Complete Phase Diagram of a Charged Colloidal System: A Synchrotron X-Ray Scattering Study

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High-resolution, small-angle, synchrotron x-ray-scattering techniques were used to determine the phase diagram, structure factor, and pair distribution function for a charged colloidal suspension from 6% to 30% volume fraction. The expected correlated liquid and fcc and bcc solid phases were observed along with a glass phase at high concentration with structure similar to metallic glasses. At high volume fractions the finite core size leads to substantial deviation from predictions resulting from a screened Coulomb interaction.

Charge and sterically stabilized colloids have been increasingly used as ideal model systems for studying the static and dynamic properties of strongly interacting particles both in equilibrium and under various applied fields. In previous studies uncharged particles have been used as physical manifestations of hard spheres[1,2] while charged particles at high dilution were used for soft-potential studies.[3] Most of the structural studies have been based on light scattering techniques which are strongly constrained by multiple-scattering considerations. As a result, studies have divided into those on very dilute charged-particle systems and those on unchanged particles which can be more readily index matched to organic solvents. X rays, on the other hand, scatter much more weakly, and it is possible to use the Born approximation to directly obtain quantitative measurements of the structural correlations in these systems over a wide concentration range.

In this Letter we report on high-resolution, small-angle, synchrotron x-ray scattering experiments on charged polystyrene spheres (polyballs) as a function of concentration and range of interaction. We find a strongly correlated liquid phase and bcc and fcc solid phases as expected for screened Coulomb systems, and fcc and glass phases as expected for hard spheres. The glass phase is obtained by an effective "quench" from high electrolyte concentration over a period of several days, illustrating the long time scales present in these systems as opposed to conventional atomic or molecular glasses. The glass phase is distinguished from the liquid both by its larger and sharper peaks in $S(q)$ and by the presence of considerably more extended fcc-like or random close-packed-like local structure. In fact, the pair correlation function in the glassy phase bears a remarkable resemblance to those found for metallic glasses, indicating that these colloidal systems may also be regarded as model systems for real metallic glasses.

The experiments were carried out on Exxon beam lines at both the National Synchrotron Light Source (NSLS, beam line X10A) and the Stanford Synchrotron Radiation Laboratory (SSRL, beam line VI-2). The high-resolution, small-angle, x-ray scattering setup on these beam lines has been described elsewhere.[4] It provides the capability of measuring $S(q)$ for a minimum q vector of 0.004 Å with a resolution width of $\sim 2.5 \times 10^{-4}$ Å^{-1} (FWHM). For these experiments the incident wave vector was 4.075 Å^{-1} and the samples were placed in 2-mm-diam quartz capillaries. In crystalline phases, we continuously rotated the sample in order to obtain a good powder average.

In order to enhance the electron density contrast between the solvent and the polyballs, a 90%-methanol–10%-water (by volume) solvent was chosen. [The electron densities for polystyrene, H_2O, and methanol are $(3.39, 3.35,$ and $2.68) \times 10^{23}$/cm^{-3}, respectively.] The nominal 455 Å radius, 0.30 volume fraction (ϕ) samples in aqueous suspension were obtained from Duke Scientific. The raw samples were sealed in a semipermeable membrane dialysis bag of known volume and placed in a gently stirred bath of methanol and mixed-bed ion-exchange resins. This resulted in an ion-free stock suspension with $\phi = 0.30 \pm 0.015$ in 90% $\pm$ 2% methanol. The samples used in these experiments were then prepared by appropriate dilution with methanol-water solvent and addition of HCl. HCl concentrations (C_{HCl}) are accurate to ± 40 μM except for zero concentration where ion-exchange resin was present in the sample capillaries. The dielectric constant of the solvent was calculated and measured to be 38 (as contrasted with 78 for H_2O) at 25 °C.

In Fig. 1 we show the typical scattering profiles of each of the four separate phases that we have observed in

