Small Angle Neutron Scattering Study of Reversible Aggregation of Colloidal Particles In a Near Critical Binary Mixture

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NCNR SHIP Symposium

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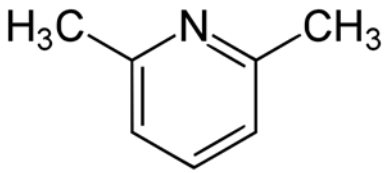
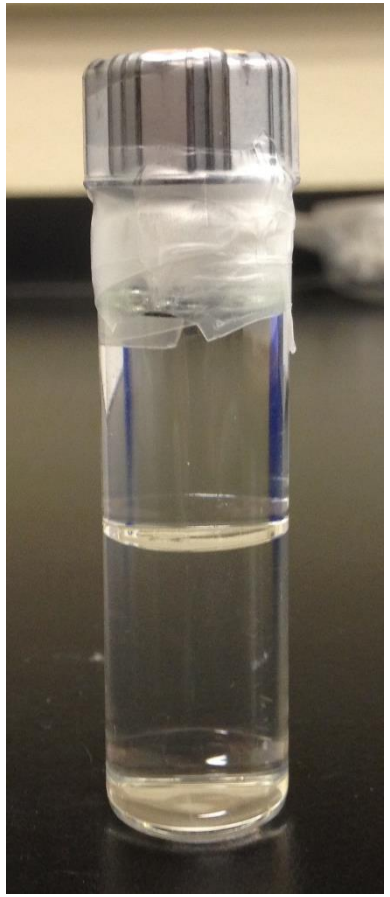
Solvent

