Phase Behavior of Thermally Responsive Microgel Colloids

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The phase behavior of poly-*N*-isopropylacrylamide (PNIPAM) nanoparticles dispersed in water is investigated using a thermodynamic perturbation theory combined with light-scattering and spectrometer measurements. It is shown how the volume transition of PNIPAM particles affects the interaction potential and determines a novel phase diagram that has not been observed in conventional colloids. Because both particle size and attractive potential depend on temperature, PNIPAM aqueous dispersion exhibits phase transitions at a fixed particle number density by either increasing or decreasing temperature.

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In many aspects, colloidal particles suspended in a liquid behave similar to large idealized atoms that exhibit liquid, glass, and crystal phases similar to those observed in atomic systems [1–6]. Phase transitions in colloidal systems have been intensively studied over the past decade not only because of the theoretical interest for addressing fundamental questions about the nature of liquids, crystals, and glasses, but also for many practical applications of colloids, especially for the fabrication of nanostructured materials [7–11]. Previous investigations on the phase behavior of colloidal dispersions, however, are primarily focused on hard-sphere-like particles such as polymethylacrylate, silica, or polystyrene; little attention has been given to those colloids where the interparticle potential is a strong function of temperature. In this Letter, we consider specifically aqueous dispersions of poly-*N*-isopropylacrylamide (PNIPAM) microgel particles that exhibit a reversible and continuous volume transition in water around 34 °C [12–29]. We show that the lower-critical-solution-temperature–like behavior of a PNIPAM microgel could affect the interparticle forces between microgels, resulting in drastic different phase behavior from those of conventional hard-sphere-like colloidal systems.

We synthesized PNIPAM microgels [26] using an emulsion polymerization method [12]. The molar ratio of the monomer (NIPAM) to cross-linker N,N'-methylene-bis-acrylamide is 78:1. The average hydrodynamic radius and the radius distribution of microgel particles were characterized using a dynamic light-scattering technique, while the radius of gyration, osmotic second virial coefficient, and the molecular weight of microgels in the aqueous dispersions were obtained using static light-scattering measurements (ALV-5000, Germany). Typically, the hydrodynamic radius of these particles was narrowly distributed with a polydispersity less than 5%. Figure 1(a) presents the particle size in an average of the radius of gyration and hydrodynamic radius $[(\sqrt{5/3}R_g + R_h)/2$. This average value is used to reduce the particle inhomogeneity effect on calculations. Figure 1(b) shows the reduced osmotic second virial coefficient (B_2/B_2^{HS}) as functions of temperature. Here, B_2^{HS} is calculated from the particle average radius assuming that they are hard spheres.

The phase transitions in aqueous dispersions of PNIPAM particles are easily observable from their appearances. Figure 2(a) shows the iridescent patterns when nearly monodispersed PNIPAM particles with the polymer concentration of 16.9 g/L self-assemble into a crystalline phase. Here, the temperature is 21 °C and the microgel spheres are fully swollen. At 26 °C, the iridescent grains disappear completely and the dispersion becomes a homogeneous liquid with small turbidity [Fig. 2(b)]. When the temperature is raised further to 35 °C, the sample becomes white and opaque, indicating a second phase separation [Fig. 2(c)]. While at low temperature the solid phase exhibits apparent characteristics of a colloidal crystal, the phase-separated state at high temperature is probably related to the metastable fluid-fluid equilibrium that will be discussed later.

A quantitative phase diagram of PNIPAM dispersions can be constructed by measuring the UV-visible absorbance spectra on a diode array spectrometer (Hewlett-Packard, Model 8543) with the wavelength ranging from 190 to 1100 nm. The turbidity of the samples was obtained from the ratio of the transmitted light intensity (I_t) to the incident intensity (I_o) as $\alpha = -(1/L)\ln(I_t/I_0)$, where L was the sample thickness (1 cm). In the crystalline phase, the UV-VIS spectrum exhibits a sharp attenuation peak due to the Bragg diffraction arising from ordered colloidal structures [14]. Above the crystalline melting temperature, the peak disappears. On the other hand, as the temperature rises to the phase separation temperature, the turbidity increases sharply in the entire range of visible light wavelengths. The melting temperature is determined by observing the disappearance of the turbidity peak.

