

Real-Space Structure of Colloidal Hard-Sphere Glasses

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The real-space structure of hard-sphere glasses quenched from colloidal liquids in thermodynamic equilibrium has been determined. Particle coordinates were obtained by combining the optical sectioning capability of confocal fluorescence microscopy with the structure of specially prepared fluorescent silica colloids. Both the average structure and the local structure of glasses, with volume fractions ranging from 0.60 to 0.64, were in good agreement with glasses and random close packings generated by computer simulations. No evidence of a divergent correlation length was found. The method used to obtain the three-dimensional particle coordinates is directly applicable to other colloidal structures, such as crystals, gels, and flocs.

Despite recent progress, neither the glass transition nor the structure of glasses is fully understood (1–6). For instance, it is an open question whether there is a thermodynamic phase transition, with diverging length scales, that underlies the freezing of a metastable liquid into an amorphous solid, or whether the arrest of relaxations is purely kinetic (1, 5, 6). Because the immense cooling rates (10^{12} K s⁻¹) necessary to prevent crystallization have not been realized experimentally, it has not yet been possible to make glasses of atomic systems with spherical symmetric interaction potentials (1). Therefore, the structure of hard-sphere random packings made from ball bearings was investigated instead (7). Later, these dense packings were generated with computer algorithms (8, 9). Computer simulations of the generation of hard-sphere glasses by very fast quenches of hard-sphere liquids have also been carried out (4, 10, 11).

Colloidal hard spheres, which have the same thermodynamic equilibrium phases as atomic hard spheres (12), form glasses relatively easily; their glass transition, which starts at a volume fraction $\phi \approx 0.57$, has been studied with light scattering (13). However, much information about the local structure of the glasses is lost because of the radial averaging of scattering techniques. From computer simulations and theoretical work, it is clear that the local structure—as expressed, for instance, through correlations of the orientational order of near-neighbor bond angles—is the key to a better understanding of the properties of glasses and of the glass transition itself (2, 3). The finite sizes of the systems studied in

computer simulations can become important, especially if the goal is to find a divergent correlation length (5, 6). We can now compare the computer simulations with an experimental system in three-dimensional (3D) real space that has a macroscopic system size.

The improved resolution and sectioning capability of fluorescence confocal scanning light microscopy (14–16) can be fully exploited with the use of digital image analysis to obtain the coordinates of colloidal spheres with high accuracy (Fig. 1). We studied silica spheres with a fluorescent core (dye, fluorescein isothiocyanate), a core ra-

dius of 200 nm, a total radius of 525 nm, and a polydispersity in size of 1.8%. The synthesis and characterization of these hybrid organic-inorganic spheres are described in (17). The hard-sphere potential was created by dispersing the particles in dimethylformamide (in which the refractive index was almost matched) to decrease the van der Waals forces and by adding 0.1 M LiCl to decrease the double layer to a very small value relative to the radius. As measured by confocal microscopy, the average distance of closest approach of the particles was 1052 nm in a dried glass and 1082 nm in the glass with solvent; the difference is probably attributable to a solvation layer that protects the particles from aggregation. The crystallization and melting volume fractions calculated from this interaction distance of closest approach were 0.50 and 0.55, respectively, in excellent agreement with reported data (12). The fluorescence confocal micrographs were made with an excitation wavelength of 488 nm (18). In the x-y plane perpendicular to the optical axis, the experimental resolution is ~ 200 nm; along the z axis it is ~ 600 nm (14, 18). The particle coordinates were obtained by fitting the three-dimensional data set to the measured particle-microscope response function of a two-dimensional layer of the same spheres (error, ~ 10 nm in x-y coordinates and ~ 15 nm in z coordinates) (19). Previously, it was

