

Investigation of Stability of Silica Particles in Lutidine/Water Solvent

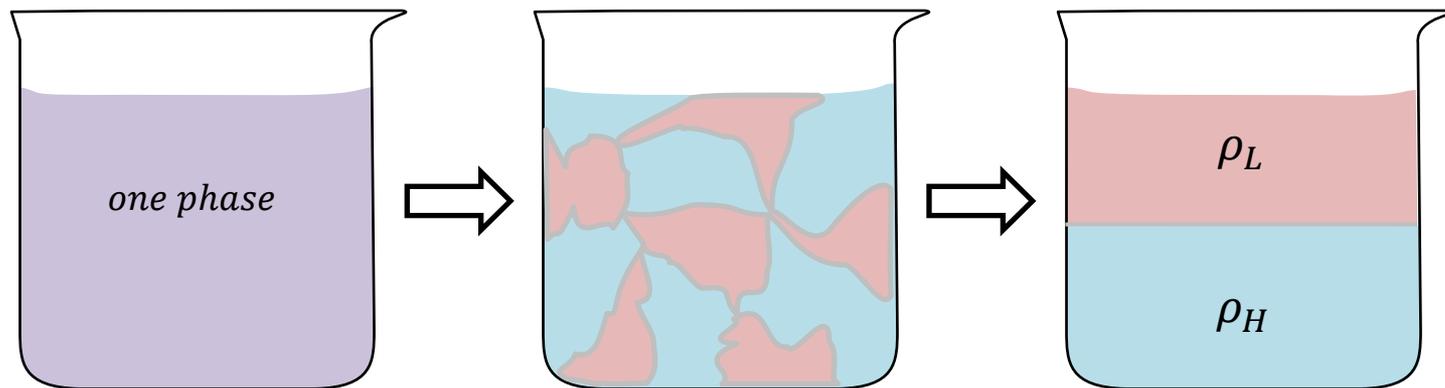
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Density Fluctuations in a Binary Solution

- A binary liquid approaching its binodal temperature will gradually separate into regions of constituent substances that have fluctuating size and shape.
- This results in density fluctuations within the system.

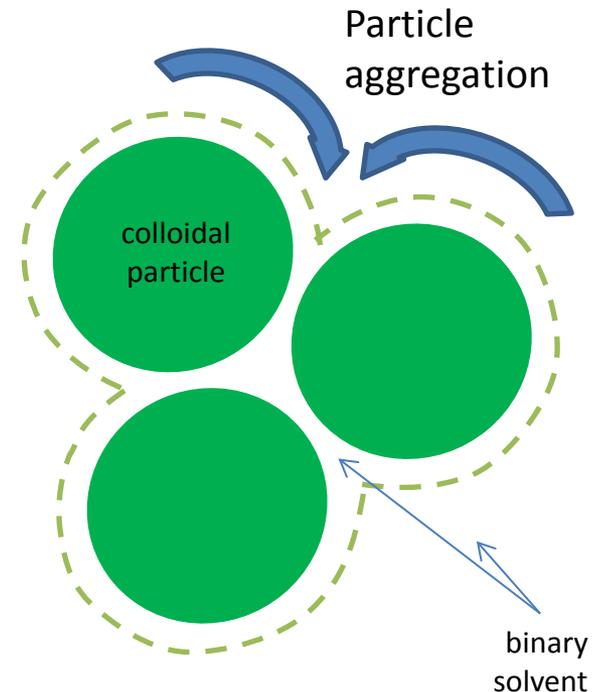


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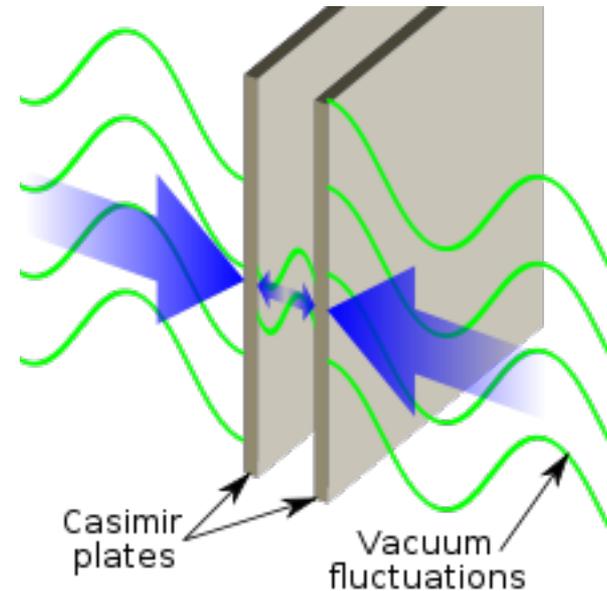
Critical Casimir Force on Colloidal Systems

- Near the system's binodal temperature, critical Casimir force affects the interaction between colloidal particles, forming a "structure."
- The interaction is predicted to be based on density fluctuations in the binary solvent near the binodal temperature. This affects the interaction and solution stability.
- Far from the binodal temperature the critical Casimir force should be negligible.
- Thus, the critical Casimir force is the attractive force between colloidal particles induced by density fluctuations in the solvent



