Order parameter and interfacial tension of a colloid-polymer system

B.-H. Chen,[1,*] B. Payandeh,[2] and M. Robert[1,2,†]

[1]*Department of Chemical Engineering, Rice University, 6100 South Main Street, Houston, Texas 77005*
[2]*Rice Quantum Institute, Rice University, 6100 South Main Street, Houston, Texas 77005*
(Received 26 February 1999; revised manuscript received 17 November 1999)

The order parameter and interfacial tension of a colloid-polymer system consisting of grafted silica particles in cyclohexane in the presence of the soluble polymer polydimethylsiloxane are determined experimentally in the entire liquid-liquid coexistence region, from the liquid-solid boundary to the critical point. The renormalized critical exponents of the order parameter and interfacial tension are found to be, respectively, $\beta^* = 0.371 \pm 0.026$ and $\mu^* = 1.30 \pm 0.08$, and are discussed in the light of theoretical predictions.

PACS number(s): 82.70.Dd, 64.60.Fr, 68.10.−m, 68.10.Cr

INTRODUCTION

Colloidal systems are ubiquitous and fascinating and, in spite of the complexity of their interactions [1], share many features with simpler atomic or molecular systems. In particular, they exhibit, under suitable conditions, solid, liquid, and vaporlike phases [2].

While the liquid-solid phase transition has been and remains actively studied at a fundamental level, in particular to shed light on the remarkable features of two-dimensional ordering [3], the liquid-liquid phase transition is more subtle and remains poorly understood.

A necessary but not sufficient condition [4] for the occurrence of a liquid-liquid phase transition is the presence of an attractive force. A well-known [5] way to provide for it in colloidal systems is by adding a soluble polymer that, if concentrated enough, will induce a short-ranged depletion force between the colloidal particles, provided the size of the polymer is sufficiently large compared to that of the colloidal particle, so that no polymer can lie between two colloidal particles if the latter are close enough to each other (see Fig. 1). While the depletion force was predicted many years ago [5], it is only recently that it has been measured, by laser-radiation pressure, a surface force apparatus, atomic-force microscopy, and other optical microscopy techniques [6].

Liquid-liquid phase equilibrium has been found in some colloid-polymer systems in an aqueous [7] or organic solvent [8]. Approximate statistical mechanical calculations for effective one-component models predict [9] that for three-dimensional colloid-polymer systems, liquid-liquid phase coexistence occurs for $a < 3r_g$, where a is the radius of the colloidal particle and r_g is the gyration radius of the polymer (see Fig. 1), confirming the experimental observations of Sperry [10]. More recently, the partitioning of polymer between the coexisting phases has also been taken into account in theoretical calculations [11].

When two colloidal phases coexist at equilibrium, one rich and the other lean in colloidal particles, they are separated by an interface to which is associated a free energy, the interfacial tension. When both phases are liquid, the interfacial tension is expected to decrease as the critical point is approached, ultimately vanishing at the critical point itself. In colloid-polymer systems, the interfacial tension is moreover expected to be very low, even far from any critical point. This is confirmed by an approximate calculation and a preliminary measurement [12].

For common systems such as simple fluids or uniaxial ferromagnets, which have a scalar (one-dimensional) order parameter, theory predicts [13] not only the critical behavior of the order parameter (respectively equal to the magnetization and the difference between the compositions of the coexisting fluid phases, which is proportional to that between their densities [14]), but also the critical behavior of the interfacial tension [15].

In contrast to that of such simpler systems, the critical behavior of colloidal systems is not known experimentally. It is the purpose of this paper to report on the order parameter and interfacial tension of a well-defined colloid-polymer system consisting of silica particles grafted with stearyl alcohol in cyclohexane, in presence of the soluble polymer polydimethylsiloxane (PDMS).

EXPERIMENTAL METHOD

Aqueous silica (Ludox TMA colloidal silica, 34 wt %, DuPont) and polydimethylsiloxane 200 fluid (molecular

*Present address: Department of Chemical and Environmental Engineering, The National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore. E-mail address: checbh@nus.edu.sg
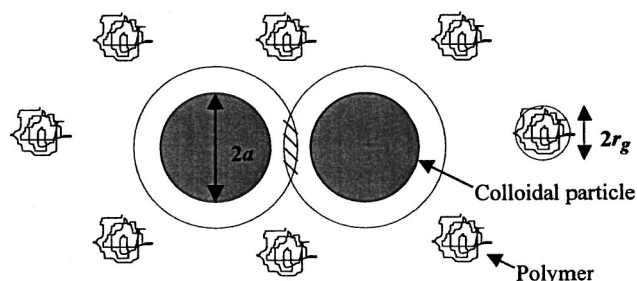
†Corresponding author.

