Large, defect-free FCC colloidal crystals under microgravity

Qian Lei¹, Boris Khusid¹, Lou Kondic², Paul M. Chaikin³, Andrew D. Hollingsworth³, Alton J. Reich⁴, Richard B. Rodgers⁵, William V. Meyer⁶

¹Otto H. York Dept. of Chemical and Materials Engineering, New Jersey Institute of Technology
²Dept. of Mathematical Sciences, New Jersey Institute of Technology
³Dept. of Physics, New York University
⁴Streamline Automation LLC, Huntsville, AL
⁵NASA Glenn Research Center, Cleveland, OH
⁶USRA at NASA Glenn Research Center, Cleveland, OH

Abstract

Here we report the results of microgravity experiments performed on the International Space Station (ISS) to study crystallized, metastable colloidal liquids in the region of the hard sphere phase diagram that has been found to be glassy on Earth. Using confocal microscopy, we observed the self-assembly of high density, three-dimensional colloidal crystals from micron-size hard spheres suspended within a fluid medium. The largest face-centered cubic (FCC) phase measured 27 x 1.5 x 0.15 mm. From a practical aspect, the fact that a single, topological defect-free FCC colloidal crystal can be grown in microgravity and the crystal returned from orbit suggests new routes for manufacturing colloidal devices, particularly optical elements in space.

Key words

Colloidal crystals, model hard sphere, 3D photonic crystals, colloidal self-assembly

Introduction

The goal for the Advanced Colloids Experiment with Temperature Control-11 (ACE-T11) ISS experiment was to study hard-sphere colloidal dispersions at particle volume fractions above $\phi \sim 0.58$. At these concentrations, samples generally remain disordered or 'glassy' on Earth because of gravitational sedimentation and particle jamming (Hunter and Weeks, 2012). Micron-sized poly(methyl methacrylate) (PMMA) spheres dispersed in a refractive index matching oil were prepared, and the effective hard sphere volume fraction was set by the predicted disorder-order transition.

Crystallization rate and structure

Our Physics of Hard Spheres Experiment (PHaSE) microgravity experiment confirmed that FCC is the stable equilibrium structure, exhibiting slow growth rates during crystal annealing (Cheng *et al.*, 2002). Recent computer simulations showed that the interfacial free energy of the HCP solid may be slightly higher than that of the FCC phase, resulting in a greater likelihood that FCC will nucleate from the (metastable) liquid compared with HCP (Sanchez-Burgos *et al.*, 2021). The ACE-T11 microgravity experiments, as well as earlier studies by our group (Zhu *et al.*, 1997), were designed to investigate the nature of phase transitions in colloids in the absence of gravity. The results reported here were achieved at the particle level using an established optical imaging technique for increasing optical resolution and contrast by means of using a spatial pinhole to block out-of-focus light in image formation.

In addition to theoretical interest, we can take advantage of the self-assembly of colloidal materials—the spontaneous organization of microscopic particles into ordered structures—to produce materials ideally with targeted properties. The implementation of this strategy allows colloidal particles to function as building blocks of new materials in myriad

technologies including materials engineering, electronics, and optics, as well as life science, chemical and pharmaceutical industries.

Materials and Methods

The colloidal particles were synthesized using established dispersion polymerization methods (Antl *et al.*, 1986; Pathmamanoharan *et al.*, 1997). The dispersant required to prevent particle aggregation was prepared according to Elsesser and Hollingsworth (2010). This polymeric stabilizer is poly(12-hydroxystearic acid)-*graft*-poly(methyl methacrylate) or PHS-*g*-PMMA, a comb-graft copolymer dissolved in an acetates and toluene mixture at about 40 weight percent non-volatiles. The ACE-T11 samples featured a rhodamine-fluorescein hybrid dye called julolidine rhodol (Sauers *et al.*, 1987; Dickinson *et al.*, 2010), which proved to be superior to commercially-available rhodamine isothiocyanate (RITC). We measured the excitation and emission spectra, which are presented in Figure 1, along with a vertical line denoting the frequency-doubled Nd:YAG (532 nm) laser system in the Light Microscopy Module (LMM). The dye was esterified with an acrylate monomer in order to co-polymerize it with methyl methacrylate and methacrylic acid. An SEM image of the PMMA particles is presented in Figure 2.

