Colloidal Interactions in Solutions

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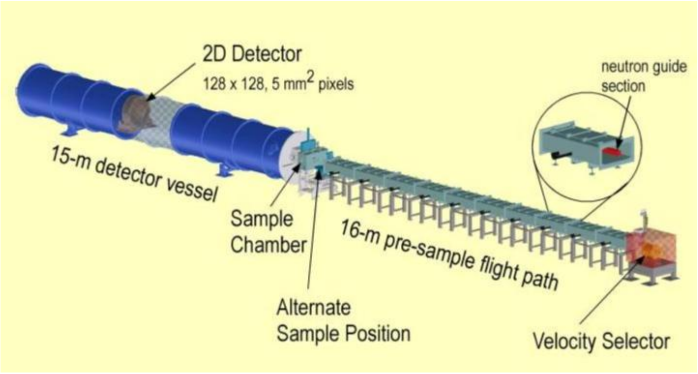
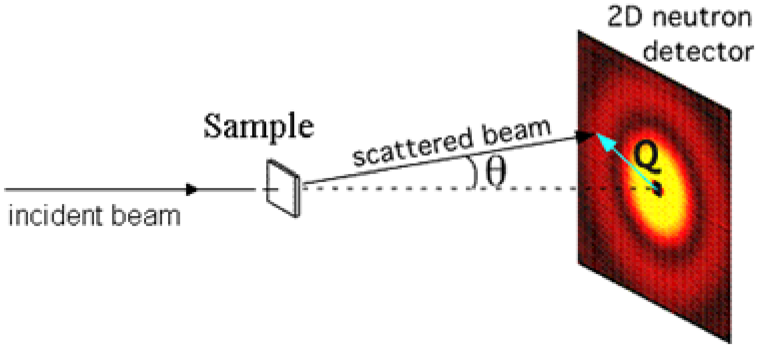
Outline

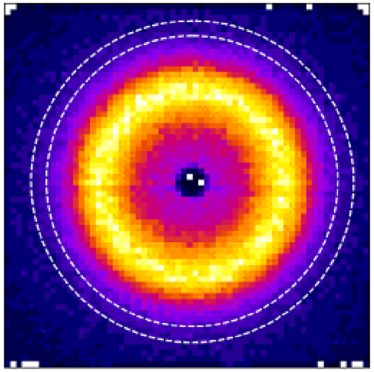
1. Introduction: Small Angle Neutron Scattering Spectrometer





NCNR NIST (http://www.ncnr.nist.gov/programs/sans/index.html)

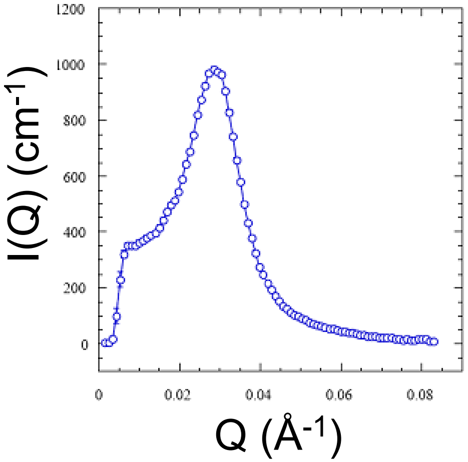
2D image

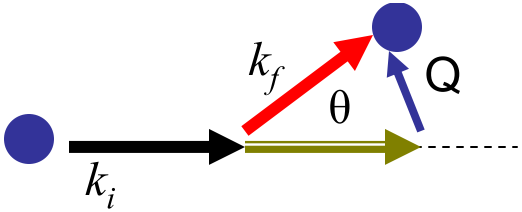


$I(Q_x,Q_y)$: intensity distribution

Annulus average

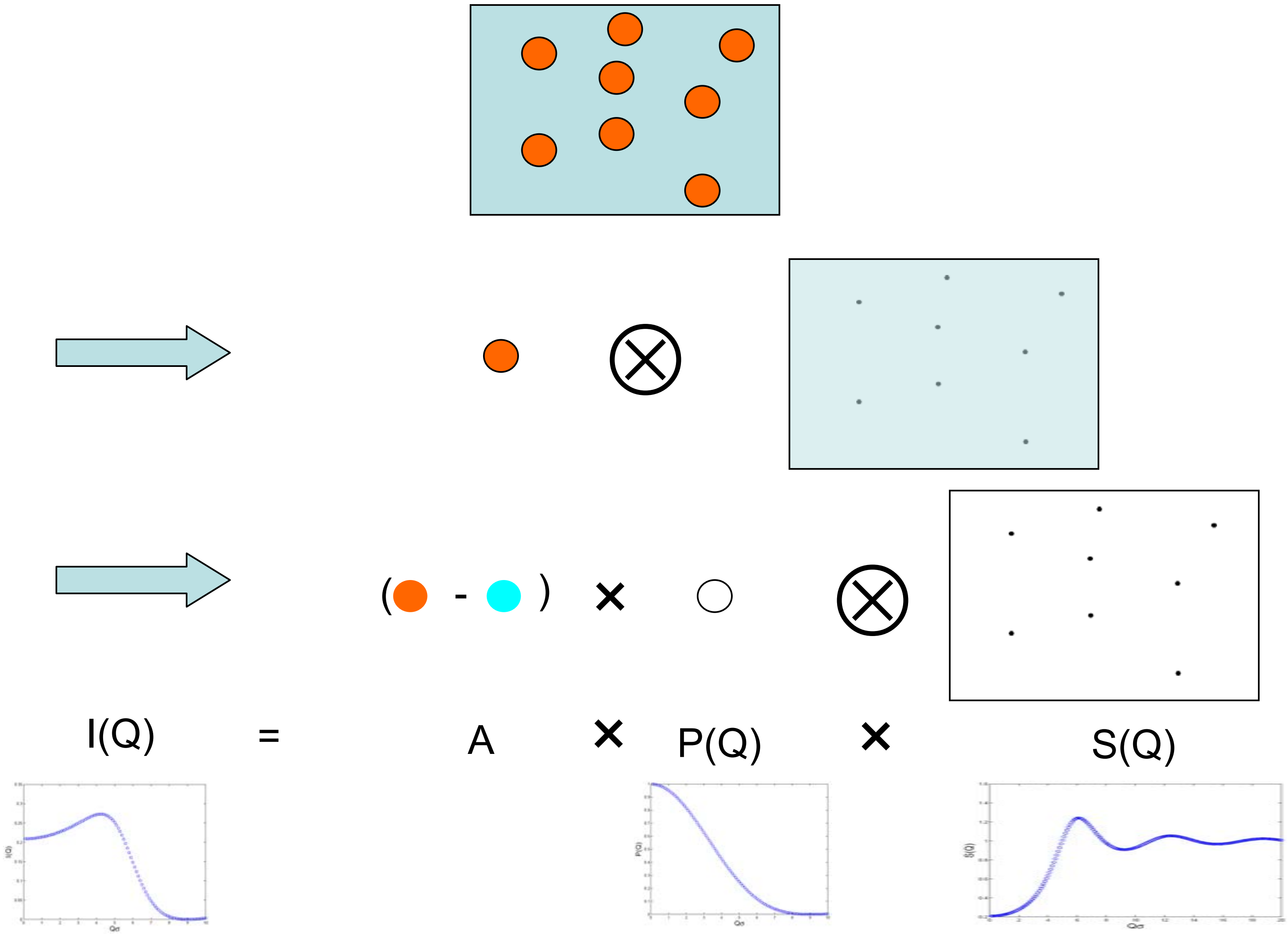
1D data





1. Introduction: What SANS measures?

I(Q) (Scattered neutron intensity distribution)



1. Introduction: Factorization Approximation

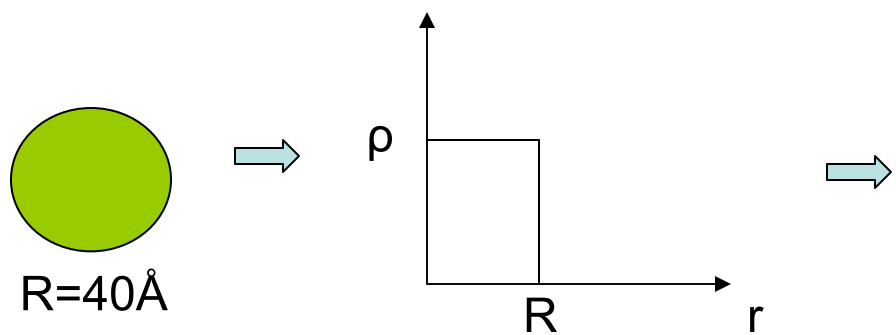
$$I(Q) = A \times P(Q) \times S(Q)$$

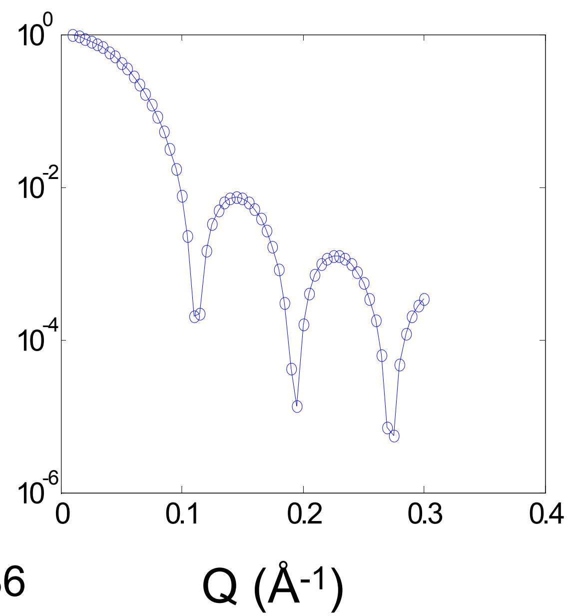
A: contrast term $A = nv^2 \Delta\rho^2$

n: number density
v: volume of a colloidal particle
Δρ: scattering length density difference

P(Q): Normalized form factor (or intra-particle structure factor)

$$P(Q) = \left| \int \rho(r) e^{-iQ\cdot r} dr^3 \right|^2 / \left| \int \rho(r) dr^3 \right|^2$$





S.-H. Chen *Ann. Rev. Phy. Chem.* **37** 351 1986

1. Introduction: Factorization Approximation

$$I(Q) = A \times P(Q) \times S(Q)$$

S(Q): Inter-particle structure factor determined by inter-particle potential.

$$S(Q) = \frac{1}{N}\sum_{j,k} e^{-iQ\cdot r_j} e^{iQ\cdot r_k}$$

$$= 1 + \frac{1}{N}\sum_{j\neq k} e^{-iQ\cdot r_j} e^{iQ\cdot r_k}$$

$$= 1 + n\int (g(r) - 1) e^{iQ\cdot r} dr^3$$

n: number density
$g(r)$: pair distribution function

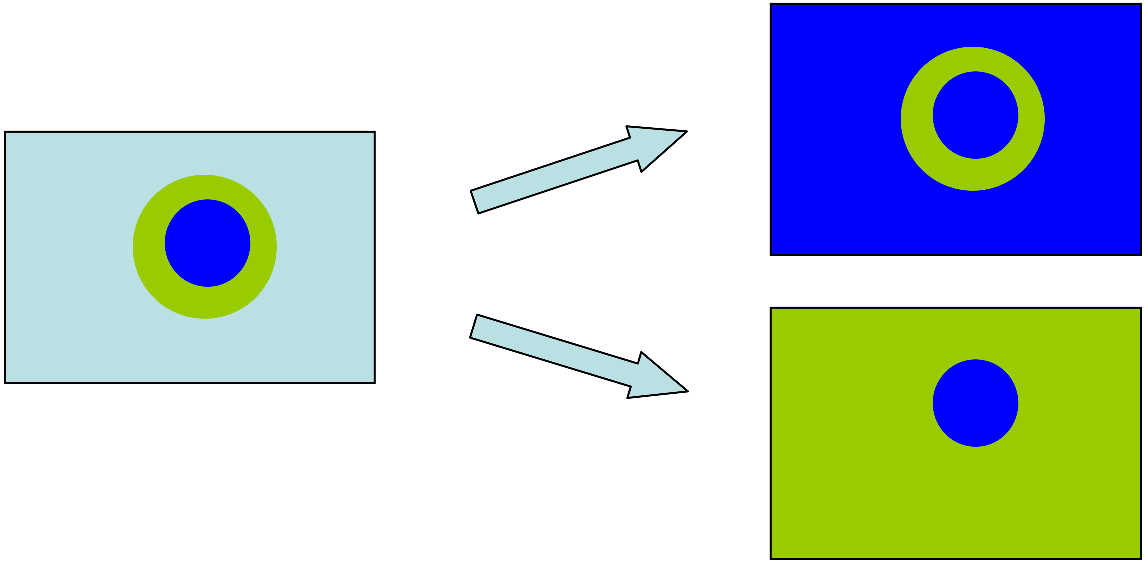
S.-H. Chen *Ann. Rev. Phy. Chem.* **37** 351 1986

2. Contrast: Selectively observe a structure

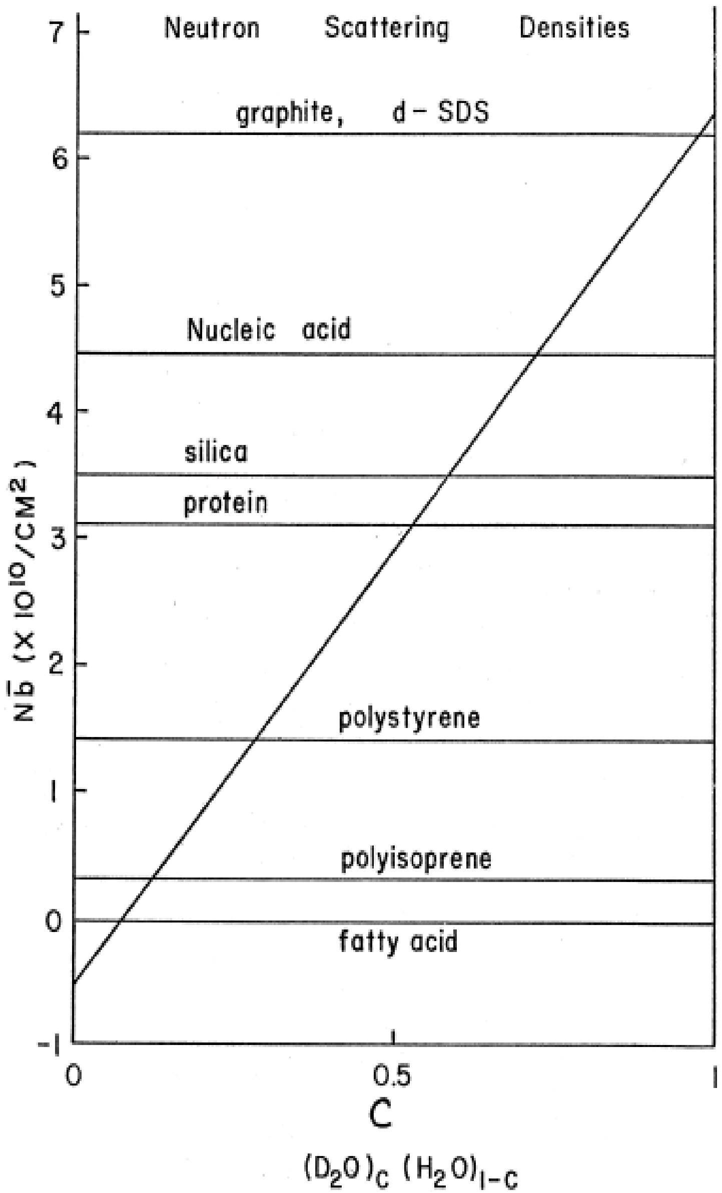
$$I(Q) = A \times P(Q) \times S(Q)$$

1. **A**: Contrast term $A = nv^2 \Delta\rho^2$

Change scattering length density: isotope replacement



2. Contrast: Selectively observe a structure



$$I(Q) = A \times P(Q) \times S(Q)$$

By changing relative ratio of D_2O/H_2O, the scattering length density can vary in a large range to match the scattering length density of different materials.

View graph from Charles Glinka

http://www.ncnr.nist.gov/programs/sans/pdf/SANS_dilute_particles.pdf

3. Form factor: shape, volume, density profile

$$I(Q) = A \times P(Q) \times S(Q)$$

P(Q): Normalized form factor (or intra-particle structure factor)

At dilute concentration, $S(Q) \approx 1$.
Therefore, $I(Q) = A \times P(Q)$.

Shape, volume, density profile
(Not necessarily spherical particles)

1. J. S. Pederson, Adv. Colloid Interface Sci. **70**, 171-210 (1997).
(Form factors of 26 models are presented in this paper).

