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Citation: The Journal of Chemical Physics **143**, 084704 (2015); doi: 10.1063/1.4929347 View online: http://dx.doi.org/10.1063/1.4929347 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/143/8?ver=pdfcov Published by the AIP Publishing

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# **Direct observation of critical adsorption on colloidal particles**

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(Received 8 July 2015; accepted 6 August 2015; published online 25 August 2015)

Despite the fundamental role adsorbed solvent layers play in generating critical Casimir forces between colloidal particles, the structure of these layers has yet to be directly determined. Using small-angle neutron scattering, we have measured critical adsorption on the surface of small spherical silica particles suspended in a binary mixture of lutidine and water. The surface concentration profile and excess adsorption  $\Gamma$  were studied as functions of temperature at the critical concentration and three off-critical concentrations. We are able to differentiate three distinct contributions to the excess adsorption including the intrinsic shape of the concentration profile. The adsorption associated with the profile shape is found to increase monotonically with increasing 2,6-lutidine concentrations for curvature induced corrections to planar adsorption and leads to  $\Gamma \sim |(T - T_c)/T_c|^{-0.52}$ , where  $T_c$  is the critical temperature. This scaling relation corresponds to a stronger divergence than found in the planar case, but a substantially weaker divergence than found previously. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4929347]

### I. INTRODUCTION

Critical concentration fluctuations produce long-range solvent-mediated interactions between colloidal particles suspended in near-critical binary mixtures.<sup>1</sup> These interactions are called critical Casimir forces and are, in many regards, analogous to the Casimir forces induced by vacuum fluctuations between conducting plates.<sup>2</sup> Early on it was realized that critical Casimir forces could strongly affect colloidal stability.<sup>3</sup> In contrast to the quantum-mechanical case, surface adsorption plays a significant role in determining the strength of critical Casimir forces between colloidal particles in binary mixtures.<sup>4</sup>

In general, when colloidal particles are suspended in a homogeneous binary solvent, one component can be preferentially adsorbed on the surface of the particles. As the solvent critical (demixing) point is approached, the size of this adsorbed layer grows with the correlation length of the solvent fluctuations, a phenomenon known as critical adsorption.<sup>5</sup> A thorough understanding of critical Casimir forces and their effect on colloidal stability require detailed information about the dependence of critical adsorption phenomena on temperature, solvent concentration, and particle size and surface chemistry.

Critical adsorption in colloidal systems is asymmetric with respect to the critical solvent concentration  $w_c$ . Notably, this asymmetry is reflected in an observed reversible aggregation region.<sup>6</sup> Using static light scattering, Gurfein *et al.*<sup>7</sup> demonstrated that the excess adsorption is significantly stronger for solvent concentrations poor in the adsorbed component, relative to the critical concentration. However, the microscopic origins of this asymmetry remain unresolved. Light scattering techniques are widely used, but largely insensitive to the detailed shape of the surface concentration profile because the wavelength of light is large compared to the typical size of adsorption layers. Specific features of adsorption layers can only be examined by employing an experimental tool with greater spatial resolution. To this end, neutron reflectometry has been previously employed to measure critical adsorption concentration profiles at planar surfaces.<sup>8</sup> While this technique is capable of probing solvent-structure over adsorption-relevant length-scales, it cannot be easily extended to colloidal particles with curved surfaces. It is important to note that the study of adsorption on curved surfaces introduces additional degrees of complexity, since adsorption phenomena are expected to be curvature dependent.<sup>9</sup> Recently, Omari et al.<sup>10</sup> reported curvature-induced deviations in the behavior of the excess adsorption from measurements of the single-particle diffusion coefficient with fluorescence correlation spectroscopy (FCS).

Here, we report small-angle neutron scattering (SANS) measurements of silica particles (R = 13 nm) suspended in lutidine/water mixtures at the critical concentration and three offcritical concentrations. These measurements make it possible to directly elucidate aspects of surface concentration profiles and excess adsorption, including the effects of solvent composition and particle curvature.