Next, the particles were transferred to a refractive index fluid, typically a mixture of decahydronaphthalene (45% w/w) and tetrahydronaphthaline (55% w/w). The decalin/tetralin mixture matched the (equilibrated) particle and fluid refractive indices, n_D = 1.5097 at a wavelength of 589 nm. In this process, the particle and fluid masses are carefully weighed according to the desired effective volume fraction. A heat shock step is

required to equilibrate the 'good' solvent (tetralin) with the PMMA (Kodger *et al.*, 2017). Following this step, one or two test samples are prepared at just below and above the freezing volume fraction to observe colloidal crystals (coexistence phase). Finally, the effective volume fraction of the samples is determined by constructing the phase diagram using the sedimentation method and calibrating with respect to the known freezing point, *i.e.* setting 0.494 as the lowest volume fraction which first shows crystallization (Phan *et al.*, 1996). This step identifies the PHS layer thickness, typically 10 to 15 nm, and volumetric swelling ratio 1.29.

Each suspension was loaded into an individual capillary through a filling port that was then sealed using indium metal (Belser, 1954). The capillaries (Electron Microscopy Science P/N 63825-05; Corning 7740 borosilicate glass capillary, 0.20 x 2.0 x 50 mm) were mounted on a copper thermal bridge equipped with thermistors to control a temperature gradient across the length of the capillary. Loading and mounting of six capillaries with colloidal samples in two sample modules was conducted at ZIN Technologies' facilities. The sample modules were delivered to the ISS on March 6, 2020, on SpaceX-20. Samples in one module were studied in September–October 2020 and in the other in January–February 2021. Imaging of colloidal samples was conducted with a 100x oil immersion objective on a confocal microscope in the Light Microscopy Module (LMM). The LMM confocal microscope was operated from the ground NASA GRC Payload Operations

Center (GIPOC) without the crew participation. We used ImageJ and MATLAB software for image processing and analysis of data collected in the ISS experiments.

Results

Three concentrated samples were prepared for ACE-T11: $\phi = 0.52$ (coexistence), 0.55 (crystal), 0.58 (glassy). The particle suspensions were homogenized in 1-g just prior to launch on SpaceX-19 (CRS-19), a Falcon 9 rocket sent into orbit on December 4, 2019. At $\phi = 0.58$, the nucleation and growth of the crystals are greatly hindered in a gravitational field and we expect that particles would remain in an amorphous state. Indeed, experimental evidence suggests that a hard-sphere glass transition, if it exists, would occur in the range $\phi \sim 0.56$ (random loose packing) to $\phi \sim 0.64$ (random close packing).

This was not the case with the sample in capillary C3, which gradually crystallized upon exposure to the microgravity environment. In this sample cell, a *topological defect-free*, face-centered cubic (FCC) phase, 27mm x 1.5mm x 0.15mm single colloidal crystal was grown from solid spheres on the ISS as indicated by the confocal microscopy images in Figures 3 and 4. For the ACE-T11 samples in the other two sample module positions, the particle sediment proved to be too viscous to manipulate the metal stir wires. In capillary C2, small crystallites did form however, within a 5 μ m layer near the top cover. A vertical temperature gradient was used unsuccessfully to induce thermophoretic particle mobility, which was hoped to produce sample mixing. No significant particle displacement was observed after several hours. We note that the ACE-T11 experiments were designed to impose temperature gradients to explore the effect of thermophoresis on crystallization of hard-sphere colloids. It was found that these temperature gradients—even a 40 °C vertical gradient across a 2 mm gap using a temperature-controlled sample and oil immersion optics maintained at ambient temperature—did not perturb the PMMA particles in an index matched medium comprised of the refractive index matching decalin-tetralin mixture. Notably, there was no detectable 'Soret effect' or thermal diffusion induced by an imposed temperature gradient as described, for example, by Piazza and Parola (2008).

The NJIT and NYU investigators worked in close collaboration with researchers from the NASA Glenn Research Center to record, process and analyze confocal microscopy images of colloids collected in the ISS experiments in 2020–2021.