- Lutidine (C_7H_9N) and water



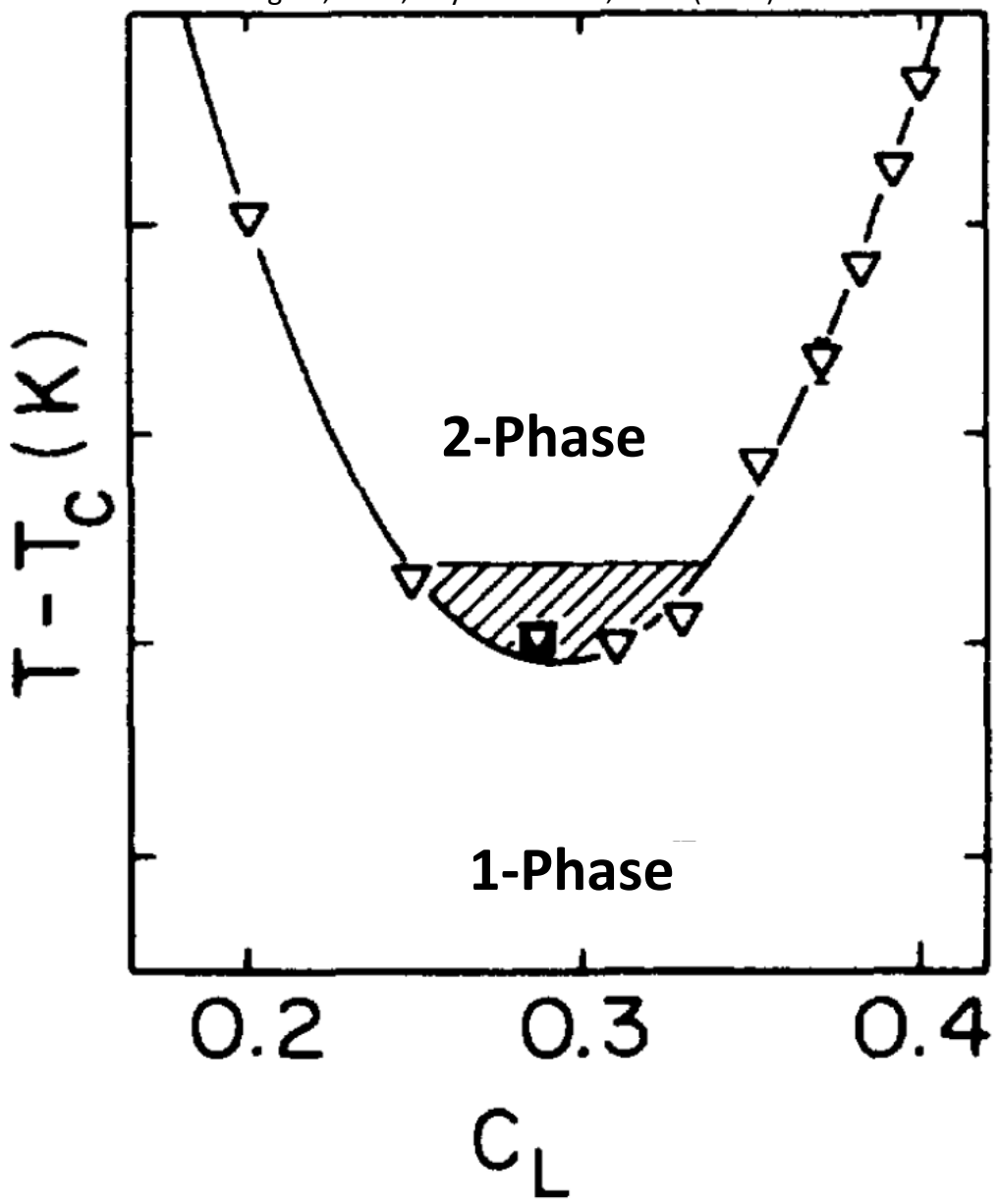
- Lower critical point at

~33.6^{o}C and 29%wt lutdine

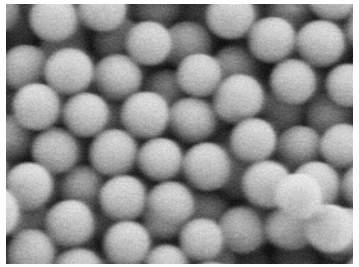


29%wt lutidne/water
Phase Separated

P. D. Gallagher, et al., Phys. Rev. A **46**, 7750 (1992)



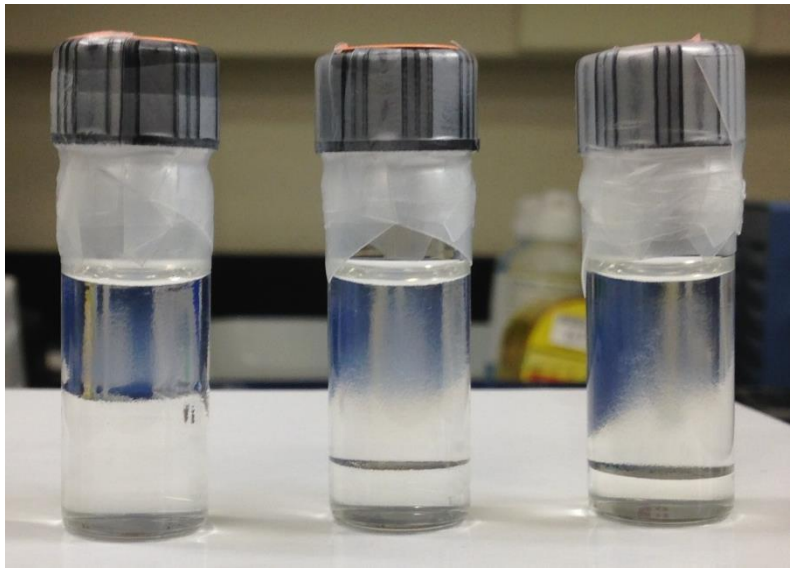
Solvent + Colloidal Particles



- Silica (SiO_2) nanoparticles
- Diameter ~ 30nm
- Exhibit reversible aggregation while approaching the coexistence curve from below

From Left to Right:

1. 25%wt lutidine/water and 3%vf Silica
2. 29%wt lutidine/water and 3%vf Silica
3. 33%wt lutidine/water and 3%vf Silica