#### **II. EXPERIMENT**

For reference, the phase diagram for lutidine and water mixtures is shown in Fig. 1. In this work, four lutidine mass fractions, w = 0.25, 0.29, 0.31, and 0.33, were studied at the particle volume fraction  $\phi = 0.001$ . Silica particles were

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FIG. 1. Phase diagram of lutidine and water mixtures. Points indicate the location of measurements described in this work. The lower critical point is located at  $T_c = 33.3$  °C and  $w_c = 0.29$ .

obtained in the form of Ludox TM-50 colloidal silica solution from Sigma-Aldrich as was 2,6-dimethylpyridine (lutidine) (>99%).<sup>11</sup> Milli-Q water (18.2 M $\Omega$  cm) was used in the preparation of all samples.<sup>11</sup> When silica is added to lutidine/water mixtures, the preferred solvent component depends on both the particle surface charge density<sup>12</sup> and the solvent ion content.<sup>13</sup> In agreement with previous reports,<sup>14</sup> the Ludox particles used here were found to have a strong preference for water. Small angle neutron scattering measurements were performed at the NIST Center for Neutron Research with an incident neutron wavelength of  $\lambda = 0.6$  nm. The instrument was configured to probe length-scales between roughly 1.6 nm and 160 nm by varying the scattering angle  $\theta$ . Representative scattering curves are shown in Fig. 2. The temperature was controlled to within 0.1 °C by connecting a circulating bath to the sample block.



FIG. 2. Comparison of scattering intensities at w = 0.25 and 0.33. All data have been shifted by the same constant to highlight variations over the entire Q range. Solid lines are fits to Eq. (1). Errorbars representing one standard deviation are contained within the size of the majority of points. For w = 0.33, the crossing of data at small Q values is a clear indication of water adsorption.

#### III. SANS MODELLING

SANS measures the differential cross section per unit volume, denoted here by *I*, as a function of  $Q = (4\pi/\lambda) \sin(\theta/2)$ , the magnitude of the scattering vector. For the purposes of interpreting our data, it is useful to view the total scattering as the sum of contributions from solvent (s) and particle (p) scattering, specifically,

$$I(Q) = I_{s}(Q) + I_{p}(Q) + B_{inc},$$
 (1)

where  $B_{inc}$  is the Q-independent incoherent background.

The intensity of solvent scattering depends on the contrast between the scattering length densities of water ( $\hat{\rho}_W = -0.56 \times 10^{-4} \text{ nm}^{-2}$ ) and lutidine<sup>15</sup> ( $\hat{\rho}_L = 1.16 \times 10^{-4} \text{ nm}^{-2}$ ) and is well described by the Ornstein-Zernike approximation<sup>16</sup>

$$I_{\rm s}(Q) = (\hat{\rho}_{\rm W} - \hat{\rho}_{\rm L})^2 \frac{\chi}{1 + (\xi Q)^2},\tag{2}$$

where  $\chi$  is proportional to the isothermal osmotic compressibility and  $\xi$  is the solvent correlation length.

The scattering cross section for colloidal suspensions<sup>17</sup> is the product of intraparticle correlations, characterized by the form factor P(Q), and interparticle correlations, characterized by the structure factor S(Q). In the dilute solution limit,  $S(Q) \approx 1$ , and the scattering pattern depends only on the form factor as

$$I_{\rm p}(Q) = nP(Q),\tag{3}$$

where *n* is the number density of silica particles. The form factor is related to the spatial variation of the local particle scattering length density  $\hat{\rho}(\mathbf{r})$  and the average solvent scattering length density  $\hat{\rho}_s$  by a Fourier transform,

$$P(Q) = \left| \int d\mathbf{r} \ e^{i\mathbf{Q}\cdot\mathbf{r}} \left[ \hat{\rho}(\mathbf{r}) - \hat{\rho}_{\rm S} \right] \right|^2. \tag{4}$$

To characterize the bare silica particles independently, we have measured the scattering from a dilute suspension ( $\phi = 0.001$ ) of silica in pure water. The scattering length density profile of a silica sphere<sup>15</sup> ( $\hat{\rho}_{SiO_2} = 3.46 \times 10^{-4} \text{ nm}^{-2}$ ) in water was represented by a step-function centered at the sphere's radius *R*. Polydispersity of the particle size was modeled by averaging the cross section over a Schultz distribution<sup>18</sup> of mean radius  $\bar{R}$  and width  $\sigma_R$ . The polydispersity index of the sample is defined by  $p \equiv \sigma_R/\bar{R}$ . The extracted fit parameters for the particles are  $\bar{R} = 13$  nm and p = 0.18.

