Controlling the Formation of Capillary Bridges in Binary Liquid Mixtures

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We study the formation of capillary bridges between micrometer-sized glass spheres immersed in a binary liquid mixture using bright field and confocal microscopy. The bridges form upon heating due to the preferential wetting of the hydrophilic glass surface by the water-rich phase. If the system is cooled below the demixing temperature, the bridges disappear within a few seconds by intermolecular diffusion. Thus, this system offers the opportunity to switch the bridges on and off and to tune precisely the bridge volume by altering the temperature in a convenient range. We measure the bridge geometry as a function of the temperature from bright field images and calculate the cohesive force. We discuss the influence of the solvent composition on the bridge formation temperature, the strength of the capillary force, and the bridge volume growth rate. Furthermore, we find that the onset of bridge formation coincides with the water–lutidine bulk coexistence curve.

Introduction

Capillary bridges at solid contacts can occur if a liquid (e.g., water) condenses out of an ambient gaseous phase. A liquid meniscus is then formed around surface contact sites exerting a strong force between the adjacent solid bodies. This cohesive force is large compared to other surface forces, for example, the van der Waals interaction, and has a tremendous effect on the material physical properties. For example, granular matter turns into a pastelike material upon adding a small amount of liquid. Material physical properties. For example, granular matter turns into a pastelike material upon adding a small amount of liquid.2,3 The understanding of this cohesive force has wide industrial applications such as sintering and powder agglomeration processes. Capillary attractions were also identified in biology, where they are discussed as possible contributions to gecko adhesion.4,5 However, recent findings indicate that capillary adhesion is caused by the change in the elastic properties of the gecko’s spatula with increasing humidity.6 Moreover, capillary bridges have been observed in liquid mixtures such as microemulsions6 and polymer solutions7,8 and in nematic liquid crystals.9 In these cases, the liquid undergoes a surface-induced phase transition with the two coexisting phases separated by a meniscus. In particular, the formation of capillary bridges in binary liquid mixtures has experienced great interest in recent years.10,11 Beyens and Esteve12 studied the aggregation of colloidal silica particles in lutidine–water mixtures.

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of grains immersed in an index-matching organic solvent.\(^{23,24}\)
However, this procedure has the clear disadvantage that the bridge size cannot easily be tuned. Once the fluorescent water has been added, it cannot be removed. In contrast, our system offers the opportunity to control the bridge size. By altering the temperature, we are able to precisely tune the capillary forces.

The outline of this paper is as follows: First, we summarize the theoretical expressions for the capillary force and bridge volume. Second, we describe our experimental setup in detail. Next, the bridge formation in a binary solvent is explained. The temperature-induced bridge formation is then demonstrated experimentally using a confocal microscope. Thereafter, we measure the bridge geometry from bright field images and calculate the cohesive force for samples with varying composition. In addition, we study in detail how the bridge formation process is influenced by the liquid mixture composition.

**The Capillary Force**

The force exerted on two particles interconnected by a liquid meniscus has two contributions. One arises directly from the interfacial tension, \(\gamma\), and the other is due to the pressure difference, \(\Delta P\), caused by the surface curvature and interfacial tension. For axisymmetric bridges between two spherical particles, the capillary force can be written as the sum\(^{25,26}\)

\[
F_b = 2\pi l \gamma - \pi l^2 \Delta P
\]

where \(l\) is the radius of the capillary neck perpendicular to the plane (Figure 1a) and \(\Delta P\) denotes the Laplace pressure. Note, that eq 1 is exactly fulfilled. Assuming that the meniscus curvature can be approximated by a circle, that is, applying the so-called toroidal approximation,\(^{25,27}\) the Laplace pressure reads

\[
\Delta P = \gamma \left( \frac{1}{r} - \frac{1}{R} \right)
\]