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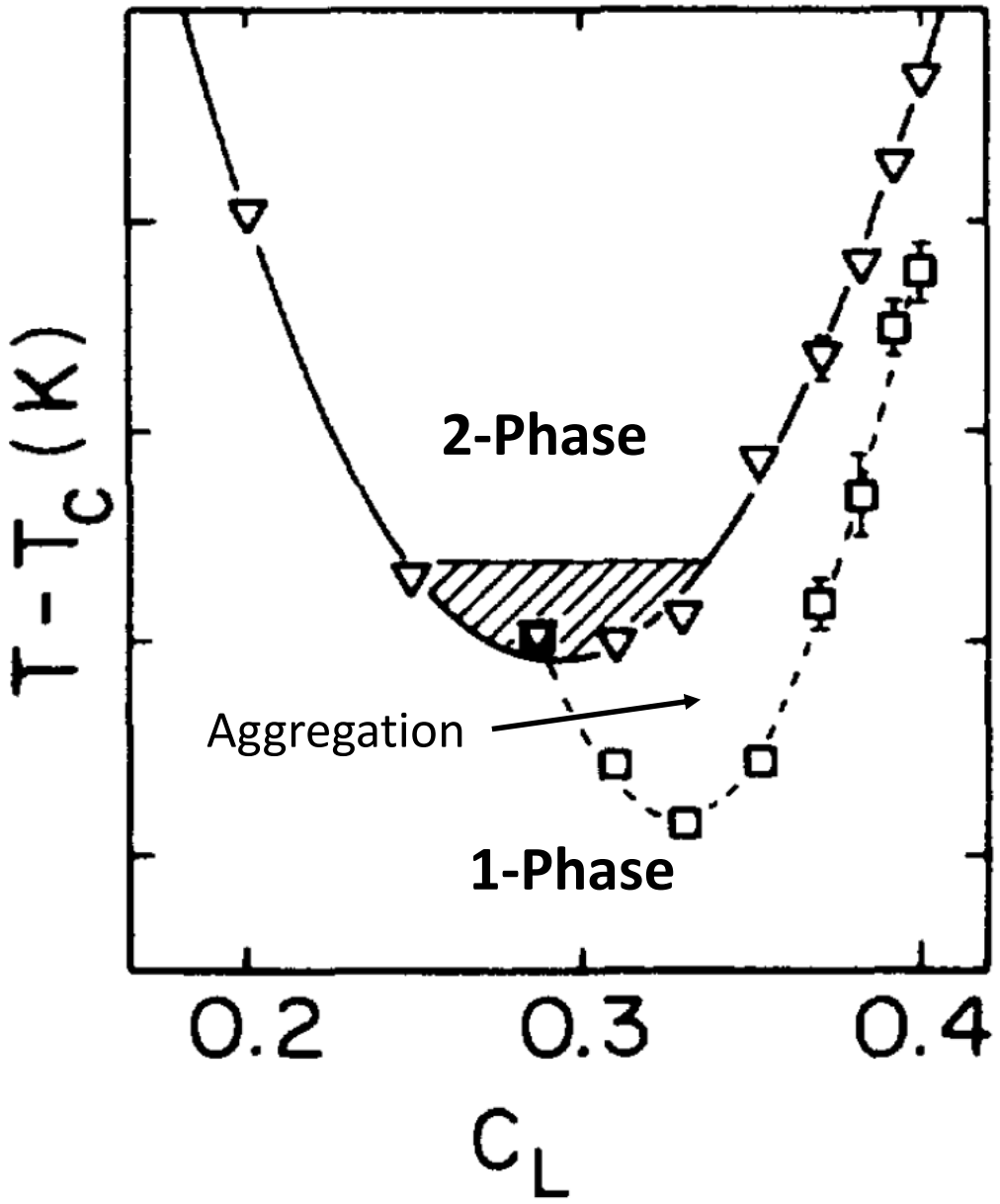
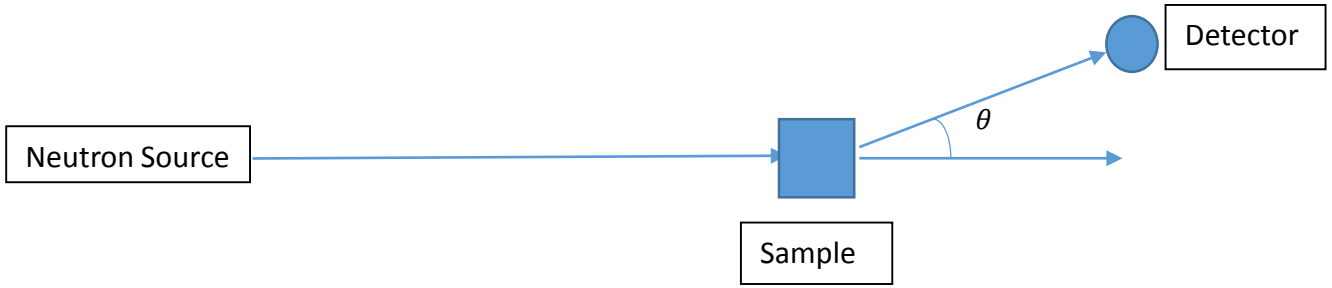


Question?