Incorporating the adsorbed surface layer into the definition of the particle form factor, P(Q), provides a convenient means of accounting for the resulting solvent-particle correlations. Thus, we define a local adsorption profile m(z) as a function of the radial distance from the particle surface z = r– R. Water adsorption corresponds to positive values of m(z). The combined scattering length density profile is now given by

$$\hat{\rho}(\mathbf{r}) - \hat{\rho}_{\rm S} = \begin{cases} \hat{\rho}_{\rm SiO_2} - \hat{\rho}_{\rm S}, & r < R\\ (\hat{\rho}_{\rm W} - \hat{\rho}_{\rm S})m(z), & r > R \end{cases},$$
(5)

where  $\hat{\rho}_{\rm S}$  is estimated from a linear interpolation between  $\hat{\rho}_{\rm W}$  and  $\hat{\rho}_{\rm L}$ . The difference in the scattering length densities of water and the bulk solvent determines the sensitivity of SANS to the preferential adsorption of water on Ludox particles.

Asymptotically close to the critical point, the adsorption profile follows the scaling law<sup>3</sup>

$$m(z) \approx B_0 |t|^\beta P(z/\xi), \tag{6}$$

where  $B_0|t|^{\beta}$  gives the (asymptotic) shape of the coexistence curve and the universal order-parameter exponent is  $\beta \simeq 0.33$ . On the basis of scaling arguments, Liu and Fisher<sup>19</sup> have proposed the following profile function:

$$P(x) = A \left(\frac{1}{x} + c\right)^{\beta/\nu} e^{-x},\tag{7}$$

where A sets the magnitude of adsorption and  $\nu \simeq 0.63$  is the universal correlation-length exponent. This form captures the expected power-law behavior at short distances and the exponential decay far from the surface. The crossover between these two regimes is controlled by the constant *c*. Because this profile diverges as  $z \rightarrow 0$ , it must be supplemented by the condition that the amplitude of the adsorbed layer saturates at the total adsorption of water, i.e.,  $\hat{\rho}(\mathbf{r}) = \hat{\rho}_w$  or m(z) = 1. Following Liu and Fisher, we simply cap the profile at this maximum value. We have tried implementing a more sophisticated scheme for incorporating surface saturation<sup>8</sup> but did not find any qualitative differences.

The crossover parameter c is, in theory, a universal constant. However, reported theoretical and experimental values of c exhibit some variation.<sup>20</sup> Based on the behavior of our data near the coexistence curve, we have used c = 0.5 for all fits. This value lies within the range of values commonly used in the literature. Within reason, different values of c do not strongly affect our results. When c is treated as a free parameter, the fits at low temperature prefer purely exponential decay (large c), whereas the fits close  $T_c$  favor smaller values of c and therefore place a greater emphasis on the power-law behavior.

#### **IV. RESULTS AND DISCUSSION**

We have fit the measured I(Q) at each temperature and concentration using the cross section given by Eq. (1) with the particle form factor corresponding to Eq. (5), averaged over a Schultz distribution. In performing these fits, we have fixed  $\bar{R}$  and p to the values extracted from silica in water. These constraints leave A,  $\chi$ ,  $\xi$ , and  $B_{inc}$  as the only adjustable parameters. Representative fits are shown in Fig. 2.

At 20 °C, the scattering curves (cf. Fig. 2) closely follow the form factor extracted from silica in pure water. As the temperature of the system is raised towards the coexistence temperature, the total scattering is affected by increases in both solvent scattering  $I_S(Q)$  and adsorption-layer particle scattering m(z). However, since the prefactor  $(\hat{\rho}_W - \hat{\rho}_S)$  multiplying m(z) in Eq. (5) is negative, while  $(\rho_{SiO_2} - \hat{\rho}_S)$  is positive, the adsorption of water reduces the scattering intensity. This explains why the small-Q scattering intensity for w = 0.33 is smaller at 32.4 °C than at 20.0 °C, even though  $\chi$  is roughly 20 times larger at 32.4 °C. Independent of fit model, the clear decrease of I(Q) at small Q indicates that water is preferentially adsorbed on the surface of the particles. The quality of the fit curves at both high and low temperatures demonstrates that the Liu-Fisher profile is adequate for the description of our data.



