Theoretical and experimental SANS study of colloidal systems: from depletion attraction to bridge attraction

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Outline

- ❑Introduction
- ❑Model description
- ❑Mapping Method
- ❑Comparison between theory and experiment
- ❑SANS experiments verification
- ❑Conclusions

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1.1 Introduction

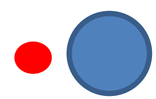
Colloidal system exists everywhere in our daily life



The key parameter deciding its function is the inter-particle interactions, which can be tuned by additions of different properties.

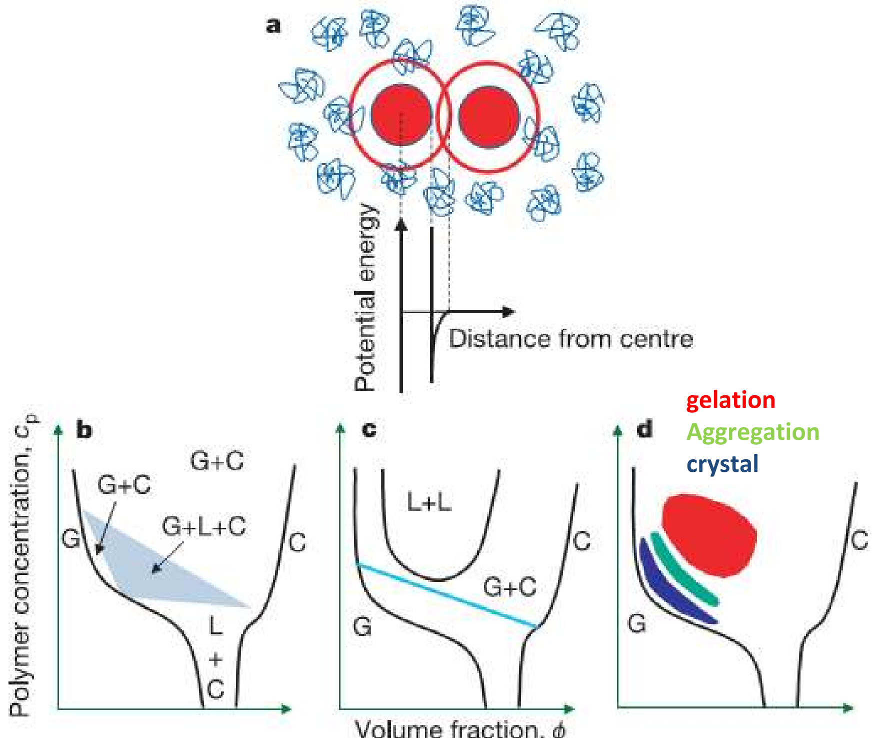
1.2 Systems Model

Small particles, such as polymer, in large colloidal system!



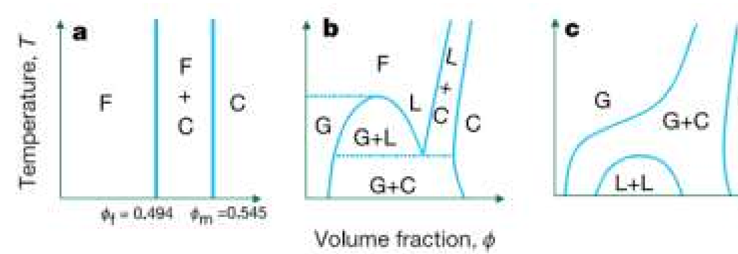
1.3 Depletion attraction-Theories

If the polymer can **not** be **adsorbed** to **large** colloidal particles :**Depletion Attraction**



Attraction from osmotic pressure caused by density difference

V.J.Anderson, H.N.W.Lekkerkerker, *Nature* **416**,811(2002)

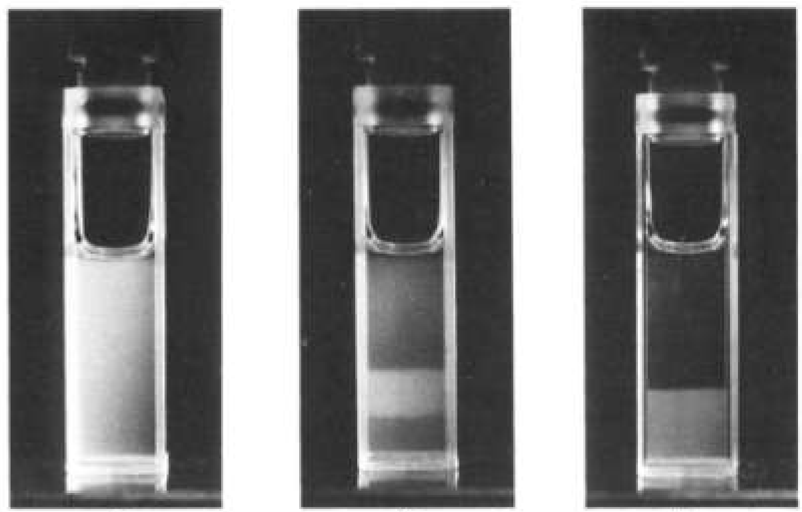


S.Asakura et al,*J.Chem.Phys* **22**,1255(1954)
N.W.Ashcroft et al, *Phys.Rev* **156**,685(1967)
E.Dickinson,*J.Chem.Soc.Faraday Trans.* **91**,4413-4417(1995)
Peter J.Lu et al. *Nature* **453**,499(2008)
……

1.3 Depletion attraction-Experiment

polymethylmethacrylate (PMMA) + polystyrene (PS)

$$x = 0.24, \phi = 0.2$$



(a) (b) (c)

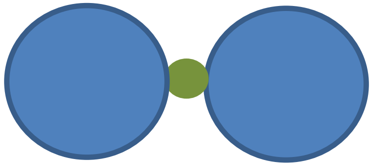
S.M.Ilett, A.Orrock,W.C.K. Poon and P.N.Pusey, *Phys.Rev.E* **51**,1344(1995)

1.4 Bridge Attraction

But what if the polymer can be adsorbed to large colloidal particles?

Physical Interaction

Chemical Interaction



1.4 Bridge Attraction

polystyrene (PS) + poly(N-isopropylacrylamide) (PNIPAM)

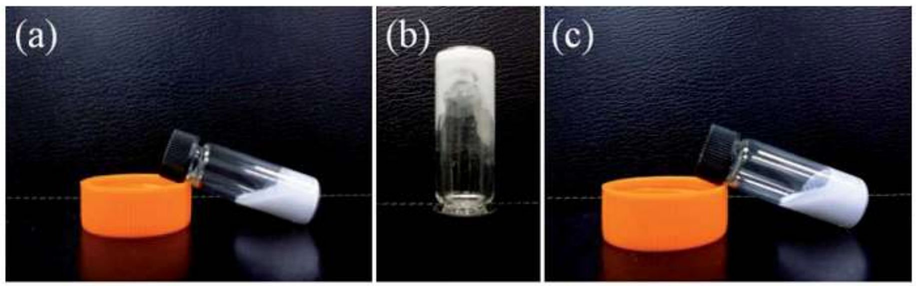


Fig. 1 Photographs of PS MS ($\phi_{MS} = 0.30$) and PNIPAM MG mixed suspension with different concentration of MG: (a) $\phi_{MG} = 0$; (b) $\phi_{MG} = 0.060$ ($\phi_{MG}/\phi^*_{MG} = 0.56$); (c) $\phi_{MG} = 0.12$ ($\phi_{MG}/\phi^*_{MG} = 1.1$).

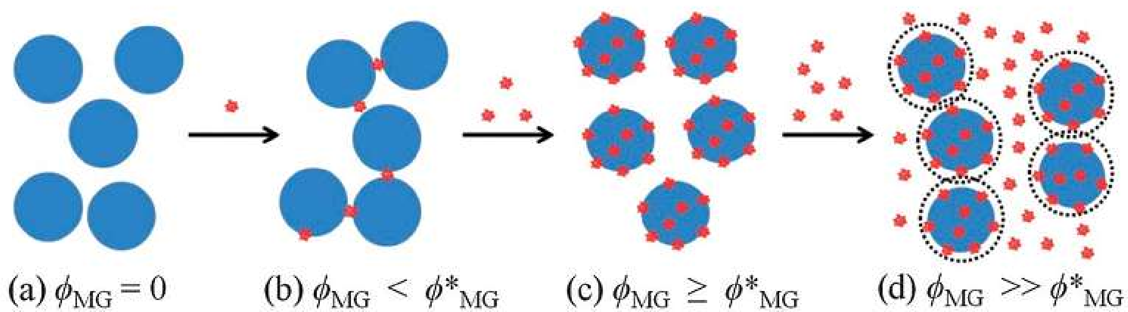


Fig. 9 A schematic illustration of the clustering (or gelation) of the MS through the MG bridge. The MS, MG and depletion layer is presented by blue circle, red circle and dotted circle, respectively.