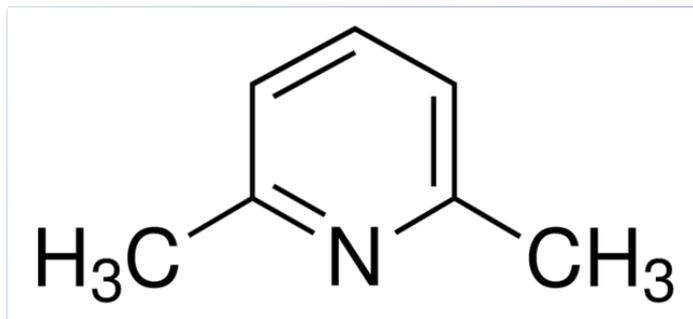
Critical Casimir Force is Different from the Casimir Effect

- The Casimir Effect is a small attractive force acting between two “close” parallel uncharged conducting plates in vacuum due to quantum vacuum fluctuations.
- The distance between the plates is smaller than the correlation length of vacuum fluctuations, so there is attraction between the plates.



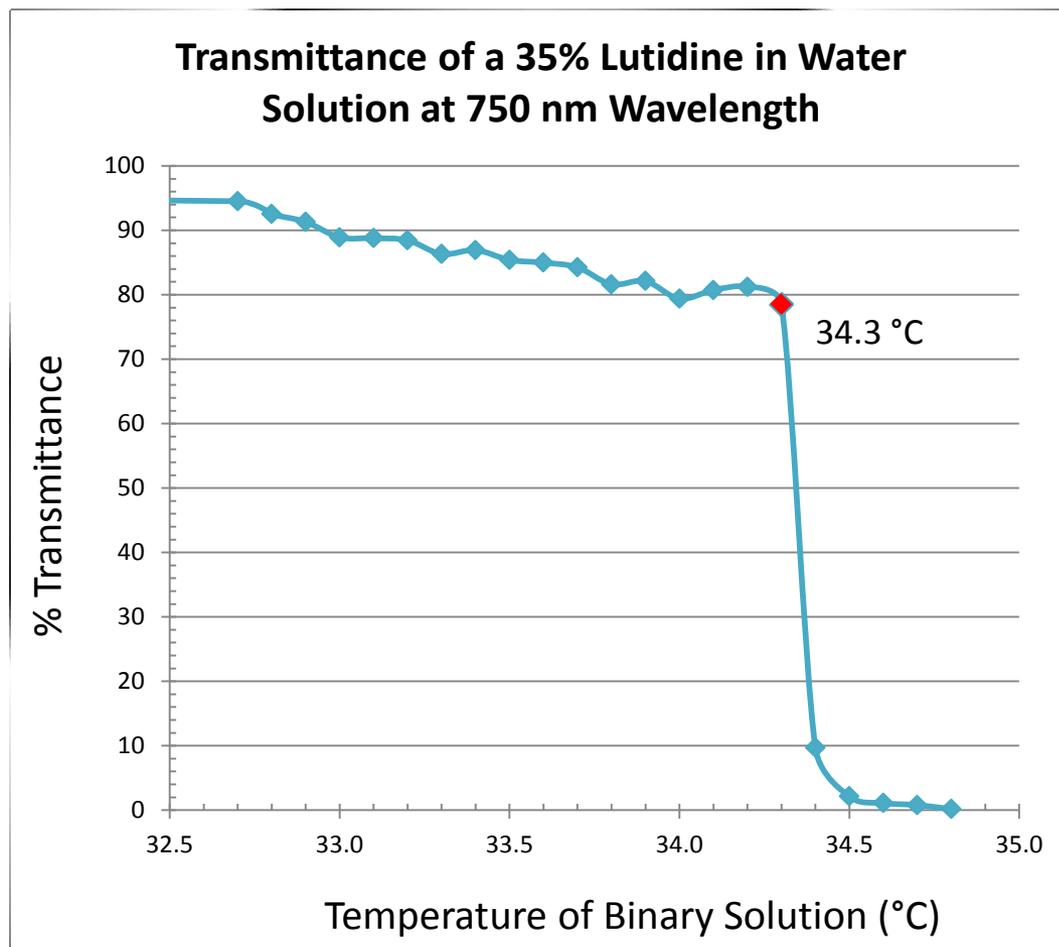
Use of Lutidine/Water Binary Solution

- Lutidine has $\rho = 0.92 \text{ g/cm}^3$
- Lutidine is chemically stable in water.