- What is the nature of the interactions between these colloidal particles as the temperature of aggregation is approached?

Small Angle Neutron Scattering (SANS)



- Scattering vector: $Q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$
- $Q \sim \frac{1}{\text{Length scale probed}}$

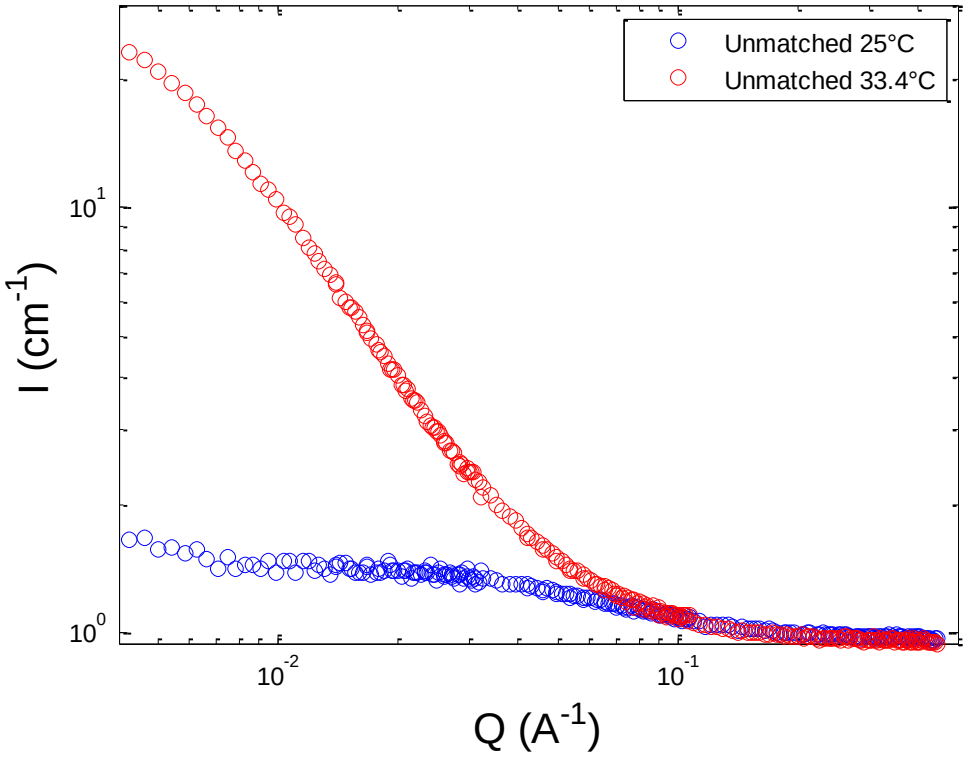
- Measured the scattering intensity:

$$I(Q) = (\hat{\rho}_{\mathrm{L}} - \hat{\rho}_{\mathrm{w}})^{2} S_{\mathrm{solvent}}(Q) + (\hat{\rho}_{\mathrm{sol}} - \hat{\rho}_{\mathrm{SiO_2}})^{2} S_{\mathrm{particle}}(Q)$$

- $\hat{\rho}$ = Scattering length density (a material property)

Contrast Match Point

- Solvent's scattering increases near the phase separation temperature
- Only want to see silica particle scattering
- Use D_2O in addition to H_2O to contrast match Lutidine
- $\widehat{\boldsymbol{\rho}}_{\boldsymbol{L}} - \widehat{\boldsymbol{\rho}}_{\boldsymbol{w}} = \mathbf{0}$
- Need ~73%wt H_2O in "water"