C.Z.Zhao et.al, *Soft Matter* **8**, 7036(2012)

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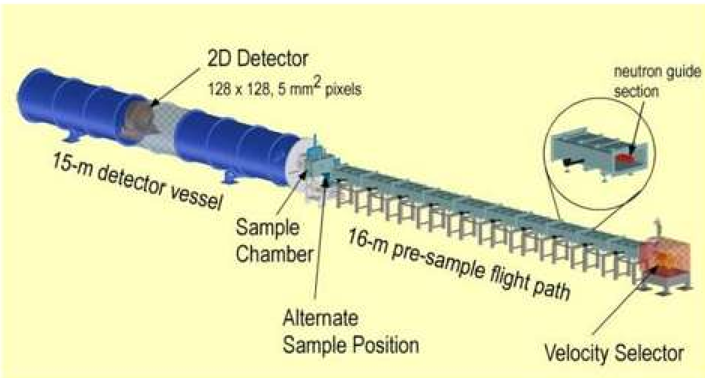
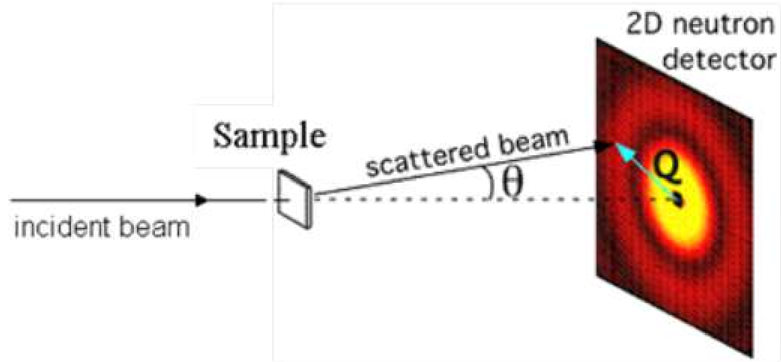
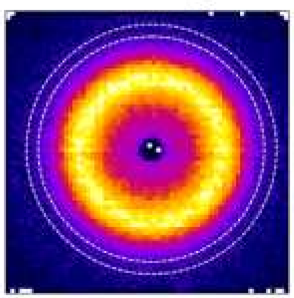
2.1 Small Angle Neutron Scattering





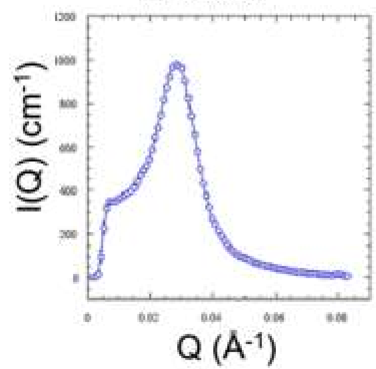
2D image

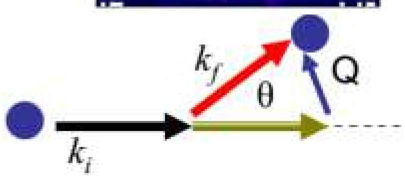


$I(Q_x,Q_y)$: intensity distribution

Annulus average

1D data



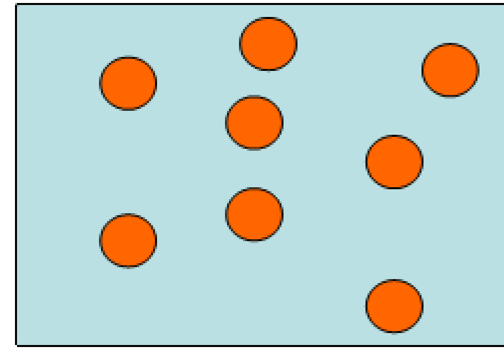


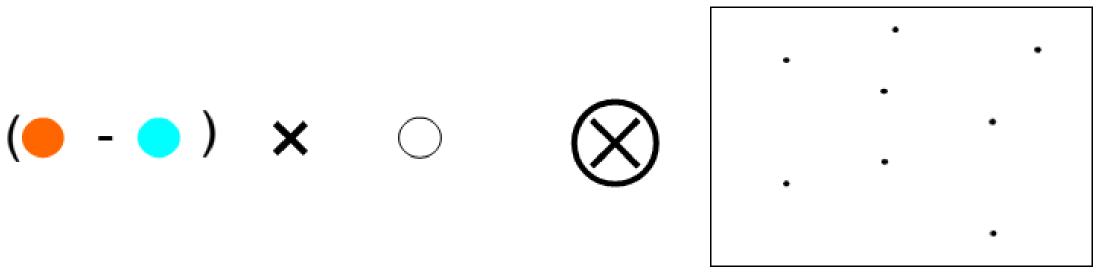
Elastic Scattering: $q = \frac{4\pi}{\lambda}\sin(\frac{\theta}{2}) \approx \frac{2\pi\theta}{\lambda}$

2.1 SANS: Scattering Pattern

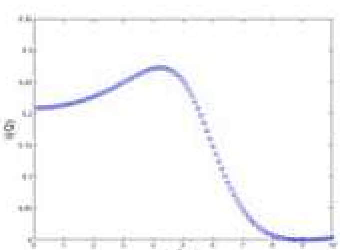
Scattering pattern: What we get in experiment after data reduction

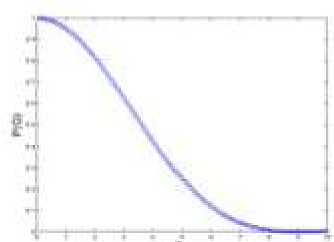
[redacted]

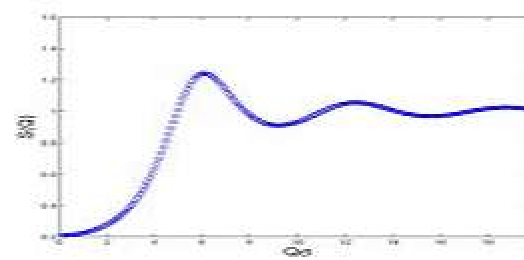




$$I(q) = A * P(q) * S(q)$$







2.1 SANS: Structure Factor

Total correlation function: $\mathrm{h}(r) = g(r) - 1$

Structure factor: $S(q) = 1 + n \int h(r) e^{iq.r} dr^3$

Ornstein-Zernike (OZ) equations:

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

c(r): direct correlation function

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

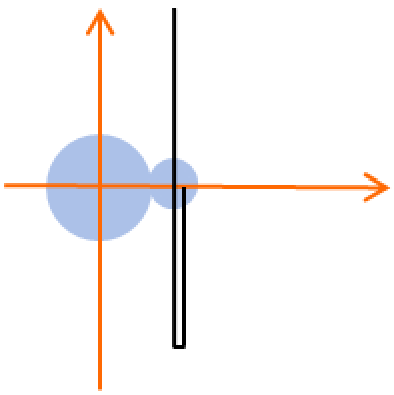
RY closure (Rogers-Young)

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

2.2 Multi-Components SHS model

- Potential

$$\beta U_{ij} = \begin{cases} \infty, & r < \sigma_{ij}; \\ \ln[12\tau_{ij}(d_{ij} - \sigma_{ij})], & \sigma_{ij} < r < d_{ij}; \\ 0, & d_{ij} < r. \end{cases}$$



- **Reduced second Virial coefficient:** $B_2^* = 1 - \frac{1}{4\tau}$

- The solution of OZ equation with Baxter's Q method is:

$$\boxed{S(q)^{-1} = I - C(q) = Q(-q)^T Q(q)}$$

$$\begin{aligned} Q_{nm}(q) =& \delta_{nm} + \frac{\pi a^3}{6}\sqrt{n_n n_m}\exp^{iqad_n/2} \times \\ & [-\lambda_{nm} d_m d_{nm}^2 j_0(qad_m/2) + \frac{3d_n d_m^2}{1-\varepsilon_3} j_0(qad_m/2) \\ & + 3a_n d_m^3 \times \frac{j_1(qad_m/2)}{qad_m/2} - i \times \frac{3d_n d_m^2}{1-\varepsilon_3} j_1(qad_m/2)] \end{aligned} \quad \text{(A1)}$$

with

$$\boxed{\begin{aligned}\tau_{nm}\lambda_{nm} =& \frac{1}{1-\varepsilon_3} + \frac{3a\varepsilon_2}{2(1-\varepsilon_3)^2} \times \frac{d_n d_m}{d_{nm}} \\ & - \frac{1}{2(1-\varepsilon_3)} \times \frac{1}{d_{nm}} \times \frac{\pi}{6}a^3 \times \\ & [\sum_k (n_k d_{nk}^2 d_k d_m \lambda_{nk} + n_k d_{mk}^2 d_k d_n \lambda_{mk})] \\ & + \frac{1}{12} \times \frac{\pi}{6}a^3 \sum_k n_k \frac{d_{mk}^2 d_{nk}^2}{d_{nm}} \lambda_{mk}\lambda_{nk}, \qquad \text{(A2)}\end{aligned}}$$