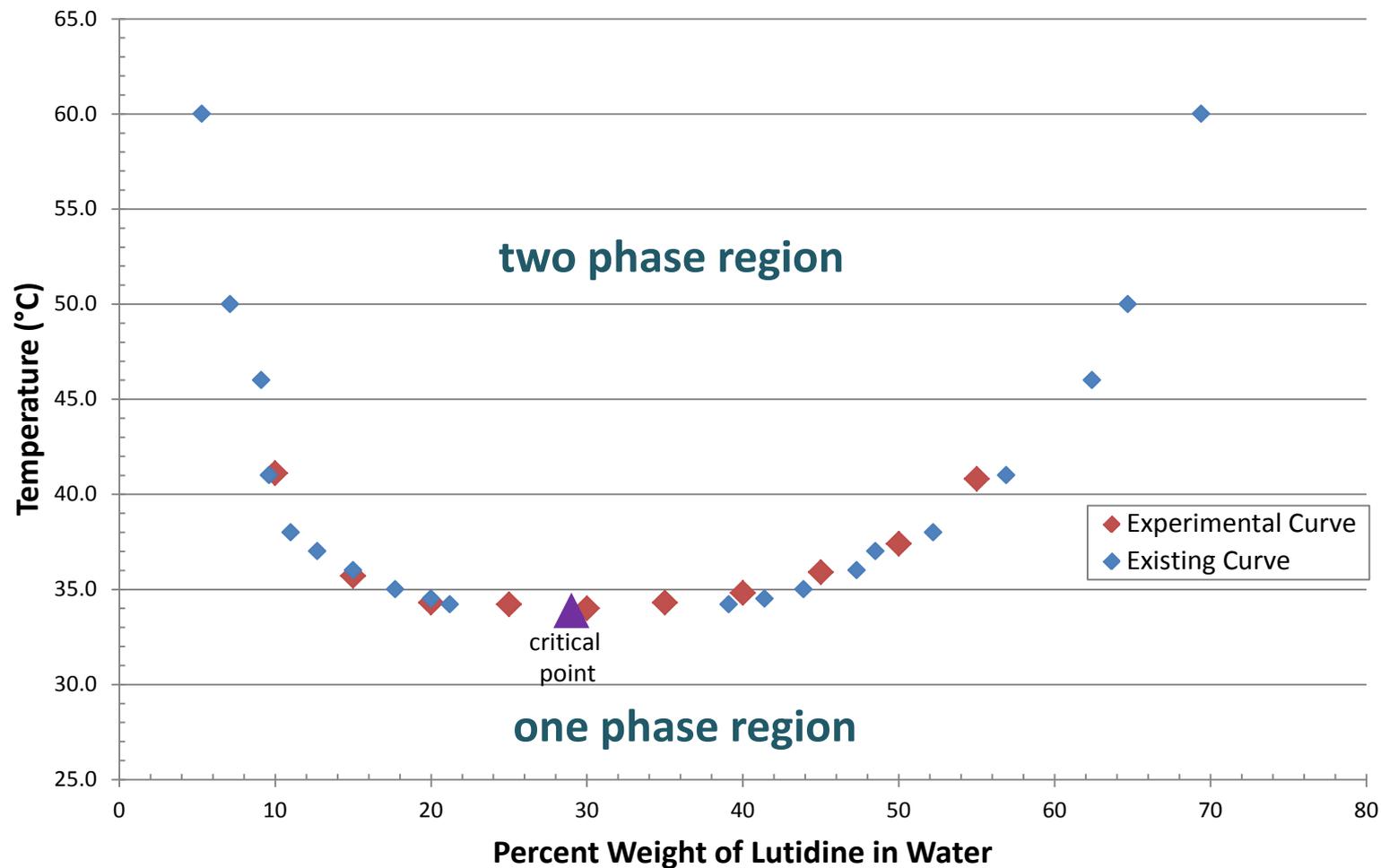


Determining the Phase Diagram of Solvent

- Due to density fluctuating in the binary system near the critical point, light is strongly scattered, resulting in critical opalescence.
- The critical point was determined using Ultraviolet-visible spectroscopy. UV-Vis spectroscopy measures the absorption or reflection of a beam of light after it passes through a sample.
- Transmittance changes result only from the scattering of light.

