Fiscal Year:	FY 2014	**Task Last Updated:**	FY 10/14/2014
PI Name:	Chaikin, Paul M. Ph.D.		
Project Title:	The Control and Dynamics of Hard Sphere Colloidal Dispersions--NNX13AR67G		
Division Name:	Physical Sciences		
Program/Discipline:			
Program/Discipline--Element/Subdiscipline:	COMPLEX FLUIDS--Complex Fluids		
Joint Agency Name:		**TechPort:**	No
Human Research Program Elements:	None		
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Space Biology Element:	None		
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Comments:	NOTE: PI moved to NYU (from Princeton U) in 2005 per A. Hollingsworth in PI's dept (7/2009). Changed email 3/30/2009 (chaikin@princeton.edu no longer valid).		
Project Type:	FLIGHT	**Solicitation:**	98-HEDS-03
Start Date:	09/06/2013	**End Date:**	09/05/2018
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No. of PhD Candidates:	5	**No. of Master' Degrees:**	
No. of Master's Candidates:	1	**No. of Bachelor's Degrees:**	
No. of Bachelor's Candidates:		**Monitoring Center:**	NASA GRC
Contact Monitor:	Motil, Brian J.	**Contact Phone:**	216-433-6617
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Flight Program:	ISS		
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Key Personnel Changes/Previous PI:			
COI Name (Institution):	Hollingsworth, Andrew (New York University)		
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NOTE (Ed., March 2014): Continuation of "The Control and Dynamics of Hard Sphere Colloidal Dispersions--NNX08AK04G", grant # NNX08AK04G with the same Principal Investigator.
Colloid science is entering a new era. Over the past 15 years, our NASA-sponsored research has mainly dealt with monodisperse suspensions of colloidal particles interacting via well-known forces. Using spherical particles and observations with light scattering and microscopy, we have gained a great deal of fundamental knowledge about different phases of matter and the dynamics and thermodynamics of their formation. In particular, our experimental results in microgravity have lead to a basic understanding of why crystals and glasses form and their properties.

During the past decade, we have made great strides in synthesizing new classes of particles with different shapes and specific, reversible or irreversible, variable range interactions. We have also found new ways to manipulate the particles

Task Description:	with flow, electric and magnetic fields, and light. We are therefore positioned at the threshold of a new technology, assembling equilibrium and non-equilibrium macroscopic structures with function and activity from well designed particles on the nano to micron scale. Of course, there are still fundamental scientific questions which we can and will address including a host of new ordered phases, frozen configurations, frustration and glasses, and the process of self-organization itself. In particular, we plan to use the microscopy and light scattering instruments, in collaboration with our European colleagues, to study particles that we prepare through emulsion and dispersion polymerization. Physical lithographic techniques will also be employed, and the particles will be modified chemically for controllable interactions. We plan to use different phoretic techniques– electro-, dielectro-, and thermo-phoresis– to control the particles density and orientation. These will also serve as the driving forces to establish the rheological properties of these new systems.
Rationale for HRP Directed Research:	
Research Impact/Earth Benefits:	Characterization of crystal formation in the microgravity environment of the ISS (International Space Station) can lead to a greater understanding of how gravity affects many kinds of colloidal materials, including monodisperse ellipsoids and cubes, colloidal clusters of silica or polymer microspheres, DNA-functionalized colloidal spheres, and 'lock-and-key' colloids. By performing these experiments in reduced gravity, we intend to accomplish the desired characterization without gravitationally-induced inhomogeneities that affect both the dynamics and equilibrium state on Earth. Understanding these complex materials should enable new ways of forming ordered phases, such as those sought for photonic devices to be used in optical communication systems. With the ability to make particles of different shapes, i.e., non spherical, we also have the possibility of having directionally dependent particle interactions. For example, we could take tetrahedral clusters of particles and attach DNA to them. The complementary single-stranded DNA 'sticky ends' can associate/dissociate via thermal activation. This arrangement could lead to tetrahedral bonding as found in diamond or in amorphous glass structures. Another approach utilizes depletion interactions. Since we can lithographically prepare particles of any shape we design in two dimensions and many shapes in three dimensions, we can fabricate lock-and-key colloids which only bind to their complementary shape. In this case, the binding is also directional since the congruent surfaces must match. We can also make such lock-and-key particles through emulsion chemistry. Our goal is to produce some simple processes with such ‘designer particles’ and interactions, to lay the foundations for self-assembly and perhaps self-replication of this new class of materials.
