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Investigating the effective interaction between silica colloidal particles near the critical point of a binary solvent by small angle neutron scattering

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An effective attractive potential can be introduced between colloidal particles dispersed in a binary solvent when the solvent condition approaches its demixing temperatures. Despite the debate of the physical origins of this effective attraction, it is widely termed as the critical Casimir force and is believed to be responsible for the colloidal stability in a wide range of particle concentration at both critical and near-critical solvent concentrations. Here, we study the effective attraction and equilibrium phase transition of charged spherical silica particles in the binary solvent of 2,6-lutidine and water as a function of the particle volume fraction and temperature at the critical solvent concentration. By analyzing our small angle neutron scattering (SANS) data, we found that at a relatively small particle volume fraction, the density fluctuation introduced attraction between silica particles can be satisfactorily explained by the function form commonly used for the critical Casimir interaction. However, at large silica particle volume fractions, an additional long range attraction has to be introduced to satisfactorily fit our SANS data and explain the large shift of the phase transition temperature. Therefore, while at relatively low volume fractions, the solvent introduced attraction may be dominated by the critical Casimir force, the physical mechanism of the effective attraction at large particle volume fractions seems to be different from the critical Casimir force. Furthermore, the range of this long range attraction is consistent with a recently proposed new theory, where the attraction can be introduced by the solvent capillary condensation between particles. We also demonstrate that the reduced second virial coefficient close to the particle phase transition is similar to the values of the binodal transition of the sticky hard sphere system. https://doi.org/10.1063/1.5038937

I. INTRODUCTION

Since first discussed by de Gennes and Fisher in the late 1970's,¹ the effective interaction between colloidal particles in a binary solvent near its critical point has been intensively studied in the past several decades.^{2–6} It causes reversible aggregation observed in many experiments when the binary solvent approaches its demixing temperature^{2,7–10} and can be used to tune the colloidal self-assemblies.^{11,12} Recently, this kind of aggregation is found to be highly sensitive to the particle size and can be utilized to efficiently separate nanoparticles by size.⁸ The colloidal system with the binary solvent has been also used as model systems to study the properties of active matter systems.¹³

When colloidal particles are dispersed in a binary solvent, they usually preferentially adsorb one component of the binary solvent. By moving the solvent condition toward the critical point, the adsorption layer thickness increases and is controlled by the correlation length of the solvent density fluctuation.¹⁴ Such a phenomenon is called critical adsorption.^{14,15} Critical adsorption has been confirmed experimentally by optical studies and neutron reflectometry.^{16–18} The adsorption of the preferred solvent molecules on colloidal particle surfaces can introduce an effective attraction between colloidal particles,^{19,20} which has been widely termed as the critical Casimir force (CCF) since the 1990's.²¹ And the CCF is believed to be responsible for particle aggregation and the instability of colloidal systems close to the demixing temperatures of the solvent. In systems with a binary solvent, changing temperature close to the critical temperature can cause gelation, glass transition,^{22,23} and crystal formation¹² at relatively high particle concentrations. The attraction induced by the solvent fluctuation has been mostly attributed to the critical Casimir force in these experiments.

Recently, one experiment using the total internal reflection microscopy showed that the interaction potential between a particle and a flat surface at or near the critical solvent

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concentration follows the theoretical prediction by the critical Casimir force.²⁰ However, when the solvent concentration is far away from the critical concentration, the bridging attraction introduced by the segregation of the solvent may dominate the attractive potential.^{19,24} Some theoretical works also studied the difference of the attraction strength between samples at critical conditions and off-critical conditions, an analog of the capillary condensation of the solvent, has been proposed to explain the attraction for samples at off-critical conditions.²⁶

Since changing the solvent composition may change the dominating contribution to the attraction force from the critical Casimir force to the bridging attraction,²⁷ it is not immediately evident if the critical Casimir force can still be the dominating attraction force when the particle concentration is increased at the critical solvent composition.^{15,28} Therefore, in this paper, we study the effective inter-particle potential for a model silica colloidal system dispersed in a well-studied binary solvent, the mixture of water and 2,6-lutidine, using small angle neutron scattering (SANS). The radius of silica particles is about 14.5 nm. Note that our particle size is significantly smaller than some experimental studies mentioned above.^{12,20}

In order to eliminate the effect of the scattering due to the solvent density fluctuation, we have mixed the heavy water (D_2O) and normal water (H_2O) to match the scattering length density (SLD) of the lutidine. As a result, the coherent scattering due to the solvent fluctuation is invisible to SANS so that we can focus on the coherent scattering intensity dominated by the particles dispersed in solution.