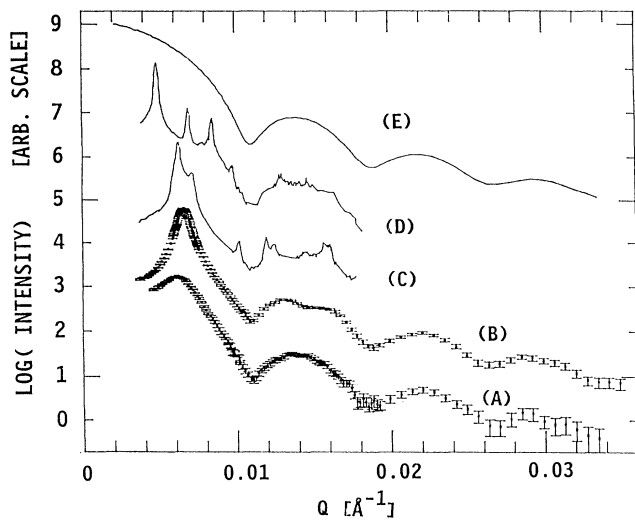FIG. 1. Typical scattering profiles of intensity vs q for, curve A, liquid ($\phi=0.24$, $C_{HCl}=2000$ μM); curve B, glass ($\phi=0.27$, $C_{HCl}=0$); curve C, fcc ($\phi=0.23$, $C_{HCl}=200$ μM); curve D, bcc ($\phi=0.10$, $C_{HCl}=10$ μM); curve E, $|F(q)|^2$ for hard spheres of $r_0=418.5$ Å with Gaussian polydispersity of 6.5%.

these experiments. The crystalline phases were easy to identify by the presence of resolution-limited Bragg peaks indexable according to their structures. Curves C and D correspond to fcc and bcc structures, respectively. The Debye-Waller factors and the dynamics of the crystalline phases are discussed in a separate paper. In curves A and B, the existence of broadened peaks implies the lack of long-range crystalline order and the presence of either liquid or glass phases.

In order to further study the noncrystalline phases it was necessary to extract the structure factor $S(q)$ $=\Sigma_{ij}\exp[iq(R_i-R_j)]$ from the intensity data by subtracting the measured background and dividing by the form factor $[|F(q)|^2]$ for the polydispersed spheres. Since $S(q)$ is smoothly varying in the liquid phases, the radius and polydispersity determine the line shape near the $F(q)$ minima. Assuming the balls have a hard-sphere density $r_0=418.5$ Å and a 6.5% Gaussian polydispersity gave the correct behavior at the minima in the disordered phases of various ϕ. Figure 1(E) shows this calculated form factor used in analyzing the data. $S(q)$ for curves A and B are shown in Fig. 2 with the data normalized to approach 1 at large q. The distinction between the glass and liquid phases was made on the basis of peak height and width in $S(q)$, along with the fact that they are observed in different regions of the phase diagram. The samples identified as being in the glass phase had structure factors which look like "smeared fcc" and had measured peak widths (FWHM) for the first peak of $S(q)$ which ranged between 5.5 $\times 10^{-4}$ and 7×10^{-4} Å^{-1}, while the peak widths in the liquid phase were greater than 1×10^{-3} Å^{-1}. In addition, the glass phase showed a first peak in the structure
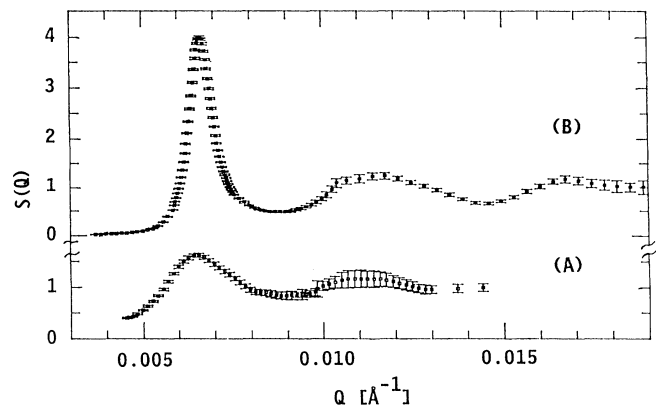
factor above the Hansen-Verlet criterion.[5] According to this criterion the height of the first peak in $S(q)$ is always less than 2.8 for the liquid state, independent of the form of the interparticle potential. This was indeed the case for samples in the liquid phase in this study.

In Fig. 3 we show the phase diagram derived from our scattering study. At zero added electrolyte concentration there would be a liquid state below $\phi=0.06$ (from previous optical studies), and then we observe, successively, bcc, fcc, and glass phases as ϕ is increased. The bcc phase exists only in a small region of the phase diagram as HCl is added, but otherwise the general progression at fixed large volume fraction is from glass to fcc solid to liquid.
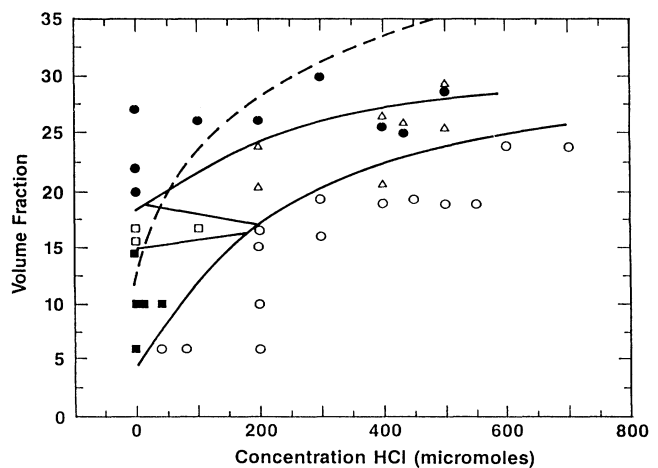