3. Form factor: Guinier plot

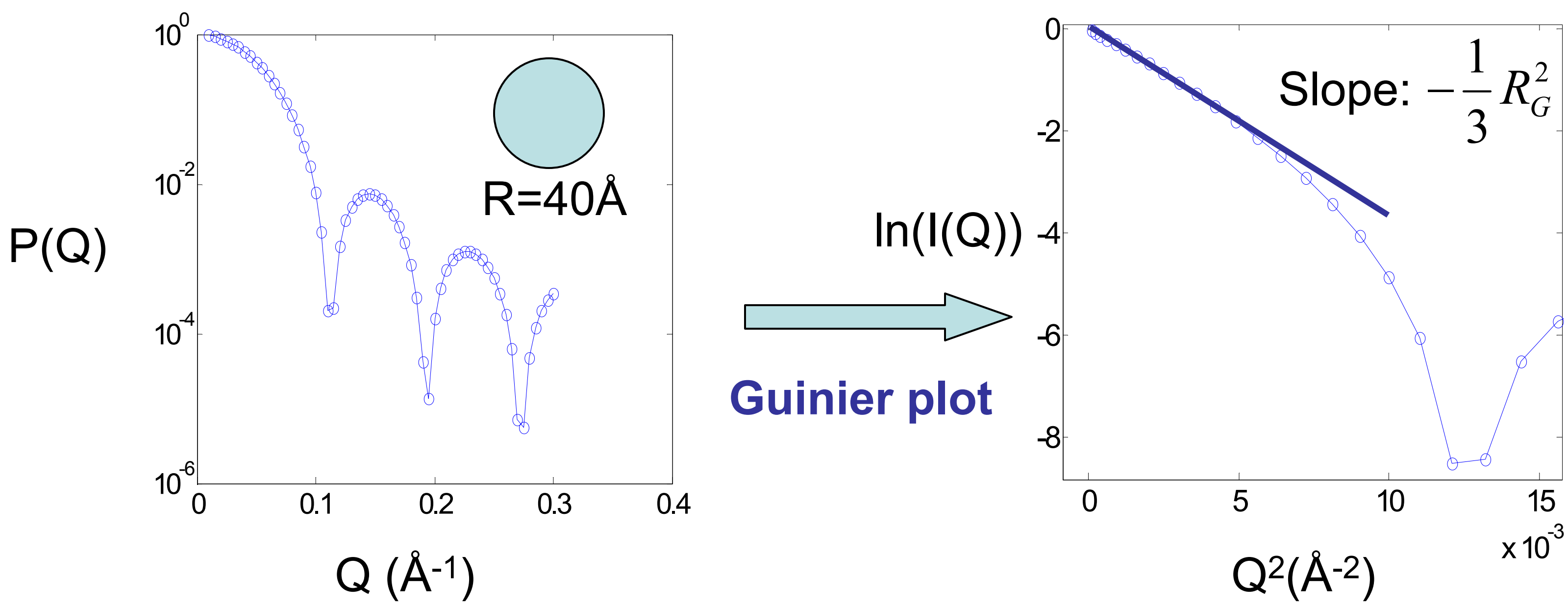
Radius of gyration R_G: a measure of size of an object

$$R_G^2 = \sum_i \gamma_i (r_i - \bar{r})^2$$

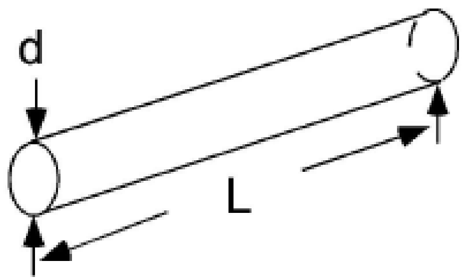
(Weighted by the neutron scattering length)

When $Ql << 1$, where l is the largest length scale in a measured object,

$$I(Q) = A\exp(-\frac{1}{3}R_G^2Q^2) \quad \text{or} \quad \ln(I(Q)) = \ln(A) - \frac{1}{3}R_G^2Q^2$$



3. Form factor: Guinier plot (cont'd)



1) QL << 1 (Guinier region)

$$I(Q) = A\exp(-\frac{1}{3}R_G^2 Q^2)$$

$$R_G^2 = \frac{L^2}{12} + \frac{d^2}{8}$$

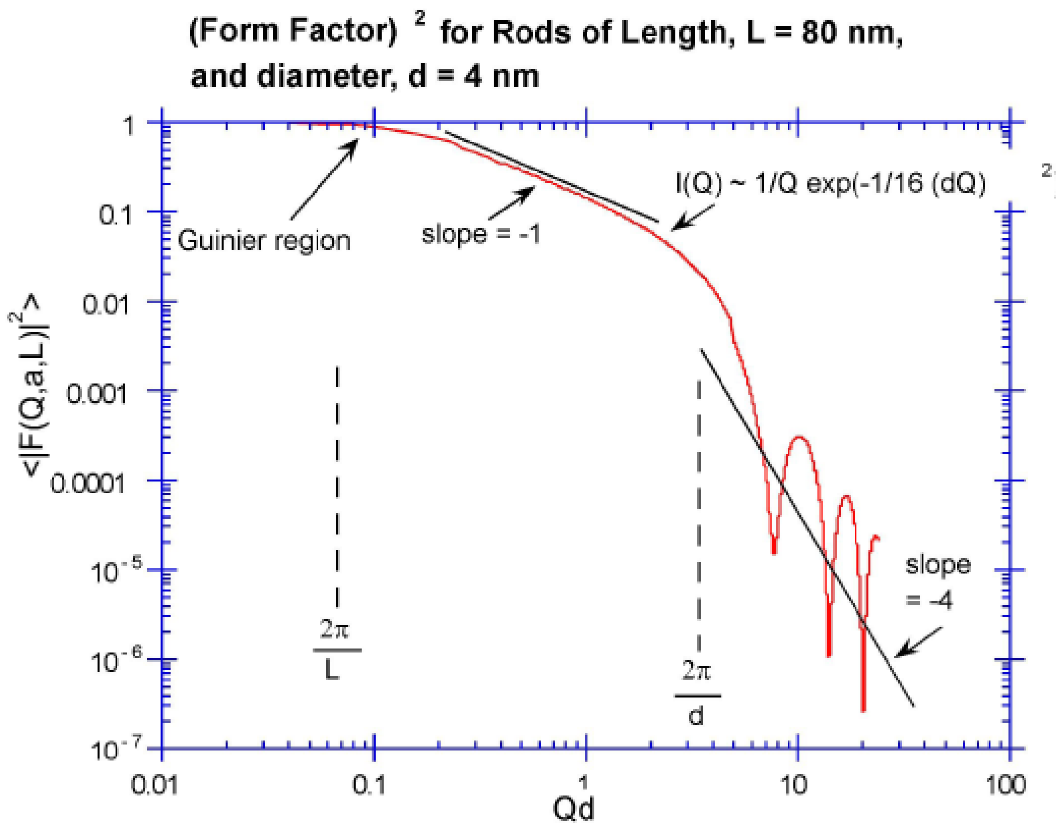
2) QL >> 1 & Qd << 1

$$I(Q) \propto \frac{\pi}{QL}\exp(-\frac{1}{16}Q^2 d^2),$$

3) Qd >> 1

$$I(Q) \propto \frac{8\cos^2(Qd)}{Q^4 L d^3}$$

(Porod law: Q^{-4} decay)



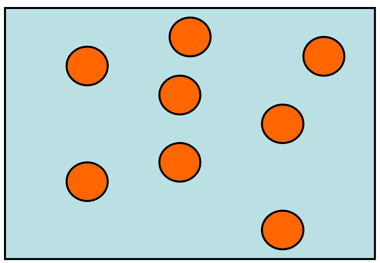
View graph from Charles Glinka

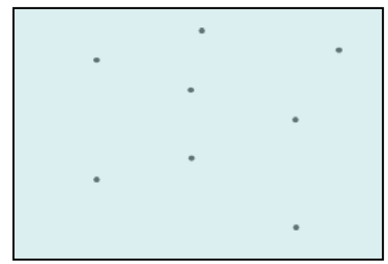
http://www.ncnr.nist.gov/programs/sans/pdf/SANS_dilute_particles.pdf

4. Structure factor S(Q): inter-particle potential

$$I(Q) = A \times P(Q) \times S(Q)$$

1. **A**: Contrast terms
2. **P(Q)**: Form factor (or intra-particle structure factor)
3. **S(Q)**: Inter-particle structure factor





$$S(Q) = \frac{1}{N}\sum_{j,k} e^{-iQ\cdot r_j} e^{iQ\cdot r_k}$$

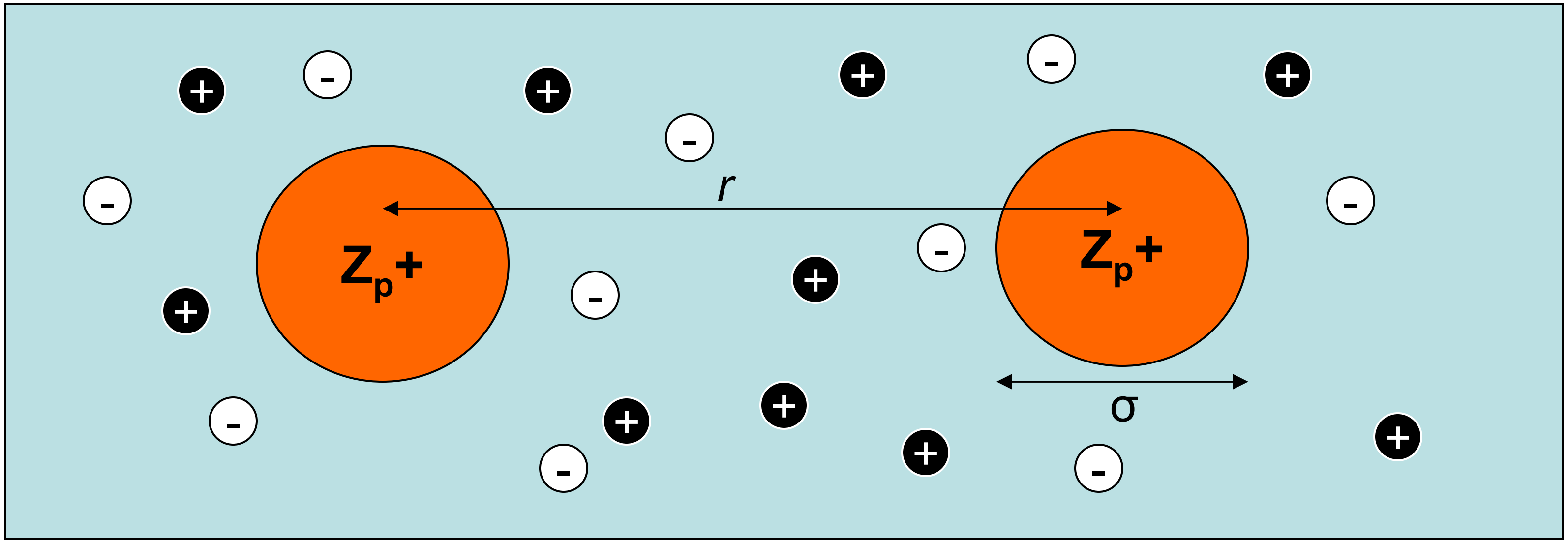
$$= 1 + \frac{1}{N}\sum_{j \neq k} e^{-iQ\cdot r_j} e^{iQ\cdot r_k}$$

$$= 1 + n\int (g(r) - 1) e^{iQ\cdot r} dr^3$$

n: number density

$g(r)$: pair distribution function

5. Colloidal interactions: effective potential



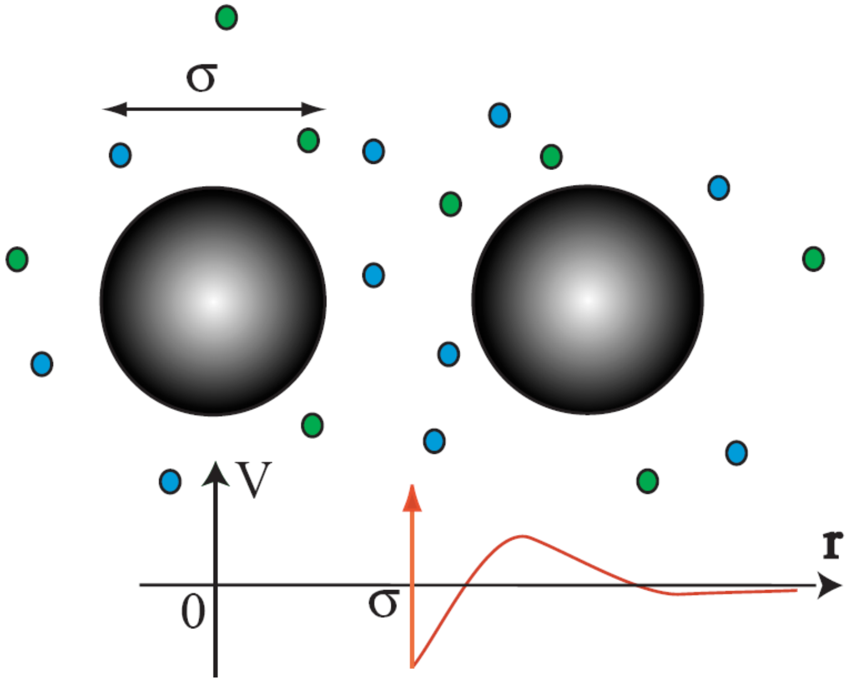
Coloumb interaction: $$U(r) = \frac{1}{4\pi\varepsilon}\frac{Z_p Z_p}{r}$$ >0, repulsive

Screened Coloumb interaction: $$U(r) = K\frac{e^{-\kappa(r-\sigma)}}{r}$$ >0, repulsive

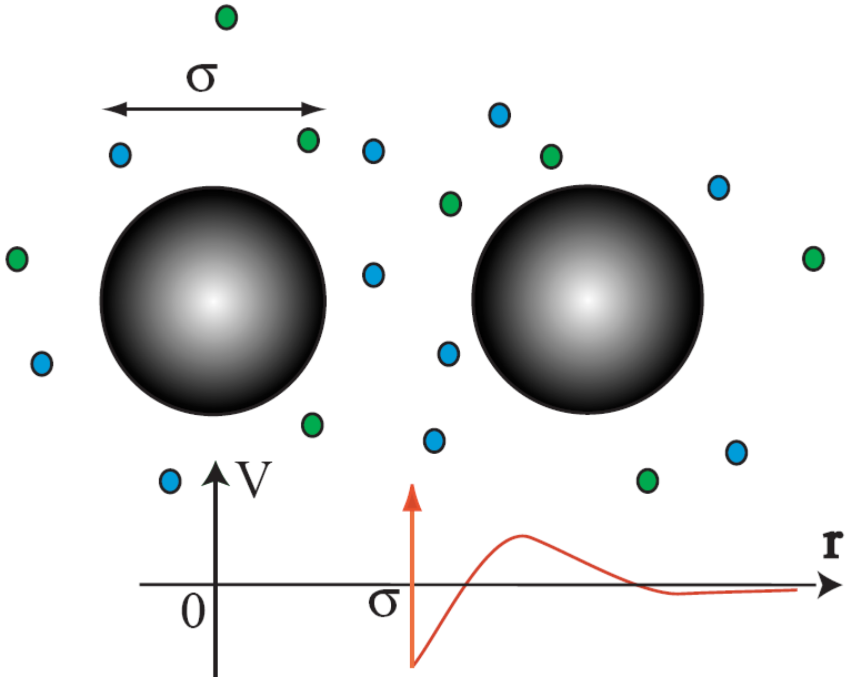
(Yukawa potential form)

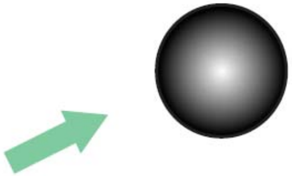
The Coloumb interaction is screened by counterions and coions in solutions and decays much faster than the bare interaction.