II. MATERIALS AND EXPERIMENTAL METHODS

Charged silica particles dispersed in normal water (Ludox TM-50) were purchased from SIGMA-ALDRICH. Heavy water (D₂O) with purity of 99.8% was purchased from Cambridge Isotope Laboratories. Milli-Q water (18.2 MΩ cm) was used whenever normal water was needed. The critical solvent composition for the normal water/2,6-lutidine system contains 29% mass fraction lutidine and 71% mass fraction of normal water. In order to match the SLD of the 2,6-lutidine, D_2O was added to prepare water with the mass ratio of 27:73 between D₂O and H₂O, which has been determined previously.⁸ Because D₂O and H₂O have different mass, when adding D₂O, we kept the mole ratio of 2,6-lutidine to water at the critical composition. Hence, the final mass concentrations of water and 2,6-lutidine of our solvent are 28.4% mass fraction of 2,6-lutidine and 71.6% mass fraction of water (mixture of D₂O and H₂O).

Samples with silica particles were prepared at 0.12%, 0.48%, 1.2%, 2.4%, 6.5%, and 9% volume fractions. Samples with the volume fraction larger than 9% are phase separated even at room temperature and are not studied here. To prepare samples, normal water is first mixed with the ludox solution. Then D_2O is added to the diluted ludox solution. Finally lutidine is added.

Dynamic Light Scattering (DLS) was performed by using the Dynapro NanoStar instrument. It measures the intensity autocorrelation function, $g_2(t)$, which is defined as²⁹

$$g_2(t) - 1 = \beta (\Sigma A_i e^{-t/\tau_i})^2, \tag{1}$$

where A_i is the amplitude of the relaxation mode, t is the correlation time, and τ_i is the characteristic relaxation time. τ_i is related to the diffusion coefficient D, which can be written as

$$\tau_i = \frac{1}{D_i Q^2},\tag{2}$$

where $Q = (4\pi n/\lambda) \sin(\theta/2)$ is the difference of the wave number between incident and scattered light. *n* is the refractive index of the solvent mixture. λ is the wavelength of the incident light in vacuum. θ is the scattering angle. For a pure water/lutidine solvent without colloidal particles, the mutual diffusion coefficient D_s is related to the critical fluctuation and can be approximated as³⁰

$$D_{\rm s} = \frac{k_B T}{6\pi\eta\xi} [K(Q\xi) + \frac{\xi_0}{\xi}],\tag{3}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity. The viscosity of the solvent mixture of 2,6-lutidine and water is obtained from published experiment results.^{31,32} $K(Q\xi) = \frac{3}{4}\{1 + (Q\xi)^{-2} + [Q\xi - (Q\xi)^{-3}] \tan^{-1}(Q\xi)\}$ is the Kawasaki function, and ξ_0 is the critical amplitude whose order of the range is of molecular interactions.

The phase transition temperature of samples with silica particles was also determined by our DLS instrument by observing the intensity change as a function of the temperature. The temperature accuracy is within 0.1 $^{\circ}$ C.