where \(r\) describes the in plane radius of curvature; see Figure 1a. Pietsch and Rumpf,\(^{28}\) and Smolej and Pejovnik\(^{29}\) derived an expression for \(F_b\), assuming a toroidal-like meniscus. The toroidal approximation has been tested thoroughly against the exact numerical solution, and good agreement has been found for zero sphere surface-to-surface separation, \(\alpha\).\(^{26,30–33}\) Since our microspheres are not monodisperse, we require an expression for the capillary force between two spheres of unequal size. For this reason, we use the analytical expression by Tselishchev and Val’tsifer\(^{34}\) for two particles with radii \(R_1\) and \(R_2\). For \(R_1 < R_2\), the bridge force is given by

\[
F_b = \pi R_1 \gamma \sin \beta_1 \left[ 2 \sin(\beta_1 + \theta) + R_1 \sin \beta_1 \left( \frac{1}{r} - \frac{1}{R} \right) \right]
\]

Figure 1. (a) Geometry of two spherical particles with a capillary bridge in between. The bridge is assumed to have a toroidal-like shape. (b) Bright field reflection image (50× magnification) of two glass spheres at contact interconnected by a capillary bridge at \(T = 40.5\,^\circ\text{C}\) and with \(w = 0.58\). The shadow between the two particles displays the capillary bridge. The width of the scale bar at the bottom right is 20 μm.

with the half opening angle \(\beta_1\), the wetting angle \(\theta\), and the two radii of curvature

\[
r = \frac{R_1 (1 - \cos \beta_1) + R_2 (1 - \cos \beta_2) + d}{\cos(\beta_1 + \theta) + \cos(\beta_2 + \theta)}
\]

and

\[
l = R_1 \sin \beta_1 - r \left[ 1 - \sin(\beta_1 + \theta) \right]
\]

The bridge volume \(V_b\) is calculated from

\[
V_b = \pi \int_{\gamma}^{\beta} dy \left[ r + l - \sqrt{\left( r^2 - y^2 \right)^2} \right] - V_1 - V_2
\]

with integration limits \(\gamma_1 = -r \cos(\theta + \beta_2)\) and \(\gamma_2 = -r \cos(\theta + \beta_1)\). The volume of the two immersed sphere caps is given by

\[
V_i = \frac{\pi}{3} R_i^3 \left( 1 - \cos \beta_i \right)^2 \left( 2 + \cos \beta_i \right) \quad (i = 1, 2)
\]

Note that a simple but instructive thermodynamic model for the formation of capillary bridges was given by Petrov et al.\(^{9}\) By approximating the liquid meniscus in between a sphere and a plate by a cylinder and assuming a complete wetting situation, these authors derived an analytical expression for the total free energy of a small capillary bridge. Using this result, Andrienko et al.\(^{35}\) discussed the first-order character of the bridging transition.

**Experimental Section**

**Materials, Samples, and Equipment.** 2,6-Lutidine (2,6-dimethylpyridine) with a purity of ≥99% was purchased from...
Sigma-Aldrich and was used as received. The index of refraction of lutidine is \( n = 1.497 \). Sodium fluorescein (Fluka) was dissolved in water taken from a Millipore ultraclean facility. This aqueous solution with a concentration of 1 mM sodium fluorescein was used to prepare all lutidine–water mixtures. The water-dissolved fluorescein has a relatively sharp adsorption maximum at 485 nm and a broad emission spectrum with a maximum at around 514 nm. The sample chambers were assembled by placing two microscope coverslips as spacers and a third one on top onto a microscope slide as described in ref 36. The height of chambers is about 170 \( \mu m \). The chambers were glued using Norland 61 optical adhesive and cured under UV-light. Afterward, these sample cells were placed for several hours in an exsiccator and coated with hexamethyldisilazane (Fluka). This procedure generates hydrophobic glass surfaces. We use GL-0179 borosilicate glass spheres (MO-SCI) with a density of 2.2 g/cm\(^3\).

The confocal images were taken with a Leica DMRXE upright microscope using a TCS SP2-xi scanning head and Leica HC PL FLUORTAR 20\( \times \)/0.50 and 50\( \times \)/0.80 objectives. For the bright field images, a Olympus BX-61 microscope with an LMPlanFl 50\( \times \)/0.50 air objective was used.