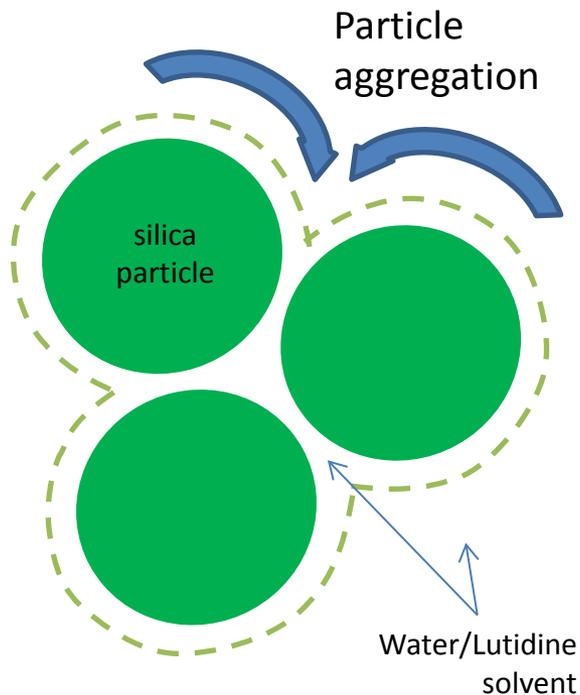


Lutidine/Water Phase Separation Curve



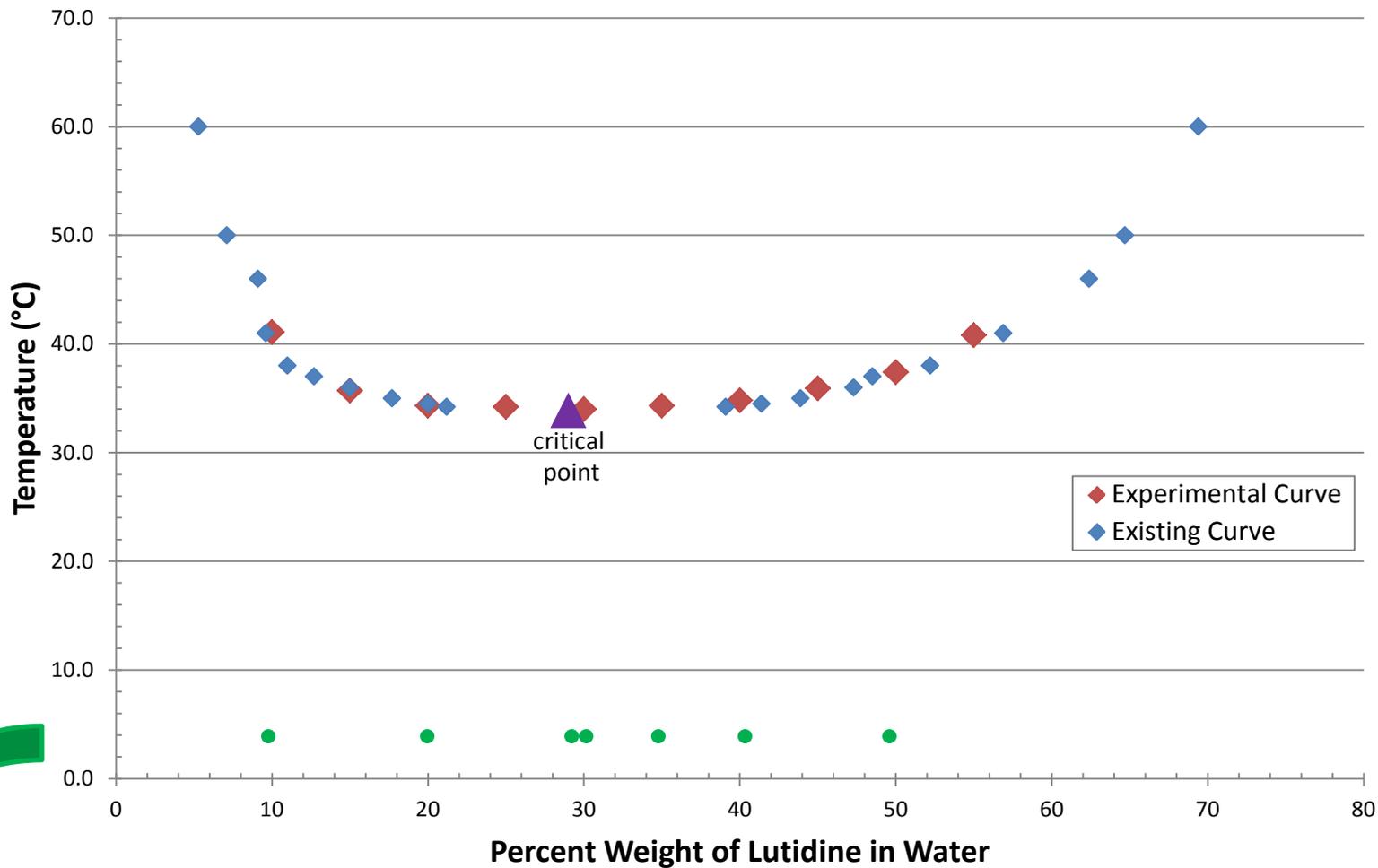
Grattoni, Carlos A., Richard A. Dawe, C. Yen Seah, and Jane D. Gray. "Lower Critical Solution Coexistence Curve and Physical Properties (Density, Viscosity, Surface Tension, and Interfacial Tension) of 2,6-Lutidine + Water." *Journal of Chemical & Engineering Data* 38.4 (1993): 516-19.