FIG. 1. Depletion force in a colloid-polymer system. Depletion zones, inaccessible to polymer coils centers, are shown around the colloidal particles, and overlap when the latter are close to each other.

weight 92 000, Dow Corning) were purchased from Aldrich. The diameter of the silica particles is 20.2 ± 1.6 nm, determined by transmission electron microscopy. Stearyl alcohol (n-C$_{18}$OH) with a purity of 99% was obtained from TCI America, and cyclohexane from Fisher Chemicals.

Neutral organophilic silica particles are prepared by grafting stearyl chains onto the silica surface according to the method described by Iler [16] and van Helden, Jansen, and Vrij [17]. Colloidal silica tends to aggregate by forming siloxane bridges in the presence of water [16,18]. Water is also the by-product of the esterification of silica and stearyl alcohol, and its presence would greatly retard esterification [19]. It is thus critical to remove water in the grafting procedure. With Ludox TMA particles, it is necessary to initially lower the pH of the aqueous dispersion below 2 during the removal of the water by azeotropic distillation with addition of 1-propanol (Fisher Chemicals). 1-Propanol is chosen because it is miscible with both water and stearyl alcohol, and forms an azeotrope with water at 87 °C. With addition of stearyl alcohol to silica alcosol, the system is then heated and esterified at 180–200 °C for 3 h under nitrogen atmosphere, after evaporation of 1-propanol and excess water at 120 °C. The grafted silica is then purified from excess stearyl alcohol by ultracentrifuging the dispersions in cyclohexane at 16 500 rpm (42 200 g) for 2 h and discarding the supernatant. The procedure is repeated three times. The grafted silica is then dried at 80 °C for at least 24 h.

Phase separation is investigated at fixed temperature, as a function of polymer concentration. The entire liquid-liquid coexistence region, from the liquid-solid phase boundary to the critical point, is found to be very narrow. The critical composition is determined by measuring the volumes of the colloid-rich and the colloid-poor phases after phase separation. As the critical point is neared, both phases have equal volumes. A series of mixtures were prepared in cyclohexane with different contents of PDMS and fixed amount of silica, which was set equal to that at the critical point. All samples are equilibrated at 24 °C for a period of at least 7 days, until both phases appear translucent and the interface between them is very sharp and mobile, confirming the liquid rather than solid nature of the denser phase. Both phases are then carefully separated with syringes and 21-G needles and transferred to different vials for interfacial tension and density measurements.

The spinning-drop method is one of the most accurate and direct methods to measure low interfacial tensions [20]. In a typical spinning-drop tensiometer, a droplet of the lighter phase is injected into an optically transparent glass tube filled with the denser phase, which is rotated at high speed. The droplet of the lighter phase becomes elongated along the axis of rotation and the equilibrium shape, mainly determined by two antagonistic forces, the centrifugal force and that due to interfacial tension, is characterized, from which the interfacial tension is calculated. If the length of an elongated drop exceeds four times its equatorial diameter, its interfacial tension is given by [20]

$$\sigma = \frac{\omega^2 r^3 \Delta \rho}{4}, \qquad (1)$$

where σ is the interfacial tension, $\Delta \rho$ is the difference be-
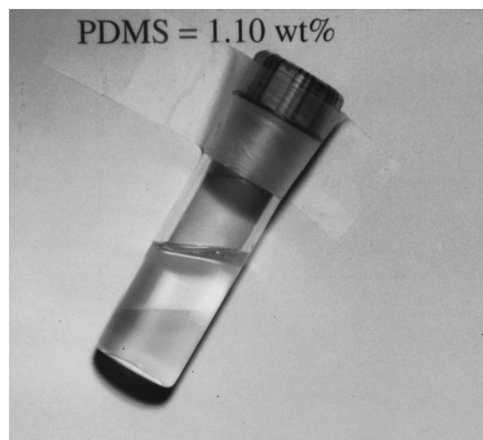

FIG. 2. Photograph of sample containing 34.4 wt % grafted silica and 1.10 wt % PDMS in cyclohexane showing liquid-liquid phase separation. The sample vial is tilted to exhibit the high mobility of the interface.

tween the densities of the two liquids, ω is the speed of rotation, and r is the equatorial radius of the drop. r cannot be measured directly. The apparent radius of the droplet is measured, with an optical magnification factor to compensate for the cylindrical lens effect of the sample tube [21,22]. This factor equals the refractive index of the fluid surrounding the droplet [22], and is independent of the refractive index and wall thickness of the sample tube [23].