Discussion

Our previous Space Shuttle experiments indicate that high volume fraction hard sphere particle suspensions might self-assemble into an ordered crystalline structure on ISS (Zhu *et al.* 1997). With this observation in mind, the ACE-T11 experiment was designed to look at the role of macroscopic and microscopic forces in structure formation. To mediate crystallization, the ACE-T11 study included heating to produce elevated sample temperatures, as well as a reversible temperature gradient to induce particle concentration gradients (Cheng *et al.*, 1999). This feature was intended to allow the disorder-to-order transition to be observed at the particle level—that is, scientists could follow this change if the particle concentration adjusted itself throughout the sample cell. Scanning across a capillary in the direction of increasing particle density, *i.e.*, towards cold side, we expected

to see the formation of crystallites in fluid (coexistence) and further along, a space-filling crystal. At the highest volume fractions that produce a glassy phase on Earth, the crystal structure should persist.

This unusual behavior is due to the absence of gravity that, on Earth, causes particle jamming, sedimentation, and convection. Observing concentrated disordered (glassy state) monodisperse collections of colloidal particles form crystals in microgravity has happened before, but at the macroscopic level. We observed this behavior in the Colloidal Disorder-Order Transition (CDOT) experiment where brilliant iridescence was attributed to the diffraction and constructive interference of visible light waves according to Bragg's law. This 'physical color'—indicative of structure—occurred when particle crystallites formed. In contrast, ACE-T11 used confocal microscopy to observe what is happening at the particle level when this phenomenon occurs.

Despite not being able to manipulate the PMMA particles with temperature gradients, the colloid in capillary C3 formed a FCC crystal nearly the size of the capillary used to contain it. FCC crystalline regions were found in capillaries C1 and C2 only near the top surface of the capillary. Furthermore, the colloidal samples used in the ISS experiments were sufficiently concentrated to survive re-entry and appeared to remain crystalline upon return to Earth. Most notably during the ACE-T11 experiment, a large, *defect-free* crystal, like nothing seen on Earth, was created on ISS. Figure 5 presents a slice from *z*-stack confocal imaging of a large 3-D crystal that has no obvious lattice imperfections. The inset shows its 2-D Fourier transform, revealing its structure. At this particle density, the sample would

have remained as a disordered glass on Earth. Yet in microgravity, capillary C3 exhibited a large 3-D crystal, made from micron-sized particles, without visible structural defects. Observations from this experiment should help ensure the future reproducibility of this important achievement.

Since the particles comprising these large, ordered structures (crystals) are the size of the wavelength of visible light, they have the potential to control light without resorting to heat producing electronics which limits miniaturization. One exciting aspect of this work is the realization that in the future we may be able to send up large quantities of these particles— monodisperse collections with different diameters, shapes and properties based on the wavelength of light we wish to control with these crystals—in these types of solvents, which do not seem to be subject to Soret effects. Upon return to Earth, these concentrated samples may exhibit desirable large 3-D, defect-free structure. Ultimately, this experiment should enable scientists to map a pathway for fabrication of multiphase micro-structured heterogeneous items from polymers, metals and ceramics. The study forms the technological foundation for the next generation of complex processes like high-resolution additive manufacturing (3-D printing).

Conclusions

Results of the ACE-T11 experiments demonstrated that molecular dynamics simulations of equilibrium phase diagram are valid only when gravitational effects are unimportant. Measurement of the motion of individual particles in crystalline and non-crystalline regions of colloids thus provides a unique opportunity for testing and validating various assumptions underlying molecular dynamics simulations of the structure and dynamics of simple liquids.

Physical realizations of the hard sphere system are almost possible with colloidal spheres dispersed in solvents of the same index of refraction. Unfortunately, index matching (to diminish the attractive van der Waals interaction and multiple scattering) is usually incompatible with density matching. Gravity tends to cause inevitable settling, preventing a uniform density at equilibrium. Moreover, the imposition of control fields such as temperature gradients leads to instabilities in any fluid phase.