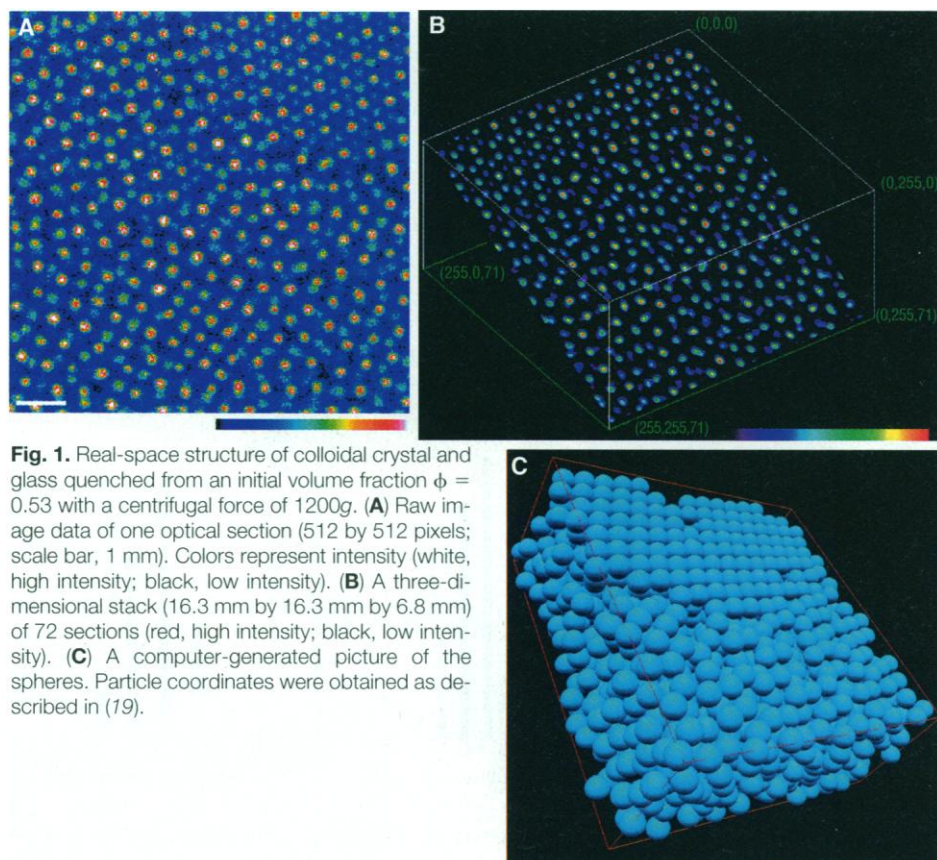


Fig. 1. Real-space structure of colloidal crystal and glass quenched from an initial volume fraction $\phi = 0.53$ with a centrifugal force of 1200g. (A) Raw image data of one optical section (512 by 512 pixels; scale bar, 1 mm). Colors represent intensity (white, high intensity; black, low intensity). (B) A three-dimensional stack (16.3 mm by 16.3 mm by 6.8 mm) of 72 sections (red, high intensity; black, low intensity). (C) A computer-generated picture of the spheres. Particle coordinates were obtained as described in (19).

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only possible to obtain particle coordinates accurately in two-dimensional colloidal systems (20). Because different data sets can be "patched" together, there is practically no limit to the size of the data set.

We created the sample shown in Fig. 1 by first allowing a dispersion of volume fraction $\phi = 0.52$ to crystallize for some time and then quenching the volume fraction very quickly with a centrifugal force. Because the quench was much faster than the crystal growth rate, the resulting sediment contained crystals dispersed in a glass. Pure glasses were made by quenching dispersions with $\phi < 0.494$, the hard-sphere crystallization

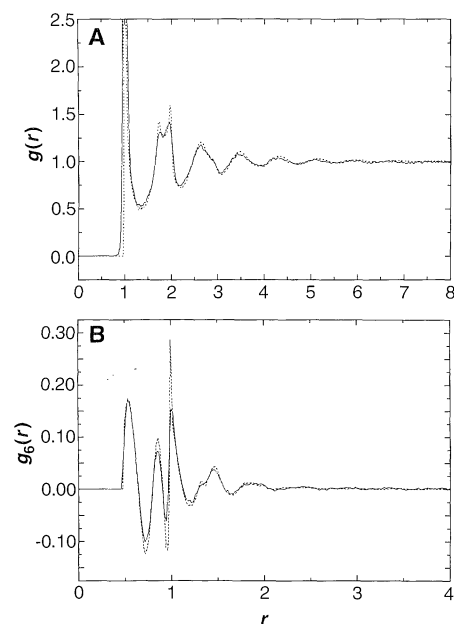
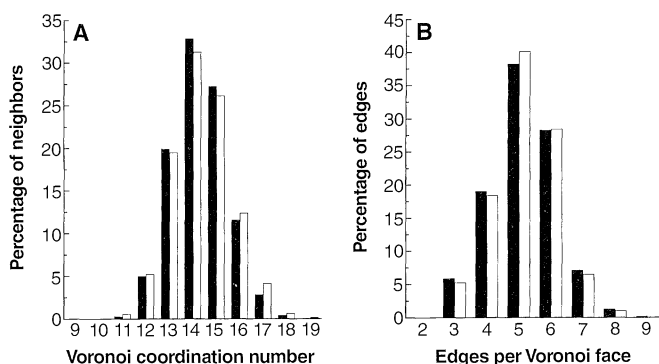


Fig. 2. Average structure of a typical pure glass with $\phi = 0.639$ (solid lines) is shown as expressed by (A) the radial distribution function $g(r)$ and (B) the bond-order correlation function $g_6(r)$ of the bond-orientational order parameter Q_6 (5, 19). A computer-generated random close packing with $\phi = 0.637$ (9) is shown for comparison (dotted lines). The distances r are scaled by the distance of closest approach (1082 nm).

