

Wetting in a Colloidal Liquid-Gas System

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(Received 28 November 2002; published 13 May 2003)

We present first observations of wetting phenomena in depletion interaction driven, phase separated colloidal dispersions (coated silica-cyclohexane-polydimethylsiloxane). The contact angle of the colloidal liquid-gas interface at a solid substrate (coated glass) was determined for a series of compositions. Upon approach to the critical point, a transition occurs from partial to complete wetting.

DOI: 10.1103/PhysRevLett.90.196101

PACS numbers: 68.08.Bc, 64.70.-p, 68.03.Cd, 82.70.Dd

Colloidal systems make convenient experimental models of simple fluids, as they are composed of particles with interactions that can be tuned in both strength and range. This Letter presents the first observations on wetting (contact angles) and a wetting transition occurring in depletion interaction driven systems.

Wetting phenomena are typical, perhaps even characteristic, for the liquid state. They occur always when three phases coexist, at least one of which is liquid, and not more than one solid. If two fluid phases are in contact with a solid, partial wetting can be characterized by the static contact angle, θ_0 , which is by Young's law related to the interfacial tensions, γ , between the three phases [1]:

$$\cos\theta_0 = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}. \quad (1)$$

Here, the subscripts S , L , and G refer to the solid, the liquid, and the gas phase, respectively. If the contact angle is 0° , the substrate is said to be completely wet by the liquid; if $0^\circ < \theta_0 < 180^\circ$, the substrate is partially wet [2]. In Eq. (1), the denominator depends only on the interaction between molecules that make up the liquid and the gas. The numerator also depends on the interaction between these molecules and the substrate. Cahn predicted that near the critical point a solid substrate is completely wet by one of the two fluid phases. At a certain temperature below the critical point, the wetting behavior may change from complete to partial. This phenomenon is called the wetting transition and is a true phase transition [3,4].

The past 25 years have seen a revival of the study of fundamental aspects of wetting phenomena in general and wetting transitions in particular [2–7]. For further investigations, it would be very convenient to control the interactions on a microscopic level. Clearly, with atomic or molecular fluids this is impossible because the interactions are given with the molecular species. As an alternative, colloidal systems make very convenient experimental model systems, because the interactions can be *tuned*, both in *range* and *strength*. Therefore, colloidal systems have played an important role in the

experimental verification of theories of condensed matter in general, and of liquids in particular [8,9].

The phase behavior of colloidal dispersions has a strong analogy with that of atomic or molecular systems. Similar to molecular systems, colloidal particles dispersed in a liquid medium can assume various states. A dilute disordered dispersion is called “colloidal gas,” a concentrated disordered one “colloidal liquid,” and a concentrated ordered dispersion “colloidal crystal.” Using colloidal model systems, the requirements for the very existence of the liquid state have been clarified, namely, the existence of an attraction with a range that is not too short, compared to the diameter of the repulsive core of the pair potential.

In order to prepare colloids in a liquid state, one proceeds as follows. Since the bare van der Waals attraction cannot be tuned, one uses colloidal particles for which this attraction is screened by dispersing them in a medium of similar dielectric permittivity (according to Lifschitz theory [10]). For such a system, the attraction, that causes gas-liquid phase separation, is generated by adding nonadsorbing polymer. This is called depletion interaction and is of entropic nature [9,11–18]. The interaction free energy of this depletion interaction is given by the product of the overlap volume of two depletion zones and the osmotic pressure due to the polymer. Similarly, there will be depletion attraction between colloidal particles and a macroscopic surface on which the polymer does not adsorb. Below the overlap concentration, the range of the attraction is twice the radius of gyration of the polymer. Hence, the depletion interaction can be varied by choosing the molar mass and the concentration of the polymer. The advantage of such systems is that the interactions (hard core repulsion/depletion attraction) are known, at least in principle. Depletion interactions between coated silica surfaces in solutions of polydimethylsiloxane (PDMS) can be measured, and have been measured for certain molecular weights and concentrations [19]. The polymer chemical potential plays a role similar to that of the inverse temperature in ordinary atomic or molecular systems [13,14,16,17]. If

the concentrations of colloidal particles and polymer are sufficiently high, the depletion interaction will lead to phase separation: A colloid poor phase and a colloid rich phase coexist.

The colloidal system used in the present study consisted of organophilic silica particles (radius, $R_c = 14$ nm), dispersed in cyclohexane [20,21]. The dielectric permittivities of silica and cyclohexane are very similar so that, in the absence of polymer, the particles behave as hard spheres [20,22]. We used PDMS as the nonadsorbing polymer. The number average molecular weight was 83 200 g/mole, corresponding to a radius of gyration, $R_g = 13$ nm, and the heterodispersity index was 1.24. The size ratio $q = R_g/R_c$ for this system equals 0.93. The liquid-gas phase behavior of similar silica/PDMS/cyclohexane systems has been studied extensively [15,23,24].