- Must also adjust %wt Lutdine to keep volume ratios the same
- Addition of D_2O will lower critical, phase separation, and aggregation temperatures

Experiment

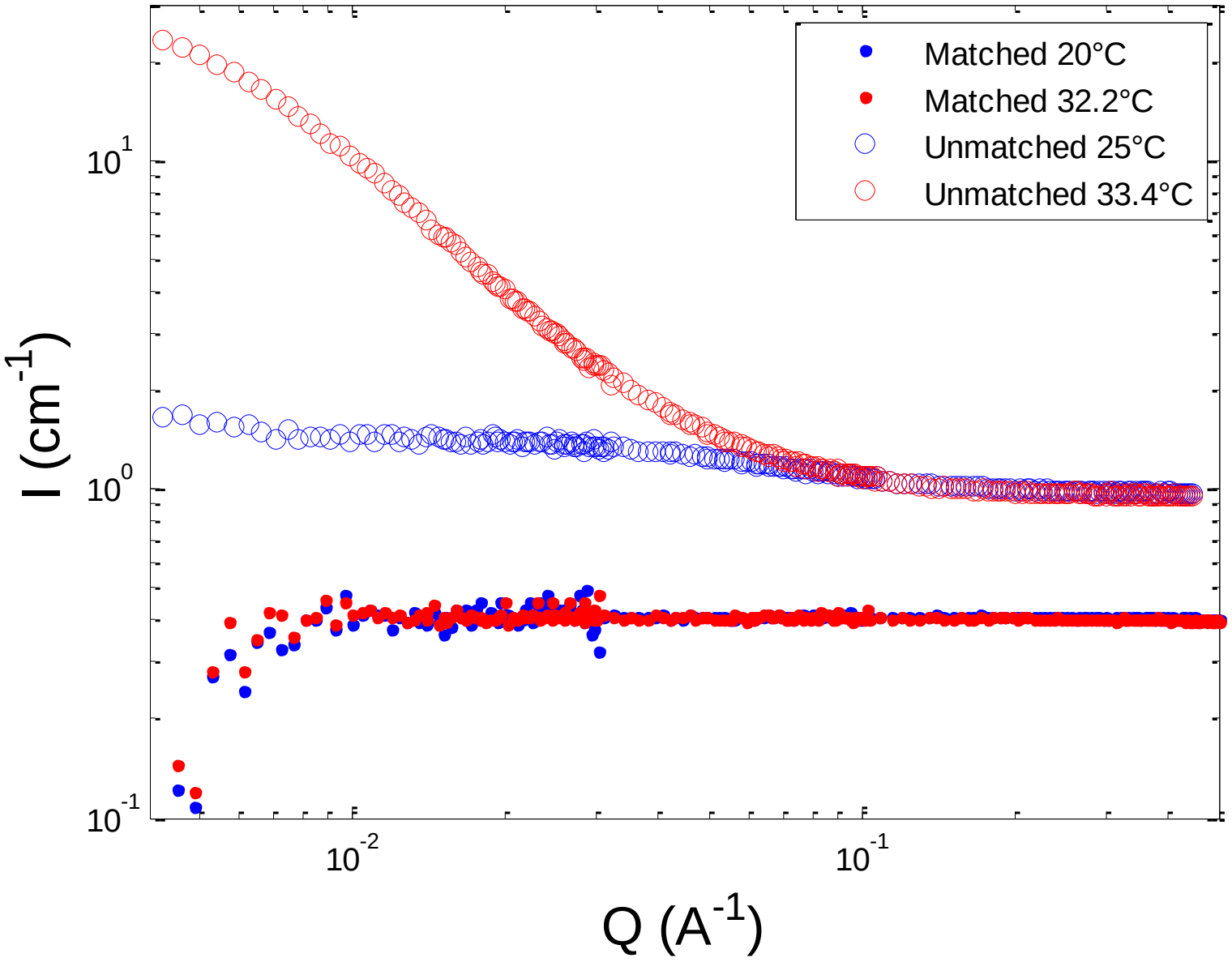
- Prepared multiple contrast matched samples at silica volume fractions ranging from 0%-5% and at 25%wt, 29%wt and 33%wt lutidine