To study the attractions between colloidal particles, small angle neutron scattering (SANS) experiments were carried out on NG7SANS and NGB30SANS from the Center for Neutron Research at National Institute of Standards and Technology (NCNR) in USA. Because the contrast between lutidine and water is tuned to zero by mixing the right ratio of D_2O and H_2O , the coherent SANS intensity is thus only from silica particles in solution.³³

In order to analyze the SANS data, the inter-particle structure factor is calculated by solving the Orstein-Zernike (OZ) equation, through which the inter-particle potential information is obtained. The previously proposed closure form is used with the implemented thermodynamic self-consistency.^{34–36} Computer simulation has been used to verify the accuracy of this method.³⁵

The ionic strength of the solvent is further estimated to calculate the screened Coulomb interaction. It is noted that accurately calculating the charge interaction between silica particles is very challenging in a binary solvent. The adsorption of one component of the binary solvent on the particle surface will change the dielectric constant of the solvent layer around a particle, which in turn affects the zeta potential and the effective charge interaction.³⁷ But we will discuss later in the paper that the challenge of accurately estimating the charge interaction will not affect our main conclusion of this paper.

The ionic strength of the solvent mixture is mainly due to the hydrolysis of lutidine in water. The ionization of lutidine is determined by the following formula:

$$\frac{[C_7 H_{10} N^+][OH^-]}{[C_7 H_0 N]} = 10^{-pK_b},$$
(4)

where [] denotes the molar concentrations of different components in units of mol/l. pK_b for lutidine is 7.4 at 25 °C. Henry's law is used to calculate the solubility *vs*. temperature of the solvent. The result can be written as pK_b = 7.4-0.035 \times (*T* - 25). The contribution to the ionic strength by dissociated ions from charged silica particles is also included in the calculation.

The charge number of the silica particles is estimated based on the measured zeta potential, which is around -36 mV.³⁸ The zeta potential is fixed at that value in the fitting. The charge number of the silica particle in the solution can be calculated by³⁹

$$C = 4\pi a^2 \epsilon \epsilon_0 \kappa \psi_{\rm eff} (1 + \frac{1}{\kappa a}), \tag{5}$$

where *a* is the particle radius, ϵ is the relative permittivity of the solvent mixture, ϵ_0 is the dielectric constant of vacuum, κ is the inverse of the Debye length, and ψ_{eff} is the zeta potential of the particle. For the solvent mixture, the relative permittivity is calculated by linear interpolation.⁴⁰ The Debye length can be calculated by

$$\kappa^{-1} = \frac{0.304}{\sqrt{I_s}},$$
 (6)

where the unit of κ^{-1} is nm and the unit of I_s is mol/l.

The screened Coulomb repulsion potential between silica particles can be calculated from the ionic strength and charge number of silica particles by the well-developed theory.^{41–43}

III. RESULTS AND DISCUSSIONS

Figure 1 shows the schematic picture of two particles immersed in a binary solvent mixture. The Ludox silica particles preferentially adsorb water on their surfaces based on a recent study.¹⁶ The thickness of the adsorption layer is proportional to the correlation length of the solvent density fluctuation, ξ .¹⁶



FIG. 1. Schematic picture of two particles immersed in a binary solvent. The red spheres are silica particles with radius a. The outer layer is the adsorption layer with the mixture of two components of the solvent. The composition of the adsorption layer depends on the composition of the solvent and the temperature. The particle surface-surface distance is D.

DLS is first used to determine the correlation length of the solvent fluctuation as a function of the temperature. It is known that ξ should follow the asymptotic power law behavior, $\xi(T) = \xi_0 |T_r|^{-\nu}$, where $\xi(T)$ is the correlation length at the temperature, T, and ξ_0 is the critical amplitude. T_r is the reduced temperature defined as $T_r = (T - T_c)/T_c$. And $\nu \approx 0.63$ is the universal correlation length exponent. Using Eqs. (1)–(3), ξ is obtained by fitting $g_2(t)$ of the binary solvent. One data set at T = 32 °C is shown in Fig. 2(a) together with the fitted curve. The obtained correlation length at different temperatures is shown in Fig. 2(b). By fitting the experimental results of $\xi(T)$ with $\xi_0 |T_r|^{-\nu}$, T_c and ξ_0 are found to be 32.4 °C and 0.2 nm, respectively, consistent with the previous result.¹⁶ Note that the use of D₂O shifts the critical temperature to a smaller value compared with that of the solvent prepared with only normal water.

