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Published 6 August 2010, *Science* **329**, 656 (2010)
DOI: 10.1126/science.1187988

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Normal Modes and Density of States of Disordered Colloidal Solids

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Materials and Methods

1 Synthesis of Microgel Particles

We synthesized the microgel colloidal particles via dispersion polymerization of N-isopropylacrylamide (NIPAm; 66.3 mmol, Acros) and acrylic acid (AA; 1.0 mmol, Alfa Aesar) with crosslinker N, N'-methylenebisacrylamide (BIS; 0.98 mmol, Acros) in Tris buffer (20 mM, 245 mL) at pH $= 8$. We used the same buffer throughout the experiment. We first dissolved all the chemicals in the buffer in 500 mL round bottom reaction flask at room temperature under nitrogen. The solution was then heated to 73°C using a heated oil bath and purged with nitrogen for 30 min under stirring. We then added initiator 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50; 0.030 g, Wako) dissolved in 5 mL Tris buffer to the flask to initiate polymerization. The reaction was maintained at 73°C under nitrogen for 4 hours. The flask was then removed from heat and diluted with additional Tris buffer. The resultant microgel particles were then cleaned with repeated centrifugation at 1000g and subsequent resuspension in buffer

solution. In this buffer, the particles can be considered sterically stabilized; the measured pair interaction potential between the particles in dilute suspension (*S1*) did not show any long range electrostatic interactions due to AA groups (Fig. S1).

2 Sample Preparation

We created fcc crystals using the microgel colloids within a glass sample chamber of dimensions $18 \times 6 \times 0.1$ mm, with the $[111]$ plane parallel to the glass surface. Because our microgel particles were temperature sensitive, we maintained the temperature of the sample using stage (WP-16; Warner Instruments) and objective warmers (Warner Instruments) to 23.8 ± 0.1°C. At this temperature the nominal volume fraction of the microgel particles was 0.64, calculated using the particle number density and the measured hydrodynamic radius of the particle. The grains within the fcc crystal had dimensions of a few millimeters parallel to the glass surface and ~ 60 μm perpendicular to the glass surface. Since the microgel particles were more than 95% water, they were almost index and density matched.

3 Data Acquisition and Data Analysis

We collected $21,500$ bright-field images at a rate of 30 frames per second of a single slice of a $[111]$ plane that was $30 - 40$ μm away from both glass surfaces and near the center of a grain using an optical microscope (Leica DMI 6000B) equipped with a CCD camera (VGA210; IMPERX), 100X oil objective (N.A. 1.4) and oil condenser (N.A. 1.25). We tracked the positions of $2,350$ particles in a field of view of 61.8 μm $\times$ 45.9 μm using particle tracking algorithms (*S2,S3*).

4 Projecting Normal Modes onto Planewaves

To project the normal modes along transverse and longitudinal planewaves, we used standard interpolation techniques. First, the mode vectors were interpolated linearly onto a regular mesh

with a spacing of 10 grid points per lattice constant. Then a finite difference of the interpolated modes on the grid was taken. The Cartesian components of the derivative were then assembled into the divergence and curl of the original mode. The discrete Fourier transform was then taken. Finally the squared amplitudes of the Fourier transforms of the divergence and curl were multiplied by the magnitude squared, q^2, of the given wavevector to obtain the projection of the original mode onto the given longitudinal and transverse planewaves.

5 Molecular Dynamics Simulation

In Fig. S5, we show the mean square displacement (MSD) computed from a molecular dynamics simulation of harmonic discs with uniform radius but random stiffness. Each particle was assigned a random stiffness from a flat probability distribution between $1k_0$ and $2k_0$ where k_0 was a constant with units of stiffness. Discs i and j interacted with a repulsive central force which was zero if they did not overlap and was equal to $F_{ij} = k_{ij}s_{ij}$ where s_{ij} was the overlap between the particles, and k_{ij} was the average stiffness of the two particles. Particles were arranged in a hexagonal lattice precisely at the close-packing point. The simulations were performed at $T = 2.5 \times 10^{-2}ak_0$ where a is the lattice spacing.