**Results and Discussion**

**Bridge Formation upon Heating.** The phase diagram of the water–lutidine mixture is sketched in Figure 2, where we plotted the temperature (ordinate) against the weight fraction of lutidine \( w \) (abscissa). The latter is defined as the fraction of lutidine with mass \( m_l \) to the total mass of lutidine and water, \( m_l + m_w \).

\[
w = \frac{m_l}{m_l + m_w}
\]  

(8)

The solid curve denotes the binodal line and the star indicates the critical point at \( w_c = 0.29 \) and \( T_c \approx 34^\circ C \). To observe capillary bridges, we proceed as follows: First, we suspend our glass spheres into the mixture with the desired weight fraction of lutidine at room temperature (point A in Figure 2). To obtain capillary bridges, we choose a mixture with a composition rich in lutidine and poor in water on the right-hand side of the critical point, that is, \( w > w_c \). Then, second, we increase the temperature stepwise, giving the sample always enough time to equilibrate, and observe the two-dimensional random packing of spheres under a microscope. When we cross the binodal line, the mixture starts to phase separate along the horizontal tie line as indicated for point B in Figure 2. The dots terminating the tie line denote the compositions of the two coexisting phases. The point on the left branch of the binodal marks the composition of the water-rich phase (and, correspondingly, lutidine-poor phase) with lutidine weight fraction \( w' \) and the point on the right branch describes the lutidine-rich phase with \( w'' \). Since we chose a solvent composition on the lutidine-rich side of the phase diagram (Figure 2), only a very small amount of the water-rich phase nucleates. This water-rich phase is adsorbed on the microsphere glass surface and a wetting layer is formed. If two particles are at contact, these wetting layers overlap and a capillary bridge is formed (see Figure 3). Note here that the undesired adsorption of the water-rich phase onto the sample chamber housing is avoided by the silane coating. If we increase the temperature further to point C in Figure 2, the amount of the wetting phase and, thus, the bridge volume increases.

To demonstrate the formation of capillary bridges described above, we show a temperature series of confocal images for a sample with \( w = 0.58 \) in Figure 4. Notice that the images in Figure 4 correspond to the state points indicated in Figure 2. The liquid mixture contains a fluorescence dye to obtain a scattering signal from the water. At 41 \( ^\circ C \) (Figure 4A), the liquid mixture is within the one-phase region and a suspension of spheres in an homogeneous background (solvent) is observed. The glass beads do not contain any fluorescent dye and, thus, appear as black disks. Upon increasing the temperature to 41.5 \( ^\circ C \), capillary bridges are formed (Figure 4B). Since the fluorescein dissolves preferentially in the water-rich phase, the dye concentration is enhanced within...
the capillary bridges. As a consequence, the bridges emit an intense fluorescence signal and appear as bright spots. The aqueous wetting layer on the microsphere surface is only a few nanometers thick and cannot be resolved by optical microscopy. If we increase the temperature to 42 °C (Figure 4C), the bridges grow in size. Moreover, we observe liquid structures interconnecting three beads (trimers). At 43 °C, a sufficient amount of water-rich phase has nucleated to form large aqueous clusters involving several particles (Figure 4D). A closer inspection of Figure 4D shows that the spheres have rearranged. We note that the morphology of liquid clusters has been studied in detail by Scheck et al. using X-ray tomography. When the sample is cooled below the demixing temperature, the aqueous phase forming the capillary bridges and liquid clusters disappears within a few seconds. Similar time scales for the interdiffusion coefficients of the water–lutidine mixture were found experimentally by Clunie and Baird.40

In Figure 5, we have evaluated the number of bridges and clusters for the confocal images presented in Figure 4. The relative frequency was obtained by dividing the number of bridges and clusters interconnecting n particles, respectively, by the total number of bridges and clusters. At $T = 41$ °C (Figure 5A), no bridges are encountered. Just above the binodal line, that is, at $T = 41.5$ °C, only bridges are observed (Figure 5B). By increasing the temperature about 0.5 to 42 °C, we observe three-sphere clusters (trimers) and quadrumers comprising 10% of all clusters (Figure 5C). At $T = 43$ °C (Figure 5D), 76% of all clusters are bridges, and large clusters are found which connect up to 15 spheres.