5. Colloidal interactions: Why study effective potential



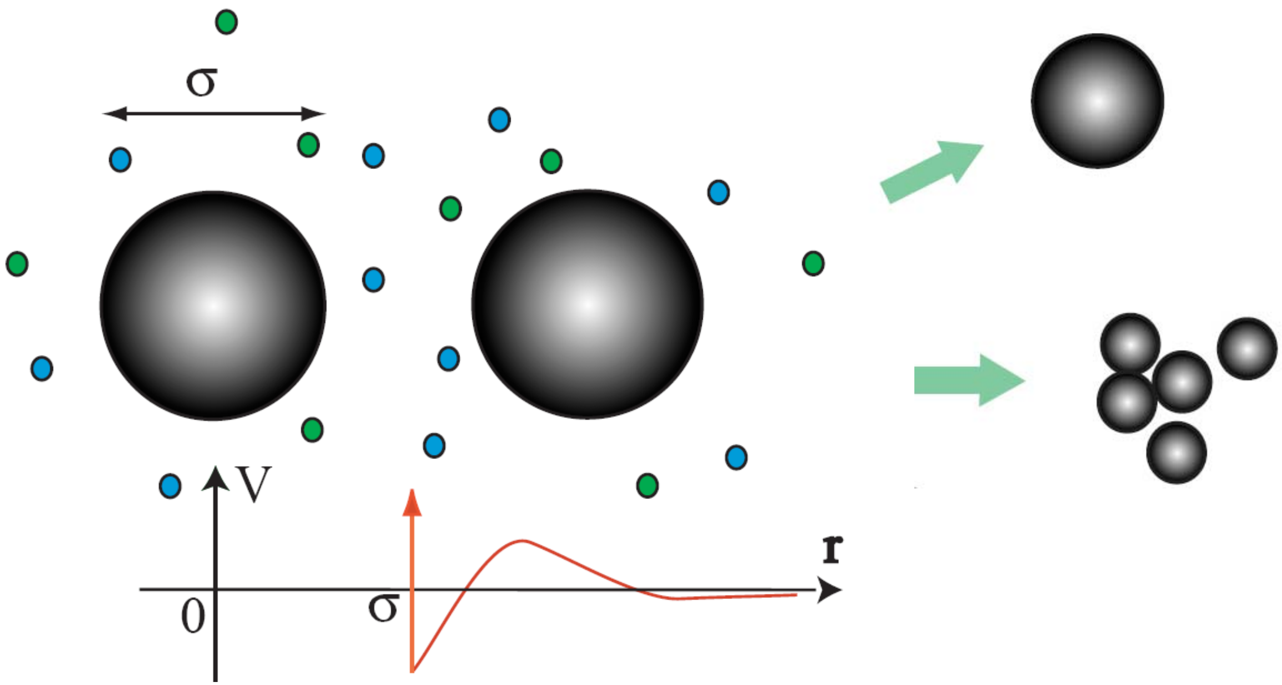
5. Colloidal interactions: Why study effective potential





Single Particle Information:
Charge, Surface Properties, …

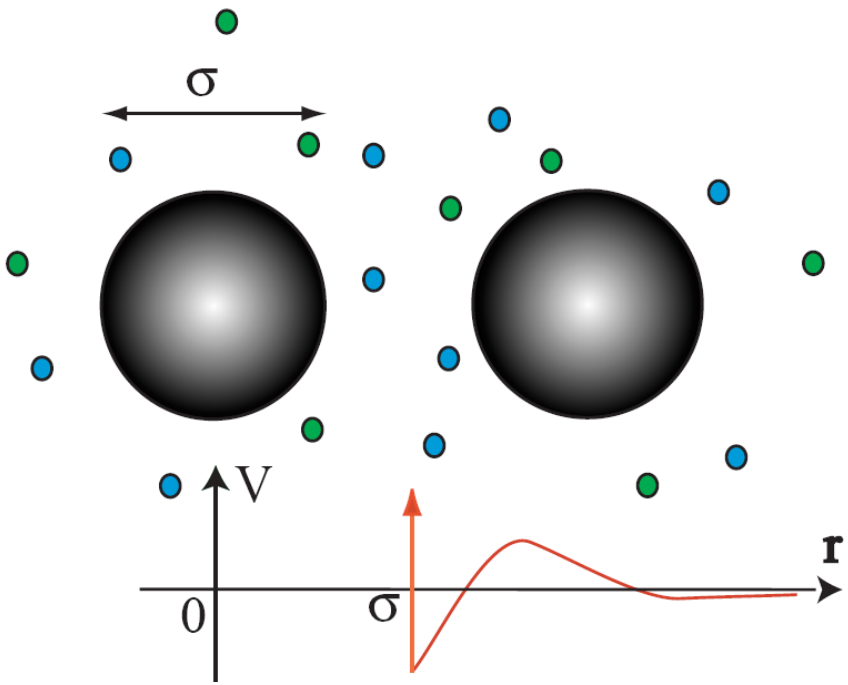
5. Colloidal interactions: Why study effective potential



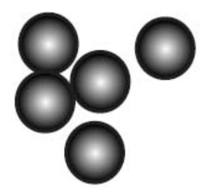
Single Particle Information:
Charge, Surface Properties, …

Collective Behaviors:
Diffusion, Clusterization, …

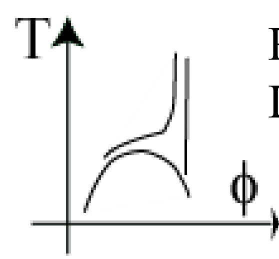
5. Colloidal interactions: Why study effective potential



Single Particle Information:
Charge, Surface Properties, …



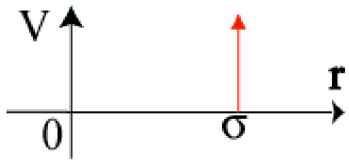
Collective Behaviors:
Diffusion, Clusterization, …



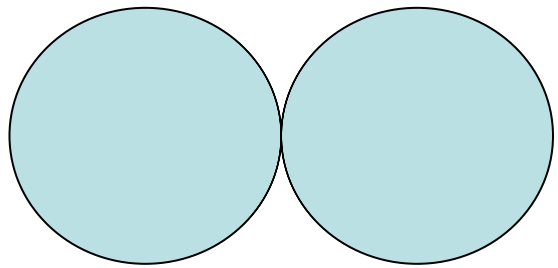
Phase Behaviors:
Liquid, Crystal, Glass, …

5. Colloidal interactions:
typical colloidal interaction potential

1. Hard Sphere Potential (Excluded volume effect)



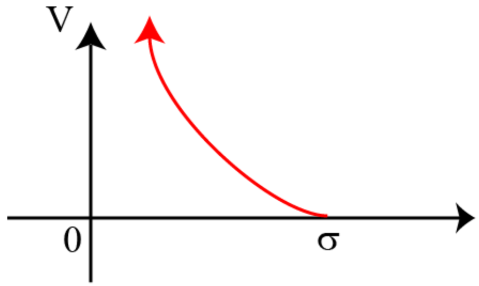
$$V(r) = \begin{cases} +\infty & r < \sigma \\ 0 & r > \sigma \end{cases}$$



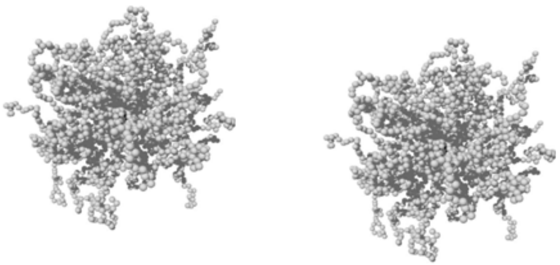
Most colloids are rigid objects: proteins, silicon nano-particle, …

5. Colloidal interactions:
typical colloidal interaction potential

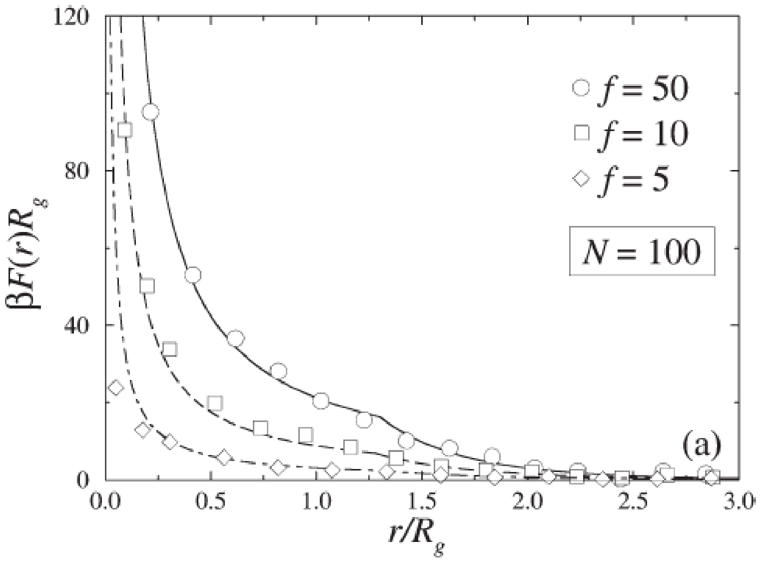
2. Soft Core Potential



$$V(r) = \begin{cases} f(r) & r < \sigma \\ 0 & r > \sigma \end{cases}$$



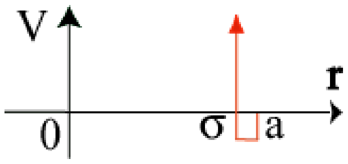
Star polymers, dendrimers



C. N. Likos, Soft Matter **2**, 478 (2006)

5. Colloidal interactions:
typical colloidal interaction potential

2. Sticky Hard Sphere, Short-Range Attraction



$$\beta V(r) = \begin{cases} \infty & r < \sigma \\ -\ln\left[\frac{1}{12\tau}\left(\frac{a}{a-\sigma}\right)\right] & \sigma < r < a \\ 0 & r > a \end{cases}$$

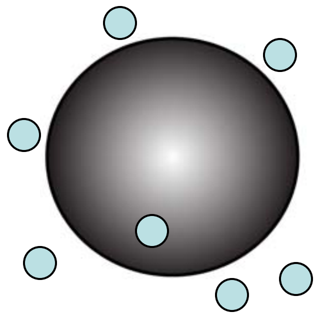
Van der Waals attraction, **depletion force** (entropic force)

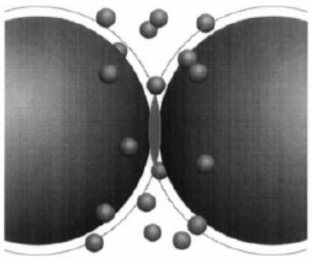
Van der Waals attraction: momentary attraction due to unevenly distributed electrons in an atom or molecule. Exists between any two atoms or molecules under any circumstances.

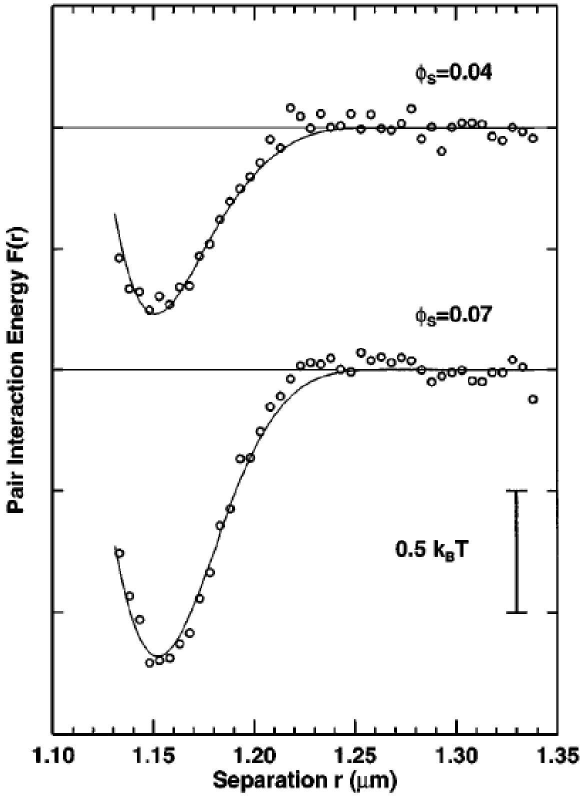
5. Colloidal interactions:
typical colloidal interaction potential

2. Sticky Hard Sphere, Short-Range Attraction

Depletion force: the overlap of the depletion zones between large particles Increases the system entropy and thus generates the effective attraction.







Large particle: 1.1 μm diameter
Small particle: 0.083 μm diameter

J. C. Crocker et al., Phys. Rev. Lett. **82**, 4352 (1999)

5. Colloidal interactions:
typical colloidal interaction potential

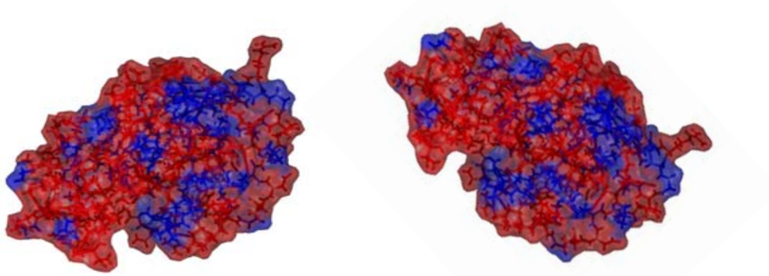
3. Electrostatic interaction

Screened Coloumb interaction: $U(r) = K \frac{e^{-\kappa(r-\sigma)}}{r}$ (Yukawa potential form)

The Coloumb interaction is screened by counterions and coions in solutions and decays much faster than the bare interaction.

Proteins, charged micelles, silica particles, …

Reliably to extract **EFFECTIVE CHARGE** of a particle!



Lysozyme protein

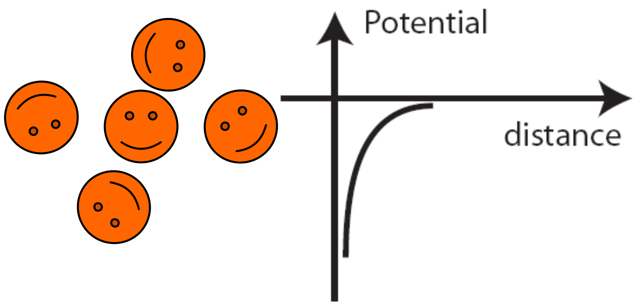
5. Colloidal interactions:

DLVO potential (Interaction between charged colloidal particles)

Derjaguin-Landau-Verwey-Overbeek potential

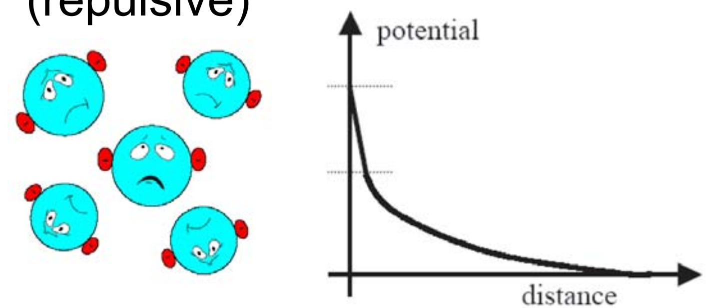
(E. J. W. Verwey and J. TH. G. Overbeek, *Theory of the Stability of Lyophobic Colloids,* Elsevier, Amsterdam, 1948)

1. Van der Waals force (attractive)



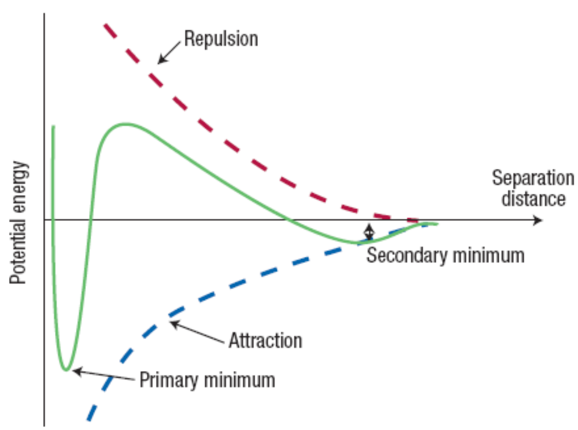
$$U_A = -\frac{A}{12}\left[\frac{1}{r^2-1}+\frac{1}{r^2}+2\ln\left(1-\frac{1}{r^2}\right)\right]$$

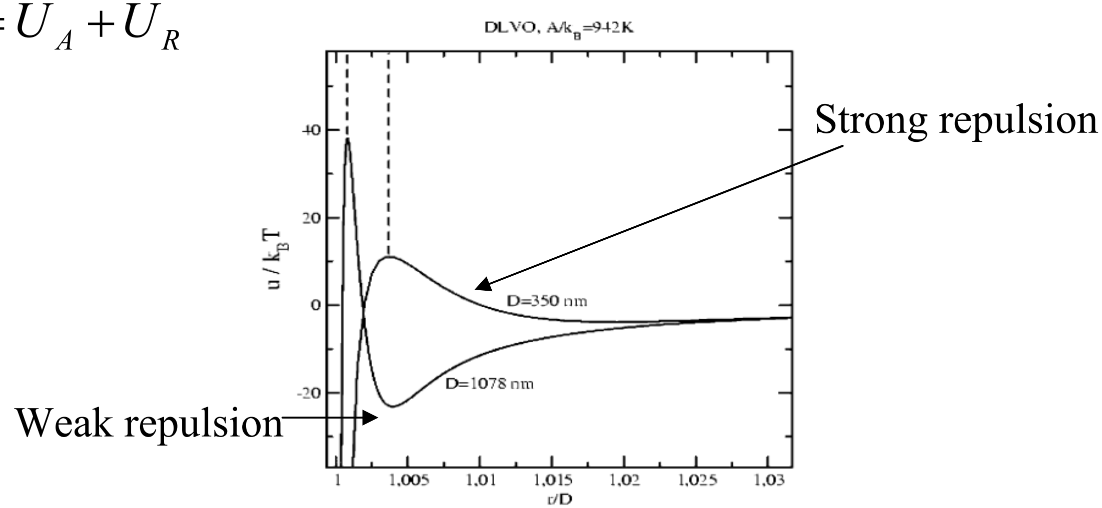
2. Screened Coloumb interaction (repulsive)



$$U_R = K\frac{e^{-\kappa(r-\sigma)}}{r} \text{ where } K = Z^2\lambda_B\frac{\exp(\kappa\sigma)}{(1+\kappa\sigma)^2}$$

3. DLVO potential: $U_{DLVO} = U_A + U_R$



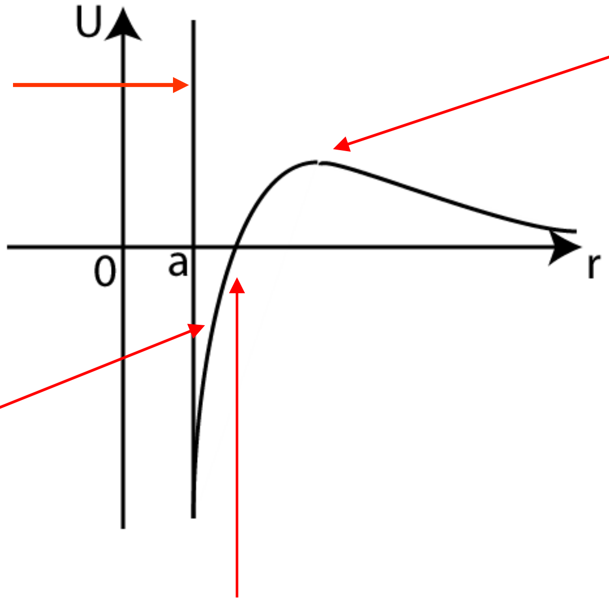


5. Colloidal interactions:

A general feature

Hard/Soft core potential:
Dendrimer,
Star polymers

Electrostatic repulsion



Short-range attraction:
Van der-Waals attraction
Depletion force,
Like charged particles

Interaction Range

6. Calculate the structure factor S(Q):

Ornstein-Zernike equation

$$S(Q) = 1 + n\int (g(r)-1)e^{iQ\cdot r}dr^3$$
$$= 1 + n\int h(r)e^{iQ\cdot r}dr^3$$

Ornstein-Zernike equation:

$$h(r) = c(r) + n\int c(|r-r'|)h(r')dr'^3$$

Closures: link pair interaction potential with *h(r)* and *c(r)*.