For all samples with silica particles, we also used DLS to observe the phase transition as a function of temperature.



FIG. 2. DLS data together with the fitting results for the pure solvent. (a) The raw data and fitting curve for $g_2(t)$ at T = 32 °C. (b) The extracted correlation length ξ at different temperatures together with the fitting curve of $\xi(T) = \xi_0 |T_r|^{-\gamma}$.

Because light scattering is very sensitive to large objects in solution, it is very sensitive to the particle aggregation in our system. When increasing the temperature, the solvent fluctuation induced attraction becomes stronger and stronger. Charged silica particles stable at room temperature begin to form clusters and eventually become phase separated. The DLS scattering intensity was recorded as a function of temperature, which is shown in Fig. 3(a). At the beginning, the intensity increases as the temperature increases indicating the formation of clusters in solution. However, at a certain temperature, the intensity begins to decrease due to the precipitation of the silica particles forming very large clusters. The temperature with the maximum scattering intensity is named "precipitation temperature," T_p . Because the light scattering only accesses a very small Q value and $T_{\rm p}$ is relatively far away from $T_{\rm c}$, the scattering intensity from the solvent can be ignored here. $T_{\rm p}$ is observed to shift to a lower temperature when the silica particle volume fraction is increased. Interestingly, T_p is



found to decrease almost linearly with the silica volume fraction, which is shown in Fig. 3(b). And the data points can be fitted with a linear line, $T_p = 32.4 - 0.61 \times \phi_s$. Note that when the particle concentration increases, it needs less attraction between particles to introduce a phase separation. It is thus expected that the transition temperature decreases when the particle concentration increases. Also, residual impurities in the ludox suspension may also affect the transition temperature.⁴⁴

To understand the inter-particle potential, SANS patterns of our samples at different concentrations were measured as a function of the temperature for $T < T_p$. For a system with monodispersed particles, the SANS scattering intensity can be expressed as

$$I(Q) = \phi_{\rm s} \Delta \rho^2 V_{\rm p} P(Q) S(Q) + I_{\rm b}, \tag{7}$$

where ϕ_s is the volume fraction of the particle, $\Delta \rho$ is the scattering length density contrast between the particle and solvent, V_p is the single particle volume, P(Q) is the form factor, S(Q)is the inter-particle structure factor, and I_b is the background mainly due to the incoherent scattering. Note that the coherent scattering of the solvent can be ignored as there is no contrast between lutidine and water prepared by mixing the right ratio of D₂O and H₂O.

The scattering length density of silica particles of Ludox TM-50 is $\rho_{sld} = (3.46 \pm 0.16) \times 10^{-6} \text{ Å}^{-2}$ that is estimated by the contrast variation method. The form factor is determined by measuring samples at two dilute concentrations with $\phi_s = 0.12\%$ and $\phi_s = 0.48\%$ at room temperature. Schultz distribution was used to account for the size polydispesity.^{45,46} The raw data and fitted curves are shown in Fig. 4. The extracted particle radius, *a*, is 14.5 ± 0.2 nm. And the polydispersity, $\sigma_R = 0.1a$, is consistent with the literature result.⁴⁷

When further increasing the concentration, the interparticle structure factor, S(Q), is not unity anymore. To calculate S(Q), we need to model the inter-particle potential. We first tried the potential form shown as below,





FIG. 4. SANS patterns of two samples with dilute silica volume fractions are shown together with the fitting curves. The error bars are shown and smaller than the size of the symbol.

where the first exponential decay term on the second line is the attraction introduced by the CCF,⁴⁸ and the second term is the screened Coulomb repulsion. *r* is the inter-particle distance normalized by the particle diameter, σ . *D* is the surface-surface distance defined as $D = (r - 1)\sigma$. The interaction potential is infinite for r < 1 due to the excluded volume effect. Z_1 is the inverse of the interaction range of the CCF. According to the literature, it should be proportional to $1/\xi$. Z_2 and K_2 are estimated from the ionic strength of the solution and the charge number.^{41–43} K_1 is the only fitting parameter for Eq. (8).

