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Measuring Dynamics and Interactions of Colloidal Particles with Digital Holographic Microscopy

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Abstract: We investigate how colloidal particles self-assemble in confined and nonequilibrium systems, including particles trapped at liquid-liquid interfaces (e.g. emulsion droplets) and inside spherical containers. Although common in industrial formulations and fundamental condensed matter studies, these systems remain poorly understood, primarily because no existing experimental probes, including confocal microscopy, can yield real-space data with sufficiently fast acquisition times to resolve 3D dynamics. We use a powerful interferometric technique, Digital Holographic Microscopy (DHM), in concert with particle synthesis and algorithm development to overcome these limitations. Preliminary data show that the technique is capable of tracking several micrometer-sized colloidal particles with 30 nm spatial precision in all three dimensions on millisecond time scales. DHM may be able to yield the most complete physical picture to date of dynamics, interactions, and assembly in colloidal suspensions.

OCIS codes: 090.1995 Digital holography ; 350.4990 Particles

1 Overview

The phenomenon of self-assembly, in both its equilibrium and non-equilibrium (driven) versions, has become a common thread linking biology, chemistry, nanoscience, and condensed matter physics. Nonetheless, it is still a difficult task to predict how or why a given system will self assemble. Recent experimental work in this area has therefore focused on simplified model systems such as colloidal suspensions, where the interactions between the particles can be controlled and measured, and the assembly process can be observed directly [1-6].

In the past decade, real-space three-dimensional studies of colloidal systems with the confocal microscope have revealed in enormous detail the mechanisms of phase transitions and nonequilibrium phenomena such as glass formation – mechanisms which cannot in general be resolved using ensemble-averaging techniques such as scattering [2-7]. Digital Holographic Microscopy (DHM) has the potential to extend the range of these studies into new timescales.. Compared to other 3D techniques such as tomography [8] and confocal microscopy [6], DHM is potentially 3 orders of magnitude faster in acquisition time. In comparison to dynamic light scattering (DLS) [9], which has even higher temporal resolution, holography has the advantage that it gives real-space information. Moreover, DHM, especially in the inline configuration, is much simpler and cheaper to build.

Colloidal particles are well-suited for holographic imaging, but relatively few articles in the recent literature describe DHM-based studies of colloids. Most of these focus on holographic particle image velocimetry for flow visualization [10-13], and many others describe interesting proof-of-concept studies [12, 14]. Recently David Grier's group has demonstrated the use of holography in both particle tracking and optical trapping [15].

As with many particle tracking techniques [16], there is some confusion over the word "resolution." It is possible to resolve the center of brightness of a *single spherical particle* to a precision on the order of tens of nanometers, well below the diffraction limit. Insofar as the center of brightness accurately represents a fixed location on the particle as it moves through the field of view, the precision to which one can measure the centroid sets the spatial "resolution" of the technique.

2 Materials and Methods

A plane wave from a collimated diode laser (Coherent CUBE, 660 nm) is used to illuminate a roughly $(1\text{ mm})^2$ area on a sample. The sample is contained in a simple sample chamber consisting of a cover glass and microscope slide with optical adhesive and a 100 μm spacer in between. We have used other sample thicknesses successfully, but thin samples such as these have the advantage that they avoid twin-image blurring. The scattered light and unscattered light from the reference beam are focused using a 0.8 NA microscope objective to a point some several cm in front of a high-speed CMOS camera (Basler A504). The unfocused, diverging image (the hologram) is captured by the camera and written directly to main memory of a computer in real time. The camera can capture up to 500 frames per second at 1280 by 1024 resolution. After the memory (2 GB) is full, the sequence of holograms is written to disk and reconstructed by the Fourier convolution method. Particles are then tracked from the reconstruction. The image processing code uses the open-source Python language and the SciPy numerical extensions. The resulting code is fast, uses well-tested numerical algorithms, runs on any platform, and is parallelizable.