MSA closure (Mean Spherical Approximation) $c(r) = -\frac{u(r)}{k_B T}$

PY closure (Percus-Yevic) $c(r) = (1 - e^{-\frac{u(r)}{k_B T}})(h(r)+1)$

HNC closure (Hypernetted-Chain) $c(r) = -\frac{u(r)}{k_B T} + h(r) - \ln(1+h(r))$

RY closure (Rogers-Young)

Other closures: Zerah-Hansen, SMSA, SCOZA, HMSA, …

Reference: C. Caccamo, Integral Equation Theory Description of Phase Equilibria in Classical Fluids, *Physics Report* **274**, 1-105 (1996).
J. P. Hansen, I. R. McDonald, Theory of Simple Liquids (Academic Press, London) 1976

6. Calculate the structure factor S(Q):

Some Analytical Solutions to OZ Equation

1. **Hard sphere system**: J. K. Percus, G. J. Yevick, Phys. Rev. **110**, 1 (1958)

   J. P. Hansen, I. R. McDonald, Theory of Simple Liquids (Academic Press, London) 1976

   (PY Closure)

2. **Sticky hard sphere system**: R. J. Baxter, J. Chem. Phys. **49**, 2770 (1968)

   (PY Closure)

3. **Short-range attraction system**:

   Y. C. Liu, S. H. Chen, J. S. Huang, Phys. Rev. E **54**, 1698 (1996)

   (PY Closure)

4. **Hard-core Yukawa Interaction**:

   One Yukawa: E. Waisman, Mol. Phys. **25**, 45 (1973).

   Two Yukawa: J. S. Høye, G. Stell, and E. Waisman, Mol. Phys. **32**, 209 (1976)

   Multiple Yukawa: J. S. Høye and L. Blum, J. Stat. Phys. **16**, 399 (1977)

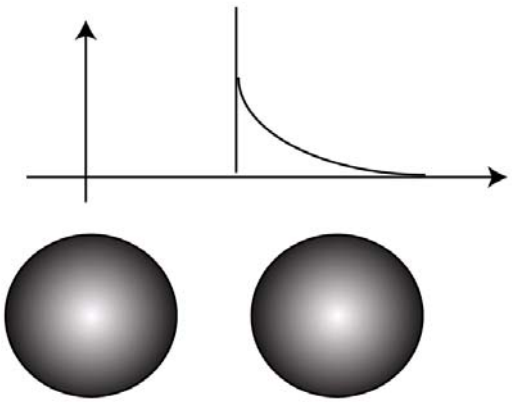
   (MSA Closure)

Implementing the algorithms is sometimes non-trivial.

6. Calculate the structure factor S(Q):

One Yukawa Hard-Core Potential: Hayter-Penfold Method

J. B. Hayter and J. Penfold, Mol. Phys. **46**, 651 (1981).
(Current citation number: > 600)
One Yukawa Hard-Core Potential



It is a powerful method for charged colloidal system.

Combing with other theories, the effective charge of a colloidal particle could be obtained.

1. The DLVO theory:

$$U_R = K\frac{e^{-\kappa(r-\sigma)}}{r} \text{ where } K = Z^2\lambda_B\frac{\exp(\kappa\sigma)}{(1+\kappa\sigma)^2}$$

It works at the dilute concentrations.

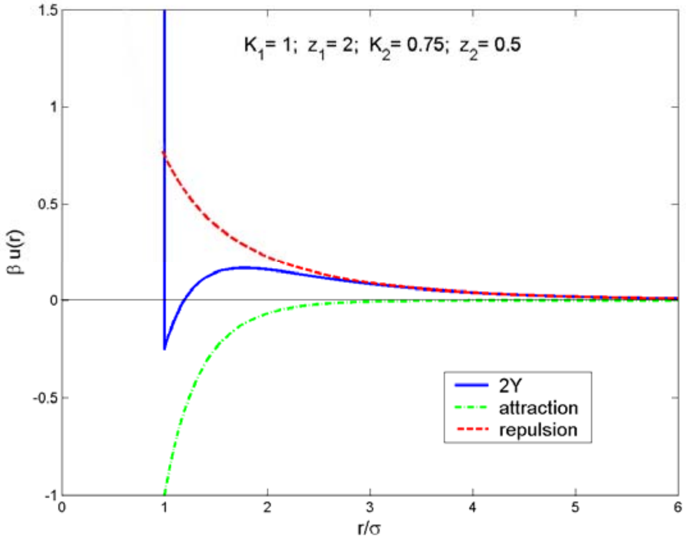
2. The Generalized One Component Macroion (GOCM) theory (Or Rescaling Mean Spherical Approximation (RMSA) theory)

Belloni, L. *J. Chem. Phys.* **1986**, *85*, 519-526
Chen, S.-H.; Sheu, E. Y. In *Micellar Solutions and Microemulsions-Structure, Dynamics, and Statistical Thermodynamics*; Chen, S.-H., Rajagopalan, R., Eds.: Springer-Verlag: New York, 1990

6. Calculate the structure factor S(Q):

Two Yukawa Hard-Core Potential

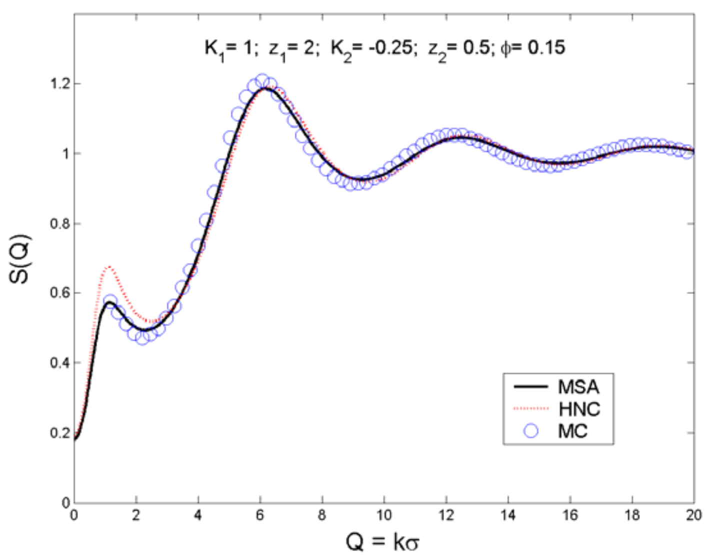
Y. Liu, W. R. Chen, S. H. Chen, J. Chem. Phys. **122**, 044507 (2005)

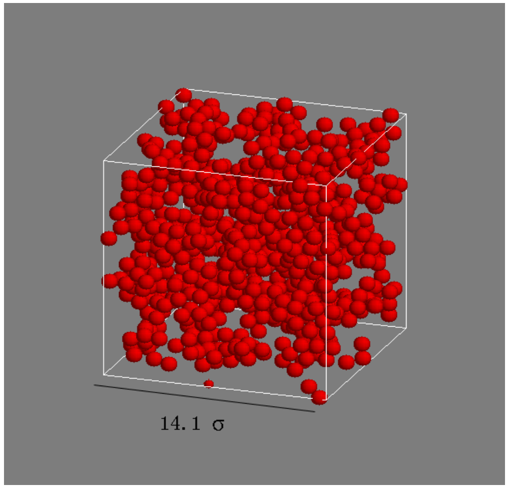


$$\beta u(r) = \begin{cases} \infty, & 0 < r \leq 1 \\ -K_1 \frac{e^{-z_1(r-1)}}{r} + K_2 \frac{e^{-z_2(r-1)}}{r} & r > 1 \end{cases}$$

It is useful for system with complicated potential.

1. Charge colloidal particles with a short-range attraction.
2. Charge colloidal particles with a soft-core.
3. Simulate the Lennard-Jones potential.





M.Broccio, D.Costa, Y.Liu, S.H. Chen, JCP 124, 084501 (2006)

6. Calculate the structure factor S(Q):

Numerical Solutions to OZ Equation

Numerical Solutions

The development of powerful computer

Advantage of a numerical methods:
- Trivial to extend the method to more complicated potential
- Easy to extend to all kinds of different closures (HNC, RY, Zerah-Hansen, SCOZA,…)
- The validity of new methods could be easily verified by computer simulations
- Relatively easy to implement the thermodynamic consistency

Application of numerical solution to analyze the scattering results of colloidal systems becomes more and more important.

Many Examples ! Such as

DLVO (HNC), One Yukawa (HNC) (protein solutions)

A. Tardieu, S. Finet, and F. Bonnete´, J. Cryst. Growth **232**, 1 (2001).

Two Yukawa (HNC) (protein solutions, micellar systems)

M.Broccio, D.Costa, Y.Liu, S.H. Chen, JCP **124**, 084501 (2006)

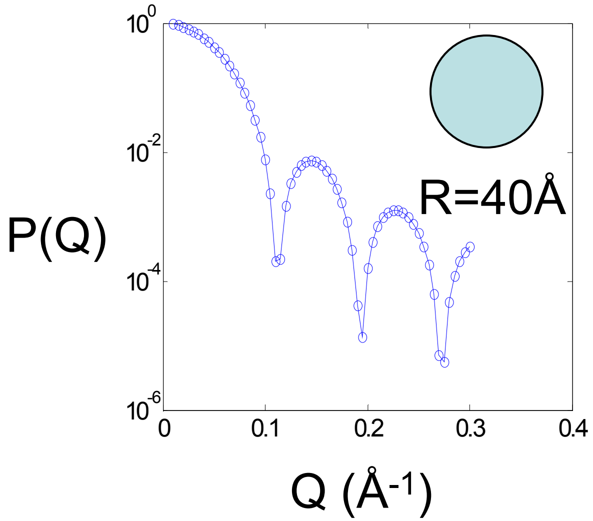
C. Caccamo, Integral Equation Theory Description of Phase Equilibria in Classical Fluids, *Physics Report* **274**, 1-105 (1996). And references therein.

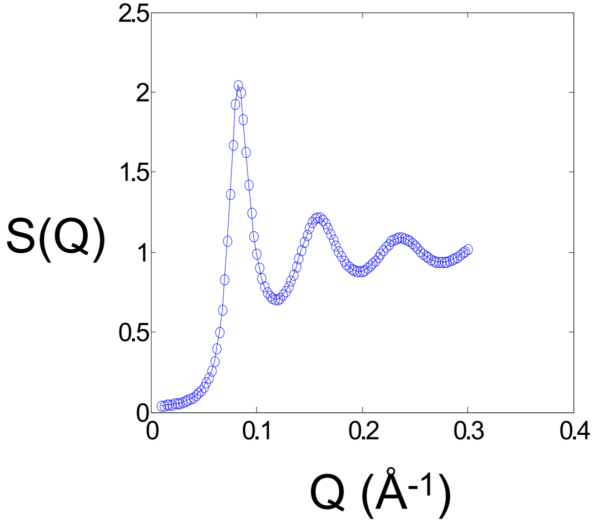
7. Example 1:

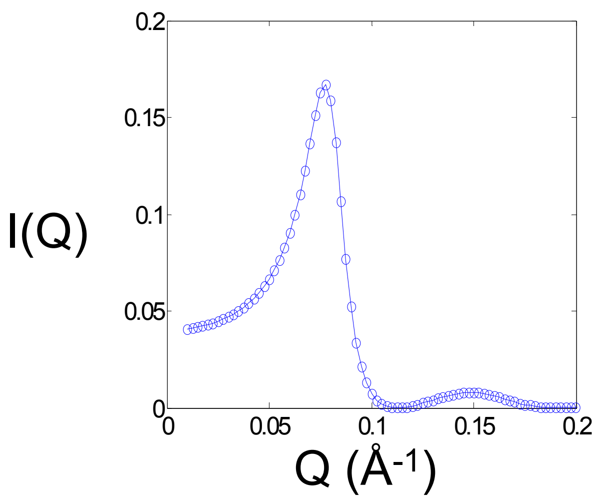
Hard Sphere Systems

$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)







Volume fraction: Φ=40%

S(Q) is calculated using PY closure.

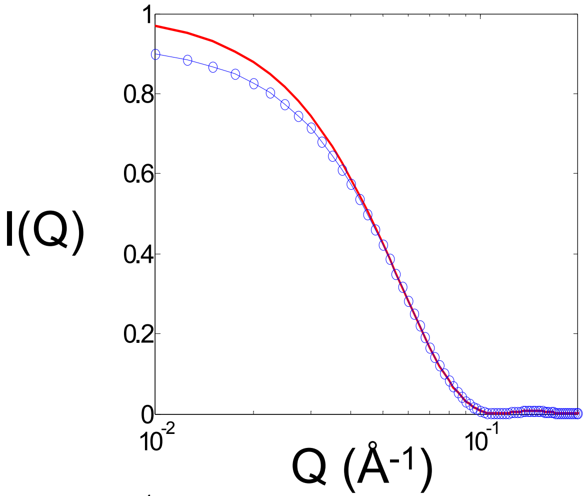
7. Example 1:

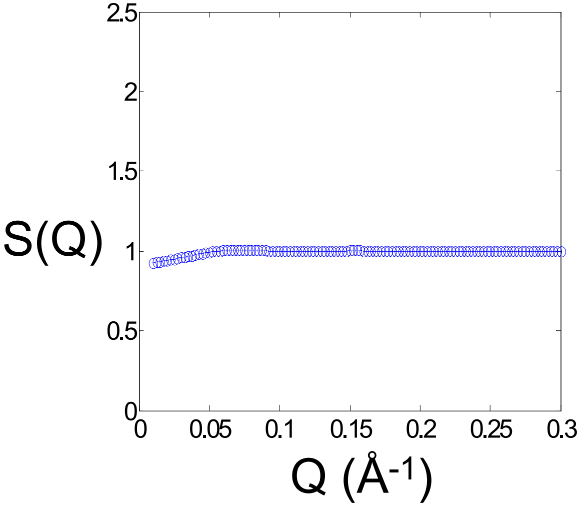
Hard Sphere Systems

$$I(Q) = A \times P(Q) \times S(Q)$$

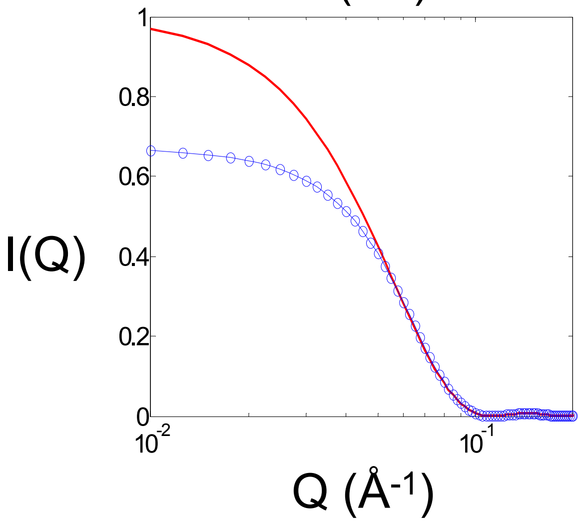
(Assume A=1)

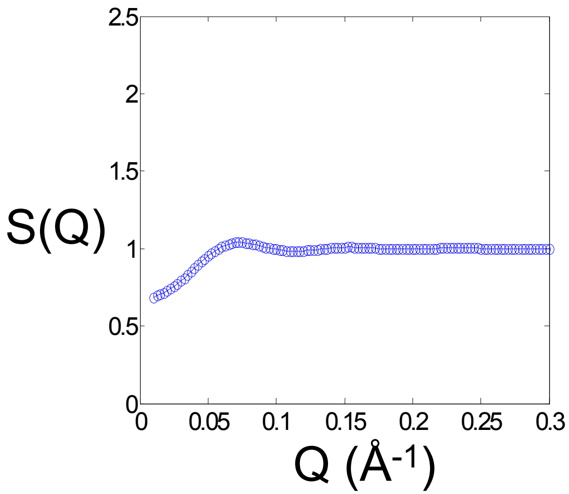
Φ=1%





Φ=5%



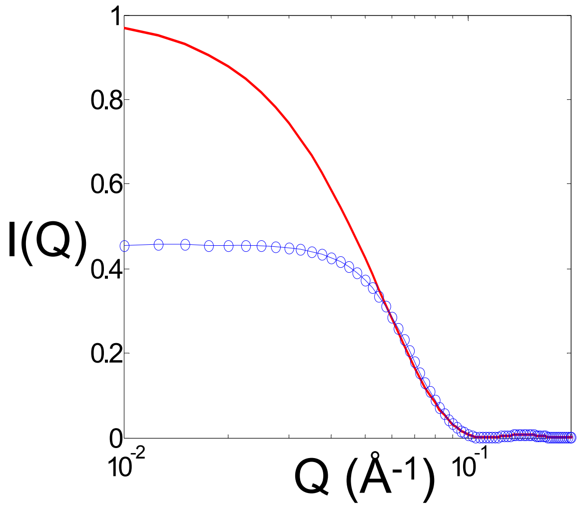


7. Example 1:

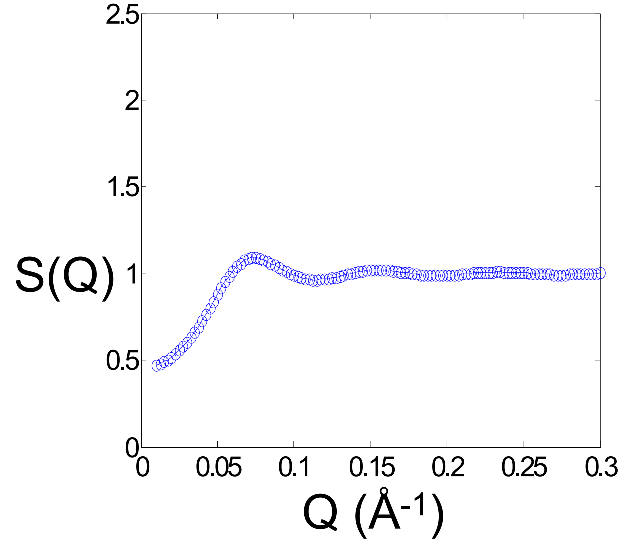
Hard Sphere Systems

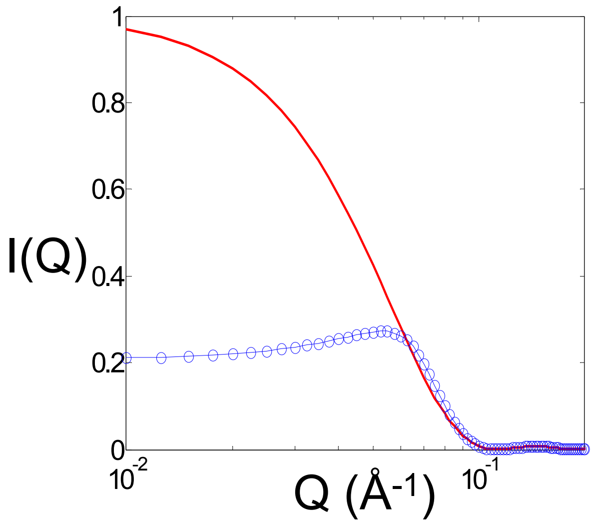
$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)