Figure 3 presents the phase diagram of a PNIPAM microgel dispersion determined from the turbidity measurements. Below the volume phase-transition

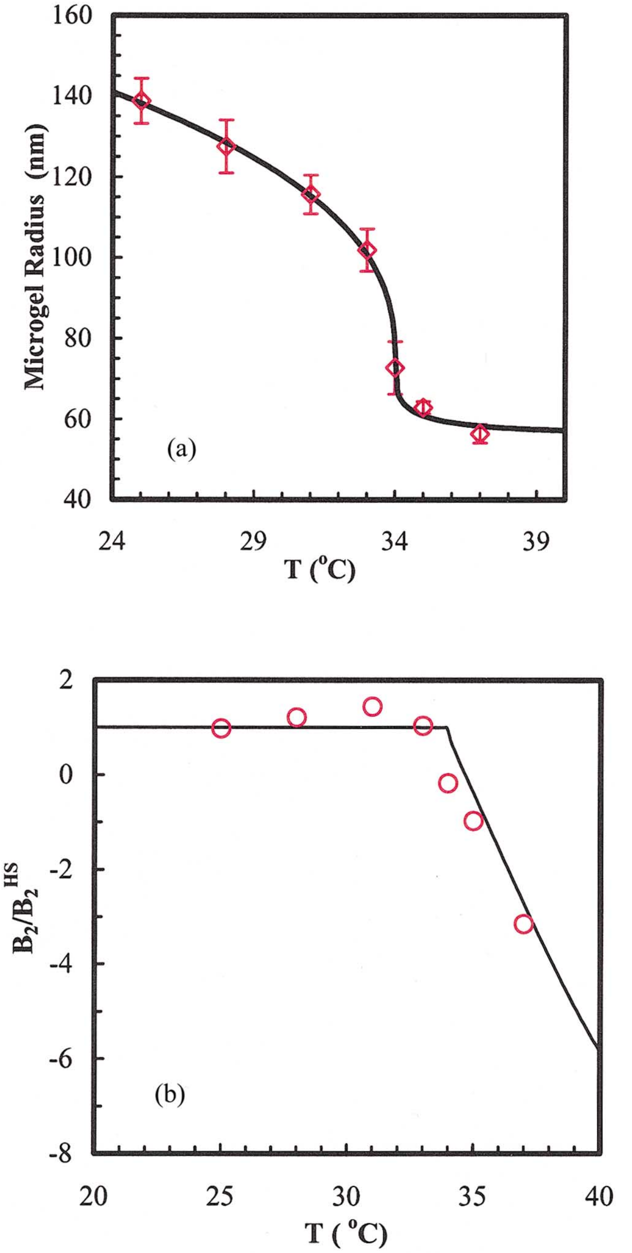

FIG. 1 (color). (a) The size of PNIPAM microgel spheres in water as a function of temperature. Here the symbols represent the averages of the hydrodynamic radius and the radius of gyration, and the line is calculated from the Flory-Rehner theory. (b) Reduced osmotic second virial coefficient from the static light scattering (symbols) and from the calculation using Eq. (1) (line).

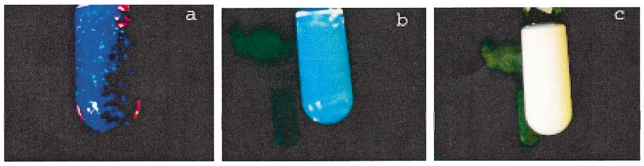

FIG. 2 (color). Color pictures of the PNIPAM microgel dispersion with polymer concentration of 16.9 g/L at various temperatures: (a) 21 °C, (b) 26 °C, and (c) 35 °C. The average hydrodynamic radius of PNIPAM microgel spheres in water at $T = 25$ °C is 133 nm. The diameter of the vial is 1 cm.

temperature, the PNIPAM dispersion exists as a clear liquid at low polymer concentration, and a crystalline solid at high polymer concentration. Above the volume-transition temperature of the microgel particles, a sharp increase in turbidity (not shown due to limited space) designates a second phase transition. In this case, no crystals are observed and the dispersion becomes opaque. No macroscopic phase separation was observed; even when the dispersion had been preserved at constant temperature for over a few weeks [Fig. 2(c)].

