

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

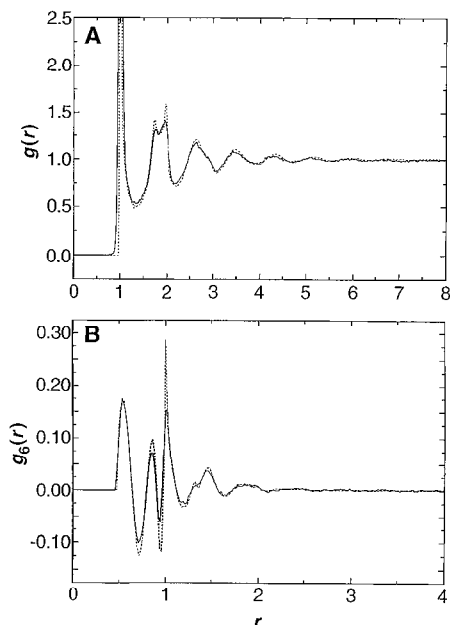


Fig. 2. Average structure of a typical pure glass with $\phi = 0.639$ (solid lines) is shown as expressed by (A) the radial distribution function $g(r)$ and (B) the bond-order correlation function $g_6(r)$ of the bond-orientational order parameter Q_6 (5, 19). A computer-generated random close packing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

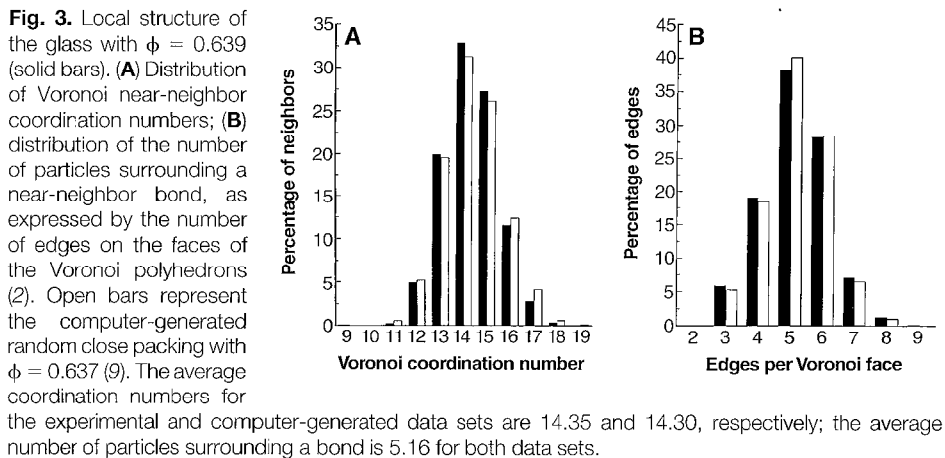


Fig. 3. Local structure of the glass with $\phi = 0.639$ (solid bars). (A) Distribution of Voronoi near-neighbor coordination numbers; (B) distribution of the number of particles surrounding a near-neighbor bond, as expressed by the number of edges on the faces of the Voronoi polyhedrons (2). Open bars 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 ($0.6 < \phi < 0.64$)

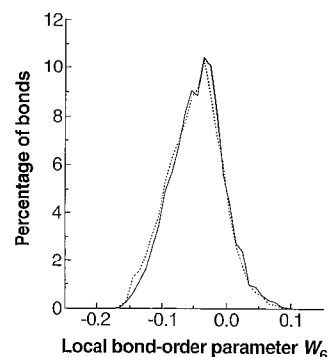


Fig. 4. Local bond-orientational order as expressed by the distribution of the local bond-order parameter W_6 (5) of the glass with $\phi = 0.639$. The average values for the experimental data set (solid line) and the simulated data set [$\phi = 0.637$ (9)] (dotted line) are -0.045 and -0.049 , respectively.

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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