N(N+1)/2 quadratic equations

$$\lambda_{nm} = 12\int_{\sigma_{nm}/d_{nm}}^{1} x g_{nm}(x)dx$$

$$\varepsilon_n = \frac{\pi}{6}\sum_k n_k (a d_k)^n,$$

$$X_n = \frac{\pi}{6}a^3 \sum_k n_k d_{nk}^2 d_k \lambda_{nk},$$

$$a_n = \frac{1-X_n}{1-\varepsilon_3} + \frac{3a d_n \varepsilon_2}{(1-\varepsilon_3)^2},$$

$$j_0(x) = \frac{\sin x}{x}, \quad j_1(x) = \frac{\sin x - x\cos x}{x^2}.$$

$$x_i = n_i/n \qquad a^3 = \sum_i x_i * (\sigma_i + \Delta_i)^3$$

$$d_i = (\sigma_i + \Delta_i)/a \qquad d_{ij} = (d_i + d_j)/2$$

B.Barboy and R.Tenne, *Chem.Phys.* **38**,369-387(1979)

2.3 System we concern

- **For our system: N=2 and $\tau_{SS}, \tau_{LL} \rightarrow \infty$ ($\lambda_{SS}, \lambda_{LL} \rightarrow 0$)**
  - **Depletion attraction: $\tau_{SL} \rightarrow \infty$ ($\lambda_{SL} \rightarrow 0$)—Two components HS system**
  - **Bridge attraction: $\tau_{SL} \neq \infty$ ($\lambda_{SL} \neq 0$)**

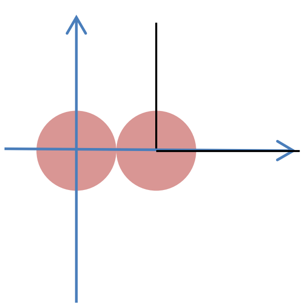
$$\lambda_{SL} = \frac{\varepsilon(1+x) + 3(\eta_S + x\eta_L)}{\frac{\varepsilon}{4x}(1+x)^2(\eta_S + x\eta_L) + (1+x)\varepsilon^2\tau_{12}} \qquad \text{(A6)}$$

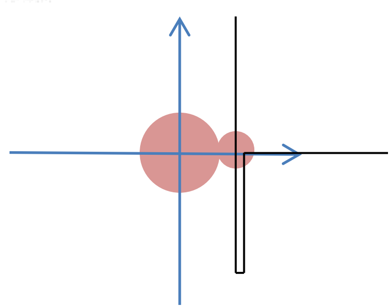
here:

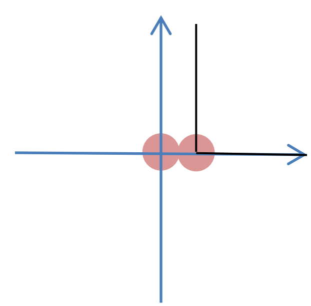
$$\eta_\alpha = \frac{\pi}{6}(ad_\alpha)^3 n_\alpha,$$

$$\varepsilon = 1 - \varepsilon_3 = 1 - \eta_S - \eta_L,$$

$$x = \frac{d_{SS}}{d_{LL}}.$$







2.4 Spinodal decomposition

$$Q_{11}(0) = 1 + \frac{4\phi_S}{\varepsilon} + \frac{3\phi_S(\phi_S + x\phi_L)}{\varepsilon^2} - \frac{(1+x)^2\phi_S\phi_L}{4\varepsilon}\lambda_{SL},$$

$$Q_{12}(0) = -\sqrt{\frac{\phi_S\phi_L}{x^3}}[\frac{(1+x)^2(1-\phi_S)}{4\varepsilon}\lambda_{SL} - \frac{1+3x}{\varepsilon} - \frac{3(\phi_S + x\phi_L)}{\varepsilon^2}],$$

$$Q_{21}(0) = -\sqrt{x^3\phi_S\phi_L}[\frac{(1+1/x)^2(1-\phi_L)}{4\varepsilon}\lambda_{SL} - \frac{1+3/x}{\varepsilon} - \frac{3(\phi_S/x + \phi_L)}{\varepsilon^2}],$$

$$Q_{22}(0) = 1 + \frac{4\phi_L}{\varepsilon} + \frac{3\phi_L(\phi_S/x + \phi_L)}{\varepsilon^2} - \frac{(1+1/x)^2\phi_S\phi_L}{4\varepsilon}\lambda_{SL}.$$

$$S(q)^{-1} = I - C(q) = Q(-q)^T Q(q)$$

[redacted]

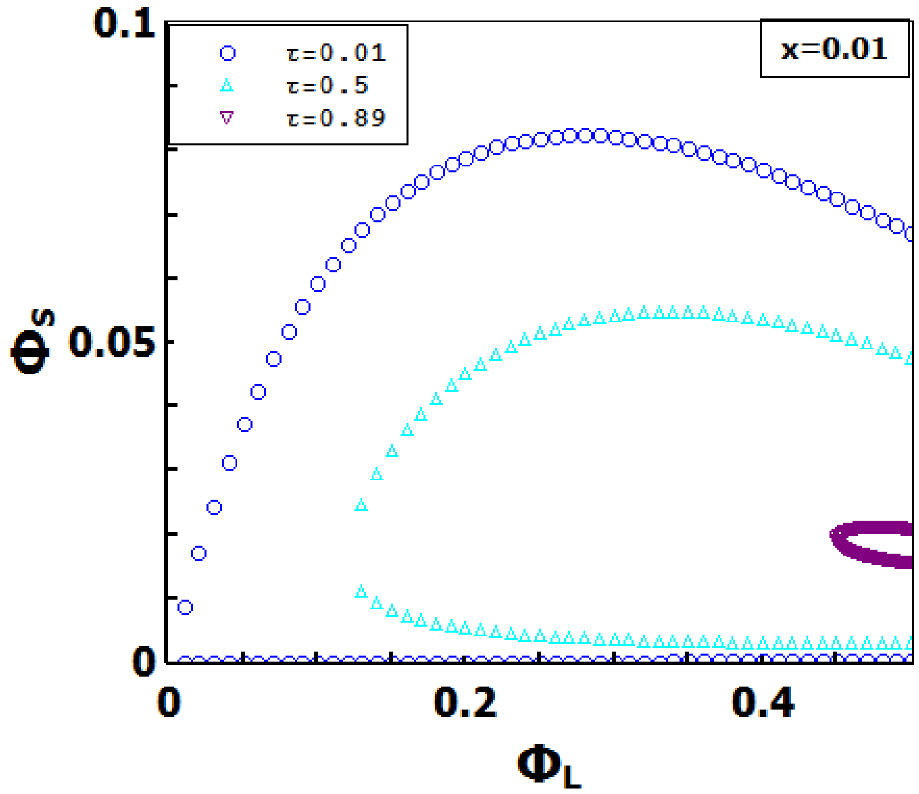
$$|Q(0)| = 0 \xrightarrow{\text{yields}} \lambda_d = \frac{3 + \sqrt{(3+\varepsilon/\phi_s)(3+\varepsilon/\phi_L)}}{\varepsilon(1+x)^2/4x}$$

$$\lambda_d = \lambda_{SL} \xrightarrow{\text{yields}} \boxed{\tau_{SL} = \frac{(1+x)[(1+x)(1-\phi) - \Delta(\phi_S + x\phi_L)]}{4x(1-\phi)(3+\Delta)}}$$

$$\Delta = \sqrt{9 + \frac{\phi(3-2\phi)}{\phi_S\phi_L}}$$

2.4 Spinodal decomposition

Calculations of spinodal decomposition for different stickiness parameters



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3.1 Map to One-Component SHS System

- Three parameters in one-component SHS system:
  stickness parameter τ, diameter d and volume fraction ϕ

- Two parameters to be mapped out:
  effective stickness parameter τ^{eff} and diameter d^{eff}

- The effective volume fraction (equal the number density):
  $$\frac{\phi^{eff}}{\phi} = (\frac{d^{eff}}{d})^3$$