The phase behavior of microgel dispersions can be semiquantitatively represented by a simple thermodynamic model. The pair potential between neutral microgel particles includes a short-range repulsion that is similar to the interaction between two polymer-coated surfaces, and a longer-ranged van der Waals-like attraction that arises from the difference in the Hamaker constants of the particle and the solvent [30]. An analytical expression for the interparticle potential that covers the entire temperature range of microgel swelling is yet to be developed. Because the phase diagram is not sensitive to the detailed function of the short-range forces [31], we assume in this work that the potential between microgel particles can be *effectively* represented by the Sutherland-like function:

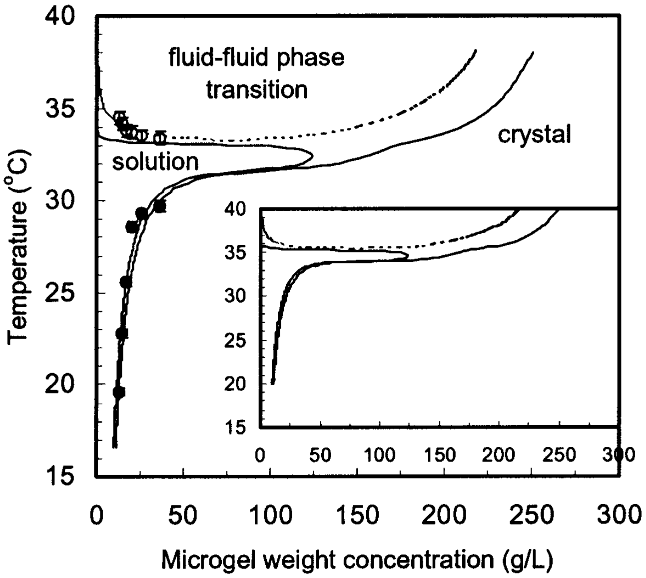

FIG. 3. The phase diagram of aqueous dispersions of PNIPAM particles determined from turbidity measurements (symbols) and from the thermodynamic perturbation theory with an empirical correction of temperature (lines). The filled and open circles represent, respectively, the melting and the second phase-separation temperatures. The inset shows the predicted phase diagram without any adjustable parameters.

$$\frac{u(r)}{kT} = \begin{cases} \infty & r < \sigma \\ -\frac{T_0}{T}\left(\frac{\sigma_0}{\sigma}\right)^{6+n}\left(\frac{\sigma}{r}\right)^{n} & r \geq \sigma, \end{cases} \qquad (1)$$

where σ is the effective diameter, r/σ denotes the reduced center-to-center distance, k is the Boltzmann constant, T is the absolute temperature, T_0 is an empirical proportionality constant that has the unit of temperature, and σ_0 is the particle diameter at a reference temperature where the conformation of the network chains is closest to that of unperturbed Gaussian chains. Introduction of T_0 and σ_0 in Eq. (1) is solely for the purpose of dimensionality. The dependence of the particle diameter σ as a function of temperature can be represented by, as shown in Fig. 1(a), the modified Flory-Rehner theory for volume-transition equilibrium of temperature-sensitive polymer gels [27]. This theory takes into account the heterogeneity of microgels and has been successfully applied to describe the volume transition of bulk PNIPAM gels. The inverse power in Eq. (1) is assumed to be $n = 8$, in considering that the van der Waals attraction between colloidal particles is short ranged in comparison to that between atomic molecules (relative to the particle size) [32]. We find that $n = 8$ gives optimum results for fitting the osmotic second virial coefficients of microgel dispersions. The temperature-independent parameters $\sigma_0 = 251.6$ nm and $T_0 = 1.884 \times 10^{-2}$ K are obtained from the average radius of microgel particles and the osmotic second virial coefficients of the microgel dispersions as shown in Fig. 1.