Using this potential form, the SANS patterns of silica particles at the volume fraction $\phi_s = 1.2\%$ can be fitted very well. The data together with the fitting curve are shown in Fig. 5(a). The inset shows the fitting of the relatively large Q range in the log-log scale. Based on the fitting, the attraction introduced by



FIG. 5. SANS data and their fitted curves. (a) The SANS data together with the fitting curves for $\phi_s = 1.2\%$ at different temperatures. (b) The SANS data and fitted curves for $\phi_s = 2.4\%$, 6.5%, and 9%. Different colors indicate different temperatures of samples. The insets are log-linear plots showing the results for the middle-*Q* and high-*Q*. The data for *Q* larger than 0.1 Å⁻¹ are not shown as they are dominated by a constant incoherent scattering background.

the solvent fluctuation can be satisfactorily explained by the critical Casimir force. Note that at the highest temperature, 31.8 °C, the correlation length of the solvent fluctuation is about 10 nm comparable to the particle radius. This correlation length is short compared with the previous experiment where the temperature is much closer to the critical temperature.²⁰ Thus, the total internal reflection microscopy used in the previous experiment may not be sensitive enough to probe such a small correlation length in our experiments.²⁰ However, both the amplitude and range of the attraction are large enough to introduce the large change of the inter-particle structure factor in our experiments, from which the effective interaction potential can be obtained.

Note that even though the adsorption of water on silica particles may slightly change the solvent composition, we do not expect this change to be significant. The shift of the solvent composition due to the solvent adsorption on silica particles can be estimated using the latest adsorption profile obtained previously by Bertrand *et al.*¹⁶ Due to the particle surface adsorption, the shift of the lutidine concentration depends on the sample temperature and volume fraction of silica particles. The largest shift is at T_p in our experiment. The final solvent composition of lutidine at T_p is estimated to be 29.3%, 29.7%, 30.7%, 31.3% for $\phi_s = 1.2\%$, 2.4%, 6.5%, 9%, respectively. The difference between solvent composition at T_p and critical composition (29%) is relatively small.

Compared with the interaction for small particle concentration (1.2%), the whole scenario is completely different at higher particle concentrations. Using Eq. (8) cannot fit the SANS patterns for particle concentrations at 2.4% or larger when T is close to T_p . A careful comparison of the experimental data and SANS patterns indicates that the theoretical pattern calculated using Eq. (8) cannot reproduce the very strong low-Q upturn when the temperature is close to T_p . This means that the range of attraction we have previously used is too short. And there should be an additional attraction, whose range is longer than ξ . Therefore, we have added an additional long range attraction term to the potential form. The new total potential is now expressed as given below,

$$\frac{V(r)}{k_B T} = \begin{cases} \infty, & r < 1, \\ -K_1 e^{-Z_1 D} + \frac{K_2 e^{-Z_2 D}}{r} - \frac{K_3 e^{-Z_3 D}}{\sqrt{r}}, & r \ge 1. \end{cases}$$
(9)

The third function form in the second line is chosen from the bridging attraction based on the capillary condensation.^{49,50} K_3 and Z_3 are the amplitude and the inverse range of this long range attraction. Both of these two parameters are free fitting parameters. The fitting results together with the experimental data are shown in Fig. 5(b). The interaction range for the third term is always significantly larger than the correlation length of the solvent at the same temperature. Hence, this indicates that the physical mechanism of the attraction for large particle concentration seems to be different from that in small concentrations.