3.2 Effective stickness parameter

- Simply equal the two structure factor at q=0

One-Component SHS system:

$$
\begin{aligned}
Q^{eff}(0) =& 1+\phi_L^{eff}\left[\frac{4-\phi_L^{eff}}{(1-\phi_L^{eff})^2}-\frac{\lambda}{1-\phi_L^{eff}}\right],\\
\lambda =& \frac{6}{\phi_L^{eff}}\Big\{\tau_L^{eff}+\frac{\phi_L^{eff}}{1-\phi_L^{eff}}-\Big[\Big(\tau_L^{eff}+\frac{\phi_L^{eff}}{1-\phi_L^{eff}}\Big)^2\\
&-\frac{\phi_L^{eff}(1+\phi_L^{eff}/2)}{3(1-\phi_L^{eff})^2}\Big]^{1/2}\Big\},\\
S^{eff}(0) =& \frac{1}{(Q^{eff}(0))^2}.
\end{aligned}
$$

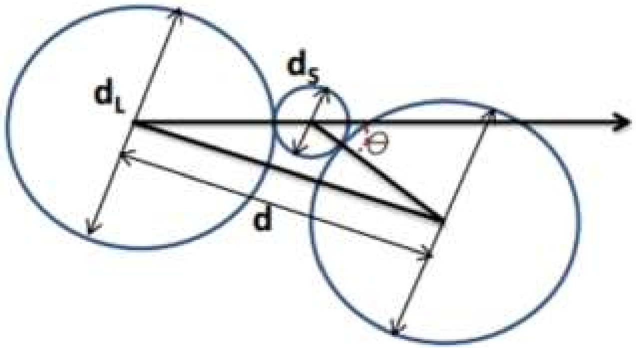
Two-component SHS system:

$$
\begin{aligned}
S_{LL}(0) =& (Q^T(0)Q(0))^{-1}_{22}\\
=& \frac{Q_{11}^2(0)+Q_{21}^2(0)}{Q_{11}(0)Q_{22}(0)-Q_{12}(0)Q_{21}(0)}
\end{aligned}
$$

$$S^{eff}(0) = S_{LL}(0)$$

$$
\boxed{
\begin{aligned}
\tau_L^{eff} =& \Big[\frac{(1-\phi_L^{eff})^2}{36}S_{LL}(0)+\frac{4\phi_L^{eff}-1}{18}\sqrt{S_{LL}(0)}\\
&-\frac{14(\phi_L^{eff})^2-4\phi_L^{eff}-1}{36(1-\phi_L^{eff})^2}\Big]\\
&/\Big[\frac{2\phi_L^{eff}+1}{3(1-\phi_L^{eff})}-\frac{1-\phi_L^{eff}}{3}\sqrt{S_{LL}(0)}\Big]
\end{aligned}
}
$$

3.3 Effective diameter



$$d_L^{eff} = \frac{\int_0^{\theta_{max}} d(\theta) P(\theta)}{\int_0^{\theta_{max}} P(\theta)}$$

$$d(\theta) = (d_S + d_L)\cos(\frac{\theta}{2}) = (1+x) d_L \cos(\frac{\theta}{2})$$

Isotropical Assumption:

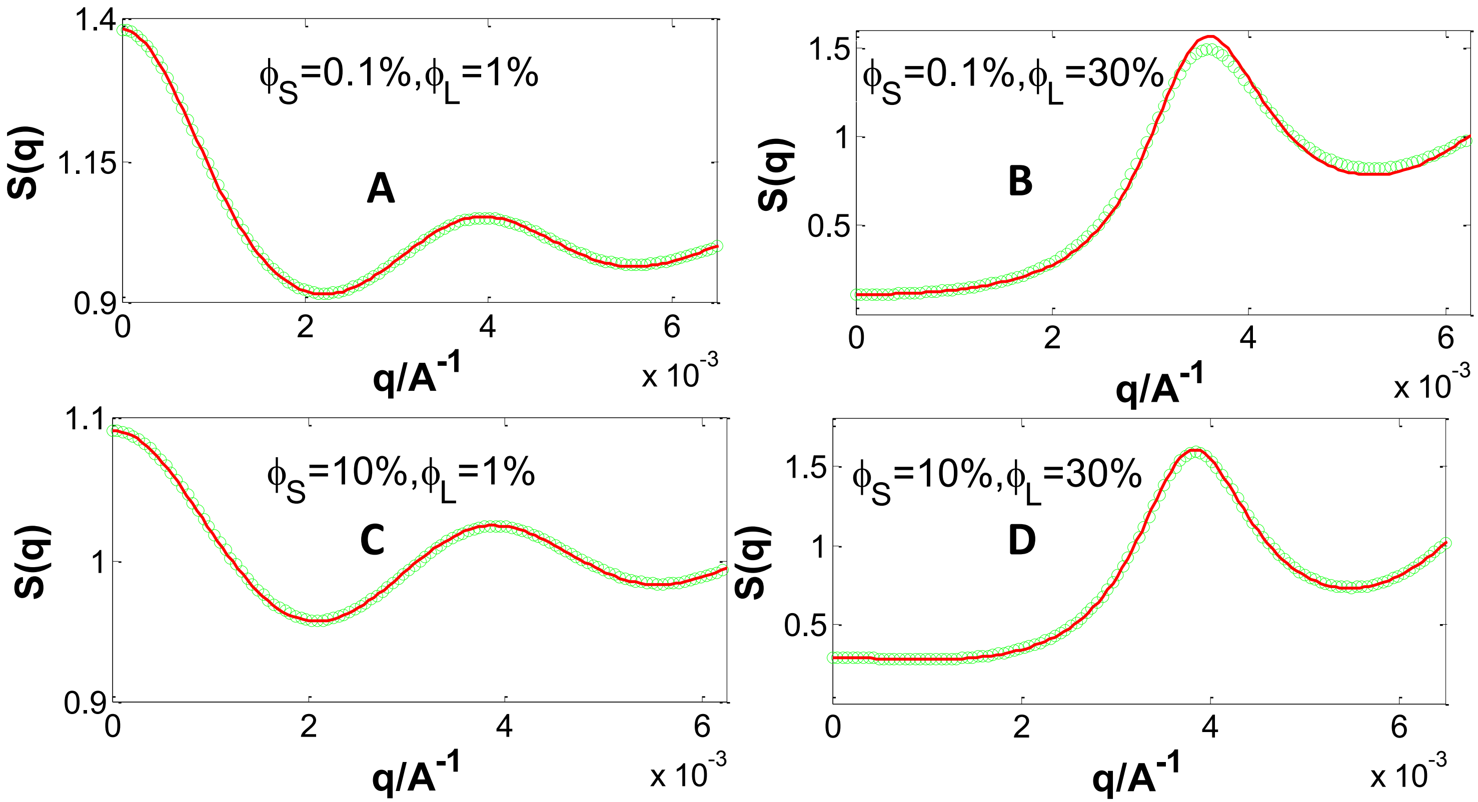
$$P(\theta) \propto 2\pi R_L \sin\theta \times R_L d\theta \propto \sin\theta d\theta$$

Hard Core Limitation:

$$\cos(\frac{\theta_{max}}{2}) = \frac{1}{1+x}$$

$$\boxed{\frac{d_L^{eff}}{d_L} = \frac{2}{3}(1 + x + \frac{1}{2+x}) \qquad \frac{\phi_L^{eff}}{\phi_L} = (\frac{d_L^{eff}}{d_L})^3}$$

3.4 Mapping results



- $d_S = 260Å, d_L = 1800Å, x = {}^{d_S}/_{d_L} = 0.1444, \tau_{SL} = 0.012$
- $d^{eff} = 1932.8Å$
- (A)$\tau^{eff} = 0.0686, \phi^{eff} = 0.0124$;(B)$\tau^{eff} = 0.7472, \phi^{eff} = 0.3715$;
  (C)$\tau^{eff} = 0.1335, \phi^{eff} = 0.0124$;(D)$\tau^{eff} = 0.2378, \phi^{eff} = 0.3715$;

2.4 Tips of the map method

- All the calculations are analytical, not any fitting;
- The "size" of big particle has changed;
- We just use one point in the structure factor (S(0)) and the results agree all the structure factor curve very well.