We use a spinning-drop tensiometer ''University of Texas at Austin Model 300.'' All measurements are made with a cylindrical glass tube of 1.9 mm internal diameter and 76.2 mm length, cleaned thoroughly by rinsing with cyclohexane. Once dried, the tube is filled with the denser fluid, followed by injection of a drop of less than 0.5 μl of the less dense fluid. The tube is then very quickly mounted in the housing of the tensiometer and spinning is initiated. Elapsed time is recorded from injection of the drop. Temperature is maintained at 24 °C. The rotation speed is about 1800 rpm and the length-to-diameter ratios are much greater than four, so that Eq. (1) applies. The measured radius is corrected with the optical magnification factor prior to the calculation of interfacial tension. At least four independent measurements of drop diameters are taken after the spinning droplets reach their equilibrium shape.

The densities are measured separately at the same temperature with a pycnometer of 1 ml (Thomas Scientific) and an analytical balance (Mettler H51AR) that provides resolution of 10 μg. The refractive indices are measured with a Bausch and Lomb Abbe-3L refractometer at 24 °C.

RESULTS AND DISCUSSION

The critical composition is found to be 34.4 wt % grafted silica and 0.91 wt % PDMS in cyclohexane. A sample having 34.4 wt % grafted silica and 0.912 wt % PDMS in cyclohexane has colloid-rich and colloid-lean phases of equal volume. However, a sample with the same composition of grafted silica but 0.906 wt % PDMS in cyclohexane exhibits a single cloudy phase after a period of 7 days. Figure 2 is a photograph showing liquid-liquid phase separation for 34.4 wt % grafted silica and 1.10 wt % PDMS in cyclohexane. The
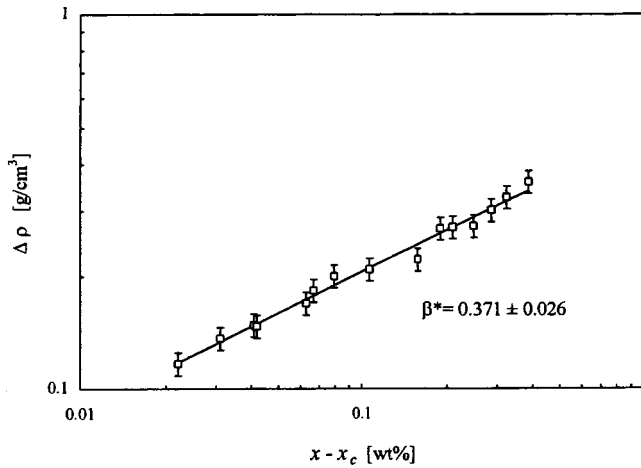
FIG. 3. Log-log plot of density difference as a function of the difference between the overall PDMS concentration x and its critical value x_c.

sample vial is tilted deliberately to exhibit the high mobility of the interface separating the liquid phases.

The difference between the densities of the coexisting phases is plotted as a function of the difference between the overall PDMS concentration x and its critical value x_c, shown as Fig. 3. A log-log plot yields a slope of 0.371 ± 0.026, equal to the exponent β^* in $\Delta\rho \approx (x-x_c)^{\beta^*}$. The error arises mainly from the separation procedure of the coexisting phases described above.