We have also formulated a model system consisting of oil-in-water emulsion droplets (with surfactant on the surface) and spherical, sterically-stabilized particles for studying the self-assembly of particles on the surface of a droplet. The system contains glycerol in the water phase to index-match the droplet to the surrounding fluid in order to eliminate scattering from the droplet interface. The particles are poly(methyl methacrylate) (PMMA) spheres stabilized by poly(dimethyl siloxane) chains grafted to their surfaces, and are nominally uncharged. In particular we examine systems containing small numbers of particles ($N < 25$). These systems are too small to form crystals, but we expect the minimum energy structures they do form to be highly sensitive to the range and depth of the interparticle forces.

3 Results and Discussion

As a preliminary test, we measured the mean-squared displacement (MSD) of a single 1 μm polystyrene sphere in water. The data show that the MSDs in each coordinate are nearly linear down to 2.5 ms in lag time and approximately 0.001 μm^2 in MSD. The linearity at short time scales indicates the precision of the technique, as the data would be expected to flatten out near a noise floor. The slopes of the MSDs for the individual coordinates vary, likely because the distance scales in x, y,and z were not calibrated separately. But the measured diffusion coefficient is accurate to within 5% of the diffusion coefficient calculated by the Stokes-Einstein equation. This experiment shows that DHM can accurately measure particle dynamics in real-space, in three dimensions, with spatial precision of about 30 nm and temporal resolution of milliseconds. It is possible to go to even higher frame rates (sub-millisecond time scales) by windowing the camera resolution.

Figure 1 shows the results of a particle tracking experiment on a system containing 10 particles bound to the surface of a droplet. We gather full three-dimensional data sets, at a rate of 30 per second, giving the instantaneous positions of all the particles at the surface. Since the system is at equilibrium, we can then use Boltzmann statistics [17] to extract parameters such as the potential of mean force (also shown in the figure), which is the interparticle pair potential averaged over the configurations of all the other particles in the system. We find that to a good approximation this potential is harmonic, consistent with the observation that the particles form an ordered arrangement on the surface in which each particle is localized about its equilibrium position. The average distance between particles is roughly 10 μm, compared to a particle size of 1 μm. The results are surprising because the range of the interactions is large even though the particles are nominally uncharged. There may be some charge acquired during the emulsification process, as has been observed in other systems [18].

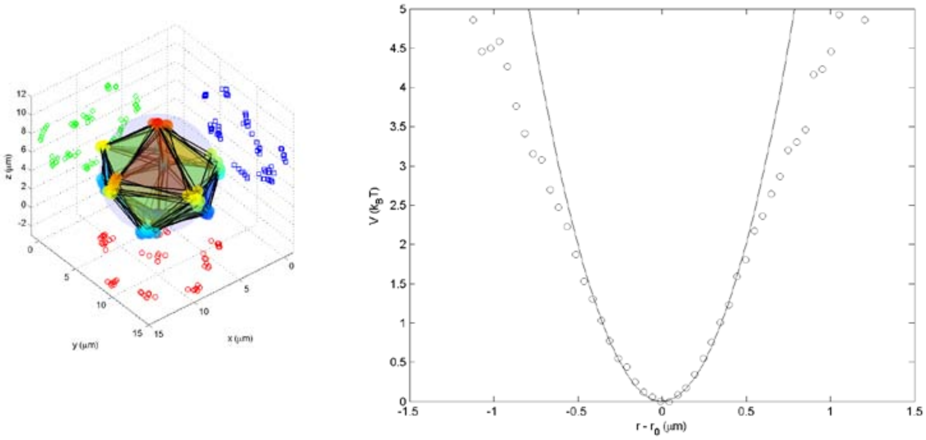

Figure 1*: Left, superposition of 7 three-dimensional reconstructions of a droplet with 10 bound particles at time intervals of 0.033 seconds. Right, average potential of mean force between particles calculated from 200 consecutive 3D reconstruction; curve is best fit to a harmonic potential.*

4 Conclusions

Self-assembly in multiphase colloids is a vast territory that remains largely unexplored due to the dearth of experimental tools that are capable of resolving the particle positions and dynamics in these small, rapidly changing and isolated systems. DHM is a key advance that makes many such experiments possible. The power of this technique is that it gives us (in theory) *all the information* about the system at equilibrium. With each hologram we take we obtain a 3D snapshot of the system at a particular spot in its configuration space. The statistics of these configurations can be used to derive the interactions and energetics through the Boltzmann distribution.