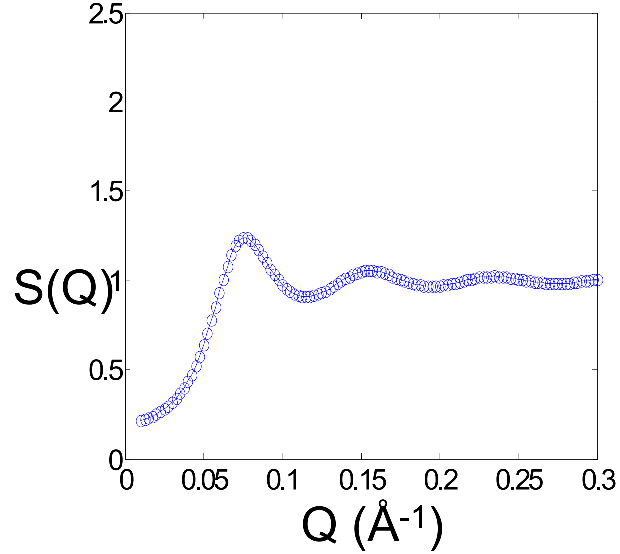


Φ=10%





Φ=20%

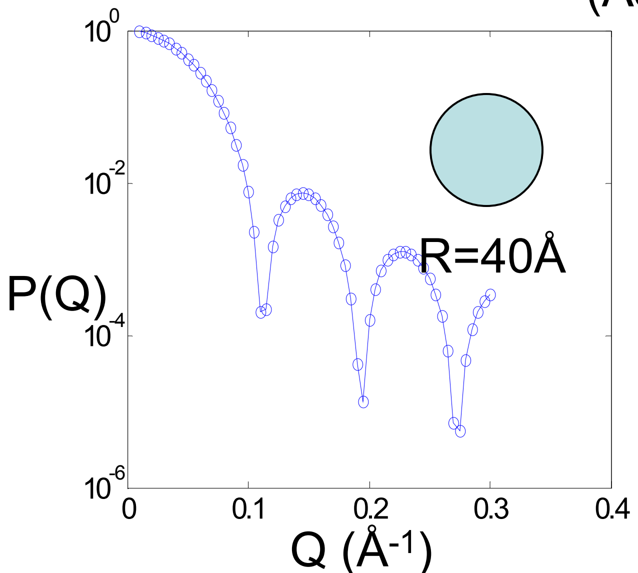


7. Example 2:

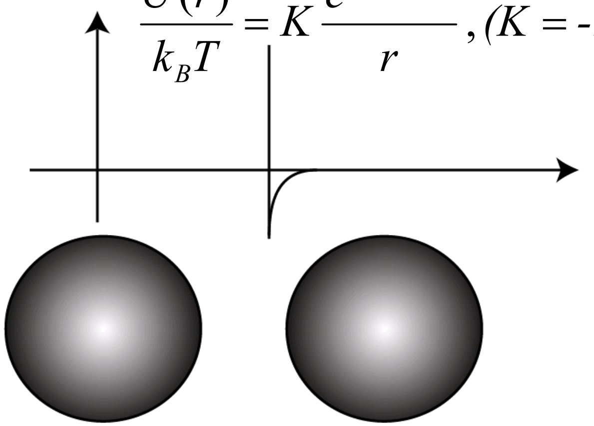
Short-range attraction systems

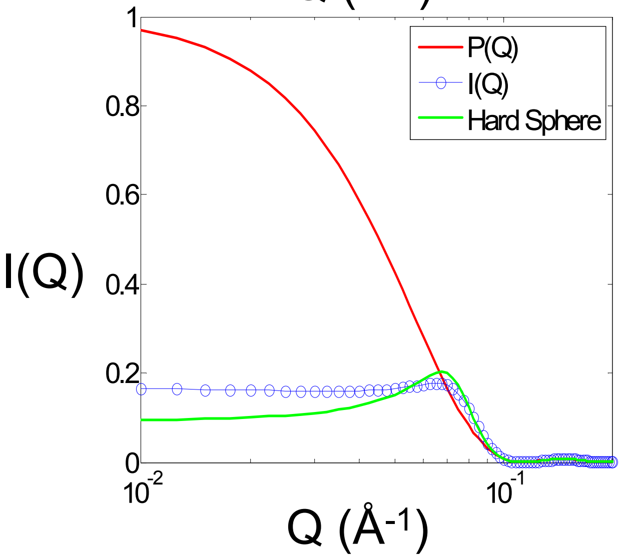
$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)



$$\frac{U(r)}{k_B T} = K\frac{e^{-\kappa(r-\sigma)}}{r}, (K = -2,\ \kappa\sigma = 10)$$





Volume fraction = 30%

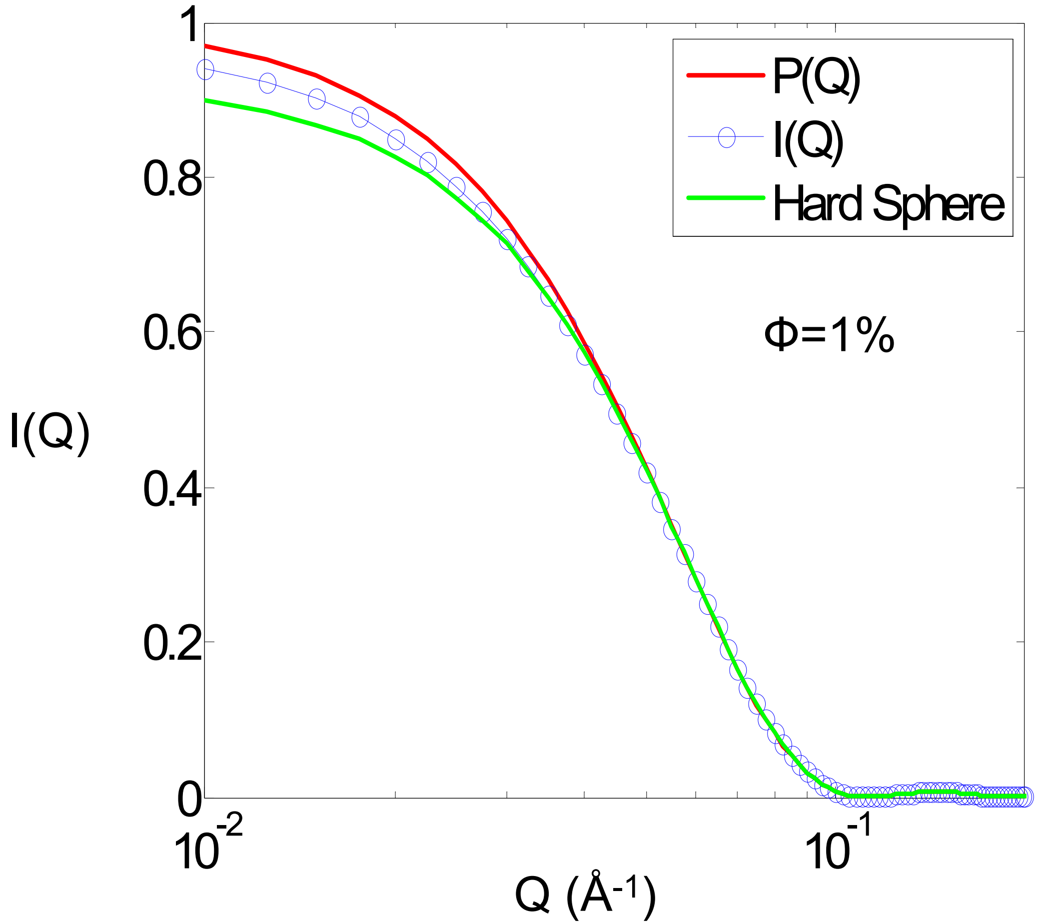
S(Q) is calculated with the MSA closure.

7. Example 2:

Short-range attraction systems

$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)



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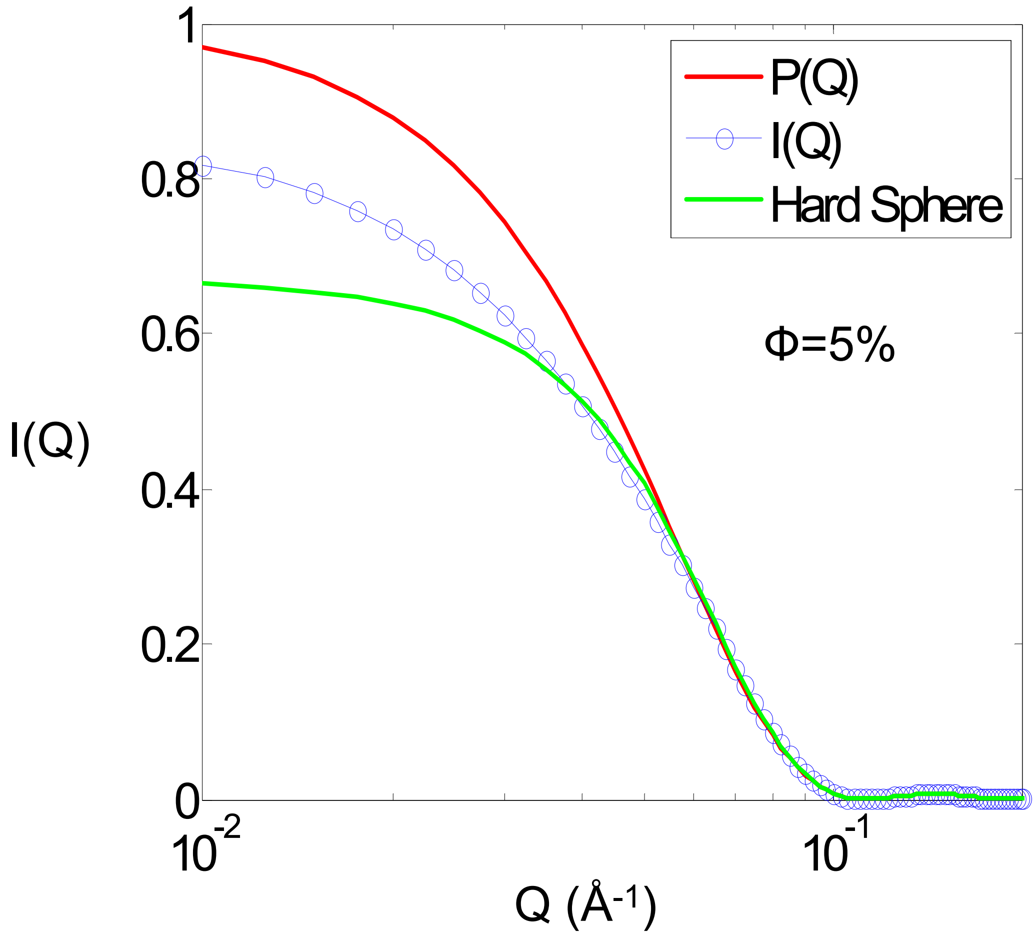

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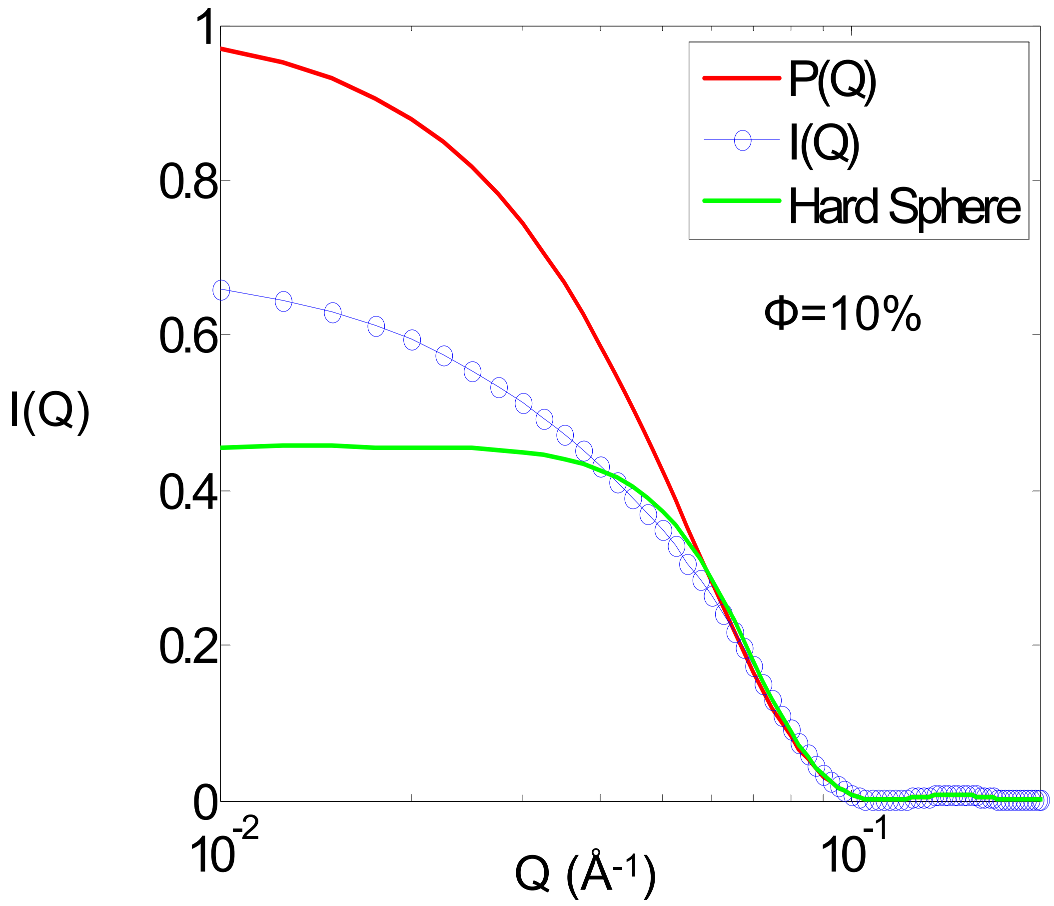