Figures

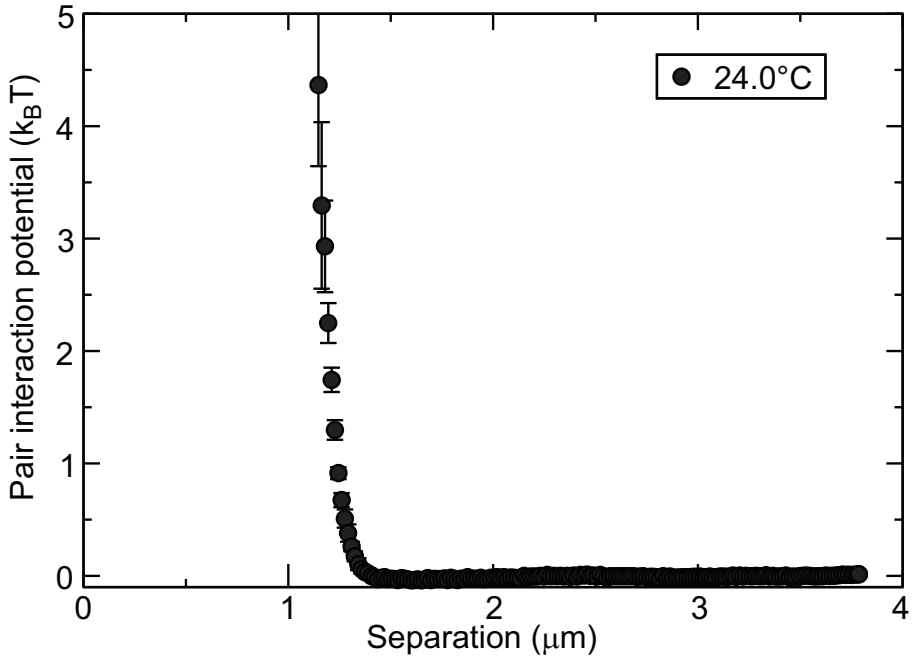

Fig. S1. Pair interaction potential of microgel colloidal particles at 24.0 ± 0.1°C and in 20 mM Tris base buffer at pH $= 8$, measured from a dilute monolayer, did not show any long range electrostatic interactions due to the acrylic acid groups present in the particles.