	NASA Contract No. NNX13AR67G: The control and dynamics of hard sphere colloidal dispersions Task Book report, Year 1: Sept. 1, 2013 to Aug 31, 2014. Principal Investigator: Paul M. Chaikin The program’s principle goal is to explain fundamental, microscopic mechanisms of self-organization. Self-organization can be described as a process leading to some form of overall order, which results from local interactions between the components of an initially disordered system. A classic example is the so-called hard sphere colloidal crystal that we have produced and studied in both 1-g and microgravity. Here, microscopic particles – similar in shape and size – spontaneously arrange themselves into structurally well-defined arrays. Thermal fluctuations trigger the (entropically-) favorable structures whose physical size and number are amplified by positive feedback. The process is called crystal nucleation and growth. This system is large enough and slow enough to be observed directly under an optical microscope, and is used extensively as a model for atomic and molecular scale phenomena. Nature produces these structures, too: the opal is composed of silica spheres, 150 to 300 nanometers in diameter, arranged in a hexagonal or face centered cubic (fcc) lattice. Opals shows a range of visible colors due to their internal structure, which causes the interference and diffraction of light passing through the microstructure. Our latest model complex fluids are composed of specially synthesized colloidal particles with well understood, well controlled and sophisticated interactions as described below. The experiments we propose feature recently introduced colloidal systems with directional, specific, and externally controlled inter-particle interactions and motility. • Colloidal particle synthesis, ‘Superballs’ We have delivered to NASA, for launch to the space station in Fall 2014, a series of samples of polymer cubes, actually superballs, with different corner roundings described by the simple equation: 1 = (x/a)^m + (y/a)^m + (z/a)^m, where m, the shape parameter, varies from 2 to 4; a is the edge length; x, y, z are spatial coordinates. The usual spheres, m = 2, pack most densely in a fcc lattice. Cubes, m = 8, pack in a simple cubic lattice. The cubes with rounded edges pack most densely in a tilted lattice taking advantage of the space at their corners (1). Most interestingly, using depletants of different sizes we can fill the edges and corners of the cubes and change the packing/crystal structure (2,3). The depletants in the flight samples are nanoparticles and the cubes are fluorescently dyed. Our more recent experiments quantitatively show the role of different sized depletants and different shaped particles in the phase diagram of these particles. To date, our experiments have been limited to two dimensions due to the disruptive action of gravity. In other words, the particles tend to sediment because of their density mismatch with the suspending media, precluding three dimensional structures. In microgravity, we hope to observe the formation of 3D crystallites. • Colloidal Swimmers In the previous report, we discussed our fabrication and early experiments with light activated colloidal swimmers propelled by a combination of osmotic and phoretic effects (4). The micron-size particles are driven by the catalytic decomposition of hydrogen peroxide into water and oxygen only when blue light is applied to the system which consists of a polymer sphere with a slightly protruding, photosensitive / catalytic hematite cube inside. We therefore have a dynamical, non-equilibrium, system which is externally controllable. This property was used to demonstrate that we can capture and move other colloidal particles, ‘colloidal dockers’, to desired positions. This special feature should allow for the directed assembly of micro- and nano-scale structures (5). We have also demonstrated that the swimmers can sense and respond to external system variations in a way usually associated only with living creatures. In particular, they can flow upstream mimicking the behavior of, e.g., salmon (6). In the presence of an external flow, when the light is off and the particles are not active, the flow advects the swimmers downstream. In a 4 micron/sec flow, when the light is turned on, the swimmers reverse direction and move upstream. In the faster flow, they direct themselves upstream but at a swimming speed of 8 microns/sec they cannot overcome the downward flow. The upstream motion results from the