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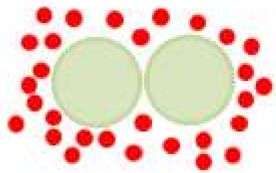
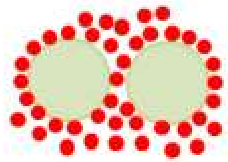
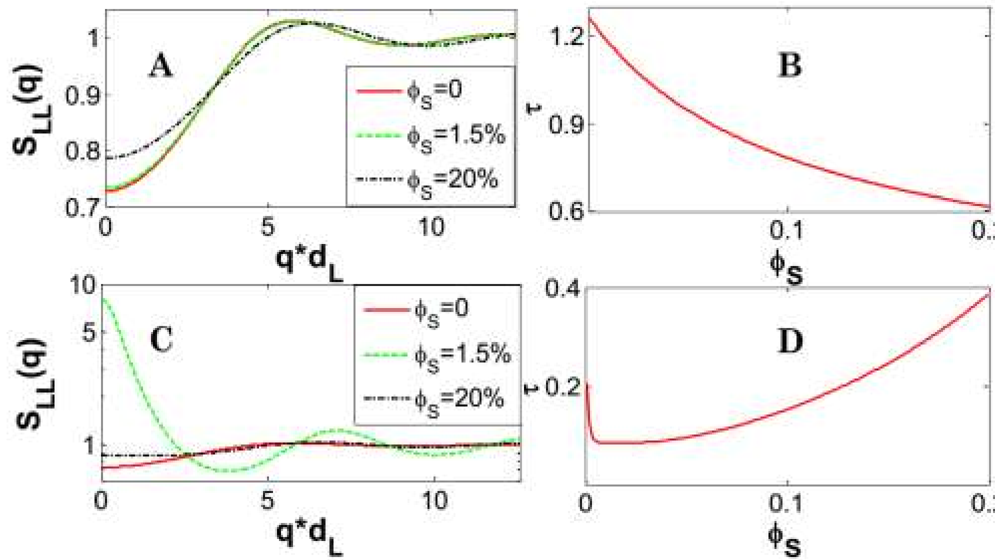
4.1 From depletion attraction to bridge attraction

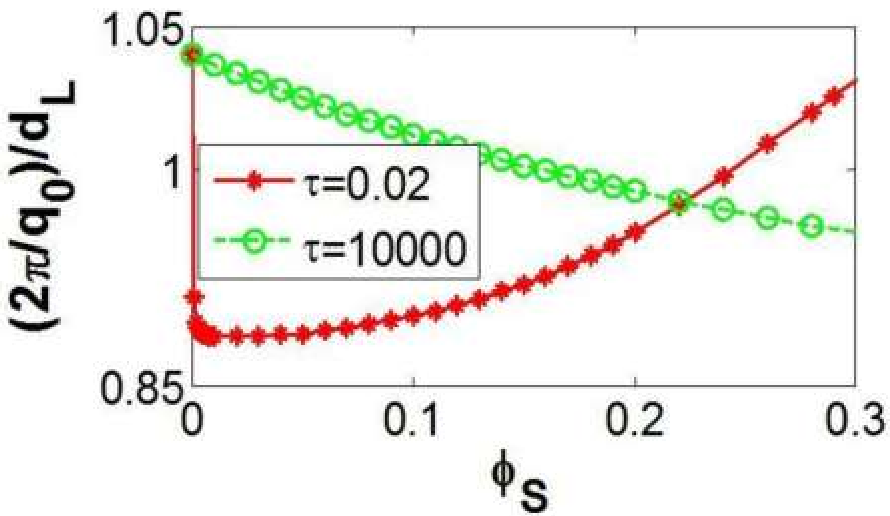
- Depletion attraction



- Bridge attraction

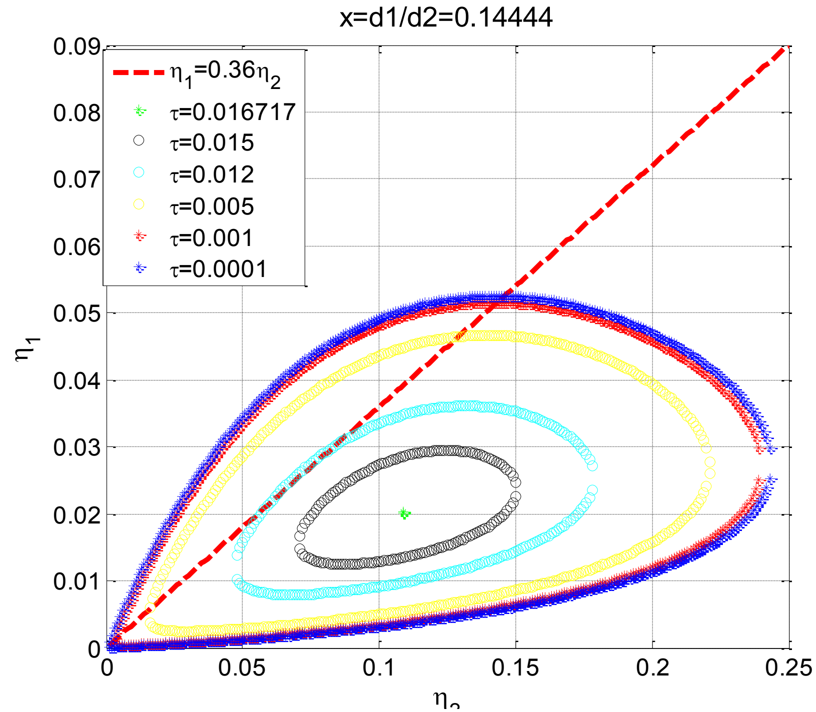






- $x = 0.1444$
- volume fraction of big particles is 4%.
- (A) and (B) are with the same attraction strength (τ_{SL} = 10000, introducing depletion attraction) between small and big particles, while it's 0.02 (introducing bridge attraction) for (C) and (D).

4.2 Spinodal Decomposition



- Spinodal decomposition lines for systems with different attraction strength between small and big particles (the legend).
- Size ratio is $x = 0.1444$,;
- Red dashed line: **the volume fraction of small particles need to cover the surface of big particles** from experiment;
- Green star: the critical "temperature", above which the system will never show spinodal decomposition phenomenon.
- So for the system we study later, we choose the attraction parameter $\tau_{SL} = 0.012$

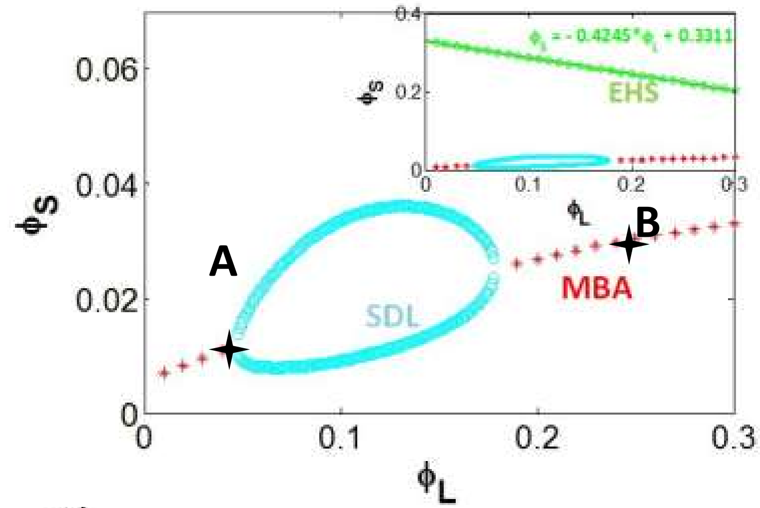
4.3 Comparison results

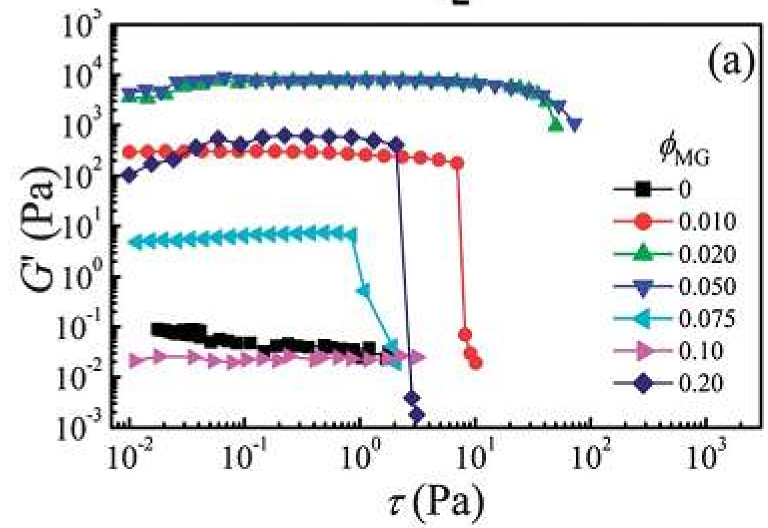
➢Consistent

- **The gelation with addition of polymers at low concentration**
- **The critical volume fraction at 0.05 (A);**
- **The gelation at $\phi_{MS} = 0.25$ (B)**

➢Inconsistent

- Re-entrance to gelation with even more polystyrene
- Gelation for high volume fraction of colloidal particles





Storage modulus of the mixed suspension as a function of applied stress with $\phi_{MS} = 0.25$, gelation between 2%-5%

C.Z.Zhao et.al, *Soft Matter* **8**, 7036(2012)