The tension of the interface between the coexisting colloid phases is also plotted as a function of the difference between the overall PDMS concentration and its critical value, shown as Fig. 4 in a log-log plot. The slope is found to be equal to 1.30 ± 0.08, giving the exponent μ^* in $\sigma \approx (x -x_c)^{\mu^*}$. The main errors consist of an extrinsic one due to measurement and an intrinsic one due to the spinning-drop tensiometer itself. The deviations of the interfacial tension are mostly within 6% around their mean value. An error analysis based on Eq. (1) indicates that much of the extrinsic error originates from the radius measurement. The intrinsic error, approximately 6%, arises from the departure of the
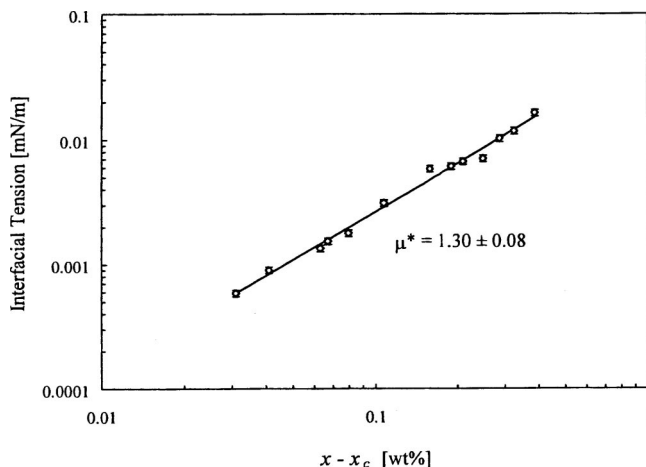

FIG. 4. Log-log plot of interfacial tension as a function of the difference between the overall PDMS concentration x and its critical value x_c.

spinning drop from gyrostatic equilibrium, due to gravity and vibration from the drive and bearings of the apparatus [22].

The theoretical description of phase transitions at critical points is most simply and conveniently given by expressing the singular thermodynamic quantities in terms of field variables, which assume identical values in distinct coexisting phases. Typical of these is the temperature, and critical exponents are thus defined in terms of distance of the temperature from its critical value. However when, as is the case here, the critical point is approached at fixed temperature, upon variation of a density (here the polymer concentration) rather than a field variable, the critical exponents change and are said to be renormalized [24]. Fisher [24] has shown that the ordinary critical exponents of the specific heat and of the order parameter, α and β, respectively, become renormalized to the values $\alpha^* = -\alpha/(1-\alpha)$ and $\beta^* = \beta/(1-\alpha)$, respectively. Note that no change occurs in mean-field theory or, equivalently, in systems with very long-ranged interactions, where $\alpha=0$. For three-dimensional systems with short-ranged interactions such as the one investigated here, $\alpha \approx 0.11$ [13], so that the values of the renormalized critical exponents are about 10% larger than the corresponding unrenormalized values. Thus, using the best current value of $\beta=0.325$, the critical exponent of the order parameter renormalizes to $\beta^*=0.365$.

The critical exponent of the interfacial tension, μ, satisfies the Widom scaling relation [15] $\mu = (d-1)\nu$, with d the dimension of space and ν the critical exponent of the correlation length so that, in view of the Kadanoff hyperscaling relation [13] $d\nu = 2-\alpha$ and the above expression for α^*, we find $\nu^* = \nu/(1-\alpha)$ from which we obtain the following renormalized value of μ:

$$\mu^* = \mu/(1-\alpha)$$
$$= (d-1)\nu^*, \tag{2}$$

which equals $2\nu^*$ in three-dimensional space. Using the value $\nu=0.63$ [13], we thus get from Eq. (2) $\mu^*=1.41$.

Comparison of these theoretical estimates with the present experimental results reveals excellent agreement for the critical exponent of the order parameter, whereas that of the interfacial tension is less satisfactory. In fact, the critical exponent of the interfacial tension is seen to be closer to its ideal, unrenormalized value $\mu=1.26$ [15] than to its fully renormalized value $\mu^*=1.41$.

It must be emphasized, however, as stressed in [24,25], that the fully renormalized critical exponents are predicted to be visible only very close to the critical point, a crossover occurring from the ideal unrenormalized value to the fully renormalized one. Therefore, in the light of these theoretical predictions, the exponent β^* determined in this study should be regarded as an effective exponent, assuming a value intermediate between those of the unrenormalized and fully renormalized exponents, whereas the exponent μ^* determined here should rather be compared to the unrenormalized exponent μ, since the critical point could not be approached very closely in the interfacial tension measurements.

We note finally that the critical volume fraction of polymer (0.0088) is much lower than that of colloids (0.2036), and the liquid-liquid coexistence region is very narrow in

polymer-concentration space (about 0.3 vol % or 0.3 wt %), so that the density difference is largely dominated by the colloids, their density being in addition about 60% larger than that of the polymer. On the other hand, a small change in the polymer concentration and in its partitioning in the coexisting liquid phases leads to a large change in the interfacial tension, which is seen to span several orders of magnitude from the critical point to the liquid-solid phase boundary. Furthermore, the spinning-drop method induces inevitable centrifugal effects, causing a small shift away from criticality. These observations account for the dominat-ing role played by polymer in the interfacial tension, and for the fact that its critical exponent departs more from its theoretical value than that of the order parameter.