Fig. 3. Local structure of the glass with $\phi = 0.639$ (solid bars). (A) Distribution of Voronoi near-neighbor coordination numbers; (B) distribution of the number of particles surrounding a near-neighbor bond, as expressed by the number of edges on the faces of the Voronoi polyhedrons (2). Open bars represent the computer-generated random close packing with $\phi = 0.637$ (9). The average coordination numbers for the experimental and computer-generated data sets are 14.35 and 14.30, respectively; the average number of particles surrounding a bond is 5.16 for both data sets.



point (12), at different quench rates and from different initial volume fractions, with centrifugal fields of 50 to 1200g (Figs. 2 through 4). At 1g, colloidal crystals were formed that were oriented with their close-packed planes perpendicular to the gravitational field. We analyzed the glass structure perpendicular and parallel to the centrifugal force and at least 20 μm from the glass wall; no differences between the two orientations were found. Close to the glass wall, a wall-induced layering was observed with a thickness of ~ 10 layers. Generally, the lower part of the sediment had a ϕ value close to 0.64, the random-close-packing limit (7–9), whereas on top there was a region (whose height depended on the experimental conditions) with a gradient in the density starting at about $\phi = 0.60$. After redispersion of the sediments, crystallization still occurred, which indicates that the spheres were not pushed through their stabilization layer. For samples of the same final volume fraction, we found no quench rate dependence in the resulting structures, in accordance with recent computer simulations (11). The analyzed data sets were four times the size of that shown in Fig. 1 and contained $\sim 10,000$ spheres.

The average structure of a glass is described by the radial distribution function $g(r)$; a typical example is compared with a computer-generated random packing (9) of similar ϕ in Fig. 2A. The function $g(r)$ describes the chance of finding a particle at a distance r away from another particle relative to a homogeneous distribution of the same density (21). The peaks in $g(r)$ indicate the ordering in coordination shells resulting from the high density; the split second peak is characteristic of glasses (although it can already be observed in a less pronounced way in the liquid phase) (1–3). The experimental data sets are very close to the computer simulation results; the only difference is that the first and second peaks of the simulation data are sharper because of the polydispersity of the spheres and the

small error in determining the experimental coordinates. The decay of the orientational order of near-neighbor bonds as expressed by the correlation function $g_6(r)$ of a local bond-order parameter (5), Q_6 , is shown in Fig. 2B. Q_6 was calculated with the near-neighbor bonds as obtained by Voronoi construction (see below and Figs. 3 and 4). No indications of diverging length scales approaching the random-close-packing limit of $\phi = 0.64$ (7–9) were found, consistent with computer simulations on glasses of particles interacting through a Lennard-Jones potential (6) and contrary to previous simulations on the same type of glasses (5).

We analyzed local structures by first determining the near neighbors of spheres in a unique way through the Voronoi construction (2, 3). A Voronoi polyhedron, analogous to a Wigner-Seitz cell in solid state physics, contains all points in space that are closer to the particle in its center than to all other particles; the whole collection of Voronoi cells fills space. Particles that share a face of their Voronoi polyhedron are called neighbors and the bonds between neighbors are perpendicular to the shared face. Distributions of the coordination numbers are shown in Fig. 3A. As expected, the average coordination number is almost exactly the same as that found in hard-sphere crystals because of the small difference in density. Also of interest is the number of particles surrounding a near-neighbor bond, as given by the edges of its face on the Voronoi cell. For any crystalline phase, this number is either three or an even number (2). In glasses and dense liquids, the number of surrounding particles is mostly five (Fig. 3B), and a structure with that symmetry cannot be extended to fill space. The differences between the experimental data and the computer-generated data were of the same order as the differences among experimental data sets, and the data for different volume fractions ($0.6 < \phi < 0.64$)