Our previous experiments show clear differences between the phase diagram, crystal structure and crystallite morphology for samples measured in 1-g and those measured in micro-g. These differences are of intrinsic interest on their own, *e.g.*, the facility of crystallization in micro-g of samples which remain in the glass phase in 1-g. The implication is that dynamical processes at volume fractions near close packing are extremely sensitive to gravity.

The main effects of gravity can be seen from the Boltzmann factor governing the particle density for dilute systems as a function of height, $exp\left(\frac{-\Delta mgh}{k_BT}\right)$, where Δm is the buoyant mass. In our samples, a gravitational height, $\frac{k_BT}{\Delta mg}$, as high as 30 microns implies, to lowest order, a factor of 20 density difference from the bottom to the top of 100 µm thick cross section. To reduce this to an acceptable level (~0.002 variation in concentration), we must

reduce the average acceleration to 10^{-4} g. Osmotic pressure effects increase the effectiveness of thermal effects and change the real requirement to $\sim 10^{-3}$ g.

The contrast in structures formed in model particle suspensions under microgravity in the ACE-T11 experiment and normal gravity on Earth revealed the salient features of the influence of a temperature gradient and gravity on non-equilibrium colloidal processes. Understanding these phenomena is essential for the development and operation of a wide range of terrestrial and space applications involving the (spontaneous or directed) self-assembly of mesoscopic materials. The particles should be dispersed in fluids which do not exhibit Soret effects (thermophoresis). The particle sizes, shapes and properties can be varied based on the wavelength of light we wish to control with colloidal photonic crystals.

Three dimensional photonic crystals have potential applications ranging from: (i) Zerothreshold microlasers with high modulation speed; (ii) Low-threshold optical switches and all optical transistors for optical telecommunication; (iii) High-speed optical computers; (iv) Microlasers operating near a photonic band edge will exhibit ultra-fast modulation and switching speeds for application in high-speed data transfer and computing; (v) Telecommunications with light without the need to for conversion to and from electrical signals; (vi) Multiple scattering of light in biological tissue providing a safe, inexpensive and non-insidious probe of brain, breast and skin tumors (Dissanayake and Wijewardena Gamalath, 2015; Johri *et al.*, 2007).

References

Antl L, Goodwin JW, Hill RD, Ottewill RH, Owens SM, Papworth S, Waters JA (1986) The preparation of poly(methyl methacrylate) latices in non-aqueous media. *Colloids Surf.* **17** 67–78. https://doi.org/10.1016/0166-6622(86)80187-1

Belser RB (1954) A Technique of Soldering to Thin Metal Films. *Rev. Sci. Instrum.* 25 180–183. https://doi.org/10.1063/1.1771017

Cheng Z, Russel WB, Chaikin PM (1999) Controlled growth of hard-sphere colloidal crystals. *Nature* **401** 893–895. https://doi.org/10.1038/44785

Cheng Z, Chaikin PM, Zhu J, Russel WB, Meyer WV (2002) Crystallization Kinetics of Hard Spheres in Microgravity in the Coexistence Regime: Interactions between Growing Crystallites. *Phys. Rev. Lett.* **88** 015501. doi: 10.1103/PhysRevLett.88.015501

Dickinson BC, Huynh C, Chang CJ (2010) A palette of fluorescent probes with varying emission colors for imaging hydrogen peroxide signaling in living cells. *J. Am. Chem. Soc.* **132** 5906–5915. https://doi.org/10.1021/ja1014103

Dissanayake SE, Wijewardena Gamalath KAIL (2015) Three-dimensional photonic crystals. *World Scientific News* **6** 57–68. EISSN 2392-2192.

