.30	96	0.25
0.40	99	0.22



Summary

- Definition of "dilute" is relative
  - Determination of intraparticle structure
  - Very useful, model independent information
- When not dilute:
  - Determination of interparticle structure
  - Information about interparticle interactions
  - Polydispersity approximations
  - Exact methods
- Other Concentrated Systems:
  - Non-spherical particles
  - Rod-like micelles
  - Much more complex analysis
  - Correlation between position and orientation