In Fig. 1, the phase diagram of the system is presented. Here the polymer concentration [25] ϕ_{pol} is plotted versus the colloid volume fraction, ϕ_{coll} . The phase diagram is constructed according to the method of Bodnár *et al.* [23]. The critical point was located by extrapolating the middles of the tielines to the binodal. In the same figure, compositions are indicated at which we performed wetting experiments. These compositions vary with respect to their proximity to the critical point. In

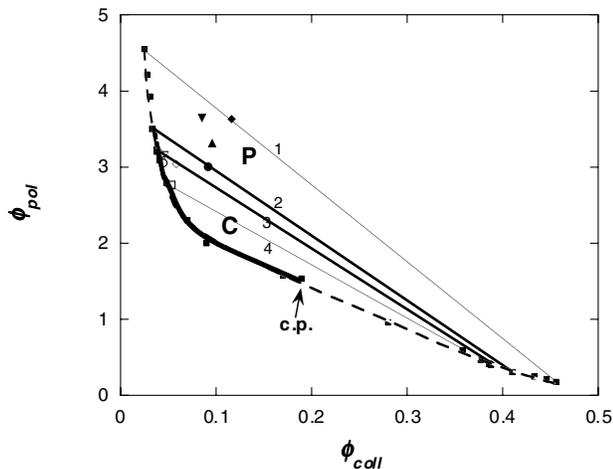


FIG. 1. Phase diagram of the silica/PDMS/cyclohexane system. The polymer concentration, ϕ_{pol} , is plotted versus the volume fraction colloid ϕ_{coll} . The binodal points are denoted by solid squares and the critical point is indicated by c.p. The binodal is represented by the dashed curve. At the tielines (solid lines), indicated by 1, 2, 3, and 4, the polymer reservoir concentrations are 5.5, 4.5, 4.3, and 4.1, respectively. The overall compositions of the samples are given by A (\blacklozenge), B (\blacktriangledown), C (\blacktriangle), D (\bullet), E (\diamond), F (∇), G (\triangle), H (\circ), and J (\square). Points E and G are on the same tieline (have the same polymer chemical potential). Where complete wetting occurs, the binodal is drawn as a fat solid line and in the interval in which the wetting transition occurs as a dotted one. The complete and partial wetting regimes are indicated by C and P, respectively.

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order to examine the wetting behavior, we chose a substrate which has only hard repulsion and depletion attraction with the particles. We used glass coated with the same organophilic groups as the particles (on which PDMS does not adsorb).

In order to make meaningful observations, we had to overcome some experimental difficulties. These are due to the low optical contrast between the phases and the small size of the meniscus. Concerning the latter, the capillary length, l_c , is an important parameter which marks the crossover between a regime where γ_{LG} dominates the shape of a meniscus and another regime where gravity dominates that shape. It is defined by $l_c = \sqrt{\gamma_{LG}/\Delta\rho g}$, where $\Delta\rho$ is the density difference between the two phases and g is the gravitation constant. Since in colloidal systems γ_{LG} is very low [24], l_c is orders of magnitude smaller (O tens of μm) than in typical molecular systems (O mm). We studied menisci around vertically suspended fibers of treated glass with a diameter of about 0.2 mm. Pictures of menisci were captured using appropriate viewing optics. We obtained the best results by illuminating the sample with a diffuse parallel light beam through the sample in the direction of objective and CCD camera. It turned out, however, that both the meniscus and its mirror image were seen, and it could not easily be decided which is which. The technical solution to this problem was to determine dynamic contact angles by moving the fiber up or down by means of an electronically controlled actuator. In this way, unambiguous and more accurate static contact angles could be obtained.

In Fig. 2, we present an image of a meniscus at the fiber of sample A (see Fig. 1). The colloidal gas and liquid phases are separated by a horizontal interface; the upper phase is the colloidal gas and the lower phase the colloidal liquid. The flat interface itself cannot be seen, but its position can be deduced by means of the mirror images it produces. Near the fiber, we can clearly distinguish the curved part of the meniscus and its mirror image.