Colloidal Nanoparticles



- Silica colloidal particles in Water/Lutidine solvent have been used as model systems to study critical Casimir force for the past few decades.
- Ludox is a 50 mass fraction suspension of SiO_2 in H_2O .
- Silica Nanoparticles in Ludox have $d \approx 30 \text{ nm}$
- Stock solution has $\text{pH} \approx 10$

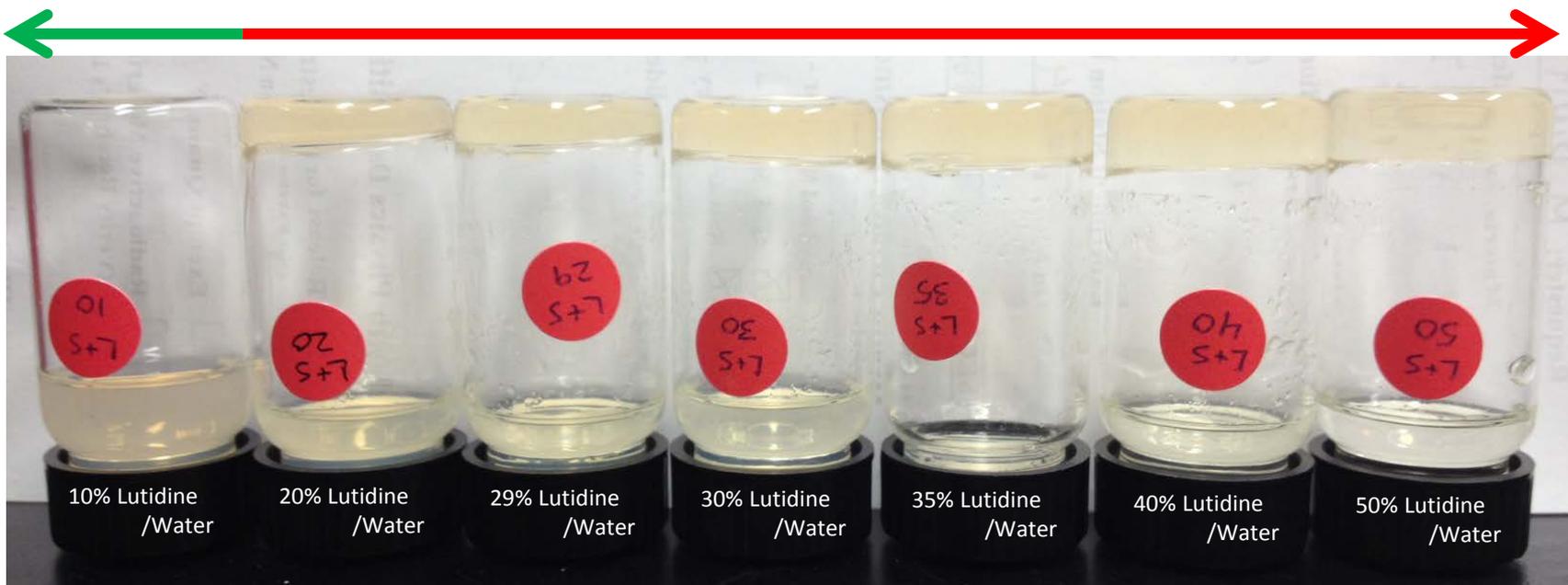
Lutidine/Water Phase Separation Curve



15% colloidal Silica by volume

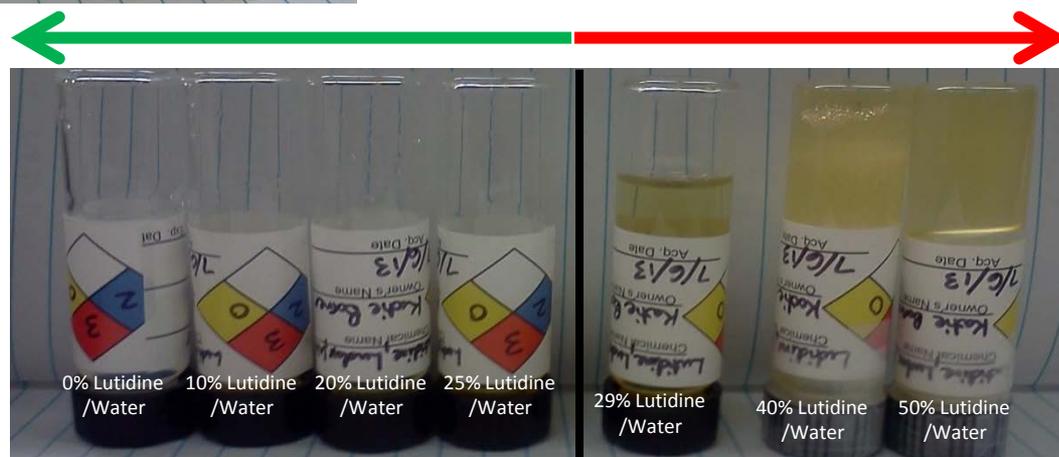
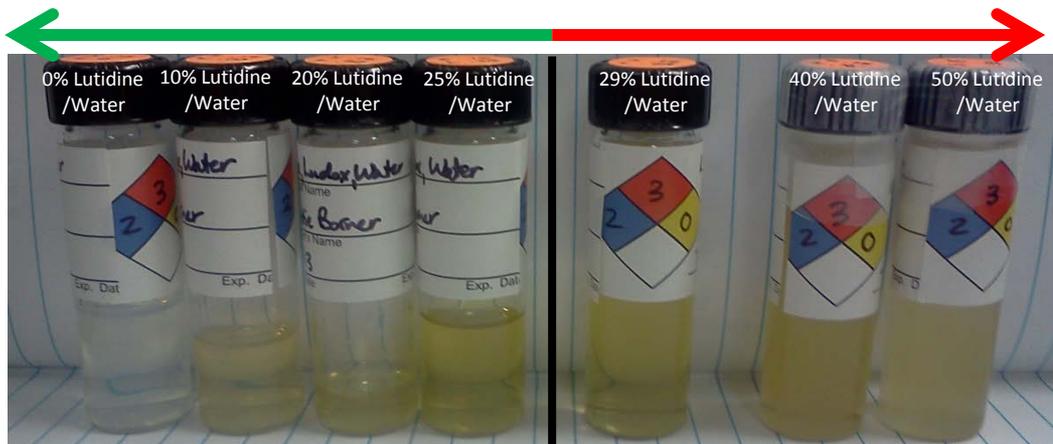
Addition of Silica to Binary Solution