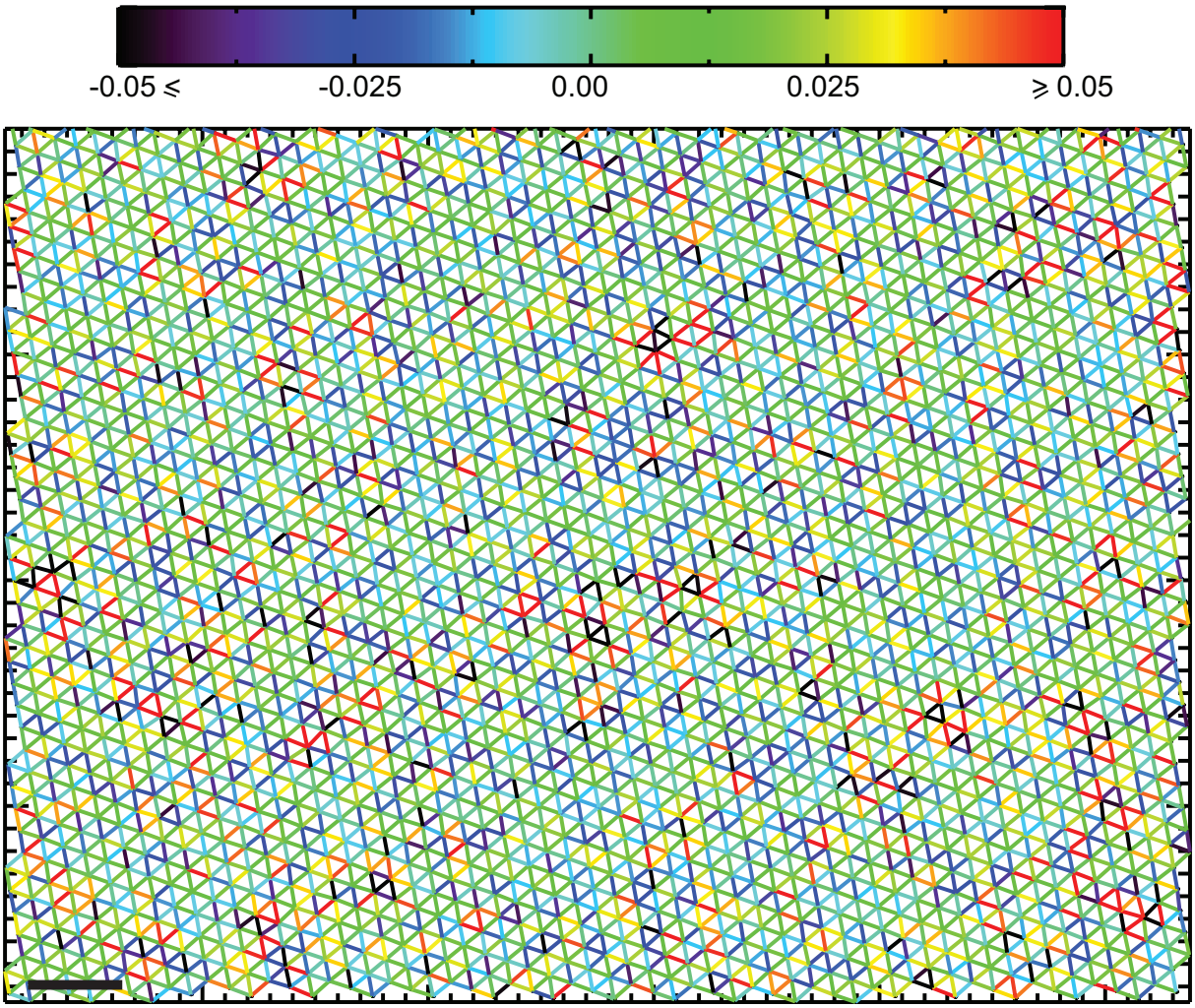

Fig. S2. Relative spatial fluctuations of the time-averaged interparticle separations, $\delta a_{ij}/a_0 = (\overline{a_{ij}} - a_0)/a_0$, for all nearest neighbor positions in the disordered crystal averaged over 21500 frames. The time-averaged nearest-neighbor separations between the particles, $\overline{a_{ij}}$, were more or less homogeneous throughout the system, demonstrating the relatively high degree of geometrical order in our system. Scale bar is 5 μm.