FIG. 3. Comparison of adsorption profiles at different solvent concentrations. The distance from the particle surface z has been scaled by the correlation length  $\xi$ . Consequently, the observed differences in m(z) are entirely attributable to the concentration dependence of P(x), as parametrized by A in Eq. (7).

Representative examples of real-space adsorption profiles corresponding to the experimental fits are shown in Fig. 3. A saturated layer of water is found on the particle surface under all experimental conditions. The structural details of this surface layer are beyond the spatial resolution of SANS. The differences in these profiles reflect differences in *A*. For a fixed correlation length, the distance from the surface at which the profile saturates is entirely determined by *A*.

Both the range  $\xi$  and magnitude  $\chi$  of concentration fluctuations increase dramatically as the coexistence curve is approached. The extracted values of these parameters are shown in Fig. 4. In terms of the reduced temperature  $t \equiv (T - T_c)/T_c$ , the measured correlation lengths and compressibilities exhibit the expected asymptotic power-law behavior:  $\xi \approx \xi_0^+ |t|^{-\nu}$  and  $\chi \approx \Gamma_0^+ |t|^{-\gamma}$ , where  $\xi_0^+$  and  $\Gamma_0^+$  are critical amplitudes and  $\gamma$  $\simeq 1.24$  is the universal compressibility exponent. For offcritical concentrations ( $w \neq w_c$ ), these scaling relations are not rigorously applicable. However, we find excellent agreement for the measured values of  $\xi$  and  $\chi$  if  $T_c$  is treated as a free parameter. In this case, the extract values of  $T_{\rm c}$  correspond to the spinodal temperature where  $\chi$  and  $\xi$  appear to diverge at off-critical concentrations. The resulting fit curves are presented in Fig. 4. The quality of these fits gives us confidence that our modeling of the SANS data is able to consistently



FIG. 4. Solvent correlation length  $\xi$  and compressibility  $\chi$  versus temperature. The solid lines correspond to fits of the data with the power-law relationships described in the text. The extracted amplitudes are  $\xi_0^+ \simeq 0.2$  nm and  $\Gamma_0^+ \simeq 0.006$  nm<sup>3</sup>.



FIG. 5. Dependence of the profile amplitude A on correlation length  $\xi$ . For a planar surface, A is expected to be independent of temperature (and therefore independent of  $\xi$  as well). The decrease in A with increasing temperature is indicative of finite curvature effects. When not shown, errorbars are contained within the size of the points. Connecting lines are shown as a guide to the eye.

differentiate the solvent and particle scattering contributions. The compressibility  $\chi$  is related to the isothermal osmotic compressibility via  $\chi = (k_{\rm B}T/\rho^2)(\partial c/\partial \mu)_T$ , where  $\rho$  is the number density of pure water, *c* is the molarity of water in the mixture, and  $\mu$  is difference in the chemical potentials of lutidine and water. This relationship accounts for why  $\chi$  has units of volume.

Values of the amplitude A extracted from the fits are shown in Fig. 5. Note that for planar surfaces, A is expected to be constant in temperature. There are two salient trends in the behavior of A. First, the relative magnitude of A increases monotonically with increasing lutidine concentration at fixed correlation length (or temperature). This trend follows that found for planar interfaces in this range of concentrations.<sup>21</sup> Second, A decreases as the coexistence curve is approached. The observed temperature dependence of A, shown implicitly in Fig. 5, can be attributed to the curvature of the silica particles. This interpretation is consistent with the mean-field calculations of Hanke and Dietrich,<sup>9</sup> who found that the intrinsic adsorption associated with the shape of the profile P(x) decreases as the solvent correlation length increases relative to the particle radius. Because A is the only free parameter related to the shape of the profile, A might be serving as a proxy for other shape related changes to P(x). The dependencies of A on w and T appear to be relatively decoupled for the conditions studied.