- Below are solutions of 15% colloidal silica with increasing Lutidine/Water concentrations from left to right
- These gelled at 4°C, the temperature at which they were stored immediately following preparation.



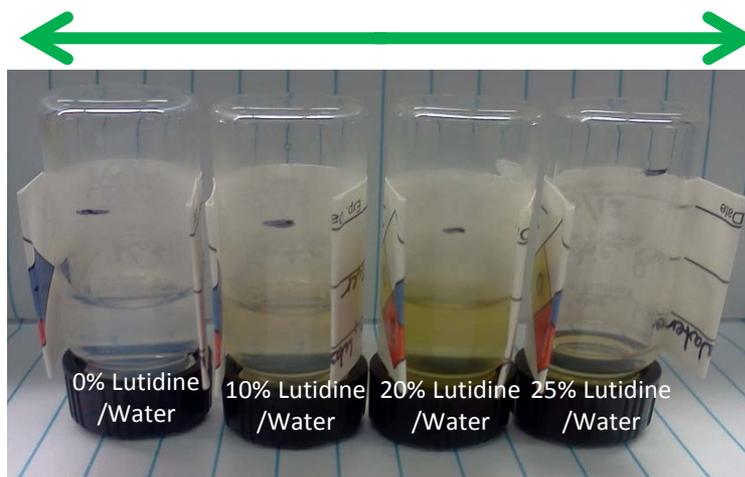
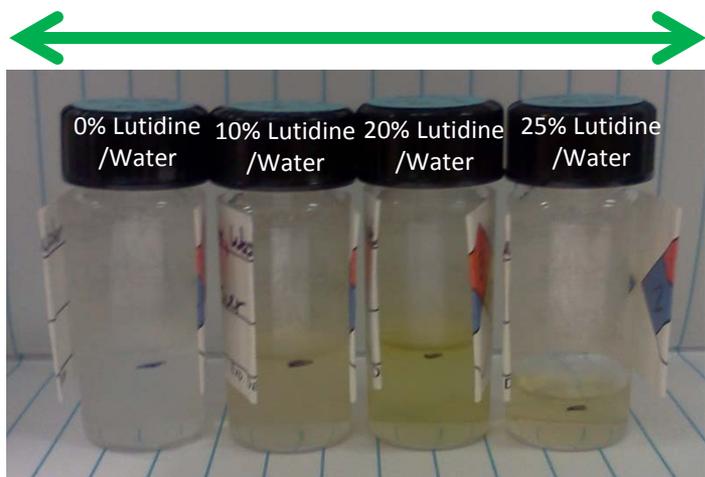
Procedure Dependent Gellation

- When we store the solutions at room temperature, after one day only the solutions $\geq 29\%$ Lutidine phase separated and/or gelled.

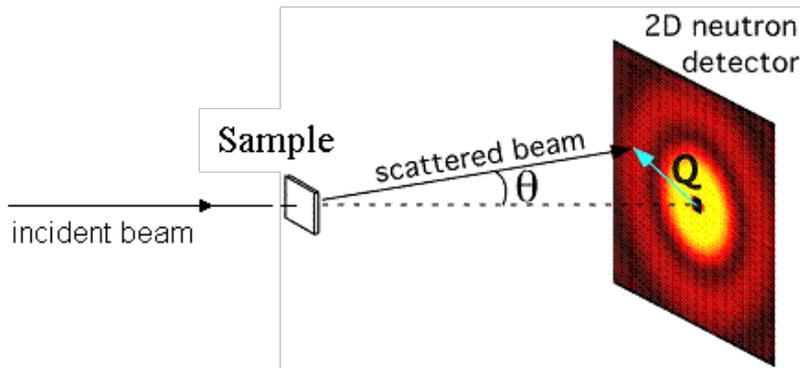


Procedure Dependent Gellation

- When the 15% silica solutions kept at room temperature were then placed into the 4 °C fridge, they remained in one phase and did not show any gellation.