- Made SANS measurements at temperatures between 15^{o}C and 33^{o}C

- Made Dynamic Light Scattering (DLS) measurements on the same samples and at the same temperatures in order to construct a phase diagram and provide comparative data

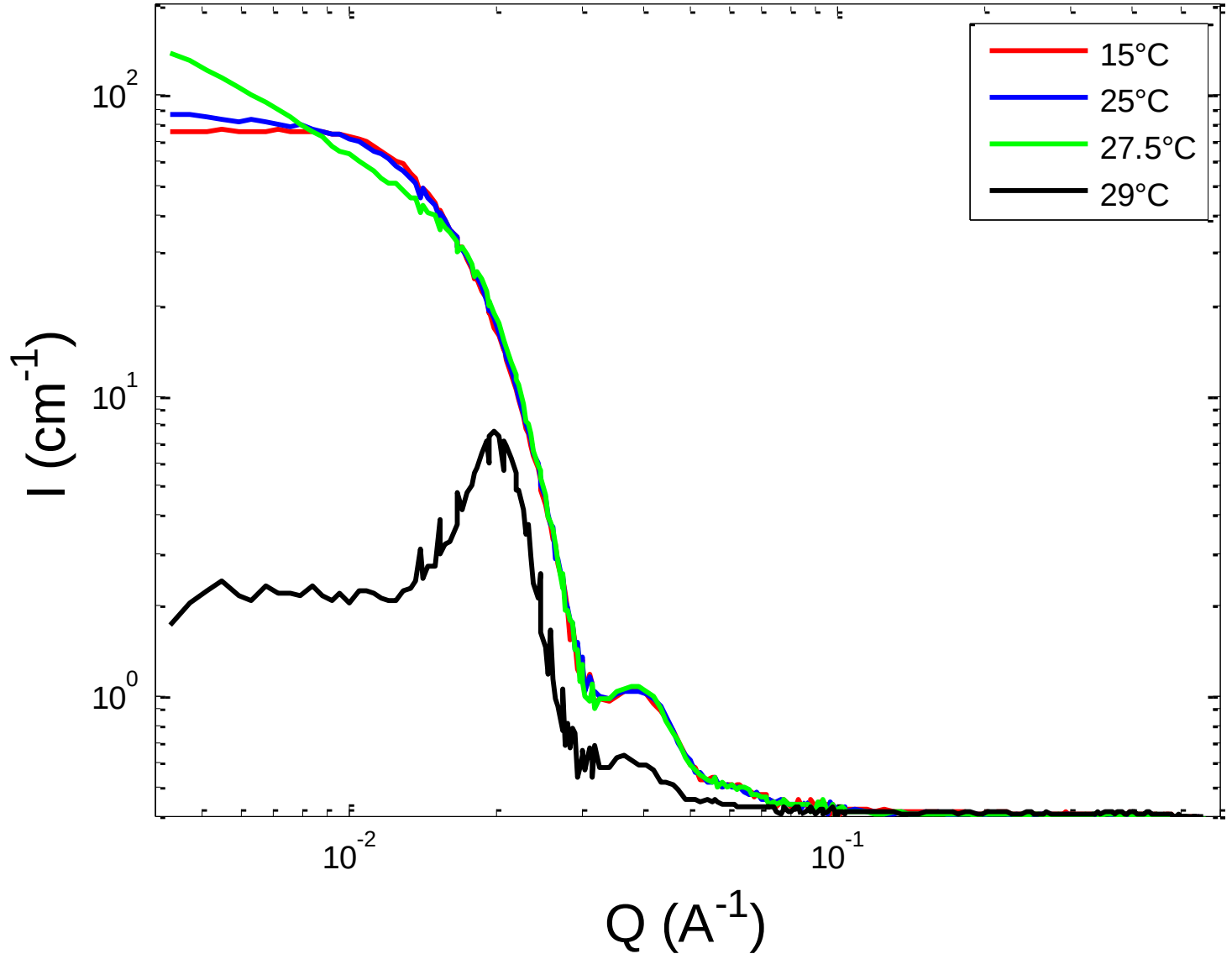
Matched Solvent

- Insignificant scattering in matched sample
- Scattering in samples will be due to the silica particles only