The excess adsorption<sup>5</sup>  $\Gamma$  is related to the scattering profile by the following integral:

$$\Gamma = \frac{N}{R^2} \int_R^\infty dr \ r^2 \left[ \hat{\rho}(r) - \hat{\rho}_{\rm S} \right],\tag{8}$$

where the normalization factor  $N = \rho_W/(\hat{\rho}_W - \hat{\rho}_L)$  converts the scattering-length density profile to a water mass-density profile. Values of  $\Gamma$  calculated with Eq. (8) are presented in Fig. 6. For planar surfaces<sup>5</sup> ( $\xi/R \rightarrow 0$ ),  $\Gamma \sim |t|^{\beta-\nu}$  with  $\beta - \nu \simeq -0.30$ . Thus, the excess adsorption diverges at the critical point. At the critical concentration, it has been predicted<sup>9</sup> that for curved surfaces  $\Gamma \sim |t|^{-\gamma}$  in the regime where ( $\xi/R$ )  $\gg 1$ . In this relation,  $\gamma \simeq 1.24$  is the compressibility exponent. Our data correspond to the regime ( $\xi/R$ )  $\lesssim 1$  and are well described by the relation  $\Gamma \sim |t|^{-0.52}$ . Hence, our data appear to diverge more strongly than the planar case, but less strongly than in



FIG. 6. Scaling plot for the excess adsorption. The excess adsorption is found to diverge more strongly than in the planar case. Increasing lutidine concentration leads to greater adsorption. The solid line corresponds to  $\Gamma \sim |t|^{-0.52}$ . When not shown, errorbars are contained within the size of the points. Connecting lines are shown as a guide to the eye.

the strong curvature regime. The recent analysis of FCS data reported by Omari *et al.* results in  $\Gamma \sim |t|^{-0.98}$  over a range of  $\xi/R$  values that include those studied here and extend to  $\xi/R \simeq 3$ . In principle, the spatial resolution and direct nature of SANS should allow for a more reliable determination of  $\Gamma$  as compared to FCS.

The high temperature data at w = 0.25 exhibit notable deviations from power-law scaling. In this case, the excess adsorption appears to saturate as the coexistence curve is approached in spite of the fact that the correlation length continues to increase as expected. It is also notable that the w = 0.29 data show a slight upward curvature as the correlation length increases. This could be indicative of a crossover to the stronger divergence predicted for greater curvature. In contrast, w = 0.31 and 0.33 apparently show no such trend.

#### **V. CONCLUSIONS**

Using small angle neutron scattering, we have successfully studied the critical adsorption profile on the surface of silica particles at critical and off-critical concentrations. We have identified three distinct factors that contribute to the excess adsorption. The first is the correlation length of the solvent fluctuations. The scaling hypothesis [Eq. (6)] forces all distances to be scaled by  $\xi$ . Based on the quality of our fits, the hypothesis appears to remain valid for off-critical concentrations and curved surfaces. In contrast, the "core-shell" model employed in light scattering studies violates this hypothesis. The correlation length is roughly symmetric with respect to the critical concentration  $w_c$ . Therefore, the differences in  $\Gamma$ observed at different concentrations cannot be attributed to differences in  $\xi$ .

The second factor contributing to  $\Gamma$  is the difference in water concentration at the particle surface and in the bulk solvent. This effect is captured by the prefactor  $(\hat{\rho}_W - \hat{\rho}_S)$  in Eq. (5) and is related to the fact that the particle surface is completely saturated with water at all conditions studied. Because excess adsorption is measured relative to the bulk concentration, compositions that are poorer in water have an inherently greater potential for *excess* adsorption. This factor creates an asymmetry in the excess adsorption with respect to

the solvent concentration that is reflected in the observed trend. However, it does not account for the entire effect because the values of A still depend on concentration for fixed  $\xi$ .

Finally, the excess adsorption is affected by the shape function P(x). In our case, changes in P(x) are parametrized by the prefactor A. As A decreases, the intrinsic extent of adsorption associated with P(x) decreases as well and the profile becomes more localized around the particles surface. For the excess adsorption, this effect is off-set to some extent by the factor  $r^2$  in the spherical Jacobian that weighs distances further from the surface more heavily. These competing effects do not completely compensate each other and we find that  $\Gamma$ diverges more strongly than in the planar case.

The temperature dependence of the excess adsorption was found to behave as  $\Gamma \sim |t|^{-0.52}$  for  $\xi/R \sim 1$ . The value of the scaling exponent in this relation is within the expected range of theoretical predictions.

#### ACKNOWLEDGMENTS

This manuscript was prepared under Cooperative Agreement No. 70NANB10H256 for NIST, U.S. Department of Commerce. The statements, findings, conclusions, and recommendations are those of the authors and do not necessarily reflect the view of NIST or the U.S. Department of Commerce.

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