FIG. 2. The structure factor $S(q)$ obtained from the raw data of Fig. 1. Curve A, liquid phase; curve B, glass phase.

FIG. 3. Phase diagram for 0.091 polyballs in 0.9-methanol-0.1-water suspension as a function of concentration ϕ, and electrolyte concentration C_{HCl}. Solid squares, bcc crystal; open triangles, fcc crystal; open squares, fcc+bcc coexistence; closed circles, glass; open circles, liquid. Solid lines are "guide to the eye" phase boundaries. Dashed line is the fcc-liquid theoretical phase boundary for a similar point-charge Yukawa system.

For charge-stabilized colloids the interparticle interactions are conventionally considered in terms of the screened Coulomb potential[3,6]: $V(r) = (Z^*e)^2 e^{-\kappa r}/\epsilon r$, where $\kappa^2 = 4\pi n e^2/\epsilon k_B T$, Z^* is the effective charge per sphere, κ is the inverse screening length, n is the total density of ions (positive and negative), and ϵ is the dielectric constant of the solvent. The range of the interaction is characterized by $\lambda = \kappa a$, where a is a measure of the interparticle spacing ($a^3 \equiv 1/\rho$ with ρ the particle density).

Qualitatively, the observed phase diagram is consistent with our expectations at volume fractions below 20%. Calculations[7-9] and experiments[3] for screened Coulomb potentials show that as the interaction strength is increased one progresses from the liquid state to a solid which is bcc for long-range interactions (small $\lambda \Rightarrow$ low ϕ and C_{HCl}) or fcc for short-range interactions. What is somewhat unexpected, and has previously never been reported for monodispersed charge-stabilized colloids, is the presence of the glass phase. (Mixtures of polyballs with two or more differently sized or charged species readily form glasses.[10]) In fact, this region of the phase diagram ($\phi > 20\%$) is reminiscent of hard-sphere systems where studies have shown a progression from liquid to solid to glass with increasing ϕ.[1,2]

The phase diagram for Yukawa or screened Coulomb systems has recently been calculated using a number of techniques which together produce a consistent picture.[7] In order to make a quantitative comparison with this theory we need to know the effective charge and from it the relevant screening lengths for our system. This was accomplished by measuring the shear modulus for some crystalline samples. The shear modulus is related to the energy density and hence the interparticle forces.[10-12] For a 12% volume fraction sample we found a shear modulus of 170 dyn/cm^2, which implies an effective charge of $\sim 135e$ per sphere. This is to be compared to an effective charge of $\sim 500e$ for the same spheres in H_2O. The effective charge can change with the density of the spheres, the amount of added electrolyte, and the dielectric constant of the solvent in a way which can be calculated.[6] In our case, the effective charge is essentially independent of ϕ at low electrolyte and decreases to $\sim 65e$ at 500 μM. To give some idea of the range of the potential we note that $\kappa^{-1} = 400$ Å and $\lambda = 3.94$ at $C_{HCl} = 0$, $\phi = 0.10$; $\kappa^{-1} = 232$ Å and $\lambda = 4.73$ at $C_{HCl} = 0$, $\phi = 0.30$; and $\kappa^{-1} = 90$ Å and $\lambda = 12.1$ at $C_{HCl} = 500$ μM, $\phi = 0.30$.