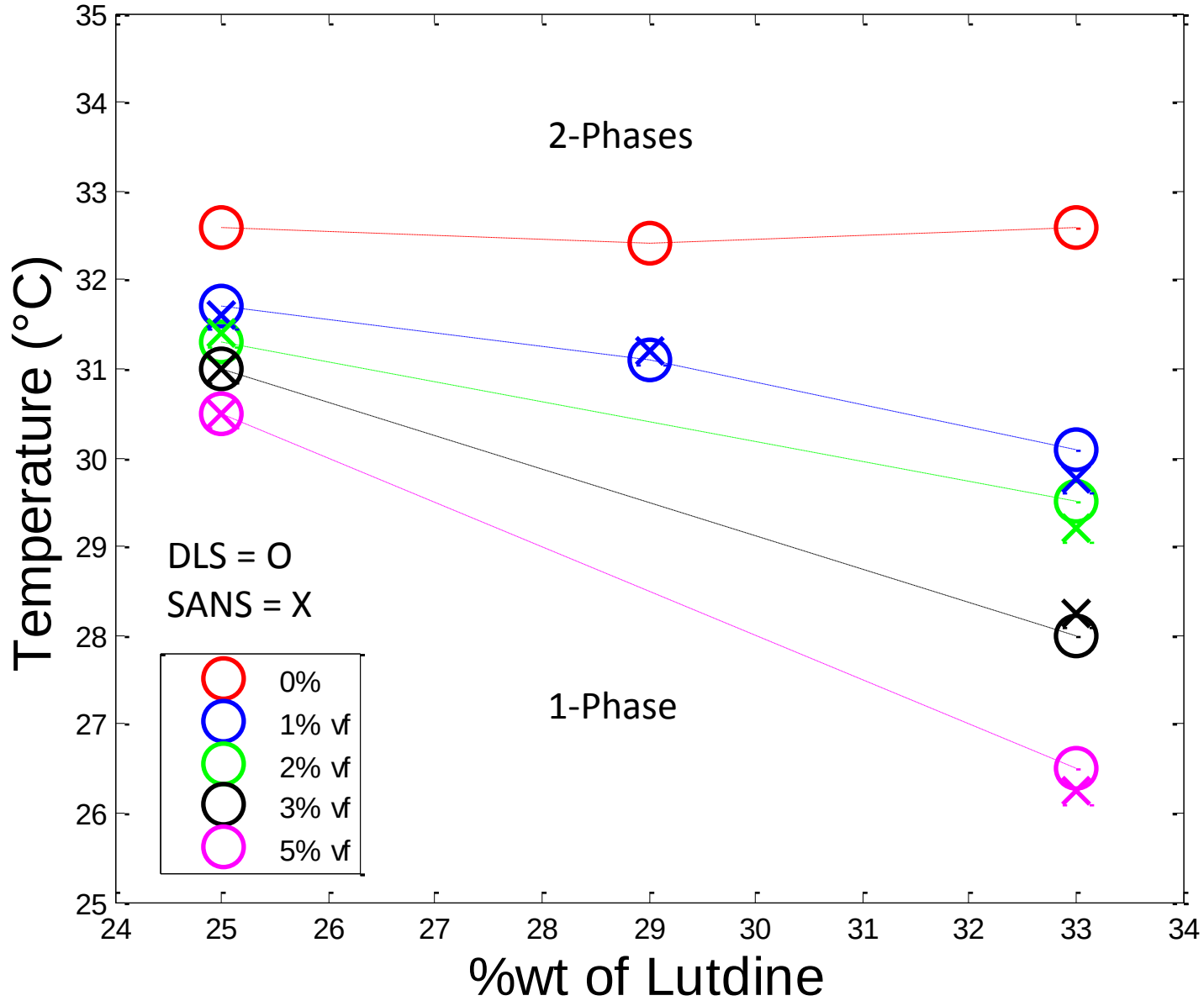
Matched Solvent with SiO_2 Particles

- Upturn at low Q as temperature increases
- After phase separation (29^{o}C), there is a large change in the scattering intensity