The overall good fitting quality achieved for all our data indicates that the overall potential extracted from our fitting is reasonably accurate. However, we have to be careful in interpreting the meaning of each fitting parameter for each individual component. We tried our best to estimate the charge interaction at the temperature far away from the demixing temperature. But the dielectric constant is estimated based on the homogeneous mixing of water and lutidine. When the temperature increases, there is a layer of the solvent adsorbed on the particle surface with more water concentration compared with the nominal water concentration in a solvent.¹⁶ As a result, there is a continuous change of the dielectric constant along the radial direction on the surface of a particle. When the layer thickness increases by increasing the temperature, the charge repulsion estimated based on the condition at low temperature may not be accurate enough. This can be partially compensated by the change of the second term in Eq. (8). For example, for 1.2% volume fraction, Eq. (8) is used with only two potential terms. If the estimated charge potential at high temperature was not accurate enough, it would be compensated by the attraction term so that the total potential is still accurate. Therefore, we only show the total potentials in Fig. 6 extracted from the data fitting instead of providing the results of each individual term of the total potential.

For the 1.2% volume fraction case, the total potential extracted from the data fitting is shown in Fig. 6(a). It can be seen that at low temperature, the total potential is dominated by a charge repulsion. When increasing the temperature, the overall interaction slowly changes from the net repulsion to the net attractive potential as increasing temperature enhances the attraction, whose function form is the same as the function form for a critical Casimir interaction. Clearly, at relatively high temperatures (T > 30.5 °C), the potential becomes overall

attractive. This is in general the trend for all samples. However, for higher concentrations, such as 9% volume fraction, the total potential becomes overall attractive even at very low temperature such as 25 °C, which is about 7.4 °C away from the critical temperature. As a result, the correlation length of the solvent fluctuation is much smaller than the range of the overall attraction.

In order to evaluate the interaction range of the long range attractive portion of the overall potential, the total potentials showing long range attraction are further analyzed. An empirical equation is used to fit the overall repulsive and attractive portion of the total potentials,⁵¹ which is expressed as

$$V(r) = A_{\rm rep} e^{-D/l_{\rm rep}} - A_{\rm att} e^{-D/l_{\rm att}}.$$
 (10)

 $A_{\rm rep}$ and $A_{\rm att}$ are the amplitudes of overall repulsion and attraction. $D = (r - 1)\sigma$ is the surface-surface particle distance. $l_{\rm rep}$ and $l_{\rm att}$ are the ranges of the repulsion and attraction, respectively. The relation between $l_{\rm att}$ and T is shown in Fig. 7. ξ of the solvent as a function of temperature is shown together as a solid line in Fig. 7. For the sample at 1.2% volume fraction, the range of attraction, $l_{\rm att}$, is actually very close to ξ indicating that at this concentration, the CCF very likely dominates the attraction between colloidal particles. However, at higher ϕ_s , the fitted $l_{\rm att}$ is always much higher than ξ at the same temperature. This indicates that at larger concentrations, the driving force between particles may be due to other mechanisms other than the critical Casimir force.

Figure 8 shows the extracted S(Q=0) for different samples as a function of temperature. The divergence of S(Q=0) is the spinodal decomposition temperature of a system. By increasing the temperature, S(Q=0), all monotonically increase and



FIG. 6. The extracted total potential as a function of the inter-particle distance, r, is shown for different samples at different temperature. (a) The results for the sample at $\phi_s = 1.2\%$. (b), (c), and (d) correspond to $\phi_s = 2.4\%$, 6.5%, and 9%, respectively.



FIG. 7. The fitted attraction range l_{att} of the total potential is shown together with the correlation length, ξ , of the density function of the pure solvent (solid line).

eventually tend to diverge. The transition temperature clearly shifts to lower temperatures when the sample concentration increases. Especially for 9% volume fraction, the shift is so large that the correlation length and the attraction strength introduced by the critical Casimir force can be too small to introduce a phase transition of colloidal particles. In fact, we have calculated S(Q = 0) of all samples by using the potential obtained by fitting the data of 1.2% volume fraction. The lines in Fig. 8 are the theoretical calculations. By increasing the volume fraction from 1.2% to 2.4%, the experimental phase transition temperature shifts to a smaller temperature by more than 0.8 °C. If the effective potential at 2.4% should be similar to that of 1.2%, in which the critical Casimir force seems to be able to explain all SANS data satisfactorily, the calculated theoretical line (red solid line) at 2.4% using similar potential should qualitatively reproduce experimental data. Instead, the theoretical calculation shows no sign of divergence until much larger temperature. Similar prediction happens for the samples at 6.5% and 9% volume fractions. Hence, this also indicates that the driving force of the phase transition of larger volume fractions seems to be due to different mechanisms other than the critical Casimir force.