Using these numbers we do not find agreement with the theoretical phase diagram of Ref. 7, although the general features are reproduced qualitatively. The theoretical phase diagram is also shown in Fig. 3. Attempts at using different effective charges or renormalizing the charge for different C_{HCl} did not yield substantially better agreement. As the authors of Ref. 7 have emphatically pointed out, they expect their model will be inappropriate at high volume fraction since they deal exclusively with pointlike particles. At very low volume fracions, Ref. 13 finds good agreement with Ref. 7 near the fcc-bcc-liquid point. Near the melting curve the rms displacement of a particle from its average position can be estimated by the Lindemann criterion[7,14] as 0.17 times the interparticle spacing. At $\phi = 0.3$ this corresponds to movements of ~ 300 Å, larger than the screening length and comparable to the spacing between the surfaces of the spheres. In this limit there will be substantial corrections to the effective charge calculations and the Yukawa approximation, and indeed the effective potentials should be considerably stiffened. This would explain the presence of the solid phase at concentrations well below the dashed line in Fig. 3. On the other hand, the presence of a solid phase at $\phi = 0.25$, $C_{HCl} = 500$ μM still requires Coulombic interactions.

We now turn our attention to the glass phase. A system which consists of a single species interacting with a spherically symmetric potential will normally form a glass phase only if it is quenched at a sufficiently rapid rate from the liquid. In this regard the deionization time of several days (from the raw liquid stock to the solid phase) appears naively as a long time. However, the fundamental time step for crystallization in atomic materials is an inverse phonon frequency, $\sim 10^{-13}$ sec, whereas for the polyballs it is the time to diffuse by an interparticle spacing (0.1 μm), $a^2/D_0 \approx 2 \times 10^{-3}$ sec, where D_0 is the Stokes-Einstein diffusion constant in the bare solvent (4×10^{-8} cm^2/sec). Thus a deionization time of 6 d for our sample is equivalent to a 10^{-4} sec quench from the liquid to well into the solid phase for a metallic glass. Of course, as one approaches the liquid-solid phase boundary it becomes easier to anneal into the crystalline state.

The structure of the glass phase is interesting. This is best seen from the pair distribution function $g(r)$ shown in Fig. 4, obtained from the Fourier transform of $S(q) - 1$ in Fig. 2. There is a great deal of local fcc-like order seen in this figure as indicated by the positions of
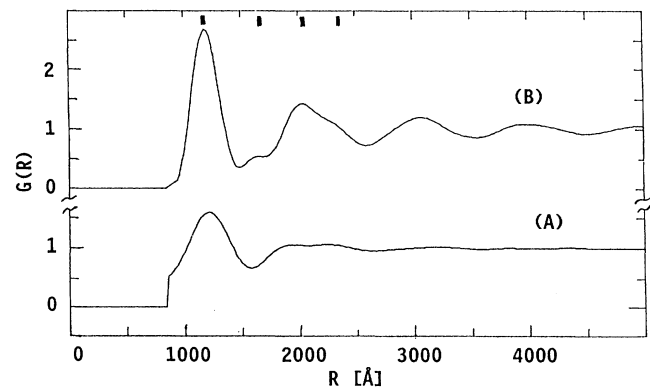

FIG. 4. Pair distribution function $g(r)$ from $S(q)$ in Fig. 2, for curve A, liquid and, curve B, glass. Vertical bars indicate positions of four nearest neighbors in the fcc structure.

fcc near neighbors corresponding to the vertical bars at the top of the figure. Such local structure is absent in $g(r)$ of the liquid phase. There is a great similarity between our $g(r)$ and that observed in some metallic glasses.[15] Previously the structure of metallic glasses has been favorably compared with a model of random-close-packed (rcp) spheres. In particular, the split second peak in $g(r)$ is often taken as indicative of rcp structure. The two parts of the split second peak are at $r_1\sqrt{3}$ and $2r_1$, where r_1 is the position of the first peak (a near-neighbor distance). There is also a small peak at $r_1\sqrt{2}$ both in our data and in the NiP metallic glass described in Ref. 15. In fact, there is a closer correspondence between our data and those in Ref. 15 than there is between either of them and rcp. In rcp there are peaks at r_1, $r_1\sqrt{3}$, and $2r_1$. In fcc crystals the first several near neighbors are at r_1, $r_1\sqrt{2}$, $r_1\sqrt{3}$, and $2r_1$. The screened Coulomb potential is also present in metallic systems, where the conduction-electron screening replaces the ions in solution and the Fermi temperature T_F replaces T. Thus we expect the interactions between the metal atoms are well modeled by the charged colloids.

In conclusion, our experiments reveal several new aspects of charged colloidal suspensions. They do not act like Yukawa particles at high concentrations, but show behavior between that of soft potentials and hard spheres. Despite the relative complexity of the interparticle interactions, the Lindemann and Hansen-Verlet criteria for melting and freezing seem to be obeyed. They, therefore, may be ideal model systems for studying the structure and dynamics of glass formation, especially of metallic glasses.

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