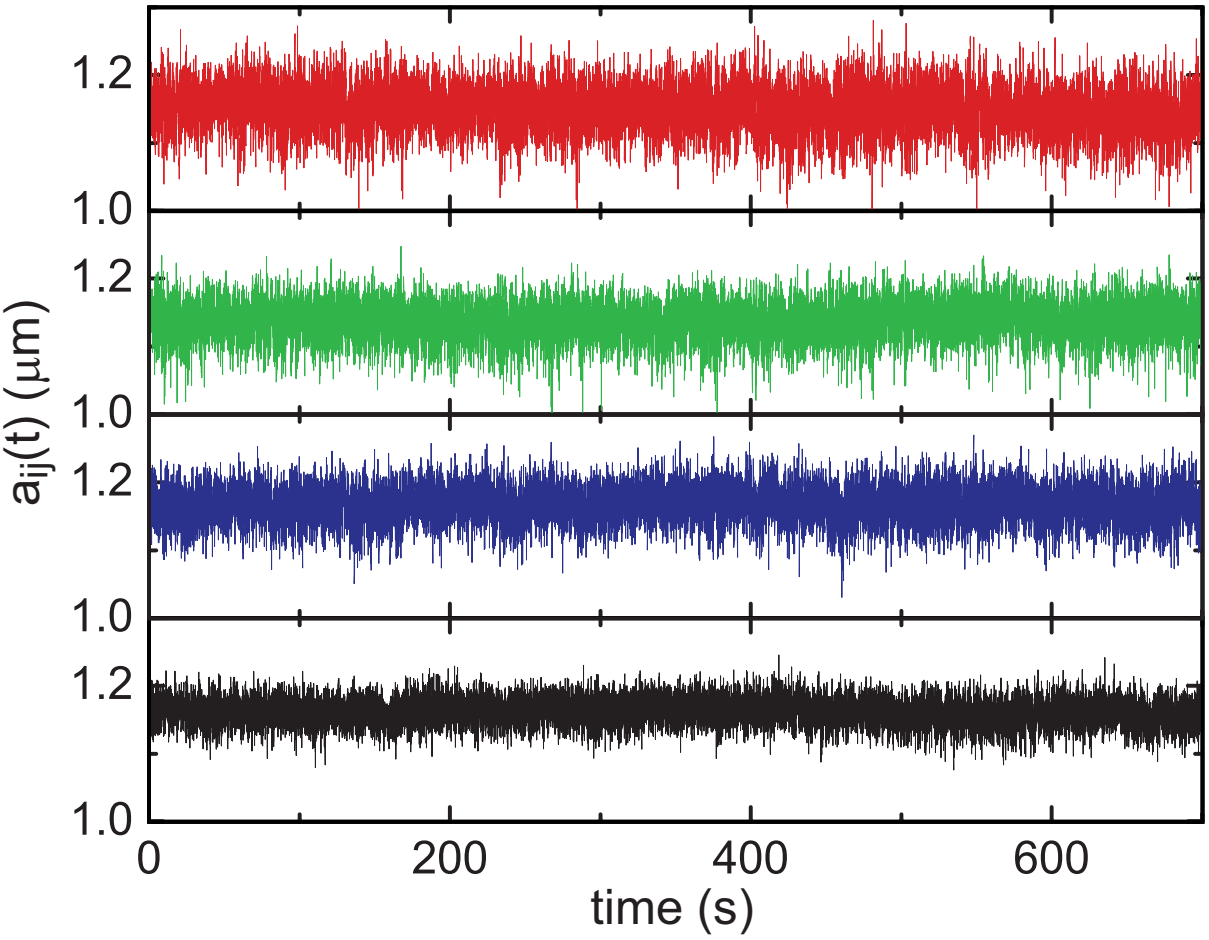

Fig. S3. The time dependent fluctuations of $a_{ij}(t)$ for four particles chosen randomly. The fluctuations in $a_{ij}(t)$ are larger than the experimental resolution in particle displacements.

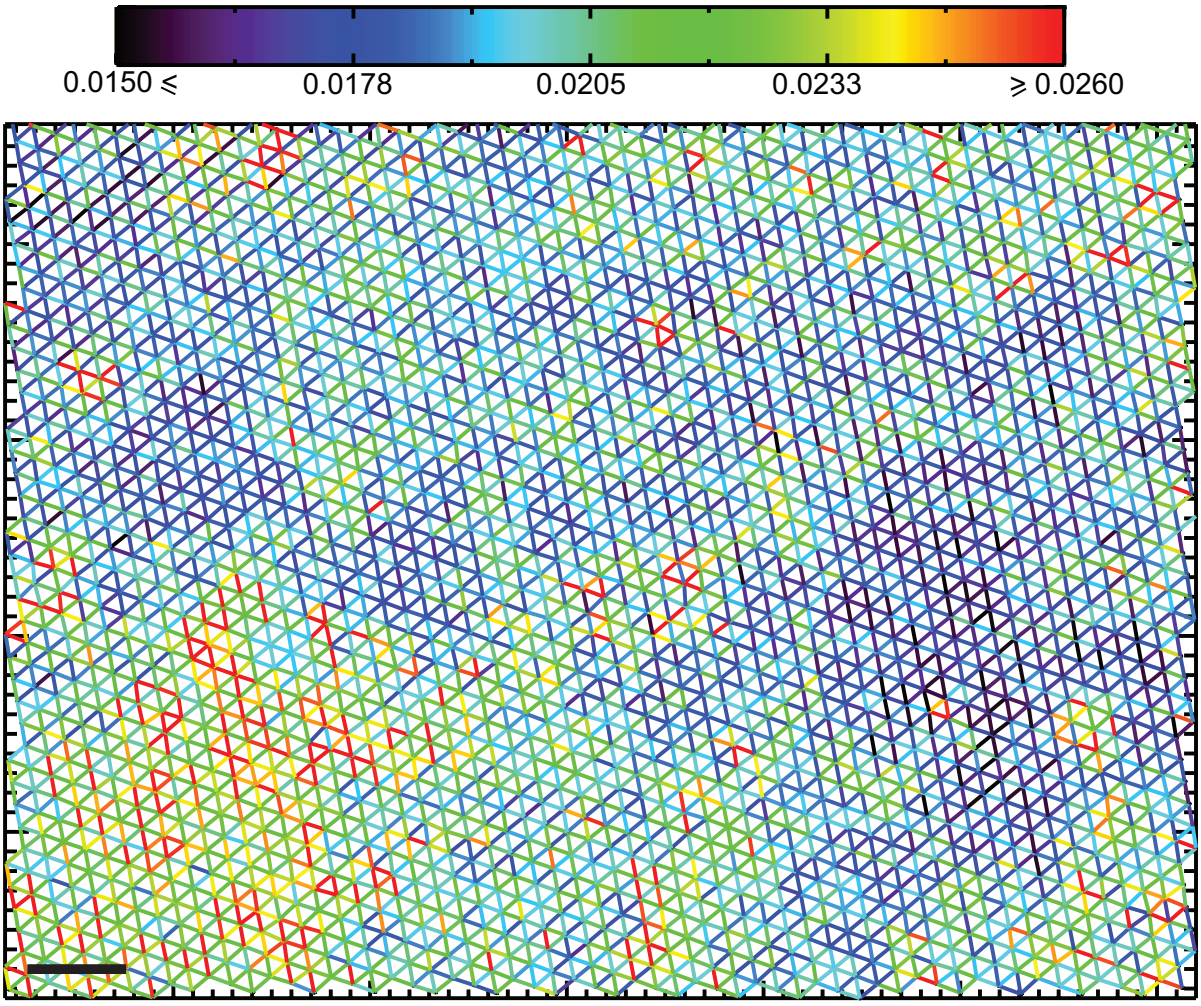

Fig. S4. Spatial distribution of relative nearest-neighbor separation fluctuations, $\Delta a_{ij}/\overline{a_{ij}} = \sqrt{\overline{(a_{ij}(t) - \overline{a_{ij}})^2}}/\overline{a_{ij}}$ averaged over 21500 frames. Solid lines connecting nearest-neighbor particles are colored blueish (reddish) to indicate lower (higher) than average Δa_{ij}. The spatial fluctuations in Δa_{ij} were five times larger than the spatial fluctuations in $\overline{a_{ij}}$. Scale bar is 5 μm.