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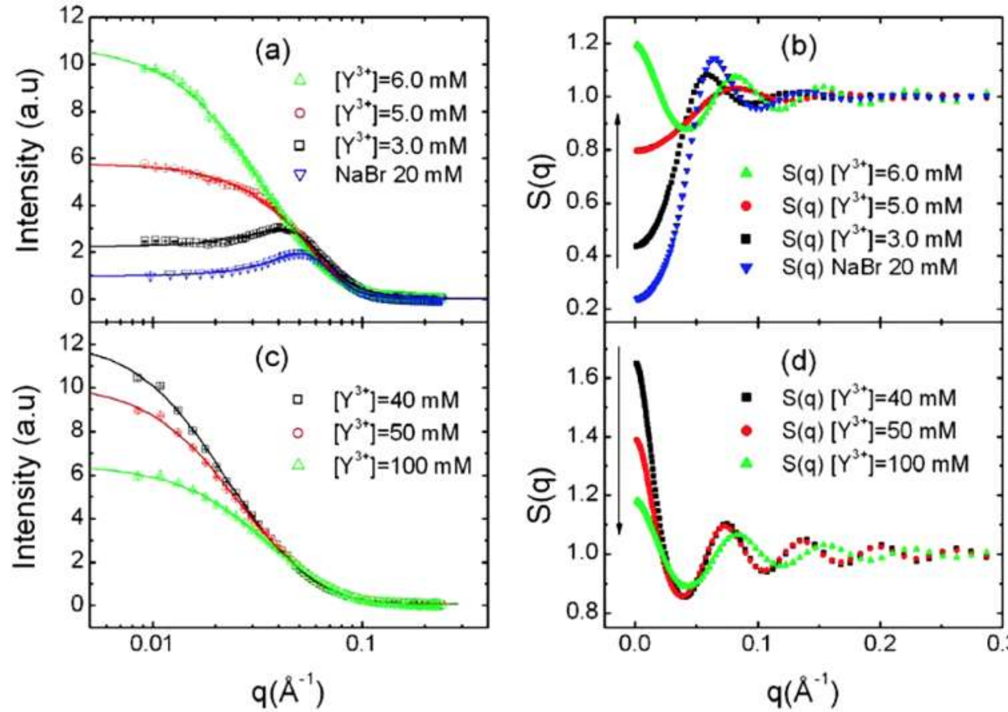
5.1 SANS Experimental Study of BSA +YCl_3

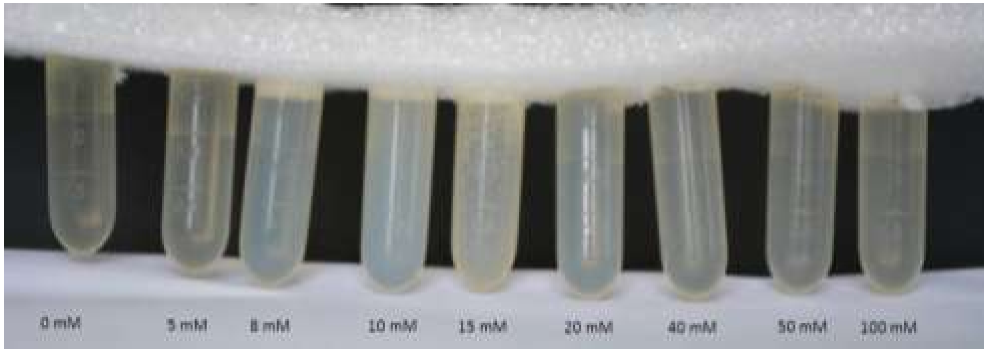
Bovine Serum Albumin(BSA)+Yttrium Chloride(YCl_3)



Zhang, F., et al. *Phys.Rev.Lett*. **101**, 148101(2008)

5.2 Samples Preparations

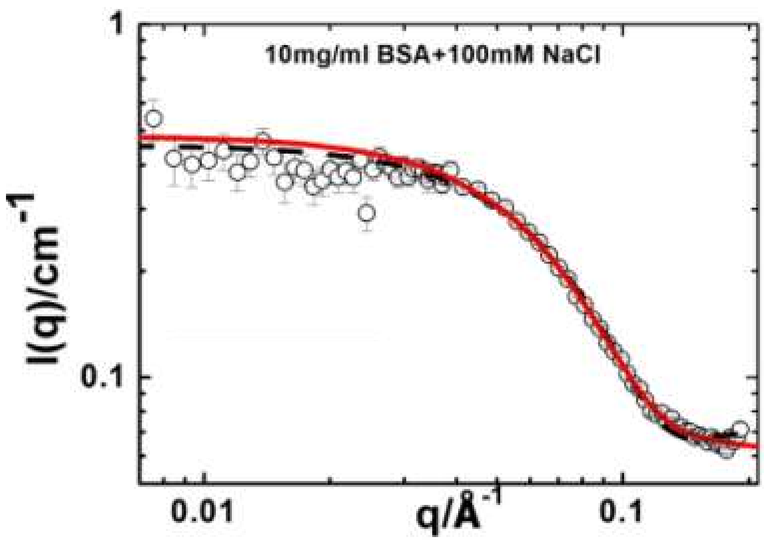
Samples prepared



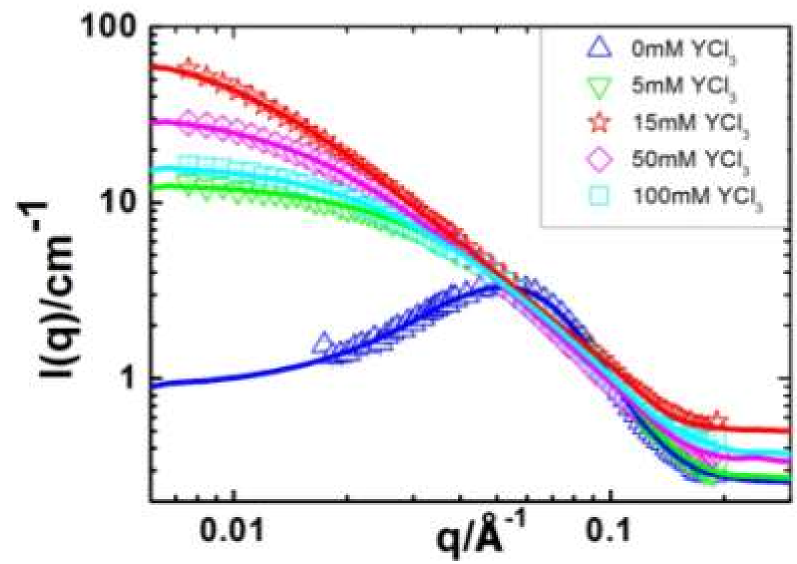
Sample #	BSA（mg/ml）	YCl_3（mM）	NaCl（mM）	**Thickness**（mm）
1	10	0	100	2
2	100	0		1
3	100	3		1
4	100	5		1
5	100	8		1
6	100	15		1
7	100	20		1
8	100	40		1
9	100	50		1
10	100	100		1
11	0	100		1

5.3 Experimental Results

BSA Form Factor



BSA +YCl_3



5.4 Fitting Parameters

c_S	$\phi_S(\%)$	$\phi_L(\%)$	$r_L(\text{Å})$	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$\rho_L(\text{Å}^{-2})$	τ_{SL}
3	0.0396	6.49	29.7	18.8	35.3	41.2	3.67E-6	0.0129
5	0.0412	8.05	28.4	18.1	36.3	39.9	3.21E-6	0.0129
8	0.0775	6.88	28.4	19.8	33.8	38.1	3.18E-6	0.0129
15	0.0733	4.21	28.1	19.7	31.5	38.8	2.14E-6	0.0129
20	0.154	7.03	28.9	23.3	36.2	39.4	2.98E-6	0.0129
40	0.215	8.09	27.2	23.0	36.0	36.9	2.48E-6	0.0129
50	0.231	8.09	27.1	22.8	34.0	38.9	2.10E-6	0.0129
100	0.412	9.41	25.0	23.0	32.3	35.6	1.56E-6	0.0129

Outline

- ❑Introduction
- ❑Model description
- ❑Mapping Method
- ❑Comparison between theory and experiment
- ❑SANS experiments verification
- ❑**Conclusions**