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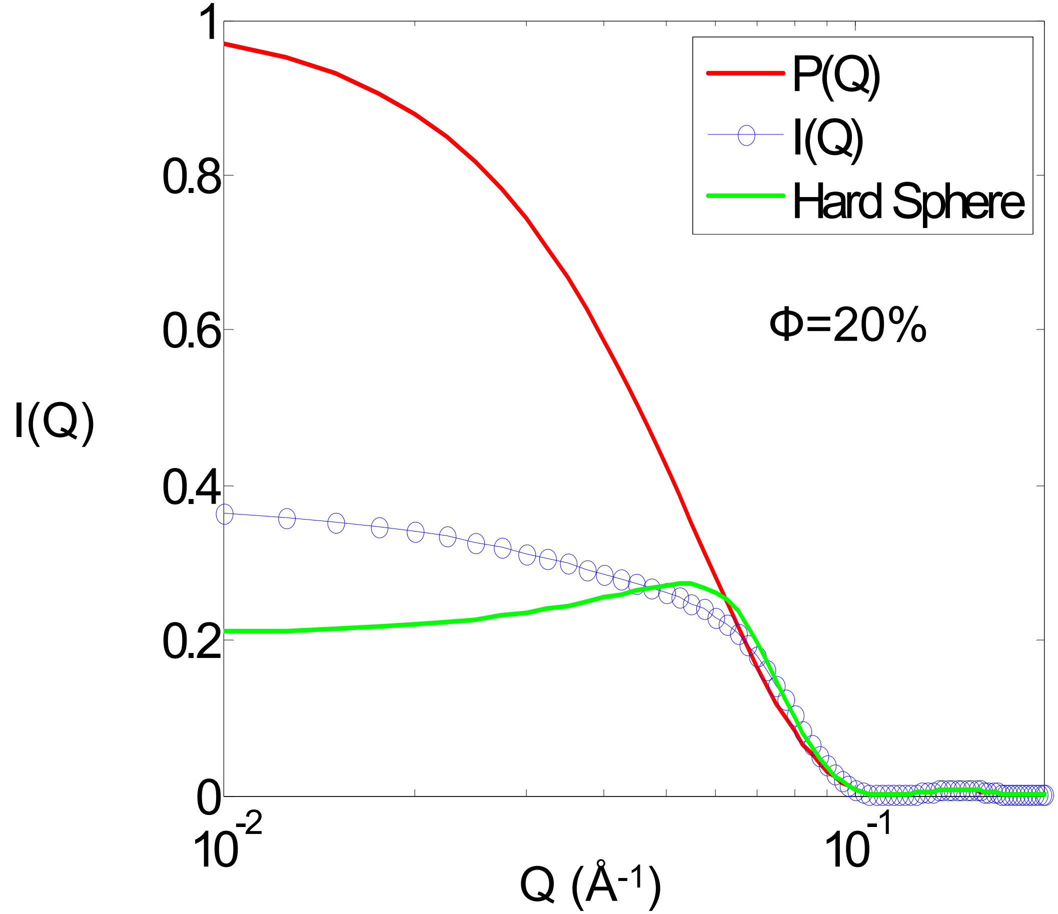
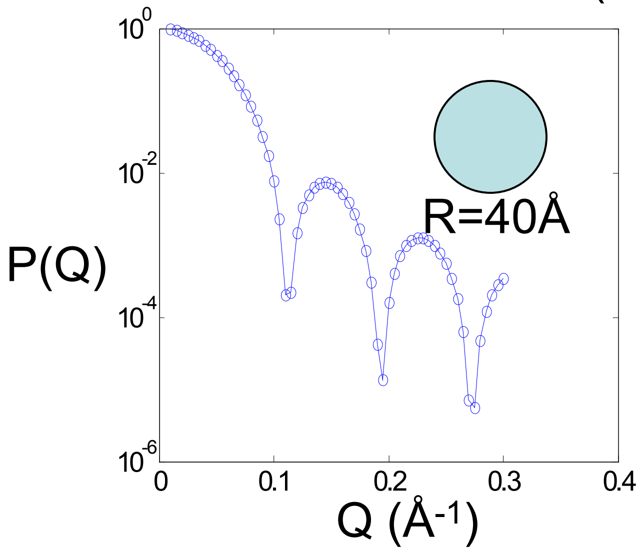


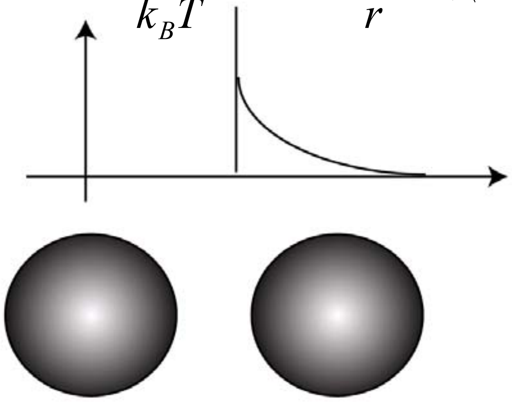
7. Example 3:
Electrostatic repulsion systems

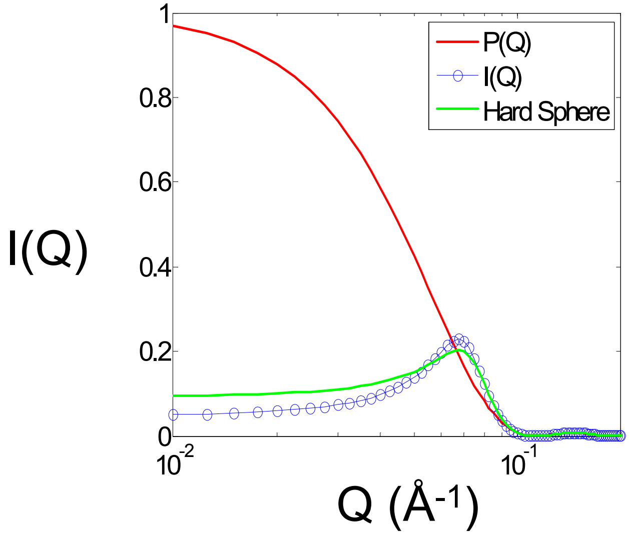
$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)



$$\frac{U(r)}{k_B T} = K\frac{e^{-\kappa(r-\sigma)}}{r}, (K = 2,\ \kappa\sigma = 4)$$





Volume fraction = 30%

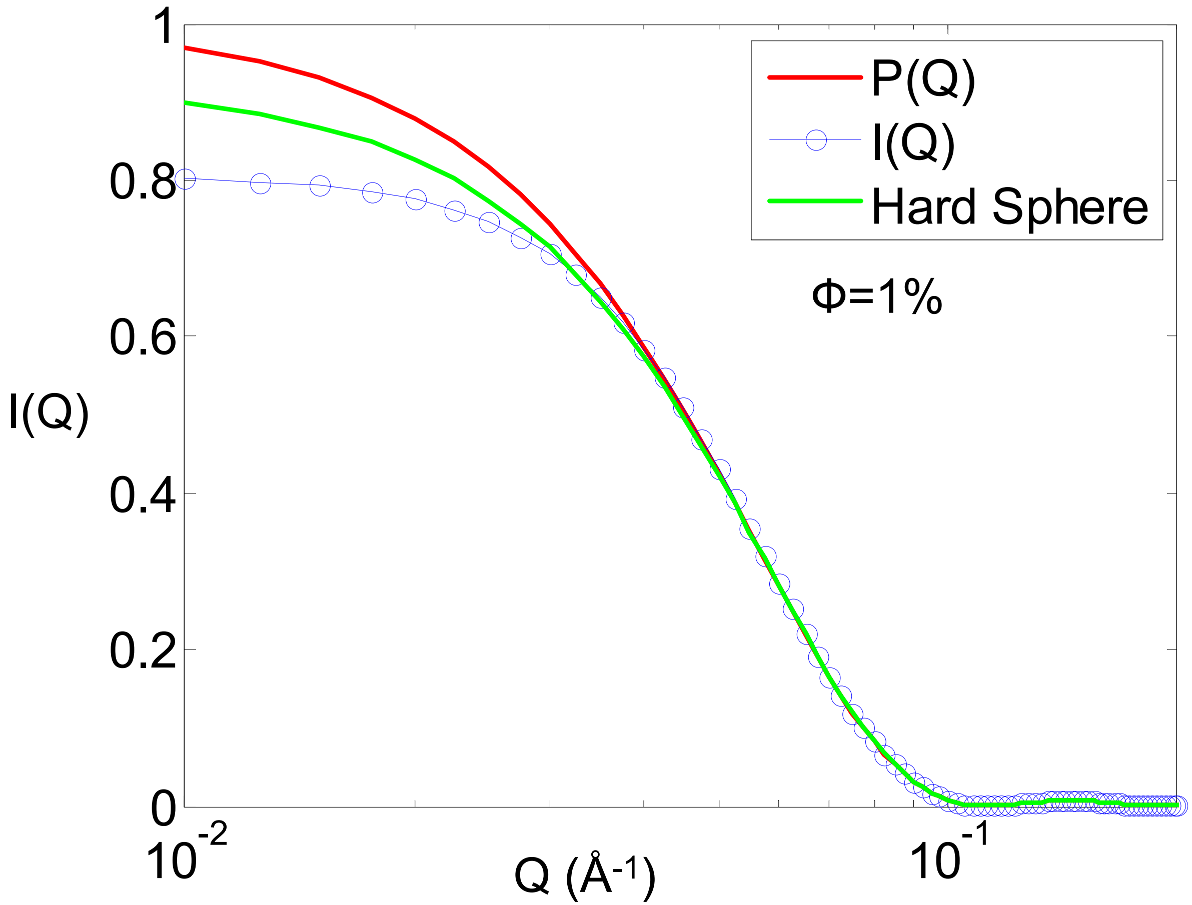
S(Q) is calculated with the MSA closure.

7. Example 2:

Electrostatic repulsion systems

$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)



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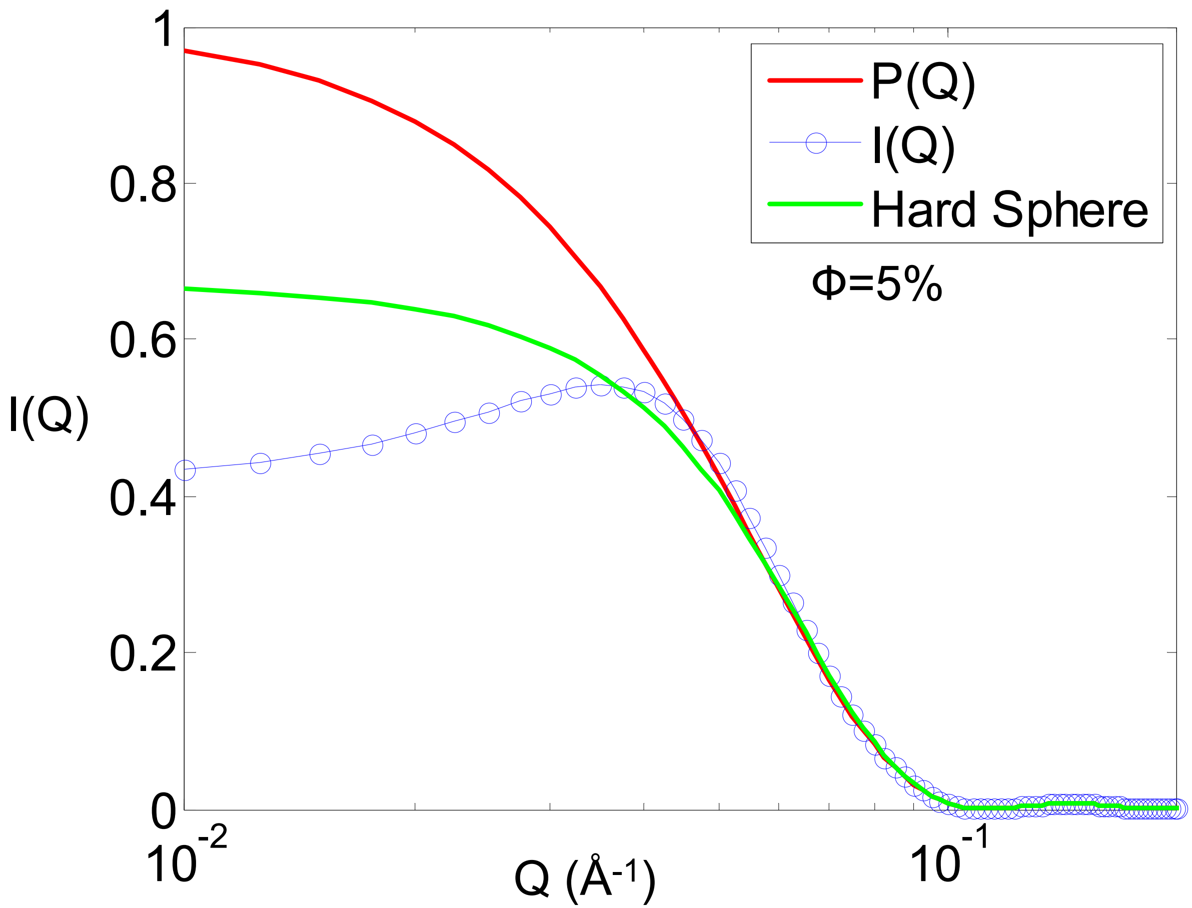

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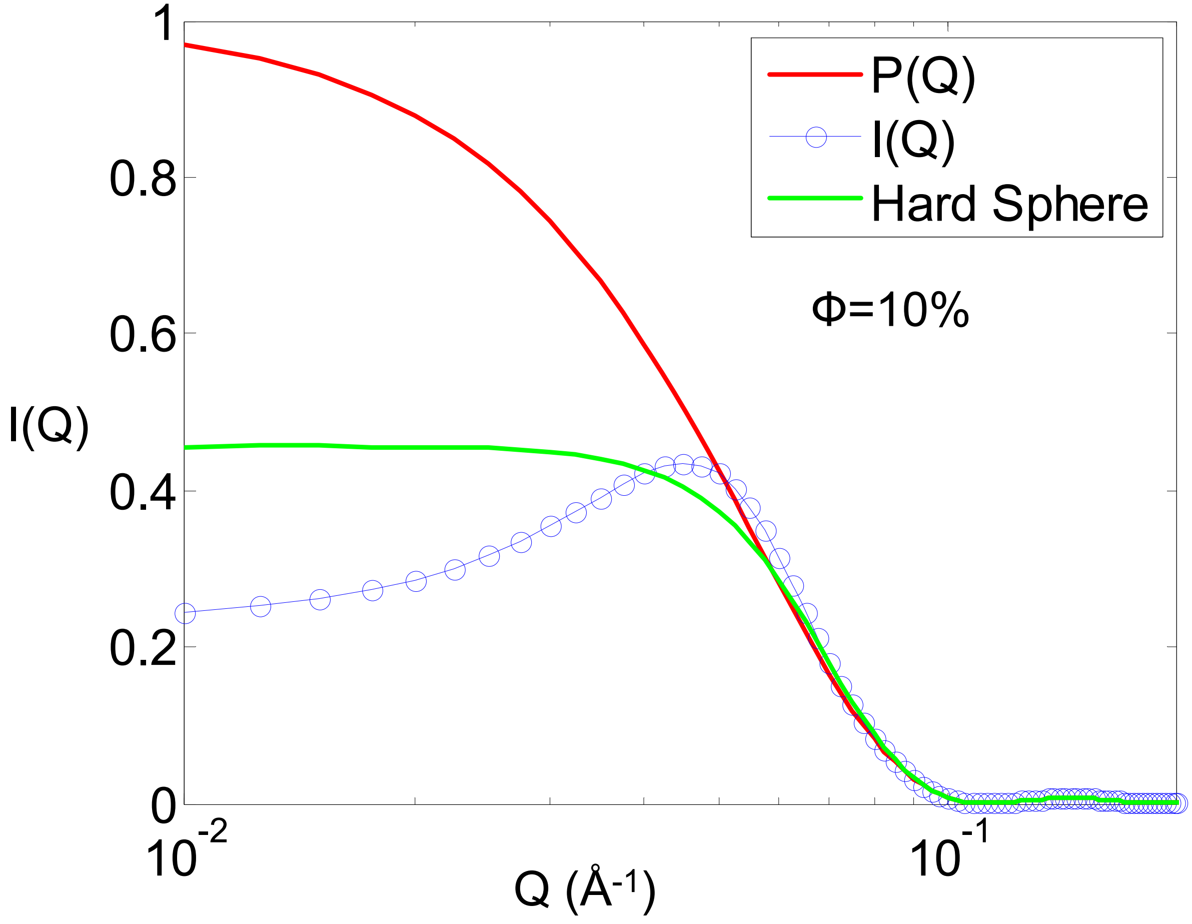

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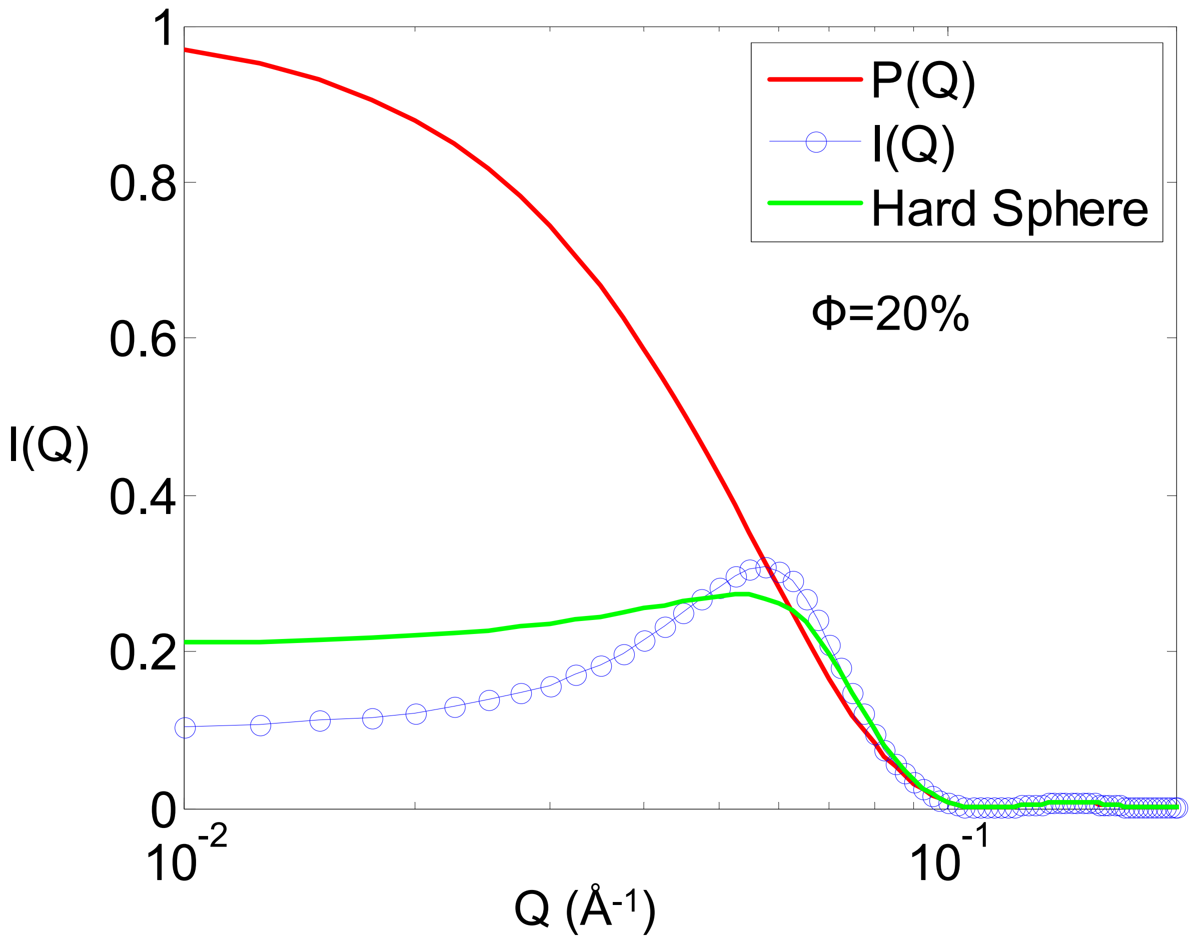