[1] See, for example, H. Löwen, Physica A **235**, 129 (1997).

[2] N. Asherie, A. Lomakin, and G. Benedek, Phys. Rev. Lett. **77**, 4832 (1996); B. Vincent *et al.*, Colloids Surface **31**, 267 (1988).

[3] For example, Q.-H. Wei, C. Bechinger, D. Rudhardt, and P. Leiderer, Phys. Rev. Lett. **81**, 2606 (1998). For a review, see C. A. Murray, in *Bond-Orientational Order in Condensed Matter Systems*, edited by K. Strandburg (Spinger-Verlag, Berlin, 1992), p. 137.

[4] S. M. Ilett, A. Orrock, W. C. K. Poon, and P. N. Pussey, Phys. Rev. E **51**, 1344 (1995); G. Stell, J. Stat. Phys. **63**, 1203 (1991).

[5] S. Asakura and F. Oosawa, J. Chem. Phys. **22**, 1255 (1954); J. Polym. Sci. **23**, 183 (1958).

[6] P. Richetti and P. Kékicheff, Phys. Rev. Lett. **68**, 1951 (1992); G. Martinelli Kepler, and S. Fraden, *ibid.* **73**, 356 (1994); D. L. Sober and J. Y. Walz, Langmuir **11**, 2352 (1995); A. Milling and S. Biggs, J. Colloid Interface Sci. **170**, 604 (1995); J. C. Crocker and D. G. Grier, Phys. Rev. Lett. **77**, 1897 (1996); Y. N. Ohshima *et al.*, *ibid.* **78**, 3963 (1997); D. Rudhardt, C. Bechinger, and P. Leiderer, *ibid.* **81**, 1330 (1998).

[7] C. Cowell and B. Vincent, J. Colloid Interface Sci. **87**, 518 (1982).

[8] H. de Hek and A. Vrij, J. Colloid Interface Sci. **70**, 592 (1979); **84**, 409 (1981).

[9] P. D. Patel and W. B. Russel, J. Colloid Interface Sci. **131**, 192 (1989); A. P. Gast, C. K. Hall, and W. B. Russel, *ibid.* **96**, 251 (1983); Faraday Discuss. Chem. Soc. **76**, 189 (1983).

[10] P. R. Sperry, J. Colloid Interface Sci. **99**, 97 (1984).

[11] H. N. W. Lekkerkerker, Physica A **244**, 227 (1997).

[12] A. Vrij, Physica A **235**, 120 (1997).

[13] For reviews, see M. E. Fisher, in *Critical Phenomena*, edited by F. J. W. Hahne (Springer-Verlag, Berlin, 1982); and J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford 1982), Chap. 9, Sec. 9.3.

[14] C. Warren and W. W. Webb, J. Chem. Phys. **50**, 3694 (1969); X. An *et al.*, J. Colloid Interface Sci. **203**, 140 (1998).

[15] See J. S. Rowlinson and B. Widom in *Molecular Theory of Capillarity* (Ref. [13]).

[16] R. K. Iler, U.S. Patent No. 2, 801, 185 (30 July 1957).

[17] A. K. van Helden, J. W. Jansen, and A. Vrij, J. Colloid Interface Sci. **81**, 354 (1981).

[18] R. K. Iler, *The Chemistry of Silica* (Wiley, New York, 1979).

[19] C. C. Ballard *et al.*, J. Phys. Chem. **65**, 20 (1961).

[20] B. Vonnegut, Rev. Sci. Instrum. **13**, 6 (1942); J. L. Cayias, R. S. Schechter, and W. H. Wade, ACS Symp. Ser. **8**, 234 (1975).

[21] A. Silberberg, Ph.D. dissertation, University of Basel, Switzerland, 1952.

[22] C. D. Manning and L. E. Scriven, Rev. Sci. Instrum. **48**, 1699 (1977).

[23] J. E. Puig, Y. Seeto, C. V. Pesheck, and L. E. Scriven, J. Colloid Interface Sci. **148**, 459 (1992).

[24] M. E. Fisher, Phys. Rev. **176**, 257 (1968).

[25] M. E. Fisher and P. E. Scesney, Phys. Rev. A **2**, 825 (1970).