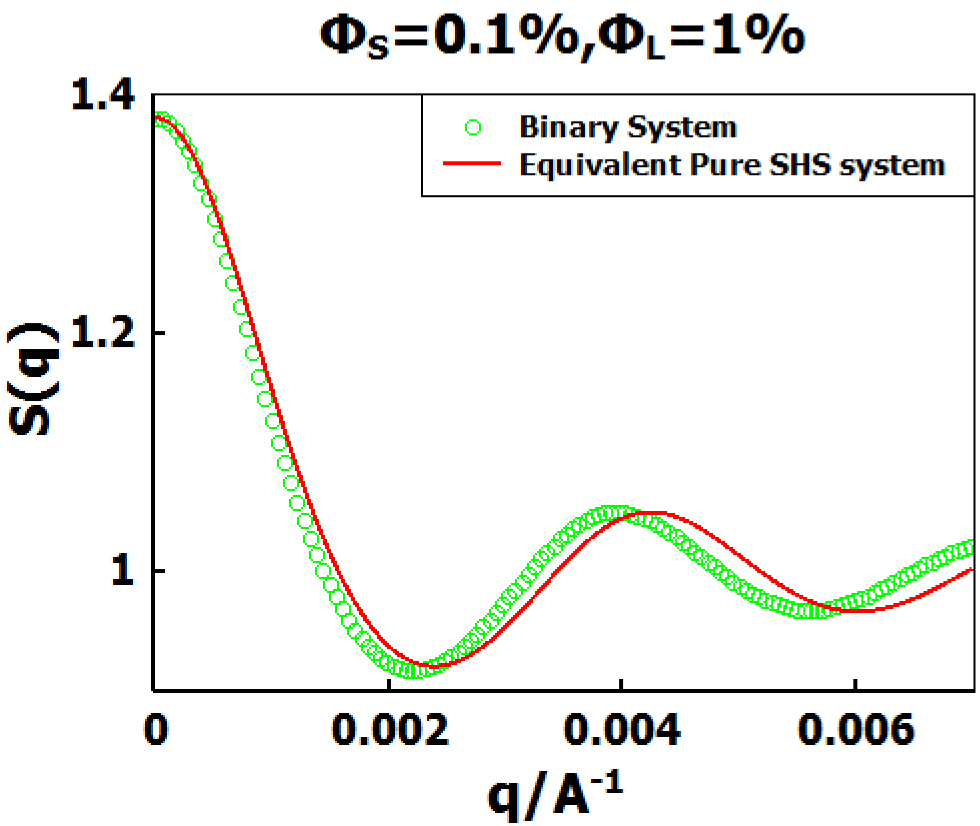
5 Conclusions

- Depletion attraction and bridge attraction are exactly two different mechanisms which will lead to different system characters;
- The two-component SHS system we study can be analytically mapped to pure SHS system;
- The phase diagram of this bridge attraction dominated system can be theoretically determined and can be used to verify the experiment .

Thanks for your attention!

S Effective diameter

- Simply take $d_L^{eff} = d_L$,so $\phi_L^{eff} = \phi_L$



- Peak shifts to left → increase inter-particle distance

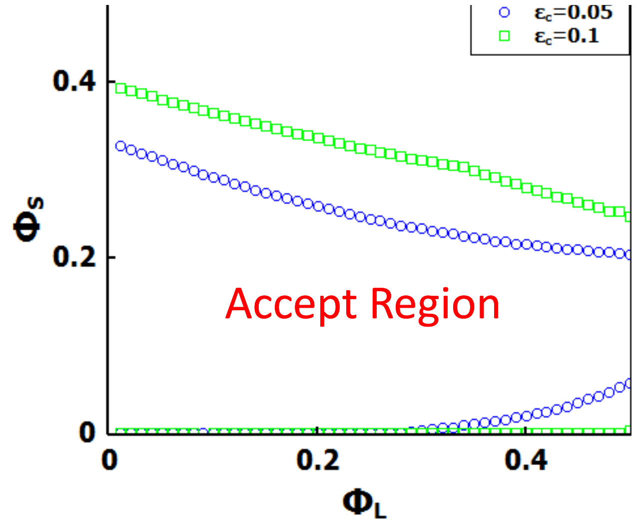
S1 Effective Map Range

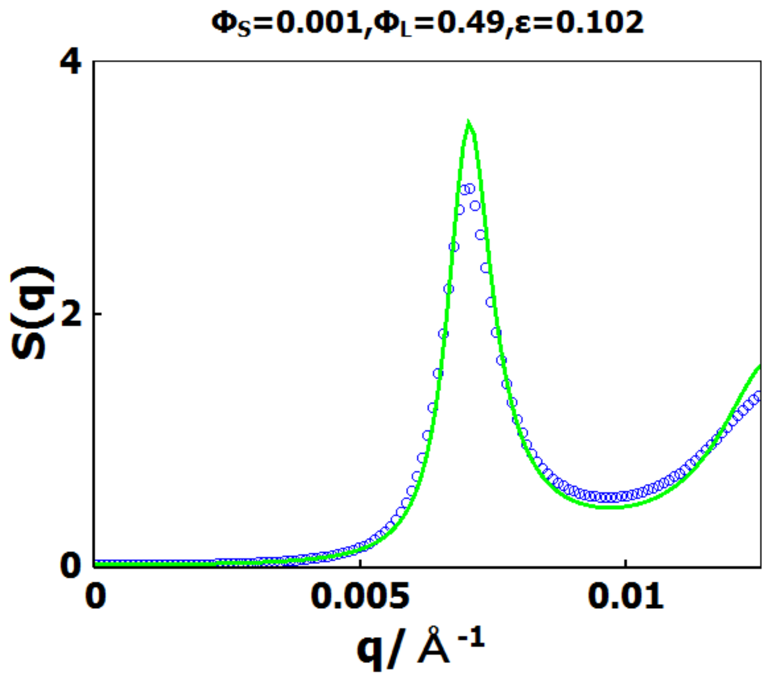
Define the error function:

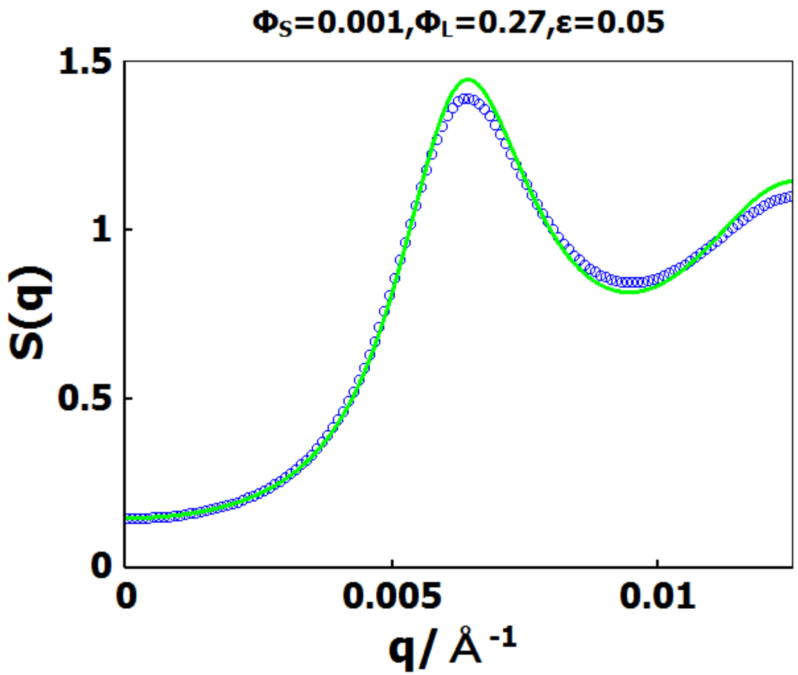
$$\varepsilon = \frac{\int_0^{4\pi} |\Delta S(qd)| d(qd)}{\int_0^{4\pi} |S_0(qd) - 1| d(qd)}$$