As a next step, the onset of the bridge formation is compared with the bulk water–lutidine coexistence curve in Figure 6. The filled blue squares indicate the state points, where we observed capillary bridges for the first time upon heating. For these samples, no critical opalescence is observed on crossing the binodal line, since the aqueous phase is adsorbed on the surface of the glass spheres. In contrast, the filled green triangles in Figure 6 denote state points, where the mixture phase separates but no bridge formation is observed. This phase separation is indicated initially by a large increase in the sample turbidity accompanied with a demixing into two macroscopic phases at later times. As seen in Figure 6, bridge formation occurs only on the lutidine-rich branch. This observation is readily understood by taking into account the microsphere wetting property and the volume fractions of the two coexisting phases. When heating up a mixture with a lutidine weight fraction smaller than the critical composition, a minor amount of a lutidine-rich phase is produced. Most of the sample volume is occupied by a water-rich phase. Since this minor phase of lutidine is hydrophobic, whereas the glass surface is hydrophilic, no wetting layer is formed. In lieu, the mixture undergoes a macroscopic phase separation. The confocal image turns dark upon crossing the coexistence curve, since the incident laser light is strongly scattered by the critical fluctuations and hardly any emitted light enters the objective. In the case of hydrophilic spheres, capillary bridges can only form for solvent compositions larger than the critical one.

For samples with $w = 0.14$ and 0.19, a close inspection of Figure 6 shows that the demixing temperatures, $T_d$, lie ~4 °C underneath the bulk coexistence curve. To investigate this shift, we prepared additional samples with the same lutidine weight fractions but without glass spheres. In addition, test samples with $w = 0.14$ and 0.19 without fluorescence dye and without spheres were mixed. For both sets of samples, we observed the same $T_d$ as previously found in samples with glass spheres. Hence, we suppose that this shift in $T_d$ is due to contaminations of the lutidine.

In summary, the formation of capillary bridges is due to the preferential wetting of the hydrophilic glass spheres by the water-rich phase of the phase-separated water–lutidine mixture. This mechanism for bridge formation is not specific for the water–lutidine system but applies for any binary liquid mixture with similar wetting properties.

Bridge Geometry and Capillary Forces. Figure 1b shows a typical bright field image of a capillary bridge. For sample compositions far away from the critical point (~10% away from $w_c$), a sharp interface is formed between the water-rich liquid bridge and the surrounding lutidine-rich phase. A closer look
at Figure 1b reveals the shadow of the toroidal-like bridge. The bridge geometry is measured from such images by fitting circular arcs of radii \( r \) and \( l \) to the in-plane curvature of the bridge and to the cross section of the neck, respectively. In addition, the two radii \( R_1 \) and \( R_2 \) of the adjacent particles are measured. The contact angle was measured for a sample with \( w = 0.58 \) for 0.25 °C ≤ \( T - T_0 \) ≤ 1.5 °C, resulting in a value less than 10. Thus, it is reasonable to assume complete wetting (\( \theta \approx 0 \)) in the following. The parameters \( r, l, \beta_1, \) and \( \beta_2 \) extracted from microscope images for samples with \( w = 0.58 \) and 0.68 are shown in Figure 7, where each data point results from the evaluation of a single bridge. We checked that the measured values for \( r \) and \( l \) coincide with those calculated from eqs 4 and 5 using \( R_1, R_2, \beta_1, \beta_2, \) and \( d = 0 \) within less than 3%. Using eqs 6 and 7, we calculated the bridge volume (Figure 8a).