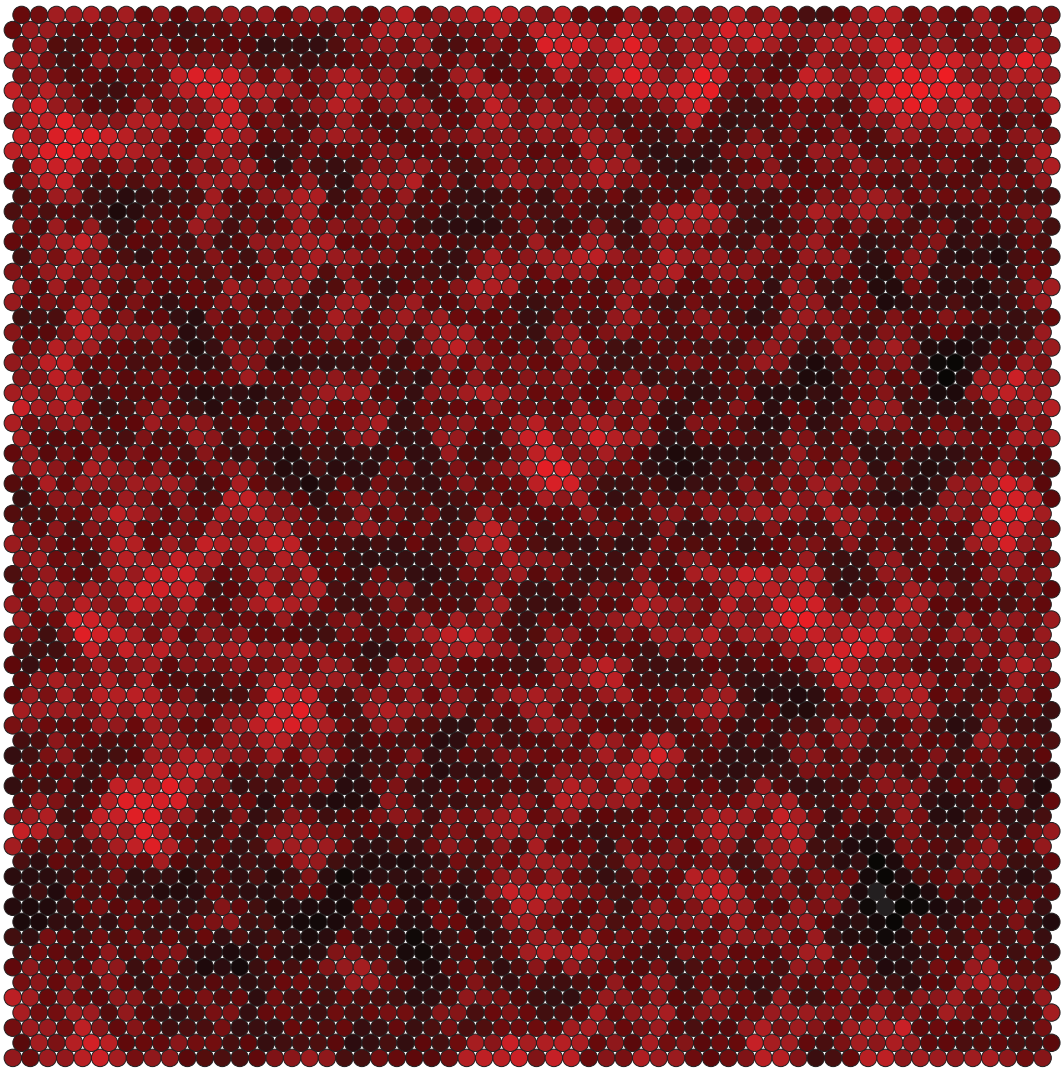

Fig. S5. Mean squared displacement (MSD) of individual particles in a molecular dynamics simulation with individual particle stiffness drawn in a random, spatially uncorrelated way. Coherent regions of large MSD arise despite the uncorrelated microscopic particle stiffness.

References

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