S1 Effective Map Range

x=0.1444,τ=0.0148

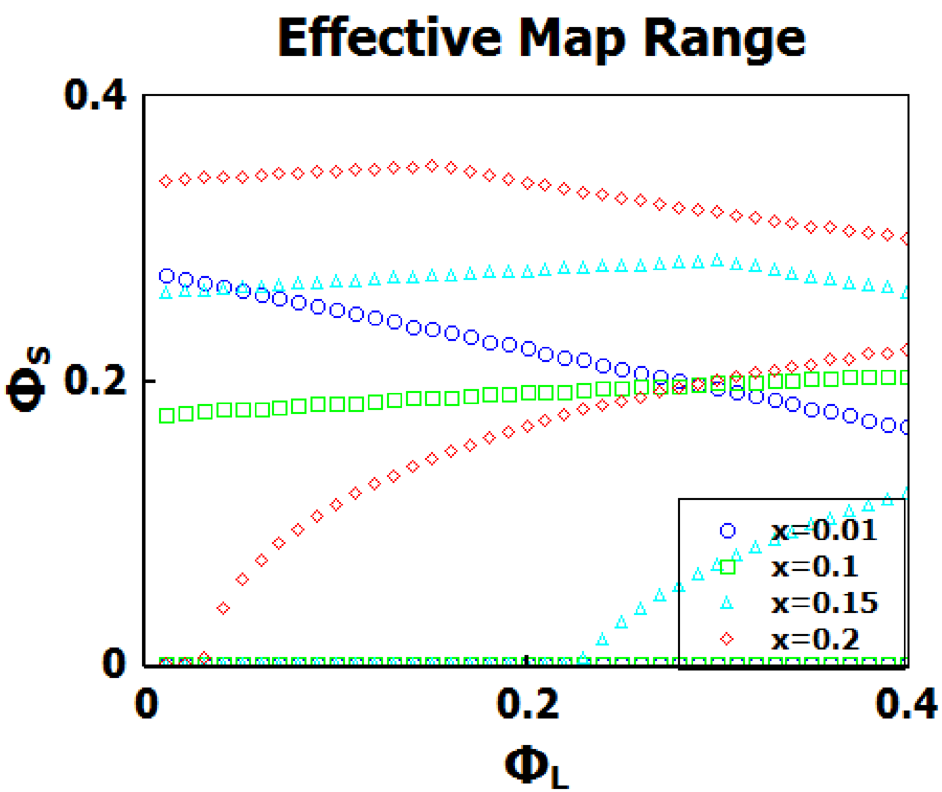


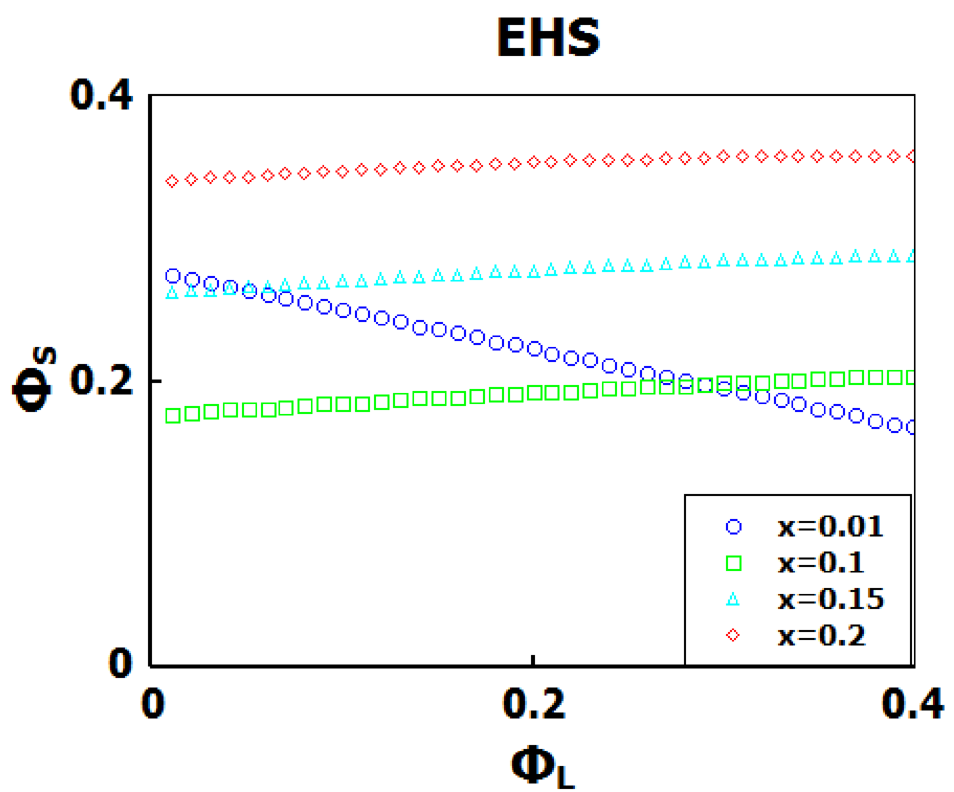




S1 Effective Map Range

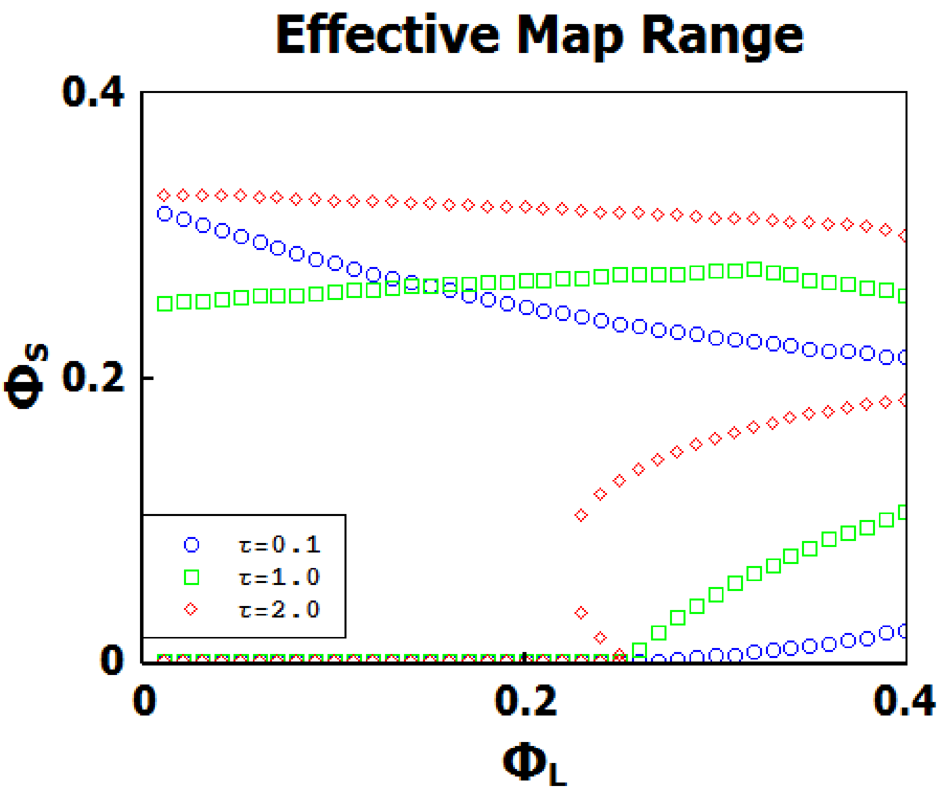
$\epsilon_c = 0.05, \tau = 1 \rightarrow B_2{}^* = 0.75$

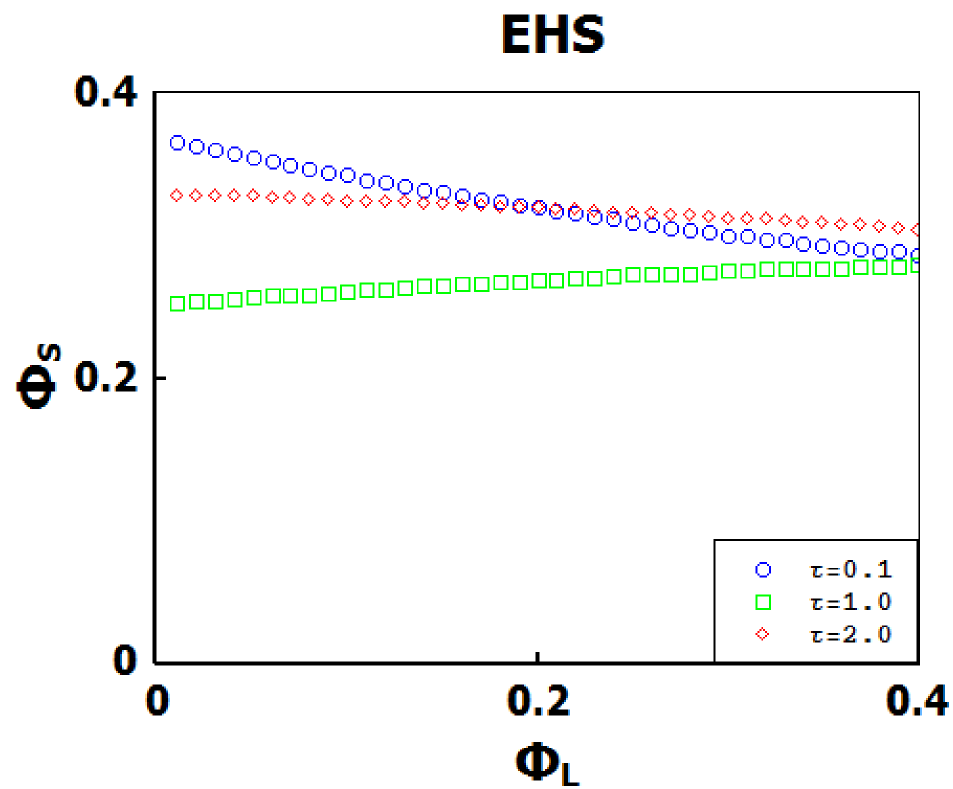




S1 Effective Map Range

$\epsilon_c = 0.05, x = 0.1444$





S1 Effective Map Range-Conclusions

- The method works well for x<0.15;
- For the experimental system (x=0.1444), this method works well even for $\tau = 2(B_2^* = 0.875)$, which means there is almost no attraction between big and small particles;
- The method works better for bigger size difference and stronger attraction;
- Recall that all the results in this method are analytical calculation, not any fitting.