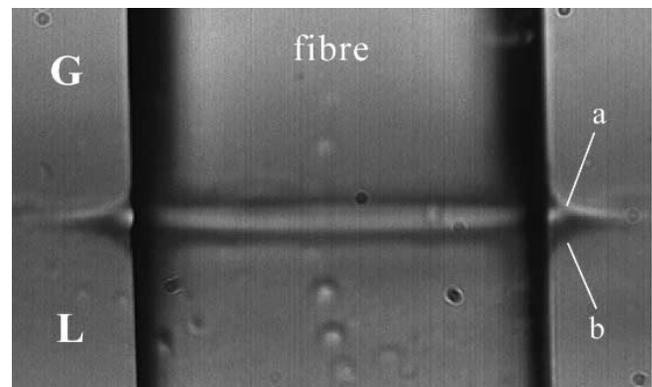


FIG. 2. Image of a meniscus at a fiber suspended in a colloidal liquid-gas system (sample A). The capitals G and L refer to the colloidal gas and colloidal liquid phase, respectively. The meniscus is indicated by a and its mirror image by b.

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The true meniscus is distinguished from its mirror image by its response to the downward or upward movement of the fiber in the dynamic experiments. This allowed us to unambiguously conclude that the static meniscus curves upwards. Hence, the contact angle is smaller than 90° but an accurate value cannot be easily determined from a static profile. Therefore we determined the static contact angle θ_0 by interpolation from dynamic contact angles measured for a large number of velocities. In Fig. 3 we present, by way of example, $\cos\theta$ for samples *A* (deep in the two phase coexistence region) and *J* (closer to the critical point) as a function of the velocity. These contact angles were determined by drawing tangents to the liquid-gas interfaces in the three phase points. Extrapolation of contact angles to zero velocity from the positive ($v > 0$) side yields the static *advancing* contact angle, and from the negative ($v < 0$) side the static *receding* contact angle. Often these two contact angles are different: At zero velocity there is a discontinuity in the contact angle-velocity curve (contact angle hysteresis). In our system, however, it seems that there is no discontinuity, within the error of the experiment. This implies that hysteresis, if any, is smaller than the scatter in our data. This justifies our interpolation procedure.

We first conclude that static contact angles for all samples in Fig. 1 are smaller than 90° , which indicates that the substrate prefers the liquid over the gas phase. This can be understood by considering the underlying interactions (particle-particle and particle-substrate). The depletion interaction is proportional to the overlap volume of the depletion zones [11,12]. Since the radius of curvature of the fiber is much larger than that of a particle, the fiber can be regarded as a flat substrate. The overlap volume between the depletion zones of a spherical particle and a flat substrate is larger than the overlap volume for two spherical particles, at the same distance. Hence, the attraction between a particle and the substrate

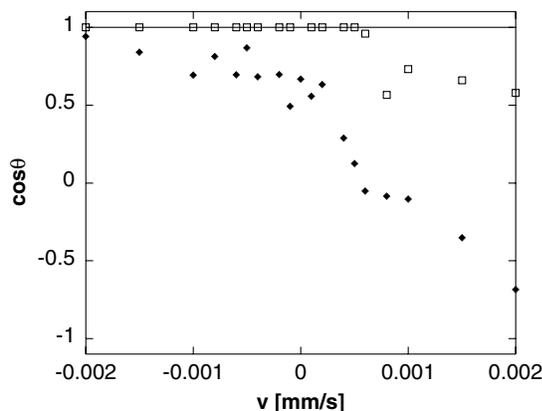


FIG. 3. The cosine of the dynamic contact angle of samples *A* (\blacklozenge) and *J* (\square) at the substrate as a function of the velocity of the substrate with respect to the colloidal liquid-gas interface. A positive velocity corresponds to an advancing contact angle and a negative to a receding contact angle.

is stronger than that between two particles. In the colloidal liquid phase, there are many more particles than in the colloidal gas phase, so the substrate attracts the colloidal liquid phase much more strongly than the colloidal gas phase. Therefore a contact angle smaller than 90° is expected.

We see that for sample *A* the static contact angle has a finite value at zero velocity, while for sample *J* this contact angle is 0° . Hence, it can be concluded that sample *A* is a case of partial wetting, and sample *J* of complete wetting. So, there must be a transition from partial wetting to complete wetting, upon approaching the critical point. In order to narrow down the range where it occurs, we measured θ_0 for all samples indicated in Fig. 1. The results appear in Fig. 4 as a plot of $\cos\theta_0$ versus an appropriate field variable [14] which measures the proximity to the critical point. For this variable there are several options. One option is to use the polymer reservoir concentration, ϕ_{pol}^r , which is related to the polymer chemical potential. This quantity cannot be directly determined experimentally. It can be estimated by correcting the actual polymer concentration (ϕ_{pol}) in the gas phase for the volume of the colloidal particles with their depletion zones by means of scaled particle theory [13,14]. However, near the critical point the polymer reservoir concentration cannot be determined in this way. As an alternative, the difference in colloid volume fraction between the liquid and the gas phase ($\Delta\phi_{\text{coll}} = \phi_{\text{coll},l} - \phi_{\text{coll},g}$) can be used. This difference vanishes in the critical point. It is known that near the critical point for most three-dimensional systems $\Delta\phi \sim (X - X_c)^{0.313}$, where X is the relevant field variable (often the temperature, but in our case it is related to ϕ_{pol}^r or the polymer chemical potential) and X_c its value in the critical point [26]. Therefore we choose in Fig. 4 to use $(\Delta\phi_{\text{coll}})^{1/0.313}$ as