FIG. 8. The experimental results (symbols) of S(Q) at Q = 0 obtained by fitting SANS data are shown together with the theoretical curves (lines). The theoretical curves are calculated by using the potential parameters obtained from the sample at $\phi_s = 1.2\%$. The upper and lower 95% confidence intervals are shown as error bars in the plot. The phase transition lines (vertical solid lines) shift to lower temperatures when the particle volume fraction is increased.

Since the driving force of the phase transition may not be dominated by the critical Casimir force, one other possibility is due to the bridging attraction similar to what has been discussed for systems, whose solvent concentration is far away from the critical concentration. A recent paper has tried to calculate the relation between the bridging attraction range and the surface-surface particle distance.²⁷ We can approximately estimate the average surface-surface distance, D_m , between particles in solution. During the estimation, face centered cubic (FCC) arrangement is used to approximate how particles are packed in solution. (Note that, the exact packing structure of colloidal particles is not important here as it only rescales the distance by a constant if different types of structures are used.) To approximately estimate D_m , we can use the following expressions

$$L_{\rm m} = (4 \times 4/3 \times \pi \times a^3/\phi_{\rm s})^{1/3}, \tag{11}$$

$$D_{\rm m} = \sqrt{2}/2 \times L_{\rm m} - 2 \times a, \tag{12}$$

where *a* is the silica particle radius, ϕ_s is the volume fraction of silica particles in solution, and L_m is the length of the cubic. D_m decreases when increasing ϕ_s . If we assume that the long range attraction introduced in Eq. (9) is due to the bridging attraction, the bridging range, R_b , can be estimated by $R_b = \sigma/Z_3$.

Figure 9 shows the result of ξ/R_b as a function of ξ/D_m . By increasing the temperature, ξ increases. ξ/R_b saturates when $\xi/D_{\rm m}$ is large enough. It is interesting to notice that at the highest temperature $(T \approx T_p)$, ξ/D_m is almost a constant value for all the concentrations in the figure and uniquely determines the phase transition. If we assume that D_m is a good approximation of the average surface-surface distance between particles, the phase separation happens when the correlation length of the solvent fluctuation is about 9% of the surface-surface distance. Note that, ξ/D_m at phase transition temperature is about 13% and 11% for the concentration at 0.48% and 1.2% that are much larger than the value at higher concentrations. This model independent parameter indicates that the driving force of the phase separation is related with the confinement of the solvent and driven by the same type of interactions.



FIG. 9. The inverse range of the long range attraction obtained by fitting SANS data is shown as a function of the correlation length normalized by the estimated mean surface-surface distance $D_{\rm m}$. Y-axis shows the ratio between the correlation length, ξ , and $R_{\rm b}$. Different symbols indicate different sample volume fractions.



FIG. 10. The reduced second virial coefficients B_2^* is calculated using the fitted total potential for different samples. The shaded area shows the binodal transition estimated using the data reported by Plattern *et al.*⁵³

In addition, at relatively high concentration, ξ/R_b also becomes almost a constant of 0.4 at large concentrations shown in Fig. 9. If we assume that R_b is the interaction range, the result is consistent with the bridging attraction predicted by Okamoto and Onuki.²⁷ We therefore believe that the bridging attraction, which is analogous with the capillary condensation, is very likely the dominating force at large particle concentrations.