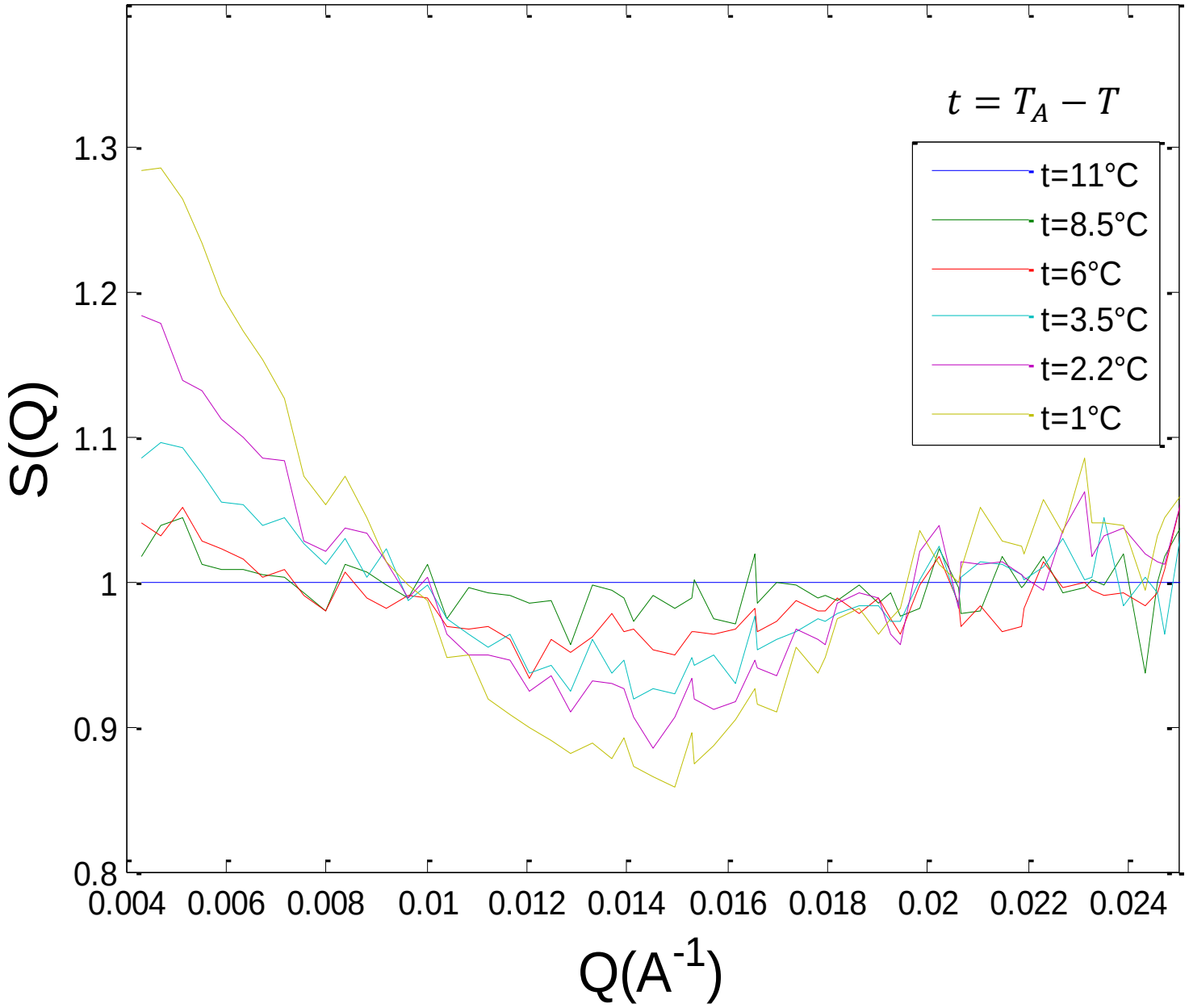
Phase Diagram

- Phase separation temperature decreases with increase in volume fraction
- Phase separation temperature decreases more significantly at higher lutidine concentrations
- DLS data correlates well with the SANS data



Structure Factor

- Increase in strength of attractive interactions with increase in temperature towards T_A



Conclusions

- Contrast matching works
- Clear change in SANS intensity data after the phase separation temperature has been reached
- The strength of the attractive interactions between particles increases as temperature increases towards phase separation
- These data help explain why the particles are aggregating

Acknowledgements:

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Questions?