Once we have the interaction potential between microgel particles, the phase diagram can be calculated using thermodynamic models for the fluid and the solid phases. The reduced Helmholtz energy F_f/NkT for the fluid phase includes a hard-sphere contribution that depends only on the particle volume fraction $\eta = \pi\rho\sigma^3/6$, and a perturbation that takes into account the short-range attraction $u_A(r)$ [33]

$$\frac{F_f}{NkT} = \ln(\eta) - 1 + \frac{4\eta - 3\eta^2}{(1-\eta)^2} + 12\eta \int_1^\infty x^2 g_f^{HS}(x) \frac{u_A(x)}{kT} dx, \qquad (2)$$

where $x = r/\sigma$, N stands for the total number of particles, ρ is particle number density, and $g_f^{HS}(r)$ is the hard-sphere radial distribution function that was calculated from the Percus-Yevick theory [2] using the analytical direct correction function, and the integral was evaluated numerically. The Helmholtz energy for the solid phase is similarly given by

$$\frac{F_s}{NkT} = \frac{F_s^{HS}}{NkT} + 12\eta \int_1^\infty x^2 g_s^{HS}(x) \frac{u_A(x)}{kT} dx, \qquad (3)$$

where the reference Helmholtz energy F_s^{HS} and the radial distribution function of the hard-sphere solid $g_s^{HS}(r)$ can be calculated from a modified cell model [33]. Like that in a hard-sphere system, an aqueous dispersion of PNIPAM microgel particles is at low cross-linking density ("softer" particles) [34]. The first-order perturbation theories for both fluid and solid phases are sufficient in this work because, when the attractions are short ranged, higher order terms make only a negligible contribution to the total Helmholtz energy [35]. The chemical potential and osmotic pressure as required in the phase-equilibrium calculations can be directly derived from Eqs. (2) and (3) following standard thermodynamic relations.

The phase diagram calculated with the thermodynamic perturbation theories is also shown in Fig. 3. The inserted plot shows the predicted results using the size and energy parameters obtained from the osmotic second virial coefficients. It can match almost perfectly with experimental data if the calculated temperature is rescaled empirically by $T' = T(15/R_g)^{0.005}$. The discrepancy is probably because the effect of osmotic pressure on the particle size is neglected in the perturbation theory or because of the slight size difference (~ 2 nm) between the microgel samples used in light scattering and in turbidity measurements. Nevertheless, the theory and experiment give the same interesting phase diagram that has not been reported before. In addition, the calculated results clearly indicate that the second phase transition is due to the metastable liquid-liquid phase transition of the microgel dispersion. That explains why crystallization is not observed at high temperatures.

The phase diagram shown in Fig. 3 is perceivably different from that for a typical hard-sphere-like colloid or that for an atomic system. First, the metastable fluid-fluid coexistence curve (the dashed line) shows a low critical temperature instead of an upper critical temperature (as observed in conventional colloids) [32]. Second, at low temperatures, the coexisting liquid and solid phases have close particle densities, similar to those observed in a hard-sphere system; however, at high temperatures, the fluid-solid transition spans over a wide range of particle concentrations. At low temperatures, the PNIPAM particles are in the swollen state and they contain up to 97% of water by weight. In this case, the van der Waals attraction between colloidal particles is negligible due to the close match in the dielectric constants of the particle and the water. As a result, the PNIPAM particles behave essentially like hard spheres as shown in Fig. 1(b). However, at high temperatures, the PNIPAM particles collapse and the polymer density within each particle rises significantly, leading to strong van der Waals attractions. The phase behavior of PNIPAM dispersion at high temperatures resembles that for strongly attractive colloids. The phase-separated state is probably related to the metastable fluid-fluid equilibrium: Fast kinetics of fluid-fluid transition leads to an amorphous fluid phase of high particle concentration. Most interestingly, Fig. 3 shows that, as observed in experiments, a microgel dispersion exhibits phase transitions by either increasing or decreasing temperature. For instance, according to Fig. 3, a microgel dispersion with 17 g/L polymer concentration is in the fluid state at 32 °C, it becomes a solid of similar particle density when the temperature drops to about 25 °C, and it will be phase separated into a dilute phase and a solid of much higher density (about 200 g/L) at about 34 °C. Whereas a conventional colloid exhibits a hard-sphere-like phase behavior at high temperature, the opposite is true in an aqueous dispersion of PNIPAM particles.

In conclusion, we have investigated the volume-transition equilibrium and the interaction potential between neutral PNIPAM particles dispersed in water using spectrometric and light-scattering experiments. We found from experiments and thermodynamic perturbation theory that aqueous dispersions of PNIPAM particles exhibit phase transitions at both high and low temperatures. The phase behavior of microgel dispersion resembles that for hard spheres at temperatures below the volume-transition temperature. However, at higher temperatures, the phase separation is driven by van der Waals attractions and a metastable liquid-liquid equilibrium exists within the fluid-solid coexistence.

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