We further estimated the reduced second virial coefficients B_2^* calculated from the fitting results. The reduced second virial coefficient is defined as $B_2^* = B_2/B_2^{HS}$ (where $B_2^{HS} = 4v_0$ for a hard sphere system with the diameter, σ , and volume $v_0 = (\pi/6)\sigma^3$.⁵² Figure 10 shows B_2^* at different temperatures for different samples. B_2^* of the gas-liquid binodals of sticky hard sphere systems can be obtained from the recent results by Platten *et al.*⁵³ Comparing the value of B_2^* of our experimental results with that of sticky hard sphere systems, we noticed that B_2^* of all our samples approaches the binodal region when the sample temperature is close to the precipitation temperature. This indicates that the precipitation is a kind of phase separation in our system, which is consistent with the results observed by Jayalakshmi and Kaler.³ And it is noted that for very dilute conditions, the second virial coefficient of charged latex particles in a binary solvent was investigated before using light scattering.²

IV. CONCLUSION

In summary, combing DLS and SANS, we have investigated the inter-particle potential of Ludox silica particles in the binary solvent of water and 2,6-lutidine. Because water can be prepared by mixing the right ratio of D₂O and H₂O to match the scattering length density of lutidine, the solvent fluctuation is invisible to SANS in our study so that we can directly measure the scattering intensity of colloidal particles only. The obtained SANS data are analyzed to extract the effective interaction potential. At low temperatures, the interaction between particles are dominated by the charge repulsion. However, by increasing the temperature, an attraction between particles becomes stronger and stronger. At relatively low particle concentration (1.2% volume fraction), all SANS data can be satisfactorily fitted with a potential including both an electrostatic repulsion and an attraction with the function form of the critical Casimir force. The overall range of the attraction is about the same as the correlation length of the solvent density fluctuation. However at larger particle concentrations (2.4%, 6.5%, and 9%), an additional long range attraction needs to be introduced in order to explain the change of the SANS patterns at higher temperatures. The range of this long range attraction is much larger than the correlation length of the solvent fluctuation at the same temperature. This indicates that for large particle concentration at the critical solvent concentration, the dominating force between colloidal particles may be due to a different mechanism instead of the critical Casimir force. This observation is further supported by the investigation of the temperature shift of the phase transition temperature when increasing the particle volume fraction. We therefore feel that the bridging attraction, which is the analog of the capillary condensation, is likely the driving force of the phase transition at high temperatures and large particle concentrations.

At the large particle concentration, we further notice that the phase transition happens almost at the fixed ratio between the correlation length of the solvent and the mean surfacesurface distance. The ratio between the correlation length of the solvent fluctuation and the attraction range converges to a similar value of about 0.4 at large particle concentrations, which is consistent with one recently proposed bridging attraction mechanism. Our results further indicate that the reduced second virial coefficient at T_p for our samples is close to the value of a sticky hard sphere system at the binodal transition. Hence, the precipitation is driven by the binodal transition of particles in solution.

As concentrated particle solutions at the critical solvent composition have been commonly used as model systems to study the reversible aggregation and glass transitions, our results indicate that even though the solvent induced attraction can be still generated by increasing the temperature, we have to be prudent when interpreting the driving force between particles, and should not always attribute it to the critical Casimir force. Other interaction forces can become dominating factors too. In our case, it seems that the bridging attraction is very likely the dominating force at large particle concentrations.

It is also noted that we may need to be careful to generalize our observation to systems with larger particle sizes close to micrometer. This is because there may be a size dependent effect on the phase separation and aggregation of particles driven by the critical Casimir force or the solvent induced bridging attraction. This kind of size effect has not been systematically studied so far. For larger particles, in order to generate the phase transition, the experiment temperature is usually much closer to the solvent critical temperature than the cases studied in this paper. At the temperature much closer to the solvent critical temperature, it is still possible that the critical Casimir force can be the dominating interaction even at large particle concentration. However, for smaller particles in our system, the solvent fluctuation induced attraction is strong enough to introduce the aggregation and phase transition at the temperature a few degrees away from the solvent critical temperature. Thus, the

dominating force at large particle concentration in our cases is not the critical Casimir force and very likely due to the bridging attraction. It is also noted that the aggregate structure of larger silica particles in water/lutdine mixture was investigated using light scattering and Ultra-Small Angle X-ray Scattering.^{9,10} It would be interesting to study the morphology of the aggregates in our systems in future.

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