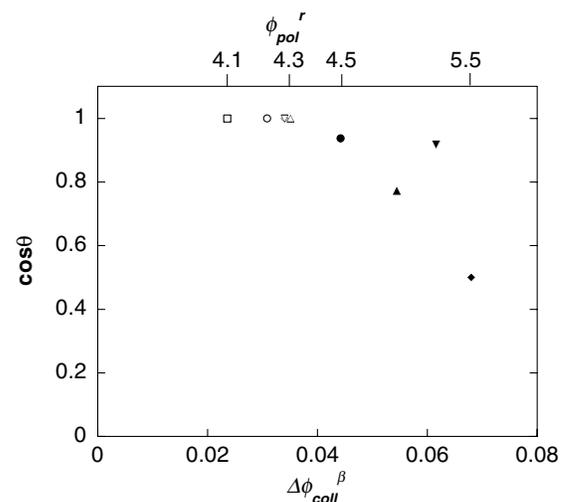


FIG. 4. The cosine of the static contact angle as a function of $\Delta\phi_{\text{coll}}^\beta$ with $\beta = 1/0.313$. The symbols are explained in the capture of Fig. 1. ∇ represents two independent measurements.

the measure for the distance to the critical point. This is the central result of our paper.

We see that at $0.034 < (\Delta\phi_{\text{coll}})^{1/0.313} < 0.044$ ($0.35 < \Delta\phi_{\text{coll}} < 0.38$) there is a transition between partial and complete wetting: $\cos\theta_0$ changes there between unity and a smaller value. This corresponds to $4.3 < \phi_{\text{pol}}^r < 4.5$. In Fig. 1, this interval is between the thick tielines 2 and 3. The occurrence of this wetting transition is in agreement with the qualitative prediction of Cahn [3]. We can make a more quantitative comparison with predictions of Brader *et al.* and Dijkstra *et al.*, who calculated the location of such a wetting transition for colloid-polymer mixtures by density functional theory and Monte Carlo simulations, respectively [16,17]. In the Monte Carlo simulations, it was found that for $q = 1$ it occurs in the region $0.011 < (\Delta\phi_{\text{coll}})^{1/0.313} < 0.012$ ($1.05 < \phi_{\text{pol}}^r < 1.10$) [27]. For the density functional calculations, we have only data for $q = 0.6$; the transition occurs at $(\Delta\phi_{\text{coll}})^{1/0.313} = 0.015$ ($\phi_{\text{pol}}^r = 0.595$). The values of both $(\Delta\phi_{\text{coll}})^{1/0.313}$ and ϕ_{pol}^r at the wetting transition are significantly lower than our experimental result, but also their binodals differ significantly from ours. The differences may be due to the fact that in the simulations and calculations the polymers are taken to be ideal, while in our experiments they are not. Within the ideal polymer model, below overlap the osmotic pressure is overestimated (as it corresponds with a larger number concentration of polymer molecules). Above overlap, it neglects the shrinking of the depletion layer thickness and the enhanced (as compared to Van't Hoff's law) increase of the osmotic pressure with increasing polymer concentration. It cannot easily be estimated what the effects of the ideal polymer approximation will be on the macroscopic (phase) behavior of a colloidal system. It turns out that it leads to an overestimation of the tendency for phase separation: In real systems the binodal is found at much higher values of ϕ_{pol} (or ϕ_{pol}^r) than is predicted by the ideal polymer model. Recent calculations of the phase diagram taking non-ideality into account lead to better, although not perfect, agreement with experiments [18]. We find predictions based on the fact that the ideal polymer approximation also underestimates for the value of ϕ_{pol}^r at which the wetting transition occurs, and to a smaller extent of $\Delta\phi_{\text{coll}}$. The accuracy of our experimental data is not sufficient to decide whether the wetting transition is first or second order.

In conclusion, we have demonstrated that wetting phenomena can be experimentally investigated using colloidal systems exhibiting gas-liquid phase behavior. The beauty of these systems is that the attractive interaction can be controlled in strength and in range. This opens up many perspectives for studying the relation between wetting phenomena and the underlying interactions, e.g., far from the critical point or close to criticality. We were able to locate a Cahn wetting transition upon approaching the critical point at $0.034 < (\Delta\phi_{\text{coll}})^{1/0.313} < 0.044$. By this

we have tested successfully the well-known Cahn prediction regarding wetting transitions [3].

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