Task Progress:	active hematite element being attracted to the surface and acting as a pivot while the flow forces the polymer sphere into a relative downstream position. • DNA Coated Colloids In previous reports we have shown how DNA functionalized colloids can be used to perform self-assembly protocols with specific recognition and association of a particle to many other different particles. We had worked out the thermodynamics of these interactions in detail but the kinetics were largely unknown. In reference (7), we have performed a detailed set of experiments and developed a model which quantitatively accounts for the rate of aggregation of these particles as a function of the DNA sequences, length, areal coverage and salt concentration. These results allow us and others to further design synthetic routes for making complex structures taking into account the different rates at which separate parts will assemble. Even more sophisticated colloidal assembly is enabled by our fabrication, along with the Weck and Seeman groups in NYU chemistry of DNA with cinnamate substituted for a set of complementary base pairs (8). Cinnamate is photocrosslinkable by exposure to UV light. Thus after particles or structures are assembled by the specific binding of complementary strands of DNA, the bonds can be made permanent by shining on UV. The usual assembly of structures with DNA hybridization is reversible upon heating, but now we can choose which links are reversible and which are permanent. • Control of defect structure using optical tweezers Our early NASA flight experiments using poly(methyl methacrylate) (PMMA) hard spheres yielded some extraordinary science from microgravity. Several researchers attempted to modify the system to get it density matched so that experiments could be done on the ground. While the hard sphere density matching did not work, the new systems became a beautiful example of charged spheres with remarkably long range interactions. We have used these systems to study Coulomb crystals and most recently to use them as ideal ways to study and manipulate topological defects such as dislocations. We performed confocal microscope imaging of the bulk system (PMMA colloids in oil) and a layer of PMMA particles which was bound by electrostatic forces to a thin water layer on a cover slip. This 2D system can be readily perturbed by introducing isolated defects using laser tweezers. In reference (9), we published our results on the formation and manipulation of grain boundaries and dislocation pairs, and dislocation reactions in this system. Our results point to many of the fundamental studies that could be done in microgravity with the addition of a laser tweezer setup to the flight confocal microscope. References 1. Y. Jiao, F. H. Stillinger and S. Torquato, Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys., 2009, 79, 041309. R. D. Batten, F. H. Stillinger and S. Torquato, Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys., 2010, 81, 061105. 2. Laura Rossi, Stefano Sacanna, William T. M. Irvine, Paul M. Chaikin, David J. Pine and Albert P. Philipse, Cubic crystals from cubic colloids, Soft Matter, 7, 4139 (2011). 3. Laura Rossi, Vishal Soni, Stefano Sacanna, Paul M. Chaikin, David J. Pine, Albert P. Philipse and William T. M. Irvine, Shape-sensitive crystallization in colloidal superball fluids, submitted. 4. Jeremie Palacci, Stefano Sacanna, Asher Preska Steinberg, David J. Pine, Paul M. Chaikin, Living Crystals of Light-Activated Colloidal Surfers, Science 339, 936–940 (2013). 5. Jeremie Palacci, Stefano Sacanna, Adrian Vatchinsky, Paul M. Chaikin, and David J. Pine, “Photoactivated Colloidal Dockers for Cargo Transportation”, J. Am. Chem. Soc. 135, 15978-15981 (2013). 6. Jeremie Palacci, Anais Abramian, Stefano Sacanna, Jeremie Barral , Kasey Hanson, Alexander Grosberg, David J. Pine, Paul M. Chaikin, Artificial Rheotaxis, to be published. 7. Kun-Ta Wu, Lang Feng, Ruojie Sha, Remi Dreyfus, Alexander Y. Grosberg, Nadrian C. Seeman, and Paul M. Chaikin, “Kinetics of DNA-coated sticky particles”, Physical Review E88, 022304-8 (2013). 8. Lang Feng, Joy Romulus, Ruojie Sha, Marcus Weck, Nadrian Seeman, and Paul Chaikin, “Cinnamate-based DNA photolithography”, Nature Materials, 12 ,747-753, (2013). 9. William T.M. Irvine, Andrew D. Hollingsworth, David G. Grier and Paul M. Chaikin, “Dislocation Reactions, Grain Boundaries and Irreversibility in Two Dimensional Lattices using Topological Tweezers”, PNAS 110,15544-15548 (2013).

Bibliography Type:	Description: (Last Updated: 05/21/2019)
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