5 References

[1] Hoogenboom, J. P.; Vergeer, P.; van Blaaderen, A., A real-space analysis of colloidal crystallization in a gravitational field at a flat bottom wall. *Journal of Chemical Physics* **2003,** 119, (6), 3371-3383.

[2] Yethiraj, A.; van Blaaderen, A., A colloidal model system with an interaction tunable from hard sphere to soft and dipolar. *Nature* **2003,** 421, (6922), 513-517.

[3] Gasser, U.; Weeks, E. R.; Schofield, A.; Pusey, P. N.; Weitz, D. A., Real-space imaging of nucleation and growth in colloidal crystallization. *Science* **2001,** 292, (5515), 258-262.

[4] Kegel, W. K.; van Blaaderen, A., Direct observation of dynamical heterogeneities in colloidal hard-sphere suspensions. *Science* **2000,** 287, (5451), 290-293.

[5] van Blaaderen, A.; Wiltzius, P., Real-Space Structure of Colloidal Hard-Sphere Glasses. *Science* **1995,** 270, (5239), 1177-1179.

[6] Weeks, E. R.; Crocker, J. C.; Levitt, A. C.; Schofield, A.; Weitz, D. A., Three-dimensional direct imaging of structural relaxation near the colloidal glass transition. *Science* **2000,** 287, (5453), 627-631.

[7] Gasser, U.; Schofield, A.; Weitz, D. A., Local order in a supercooled colloidal fluid observed by confocal microscopy. *Journal of Physics-Condensed Matter* **2003,** 15, (1), S375-S380.

[8] Xu, W. B.; Jericho, M. H.; Meinertzhagen, I. A.; Kreuzer, H. J., Digital in-line holography for biological applications. *Proceedings of the National Academy of Sciences of the United States of America* **2001,** 98, (20), 11301-11305.

[9] Berne, B. J.; Pecora, R., *Dynamic light scattering : with applications to chemistry, biology, and physics*. ed.; Wiley: New York, 1976; p vii, 376.

[10] Sheng, J.; Malkiel, E.; Katz, J., Digital holographic microscope for measuring three-dimensional particle distributions and motions. **2006,** 45, (16), 3893-3901.

[11] Pan, G.; Meng, H., Digital holography of particle fields: reconstruction by use of complex amplitude. **2003,** 42, (5), 827.

[12] Garcia-Sucerquia, J.; Xu, W.; Jericho, S. K.; Klages, P.; Jericho, M. H.; Kreuzer, H. J., Digital in-line holographic microscopy. **2006,** 45, (5), 836-850.

[13] Pu, Y.; Meng, H., Intrinsic aberrations due to Mie scattering in particle holography. **2003,** 20, (10), 1920-1932.

[14] Xu, W.; Jericho, M. H.; Meinertzhagen, I. A.; Kreuzer, H. J., Digital in-line holography of microspheres. **2002,** 41, 5367-5375.

[15] Lee, S. H.; Grier, D. G., Holographic microscopy of holographically trapped three-dimensional structures. **2007,** 15, (4), 1505-1512.

[16] Crocker, J. C.; Grier, D. G., Methods of digital video microscopy for colloidal studies. *Journal of Colloid and Interface Science* **1996,** 179, (1), 298-310.

[17] Crocker, J. C.; Grier, D. G., Microscopic Measurement of the Pair Interaction Potential of Charge-Stabilized Colloid. *Physical Review Letters* **1994,** 73, (2), 352-355.

[18] Hsu, M. F.; Dufresne, E. R.; Weitz, D. A., Charge Stabilization in Nonpolar Solvents. **2005,** 21, (11), 4881-4887.