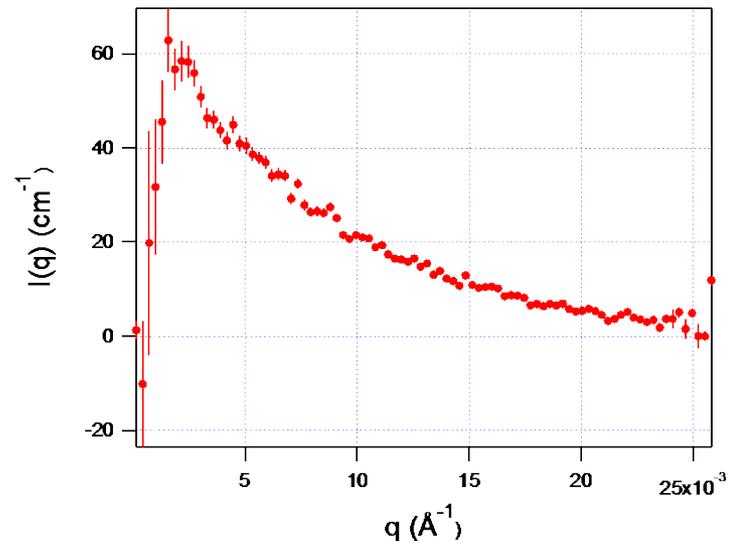
Small Angle Neutron Scattering



$$Q = 4\pi \frac{\sin\left(\frac{\theta}{2}\right)}{\lambda} = \text{scattering vector}$$

- From SANS we obtain the 1D scattered neutron intensity distribution given as $I(Q)$

Aged 0.1% Silica & 29% Lutidine sample



Small Angle Neutron Scattering Analysis

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

A: contrast term

P(Q): normalized form factor (intra-particle structure factor)