Elsesser MT, Hollingsworth AD (2010) Revisiting the synthesis of a well-known combgraft copolymer stabilizer and its application to the dispersion polymerization of poly(methyl methacrylate) in organic media. *Langmuir* **26** 17989–17996 doi:10.1021/la1034917

Hunter GL, Weeks, ER (2012) The physics of the colloidal glass transition. *Rep. Prog. Phys.* **75** 066501. doi: 10.1088/0034-4885/75/6/066501

Johri M, Ahmed YA, Bezboruah T (2007) Photonic band gap materials: Technology, applications and challenges. *Current Science* **92** 1361–1365. https://www.jstor.org/stable/24097763

Kodger TE, Lu PJ, Wiseman GR, Weitz DA (2017) Stable, fluorescent polymethylmethacrylate particles for the long-term observation of slow colloidal dynamics. *Langmuir* **33** 6382–6389. doi:10.1021/acs.langmuir.7b00852

Pathmamanoharan C, Groot K, Dhont J (1997) Preparation and characterization of crosslinked PMMA latex particles stabilized by grafted copolymer. *Colloid Polym. Sci.* **275** 897–901. https://doi.org/10.1007/s003960050164

Piazza R, Parola A (2008) Thermophoresis in colloidal suspensions. J. Phys.: Condens. Matter 20 153102. doi: 10.1088/0953-8984/20/15/153102

Phan S-E, Russel WB, Cheng Z, Zhu J, Chaikin PM, Dunsmuir JH, Ottewill RH (1996) Phase transition, equation of state, and limiting shear viscosities of hard sphere dispersions. *Phys. Rev. E* **54** 6633–6645. https://doi.org/10.1103/PhysRevE.54.6633

Pusey PN, van Megen W (1986) Phase behaviour of concentrated suspensions of nearly hard colloidal spheres. *Nature* **320** 340–342. https://doi.org/10.1038/320340a0

Pusey PN, van Megan W (1987) in Physics of Complex and Supramolecular Fluids, Safran SA, Clark NA, eds.; Wiley-Interscience, New York, 673.

Sanchez-Burgos I, Sanz E, Vega C, Espinosa JR (2021) Fcc vs. hcp competition in colloidal hard-sphere nucleation: on their relative stability, interfacial free energy and nucleation rate. *Phys. Chem. Chem. Phys.* **23** 19611–19626. doi: 10.1039/d1cp01784e

Sauers RR, Husain SN, Piechowski AP, Bird GR (1987) Shaping the absorption and fluorescence bands of a class of efficient, photoactive chromophores: Synthesis and properties of some new 3H-xanthen-3-ones. *Dyes and Pigments* **8** 35–53. https://doi.org/10.1016/0143-7208(87)85004-0

Zhu J, Li M, Rogers R, Meyer WV, Ottewill RH, STS-73 Space Shuttle Crew, Russel WB, Chaikin PM (1997) Crystallization of hard-sphere colloids in microgravity. *Nature* **387** 883–885. https://doi.org/10.1038/43141

Acknowledgments

The research was supported by the NASA grant 80NSSC19K1655 to NJIT and the NSF grants 1832260 to NJIT and 1832291 to NYU and NASA Contract 80GRC020D0003 for USRA at NASA GRC. The Carl Zeiss FESEM instrument was purchased with financial support from the MRI program of the National Science Foundation under Award DMR-0923251. The authors thank the ZIN Technologies Inc. team and the NASA GRC Payload Operations Center (GIPOC) for their support during flight operations. ImageJ is a Javabased image processing program developed at the National Institutes of Health and the Laboratory for Optical and Computational Instrumentation at University of Wisconsin.

Author disclosure statement

No competing financial interests exist.



Figure 1. Excitation and emission spectra for julolidine rhodol-labeled PMMA particles. Measurements were made using a Leica SP8 confocal laser scanning microscope.



Figure 2. SEM image of the 1.25 µm average diameter PMMA spheres (4.3% PDI) using a MERLIN (Carl Zeiss) field emission scanning electron microscope (FESEM).



Figure 3. ACE-T11 LMM 3D confocal microscopy image of large defect free 3D colloidal photonic FCC crystal grown in space.

COLLOIDAL CRYSTALLIZATION ON ISS



Confocal microscopy: Magnification 100 X, oil immersion objective

Figure 4. Typical ACE-T11 LMM typical portions from an extended slice used for constructing a confocal microscopy image of a large defect free 3D colloidal photonic FCC crystal grown in space.



Figure 5. Image from ACE-T11 experiment. 100× magnification of capillary 3 shows a slice from a large 3-D crystal that has no obvious defects. The inset shows its 2-D Fourier transform, revealing its structure.