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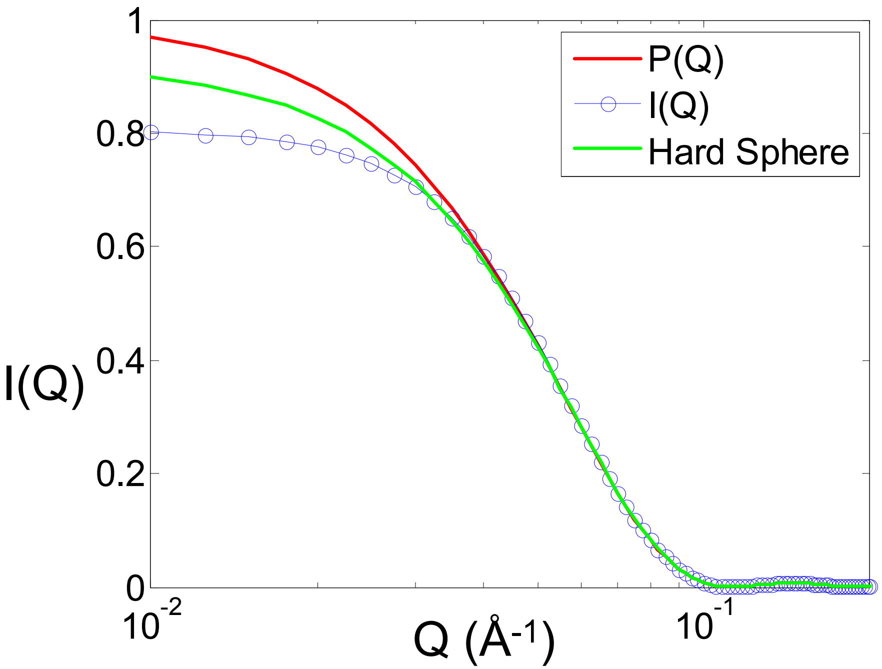
Electrostatic repulsion systems

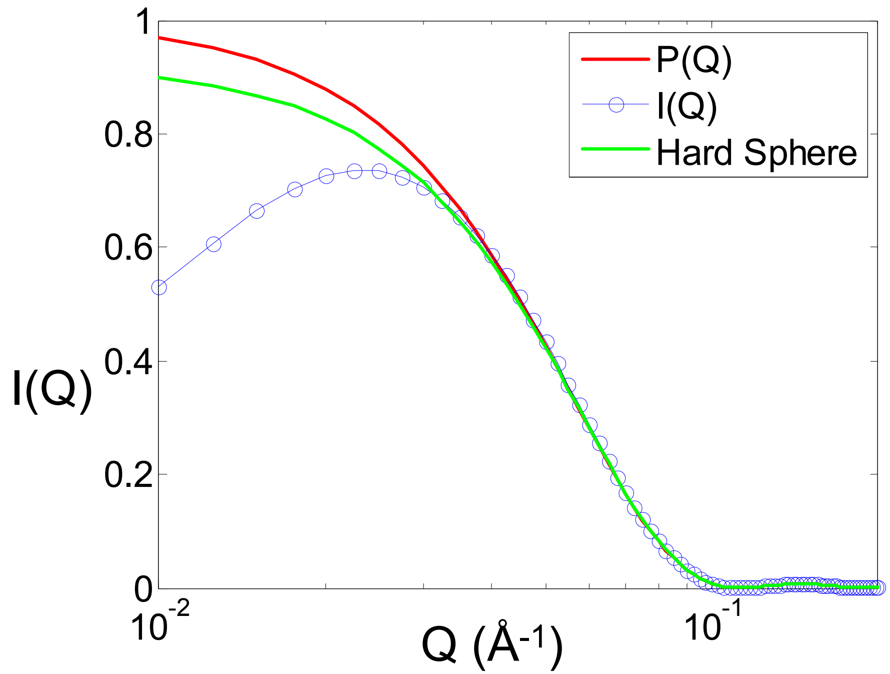
$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)

Φ=1%



$$\frac{U(r)}{k_B T} = K \frac{e^{-\kappa(r-\sigma)}}{r}, (K = 2,\ \kappa\sigma = 4)$$



$$\frac{U(r)}{k_B T} = K \frac{e^{-\kappa(r-\sigma)}}{r}, (K = 2,\ \kappa\sigma = 0.5)$$

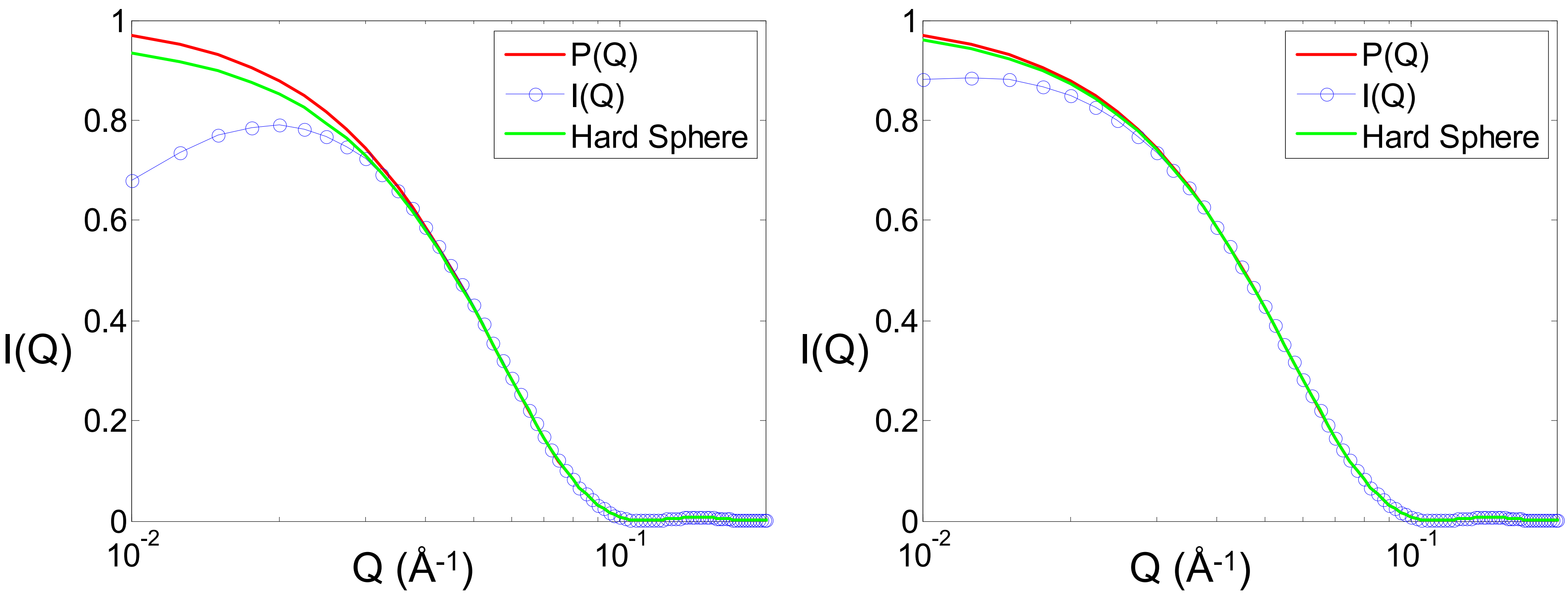
7. Example 2:

Electrostatic repulsion systems

$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)

Φ=0.5%   Φ=0.1%



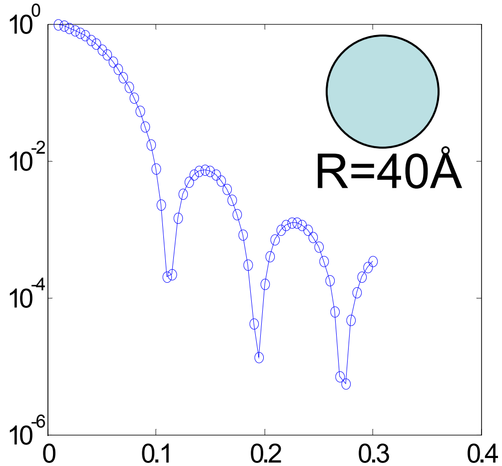
$$\frac{U(r)}{k_B T} = K \frac{e^{-\kappa(r-\sigma)}}{r}, (K = 2,\ \kappa\sigma = 0.5)$$

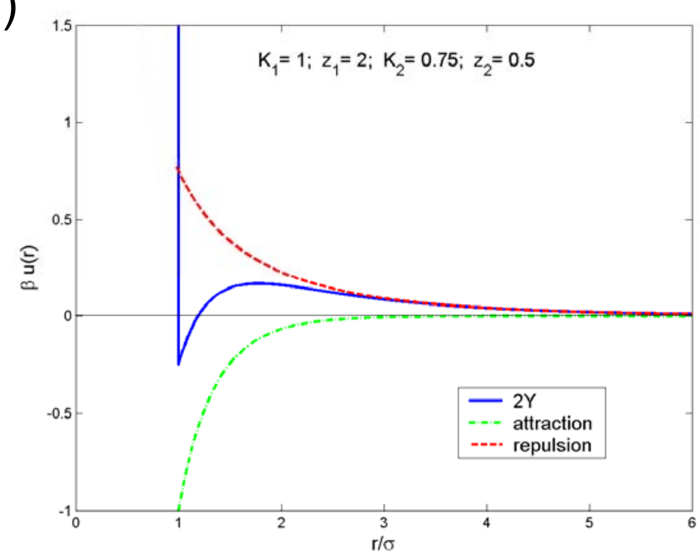
7. Example 3:

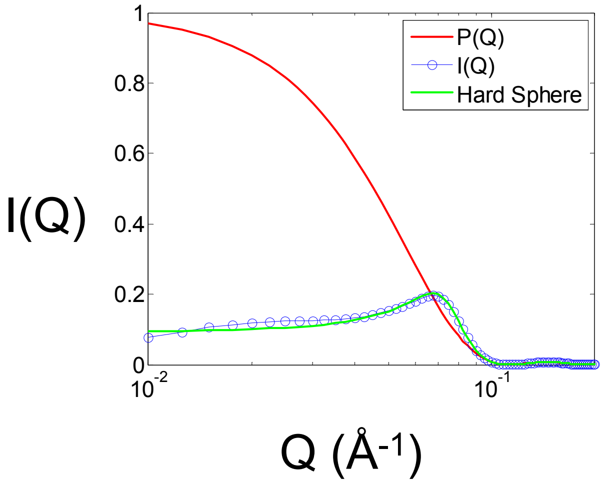
Electrostatic repulsion systems with short-range attraction

$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)







$$\beta u(r) = \begin{cases} \infty, & 0 < r \leq 1 \\ -K_1 \frac{e^{-z_1(r-1)}}{r} + K_2 \frac{e^{-z_2(r-1)}}{r} & r > 1 \end{cases}$$

Volume fraction = 30%

S(Q) is calculated with the MSA closure.

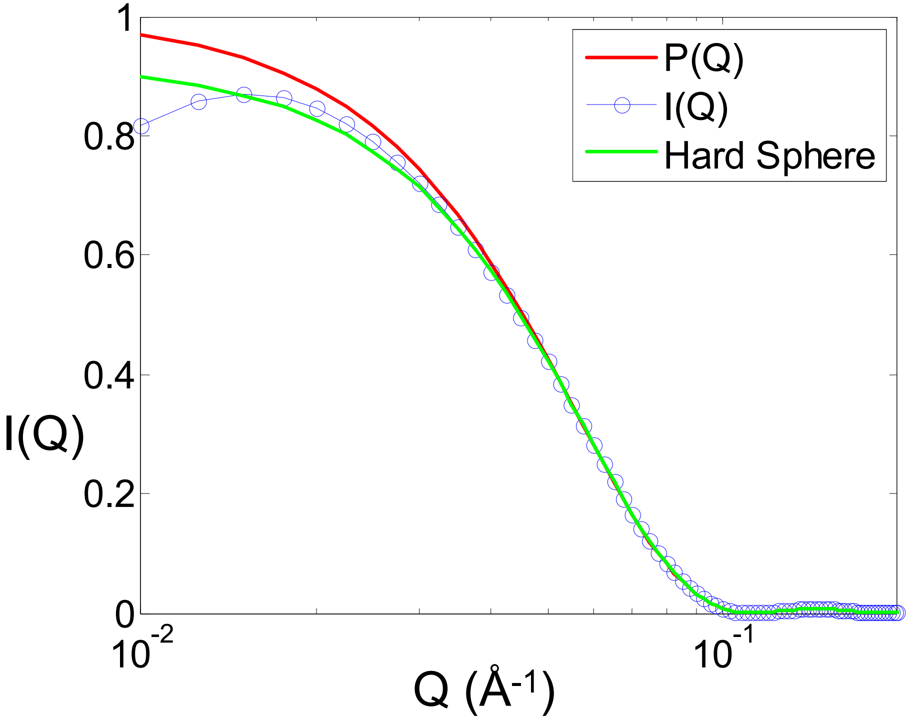
7. Example 3:

Electrostatic repulsion systems with short-range attraction

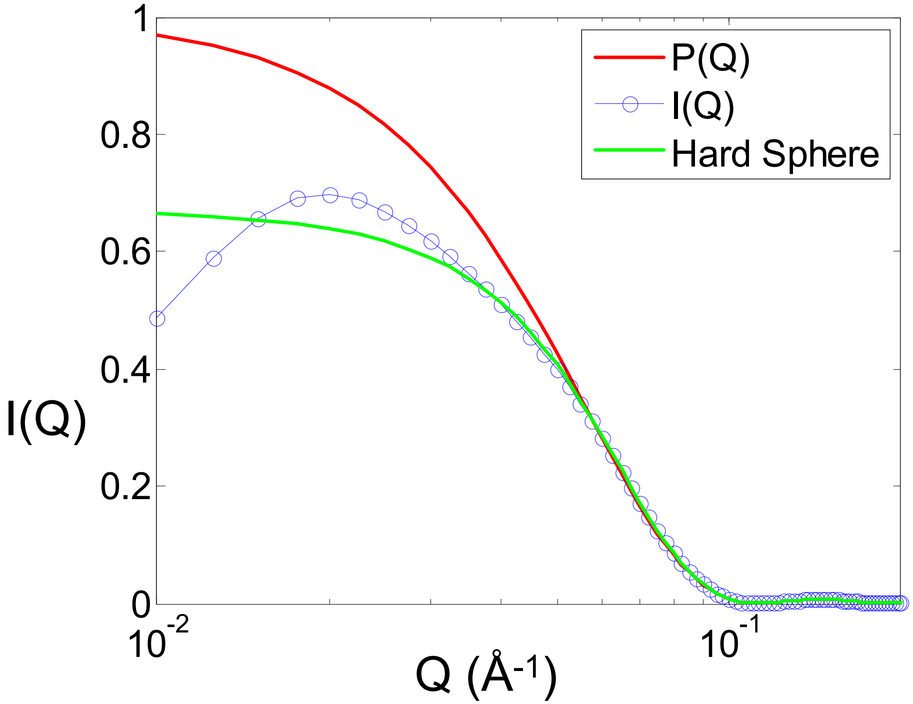
$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)

Φ=1%



Φ=5%



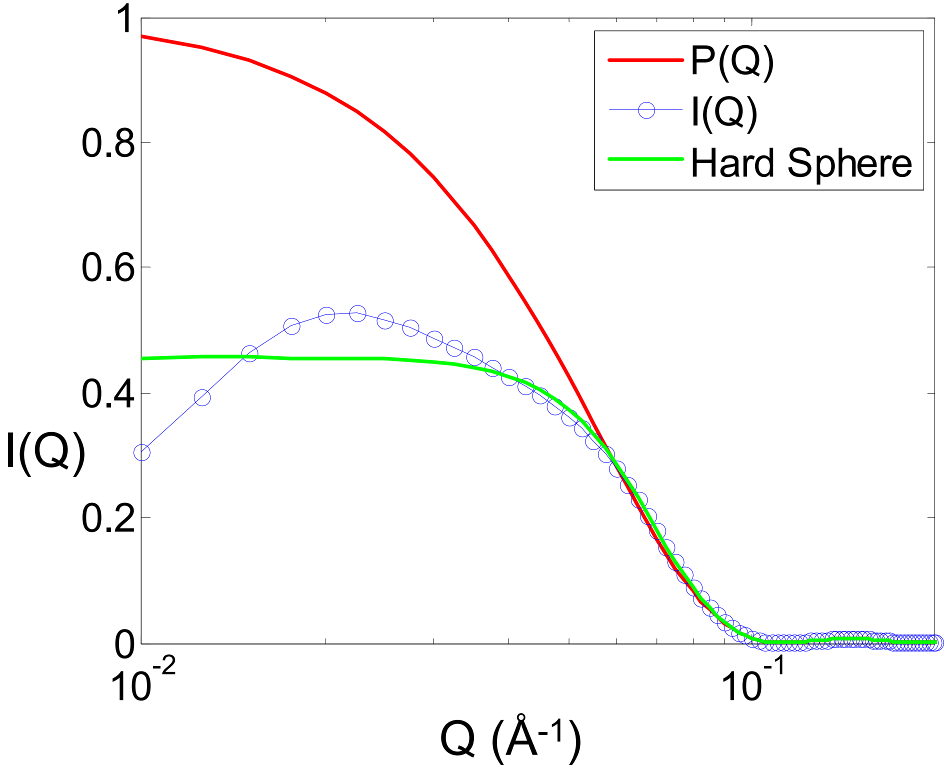
7. Example 3:

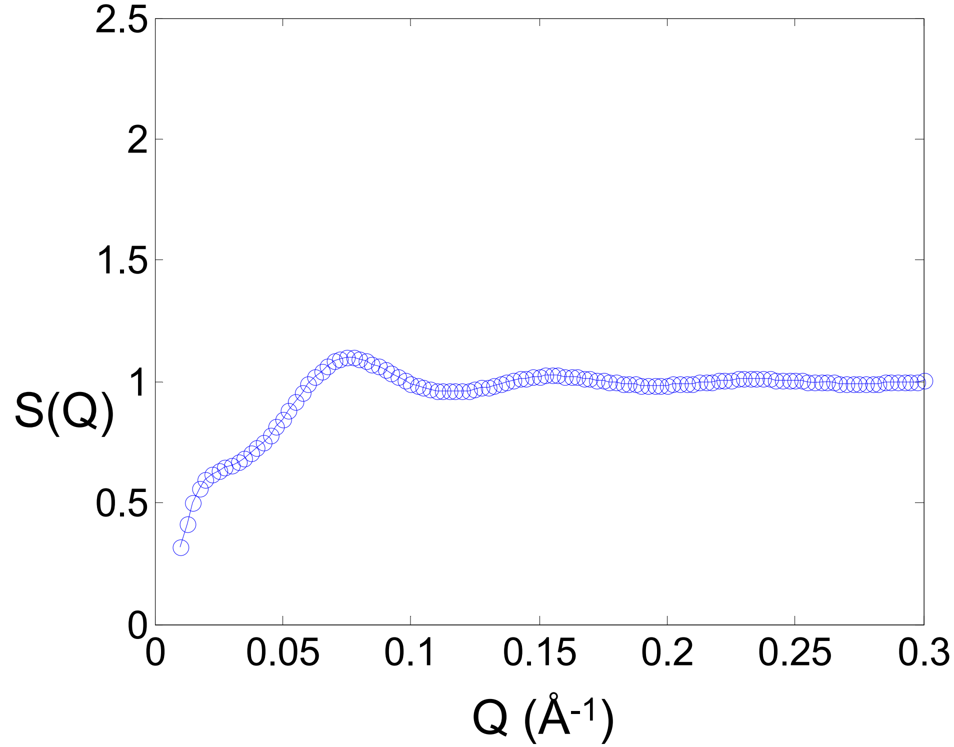
Electrostatic repulsion systems with short-range attraction

$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)

Φ=10%





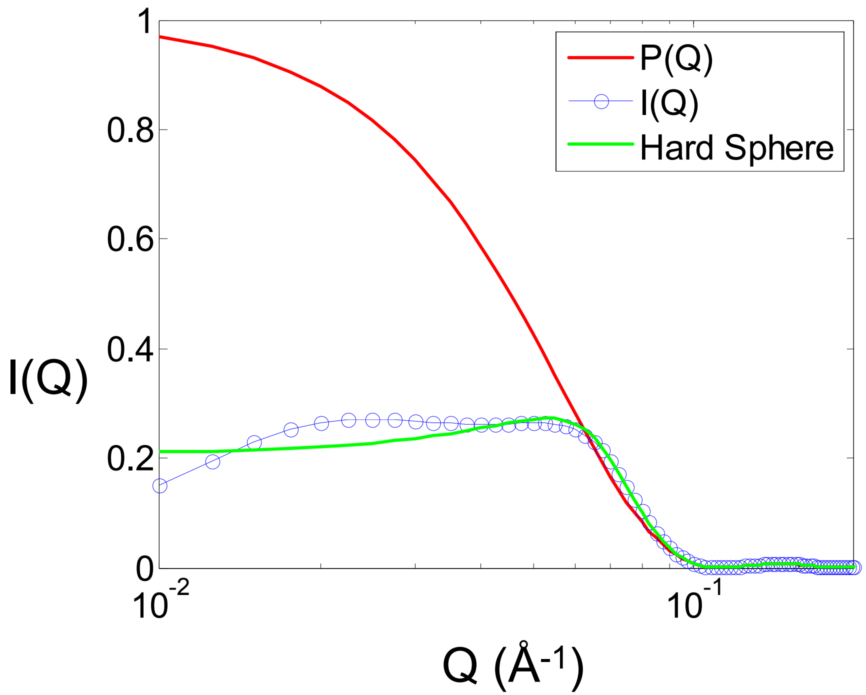
7. Example 3:

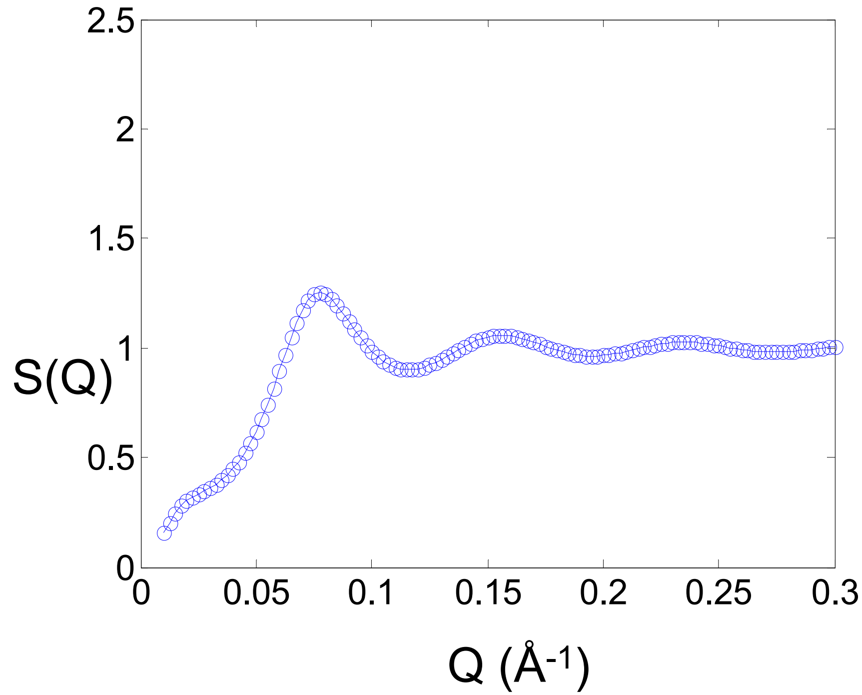
Electrostatic repulsion systems with short-range attraction

$$I(Q) = A \times P(Q) \times S(Q)$$

(Assume A=1)

Φ=20%





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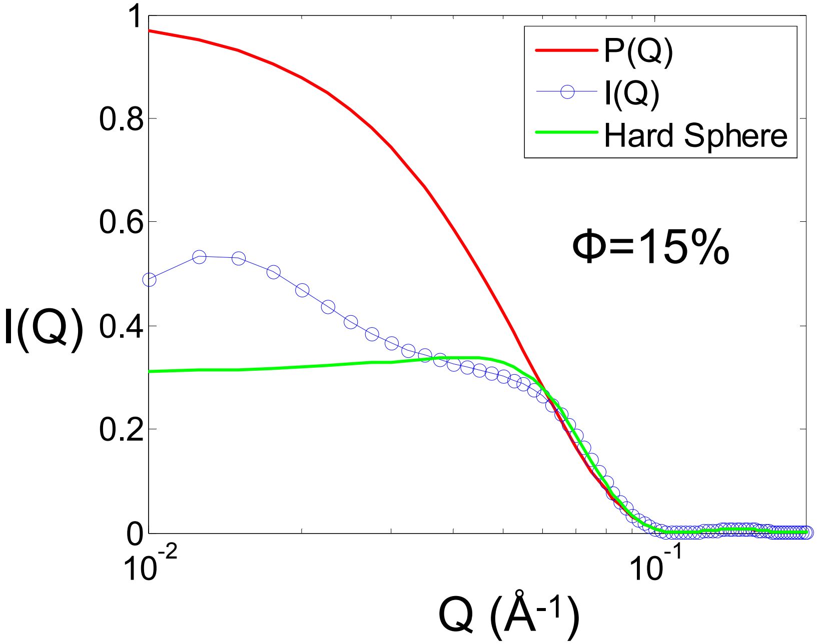
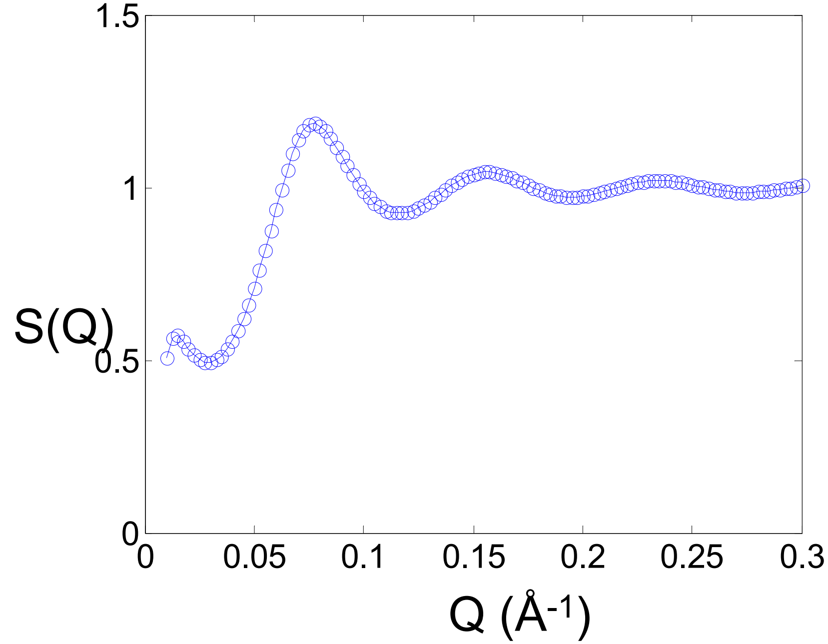
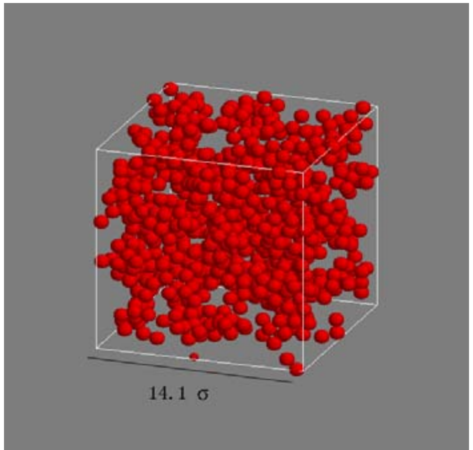




$K_1=1,\ Z_1=2,\ K_2=0.25,\ Z_2=0.5$

$$\beta u(r) = \begin{cases} \infty, & 0 < r \le 1 \\ -K_1 \frac{e^{-z_1(r-1)}}{r} + K_2 \frac{e^{-z_2(r-1)}}{r} & r > 1 \end{cases}$$



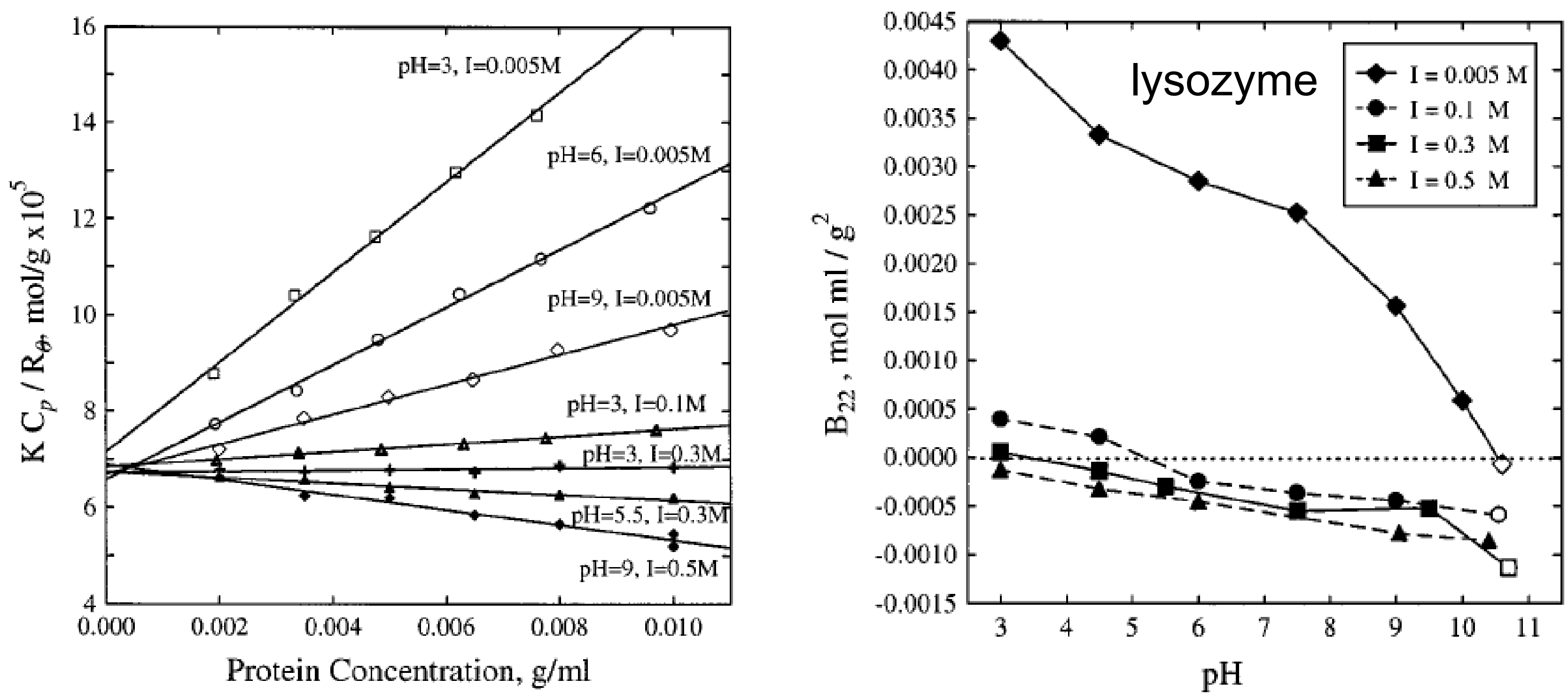
8. Relations with other methods:
Light scattering

Obtain the second virial coefficient, B_{22}, using static light scattering:

$$\frac{KC_\mathrm{p}}{R_\theta} = \frac{1}{M_\mathrm{W}} + 2B_{22}C_\mathrm{p}$$

$$B_{22}M_w N_A = -2\pi\int (g(r)-1)r^2 dr = -2\pi\int (e^{-\frac{U(r)}{k_B T}}-1)r^2 dr$$

Velev et al., Biophysical Journal **75**, 2682 (1998)



8. Summary and β-approximation

$$I(Q) = A \times P(Q) \times S(Q)$$

- Decoupling approximation: one component system with spherical particles
- Given the know information of inter-particle potential, S(Q) can be obtained by solving OZ equation: isotropic interaction

Big trouble!

- Disks, rods, …
- particles with large polydispersity
- Anisotropic interactions

8. Summary and β-approximation

$$I(Q) = A \times P(Q) \times S(Q)$$

- When polydispersity is small or the colloidal particle is close to a spherical shape

β-approximation

$$I(Q) = \frac{N}{V}\langle P(Q)\rangle [1+\beta(Q)(\bar{S}(Q)-1)]$$

$$\beta(Q) = |\langle F(\mathbf{Q})\rangle|^2/\langle|F(\mathbf{Q})|^2\rangle$$

$$\langle P(Q)\rangle = \langle|F(Q)|^2\rangle$$

$\bar{S}(Q)$ can be approximated with one component structure factor.

S.-H. Chen *Ann. Rev. Phy. Chem.* **37** 351 1986

8. Available resources

1. Available computer codes

SANS & USANS Analysis with IGOR Pro
http://www.ncnr.nist.gov/programs/sans/data/data_anal.html

- Many form factor models
- The structure factor for hard sphere system (PY), sticky hard sphere system (PY), the Hayter-Penfold method (MSA for one Yukawa hard sphere system).

Structure factor for two Yukawa hard sphere system with Matlab codes

- MSA closure. Freely available by contacting Yun Liu (yunliu@nist.gov) or Sow-Hsin Chen (sowhsin@mit.edu)

2. Website lecture notes and tutorials

NCNR SANS Tutorial
http://www.ncnr.nist.gov/programs/sans/tutorials/index.html

Lectures by Roger Pynn
http://www.mrl.ucsb.edu/~pynn/