Fiscal Year:	FY 2015	**Task Last Updated:**	FY 01/05/2016
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		
Human Research Program Risks:	None		
Space Biology Element:	None		
Space Biology Cross-Element Discipline:	None		
Space Biology Special Category:	None		
PI Email:	chaikin@NYU.edu	**Fax:**	FY 212 995-4016
PI Organization Type:	UNIVERSITY	**Phone:**	212 998-7694
Organization Name:	New York University		
PI Address 1:	Department of Physics		
PI Address 2:			
PI Web Page:			
City:	New York	**State:**	NY
Zip Code:	10003	**Congressional District:**	8
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 Changed email 3/30/2009 (chaikin@princeton.edu no longer valid).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
No. of Post Docs:	3	**No. of PhD Degrees:**	4
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
Contact Email:	brian.j.motil@nasa.gov		
Flight Program:	ISS		
Flight Assignment:			
Key Personnel Changes/Previous PI:			
COI Name (Institution):	Hollingsworth, Andrew (New York University)		
Grant/Contract No.:	NNX13AR67G		
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Performance Goal Text:			
	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.
Task Progress:	The primary goal of our research program is to gain an understanding of the fundamental microscopic mechanisms of self-organization in model complex fluid systems. The experimental samples are composed of specially synthesized colloidal particles with well understood, well controlled, and sophisticated interactions. Our experiments involve the design and assembly of complex three-dimensional structures from these small particles, which are suspended within a fluid medium. Recently introduced colloidal systems feature directional, specific, and externally controlled inter-particle interactions and motility. These so-called “self-assembled colloidal structures,” are vital to the design of advanced optical materials. In the microgravity environment, insight will be provided into the relation between particle shape, crystal symmetry, and structure: a fundamental issue in condensed matter science. Microgravity experiments: Superballs and cubic crystals During the previous grant period, we delivered to NASA, for launch to the ISS on SpaceX CRS-4 (21 September 2014), a series of samples of synthetic colloidal cubes, actually superballs, with different corner roundings. Spheres, with complete rounding, pack most densely in a face centered cubic lattice, whereas cubes pack in a simple cubic lattice. We have shown in previous publications under this grant and in more recent publications that using depletion interaction forces, we can observe these different phases. A 'depletion force' is an effective attractive interaction that arises between colloidal particles suspended in a dilute solution of smaller solutes that are preferentially excluded from the vicinity of the larger particles. Classical depletants are non-adsorbing polymers, but in our flight samples, they were nanoparticles suspended along with the micron-size cubes, which were fluorescently dyed. Ground-based fluorescence microscopy experiments at NYU (New York University) on the flight samples before delivery and subsequently on the same samples at NASA Glenn showed 2D crystallization in the cubic phase as expected. The samples were delivered to ISS and a series of experiments were carried out during several days over a period of months during 4Q 2014 and 1Q–2Q 2015. After astronaut manual homogenization of the samples using an external magnet and an internal stirbar, the samples were inspected with ground-based control using several different magnification objectives and brightfield and fluorescent illumination. Most images of the hollow cubic colloids in microgravity were obtained using a 63x air objective. The resolution was sufficiently clear to observe the hollow cubic particles. Depth scans were taken of several samples, with good quality images for depths of up to 100 microns from the surface. “Movies” were taken by sequentially capturing 30, 40, or 100 images of the same region and depth at fixed intervals. They indicated that particles in the bulk were mobile and diffusive while particles near the surfaces were immobile. Overall the microscope and ground control performed at or above expectations. Unfortunately, the microgravity samples did not show the expected three dimensional cubic crystals that were expected. We are presently studying the microgravity data and performing more ground-based tests to determine why samples from the same batch performed differently in micro-g than in 1g. One immediate difference to be investigated is the presence of dense clumps of the colloidal particles around the stirbar and the fill ports of the space samples. Such aggregation did not occur on similarly prepared samples which remained Earthbound and were studied at the same time as the observations were made on orbit. It is possible that the clustering reduced the concentration of colloids in suspension below that required for crystallization. We will try to mimic the clustering phenomena in future ground-based work. Shape-sensitive crystallization in colloidal superball fluids During this period, we continued our study of superballs to understand the effect of particle shape and the range of interactions in forming different crystal structures. Guiding the self-assembly of materials by controlling the shape of the individual particle constituents is a powerful approach to material design. We have shown that colloidal silica superballs crystallize into canted phases in the presence of depletants. Some of these phases are consistent with the so-called “lambda-1” lattice that was recently predicted as the densest packing of superdisks. As the size of the depletant is

	reduced, however, we observe a transition to a square phase. The differences in these entropically stabilized phases result from an interplay between the size of the depletants and the fine structure of the superball shape. We find qualitative agreement of our experimental results both with a phase diagram computed on the basis of the volume accessible to the depletants and with simulations. By using a mixture of depletants, one of which is thermosensitive, we could induce solid-to-solid phase transitions between square and canted structures. The use of depletant size to leverage fine features of the shape of particles in driving their self-assembly demonstrates a general and powerful mechanism for engineering novel materials. Light activated, self-propelled colloids Light-activated, self-propelled colloids were synthesized and their active motion was studied using optical microscopy. We proposed a versatile route using different photoactive materials, and demonstrate a multi-wavelength activation and propulsion. Thanks to the photoelectrochemical properties of two semiconductor materials (alpha-Fe2O3 and TiO2), a light with an energy higher than the bandgap triggers the reaction of decomposition of hydrogen peroxide and produces a chemical ‘cloud’ around the particle. The effect induces a phoretic attraction with neighboring colloids as well as an osmotic self-propulsion of the particle on the substrate. We use these mechanisms to form colloidal cargoes, as well as self-propelled particles where the light-activated component is embedded into a dielectric sphere. The particles are self-propelled along a direction otherwise randomized by thermal fluctuations, and exhibit a persistent random walk. For sufficient surface density, the particles spontaneously form ‘living crystals,’ which are mobile, break apart, and reform. Steering the particle with an external magnetic field, we show that the formation of the dense phase results from the collisions, "heads-on," of the particles. This effect is intrinsically non-equilibrium and a novel principle of organization for systems without detailed balance. Engineering families of particles self-propelled by different wavelengths demonstrate a good understanding of both the physics and the chemistry behind the system and points to a general route for designing new families of self-propelled particles.
Bibliography Type:	Description: (Last Updated: 05/21/2019)
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Journal/Magazine covers	Wang C, Shpaisman H, Hollingsworth AD, Grier DG. "Cover in journal Soft Matter for journal's 10th anniversary. Article, 'Monitoring colloidal growth with holographic microscopy.' " Soft Matter. 2015 Feb 14;11(6):1062-6. http://dx.doi.org/ , Feb-2015