Notice that we normalized \( V_b/R^3 \) to the in-plane curvature of the bridge and to the cross section of the neck, respectively. The onset of the bridge formation is observed upon heating. The green triangles denote solvent compositions, where no capillary bridges were formed. In these samples, the water–lutidine mixture undergoes a macroscopic phase separation. The solid curve is the bulk coexistence curve, and the star denotes the critical point.4

Figure 6. Onset of bridge formation in comparison to the bulk phase diagram: The blue squares indicate the temperatures, where the onset of the bridge formation is observed upon heating. The green triangles denote solvent compositions, where no capillary bridges were formed. In these samples, the water–lutidine mixture undergoes a macroscopic phase separation. The solid curve is the bulk coexistence curve, and the star denotes the critical point.4

Hence, a much steeper slope of the coexisting curve is encountered when crossing the binodal line at \( w = 0.68 \) than at \( w = 0.58 \). As stated by the lever rule, the amount of the water-rich phase and, correspondingly, of the bridge volume is proportional to \( |w - w'| \), that is, to the distance measured from the mixture composition, \( w \), to the composition of the lutidine-rich phase, \( w' \), along the tie line (see Figure 2). Thus, \( V_b \) increases faster with increasing temperature for mixtures \( w \) close to the critical composition as observed in our experiments. For comparison, we calculated the relative composition, \( f = (w'' - w)/(w - w') \), of the liquid mixture using the bulk binodal line (Figure 8b). As expected, \( f \) increases much faster for \( w = 0.58 \) than for \( w = 0.68 \). Since the overall number of bridges is unknown, we cannot compute the theoretically expected bridge volume. However, comparing the ratio of bridge volumes for \( w = 0.58 \) and 0.68 (Figure 8a) with the ratio of aqueous phases (Figure 8b) indicates that \( V_b \) increases with \( T \) at the same rate as predicted by the bulk coexistence curve.

Next, we calculated the bridge force for samples with \( w = 0.43, 0.58, \) and 0.68 (Figure 9a). The forces are computed by inserting the measured values for \( R_1, \beta_1, r, \) and \( l \) in eq 3 using the known data for \( \gamma(T) \) from ref 22. If we compare the magnitudes of the forces for the three different lutidine weight fractions at fixed temperature in Figure 9a, we observe that \( F_b \) increases drastically with increasing \( w \) at fixed \( T - T_0 \). This observation can again be
explained by looking at the phase diagram in Figure 6. As noticed before, $T_d$ stays approximately constant near $T_c$ and increases rapidly with increasing $w$ for $w > w_c$. Hence, capillary bridges are formed at a much higher temperature in a sample with $w = 0.68$ than for a mixture with $w = 0.43$. Since $F_b \sim \gamma$ and $\gamma \sim T$, $F_b$ increases with $T$. Thus, stronger capillary forces are observed for larger $w$ if the force is normalized by $\gamma$, all three data sets collapse, indicating that the differences in force are mainly caused by temperature dependence of the interfacial tension (Figure 9b).

It is interesting to notice here the low interfacial tensions encountered in our samples. $\gamma$ is about 100 times smaller than the typical surface tension between a water–air-interface ($\gamma_{\text{water–air}} \approx 72$ mN/m at 25 °C). At the same time, the capillary force is still several times stronger than the gravitational forces acting on our glass spheres ($F_g \approx 4$ nN). Therefore, $F_b$ is large enough to rearrange the particles as observed in Figure 4.

Moreover, we note that eq 3 should be applicable for particle sizes down to 1 μm. Thus, our results can be used to estimate the capillary forces in colloidal suspensions with similar wetting properties.[41]

**Conclusion**

We have directly observed the formation of capillary bridges in water–lutidine mixtures. Using optical microscopy, we demonstrated that this system provides an convenient approach to induce capillary forces by tuning the temperature. The magnitude of the forces was estimated from the observed bridge geometry. Due to the low interfacial tension, we expect capillary forces of the order of nanonewtons. We showed that the cohesive force can be easily varied over more than two decades by choosing different solvent compositions. In addition, we demonstrated that the bridge formation depends more sensitively on the temperature for solvent compositions further away from the critical point. For the relatively low concentrations of glass spheres under investigation, we find that the temperature where the onset of bridge formation is observed coincides with the bulk coexistence curve. The system studied here is particularly interesting because it might serve as a model system to investigate the commons and disparities in the physical properties of dry and wet granular matter. Direct measurements of the capillary force would be highly desirable and should be considered in the future.

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