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

At dilute concentrations, $S(Q) \approx 1$, therefore, $I(Q) = A \times P(Q)$

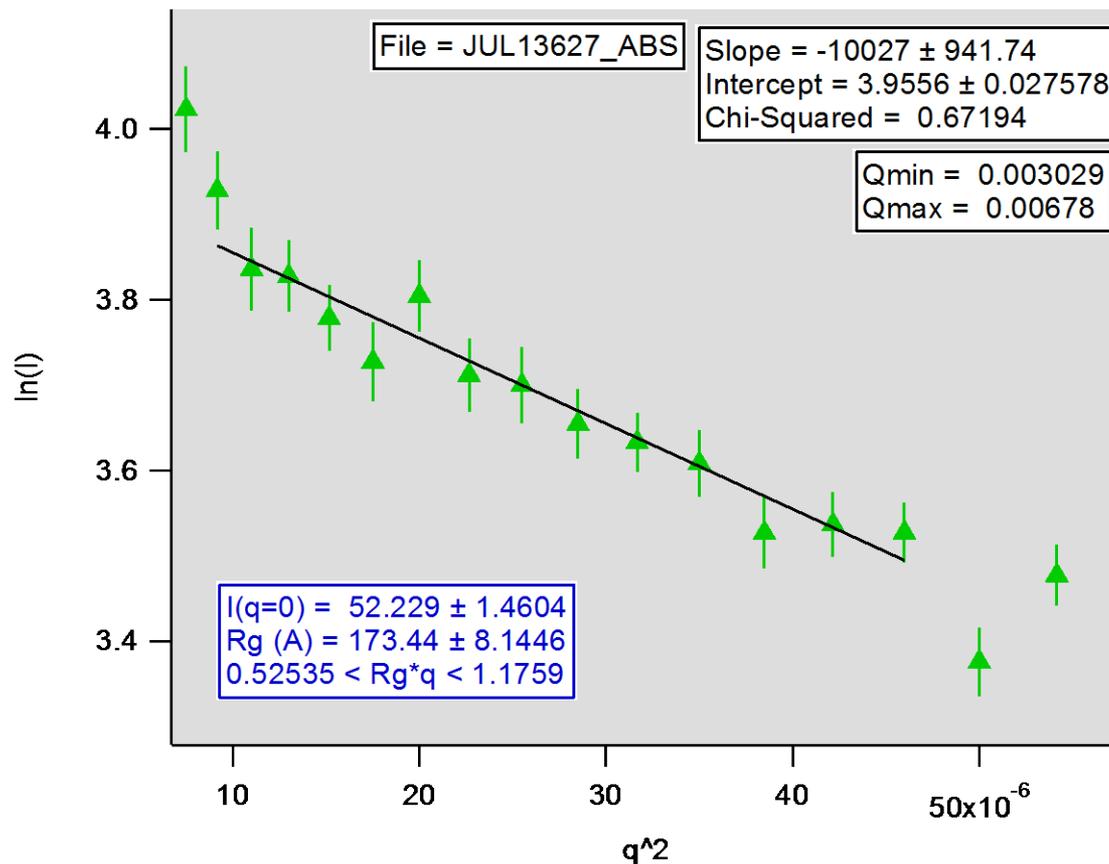
Radius of gyration, R_G : at low Q

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

Radius of Gyration Determination

Radius of gyration, R_G : approximate size of the scattering object

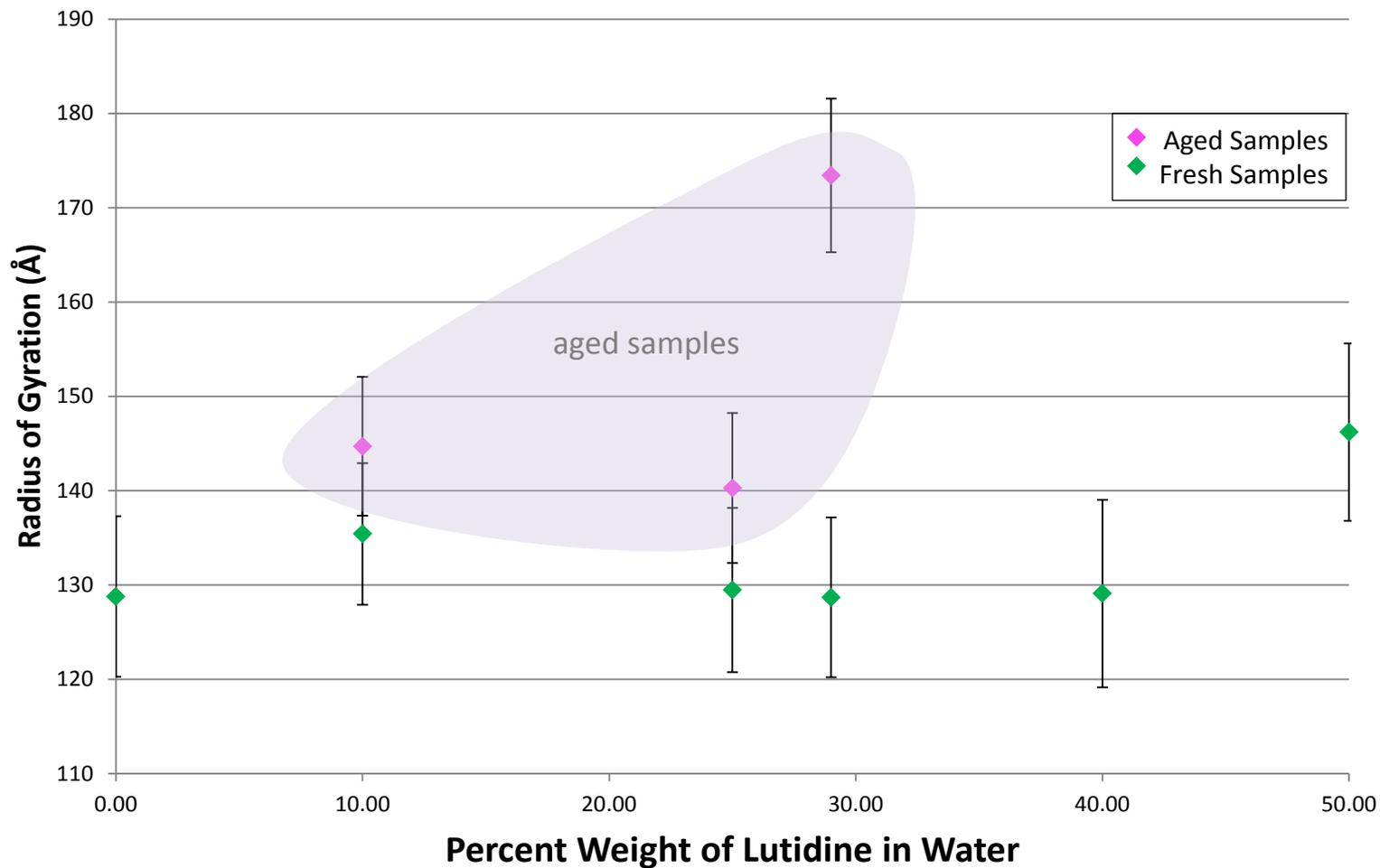
- In our case the scattering object is a silica particle cluster



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

This is the aged 0.1% Silica and 29% Lutidine sample.

Radius of Gyration for 0.1% Silica Samples at 25 °C



pH Affect of Aggregation

- SiO_2 nanoparticles have $\text{pH} \approx 10$.
- It has been shown that at near neutral $\text{pH} \approx 7$ the silica will experience natural aggregation.
- The pH value of our solutions is ≈ 10.15 .
- Gellation is not due to natural aggregation of silica particles, but due to the interaction of the silica particles with the Lutidine in solution.

Research Implications and Future Goals

- The gelation of the concentrated colloidal silica solutions is procedure dependent. It is likely due to a chemical reaction.
- Similar systems used by previous researchers could have their stability compromised above a certain silica concentration and temperature. No one has yet reported chemical reactions in this model system and their effect when studying critical Casimir force.
- Further utilize dynamic light scattering and small angle neutron scattering (SANS) to determine the scattering patterns of the colloidal particles to better determine the transition temperature and nature of interaction.

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