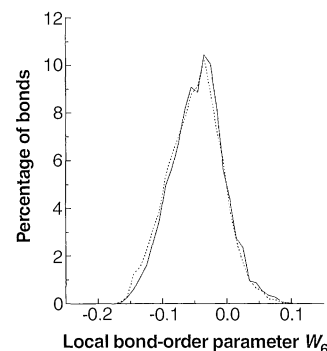


Fig. 4. Local bond-orientational order as expressed by the distribution of the local bond-order parameter W_6 (5) of the glass with $\phi = 0.639$. The average values for the experimental data set (solid line) and the simulated data set [$\phi = 0.637$ (9)] (dotted line) are -0.045 and -0.049 , respectively.

were similar. The local structure can also be characterized in terms of the local symmetry of the near-neighbor bonds as expressed through local bond-order parameters (5). One of these, W_6 , is sensitive to icosahedral order, because this order parameter peaks at a value of -0.17 if the Voronoi neighbor bonds of a central particle have a perfect icosahedral surrounding (Fig. 4). The averages were close to -0.045 for all ϕ , which is an indication of moderate icosahedral order and the absence of any substantial crystalline order. The same average values have been reported for computer-simulated glasses of Lennard-Jones systems (3).

We have shown that with confocal microscopy it is possible to study structures of fluorescent colloidal model spheres in real space with high accuracy and with no essential limit to the number of particles. Contrary to some computer simulations, we found no sign of a thermodynamic phase transition underlying the glass transition. Because colloidal dispersions form equilibrium phases analogous to those of atomic systems (22), the method allows a direct three-dimensional real-space comparison with computer simulations and theory for the atomic analogs and can be easily extended to multicomponent systems (23). Furthermore, the method is not only applicable to fundamental problems in condensed-matter physics (as demonstrated above) but can also be used to study typical colloidal problems, such as gelation and aggregation (16).

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A Carbon Nanotube Field-Emission Electron Source

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A high-intensity electron gun based on field emission from a film of aligned carbon nanotubes has been made. The gun consists of a nanotube film with a 1-millimeter-diameter grid about 20 micrometers above it. Field-emission current densities of about 0.1 milliampere per square centimeter were observed for applied voltages as low as 200 volts, and current densities greater than 100 milliamperes per square centimeter have been realized at 700 volts. The gun is air-stable, easy and inexpensive to fabricate, and functions stably and reliably for long times (short-term fluctuations are on the order of 10 percent). The entire gun is only about 0.2 millimeter thick and can be produced with virtually no restrictions on its area, from less than 1 square millimeter to hundreds of square centimeters, making it suitable for flat panel display applications.

Electron guns have numerous applications in commercial devices and for industry and research. Standard electron guns used in cathode ray tubes usually utilize thermionically emitted electrons from hot tungsten wires and heated materials with low work functions. Alternatively, electron sources based on field emission from sharp tips are used for applications requiring monochromatic electron beams, as in electron microscopy and research. However, these sources typically require ultrahigh-vacuum conditions and high voltages (1). The currents are limited to several microamperes.

Carbon fibers, typically 7 μm in diameter, have also been used as electron emitters in electron guns (2, 3). Although they operate in less stringent vacuum conditions, practical applications are limited because of poor reproducibility and rapid deterioration of the tip (4). Nevertheless, these previous studies show that despite its high work function (≈ 5 eV), graphite can be used as a material for field emitters.

Consequently, the nanometric tips of carbon nanotubes (5) are very good candidates for this purpose, although the emission current of a single tube is constrained because of its very small dimensions (≈ 10

nm in diameter and ≈ 1 μm in length), as previously observed even in the case of much larger carbon fibers (10 μm in diameter). To circumvent this practical problem, one can use an array of nanotubes, where the tubes are all oriented perpendicular to a surface. Large area films of oriented nanotubes have been recently realized (6), and we have used these to construct an electron source (Fig. 1).

The emission characteristics were determined by measuring the current collected on a plate about 1 cm in front of the grid. A typical current versus voltage (I - V) curve at a residual pressure in the vacuum chamber of $\sim 10^{-6}$ torr can be compared with the Fowler-Nordheim equation for field emission (Fig. 2): $I = aE_{\text{eff}}^2 \exp(-b/E_{\text{eff}})$, where a and b are constants that depend on the electronic work function of the surface and only slightly on the electric-field strength at the emitting surface $E_{\text{eff}} = \gamma E_0$ (7), where $E_0 = V/d$ is the average uniform field and d is the distance from the nanotube surface to the grid. The sharp tips and the geometry of the emitting surface cause the electric fields at the tips to be amplified by a factor γ compared with E_0 . For standard field emitting tips, γ is on the order of 10 (7). The electron energy distributions have been measured with an energy analyzer, and we find (for low emission currents) that they are narrow, consistent with field emission, and contain usually one, but sometimes several, peaks with widths between 0.15 and 0.2

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