Fiscal Year:	FY 2017	**Task Last Updated:**	FY 01/16/2018
PI Name:	Chaikin, Paul M. Ph.D.		
Project Title:	The Control and Dynamics of Hard Sphere Colloidal Dispersions		
Division Name:	Physical Sciences		
Program/Discipline:			
Program/Discipline--Element/Subdiscipline:	COMPLEX FLUIDS/SOFT MATTER--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 Changed email 3/30/2009 (chaikin@princeton.edu no longer valid).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 / Funding Source:**	98-HEDS-03
Start Date:	09/06/2013	**End Date:**	09/05/2019
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:	McQuillen, John	**Contact Phone:**	216-433-2876
Contact Email:	john.b.mcquillen@nasa.gov		
Flight Program:	ISS		
Flight Assignment:	NOTE: End date changed to 9/5/2019 per NSSC information (Ed., 10/2/19)		
Key Personnel Changes/Previous PI:			
COI Name (Institution):	Hollingsworth, Andrew Ph.D. (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 led 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		

Task Description:	specific, reversible or irreversible, variable range interactions. We have also found new ways to manipulate the particles 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:	Charged Particles Near an Oil-Water Interface We have continued our studies of charged colloidal particles held by image charge forces to fluid interfaces. In flat space we looked at the two dimensional glass transition. It had been theoretically (computationally) predicted that 2D glasses had a different diffusive behavior than 3D glasses. It is well known that freezing in 3D is a single first order transition while in 2D it is two second order transitions. Phase transitions significantly differ between 2D and 3D systems, but the influence of dimensionality on the glass transition is unresolved. We used microscopy to study colloidal systems as they approached their glass transitions at high concentrations and found differences between two dimensions and three dimensions. We found that, in two dimensions, particles can undergo large displacements without changing their position relative to their neighbors, in contrast with three dimensions. This is related to Mermin–Wagner long-wavelength fluctuations that influence phase transitions in two dimensions. However, when measuring particle motion only relative to their neighbors, two dimensions and three dimensions have similar behavior as the glass transition is approached, showing that the long-wavelength fluctuations do not cause a fundamental distinction between 2D and 3D glass transitions. This work resolved the controversy created by the simulations. Microrollers: Magnetically-driven Magnetic Colloids Our previously reported work on colloidal swimmers involved particles specially prepared by Prof. Stefano Sacanna. These are 3-(trimethoxysilyl)propyl methacrylate (TPM) polymer particles with an imbedded magnetic hematite cube. We found that driving these particles with a rotating magnetic field produced an entirely new set of phenomena. When rotated near a wall the particles “rolled” and produced very large fluid flows which advected nearby particles and led to strong hydrodynamic interactions and new collective effects. These include the formation of a shock front, the instability of the front, a new type of fingering instability and finally the creation of self-sustaining “critters” — clusters that broke off from the fingers and self propelled. One of the remarkable features of these critters is that they form from hydrodynamic interactions alone with no potential interactions. These microrollers and critters may lead to new ways to control microfluidic flows. Freezing in Two Dimensions We are also interested in how the 2D melting transition is frustrated by the effects of Gaussian curvature and the topological defects that it requires. As a warm-up, we studied the flat space crystallization. We found that even in a small system of charged dipoles residing at a fluid-fluid interface we could reproduce the effects previous seen in magnet dipole systems. We studied the phase behavior of a system of charged colloidal particles that are electrostatically bound to an almost flat interface between two fluids. We showed that, despite the fact that our experimental system consists of only 103–104 particles, the phase behavior is consistent with the theory of melting due to Kosterlitz, Thouless, Halperin, Nelson, and Young. Using spatial and temporal correlations of the bond-orientational order parameter, we classified our samples into solid, isotropic fluid, and hexatic phases. We demonstrated that the topological defect structure we observe in each phase corresponds to the predictions of KTHNY theory. By measuring the dynamic Lindemann parameter, and the non-Gaussian parameter of the particle displacements relative to their neighbors, we showed that each of the phases displays distinctive dynamical behavior. Freezing on a sphere: In studies recently submitted to the journal Nature, we have seen crystallization on a spherical interface despite the topological frustration. The mechanism involves the sequestration of the defects to the vertices of an icosahedron. We can see this by locating the defects on the confocal image of the colloids bound to the surface of a water droplet in oil, fitting an icosahedron to the defects positions, projecting the particle positions onto the triangular

	faces and then unfolding the icosahedron. This approach leads to some intuition on why viruses often form in an icosahedral shape. Synthesis of Monodisperse, Micron-sized Organosilica Spheres Colloidal particles of controlled size are promising building blocks for the self-assembly of functional materials. We systematically studied a method to synthesize monodisperse, micrometer-sized spheres from 3-(trimethoxysilyl)propyl methacrylate (TPM) in a benchtop experiment. Their ease of preparation, smoothness, and physical properties provide distinct advantages over other widely employed materials such as silica, polystyrene, and poly(methyl methacrylate). We determined that the spontaneous emulsification of TPM droplets in water is caused by base-catalyzed hydrolysis, self-condensation, and the deprotonation of TPM. By studying the time-dependent size evolution, we found that the droplet size increases without any detectable secondary nucleation. Resulting TPM droplets are polymerized to form solid particles. The particle diameter can be controlled in the range of 0.4 to 2.8 µm by adjusting the volume fraction of added monomer and the pH of the solution. Droplets can be grown to diameters of up to 4 µm by adding TPM monomer after the initial emulsification. Additionally, we characterized various physical parameters of the TPM particles, and we described methods to incorporate several fluorescent dyes.
Bibliography Type:	Description: (Last Updated: 06/21/2021)
Articles in Peer-reviewed Journals	Vivek S, Kelleher CP, Chaikin PM, Weeks ER. "Long-wavelength fluctuations and the glass transition in two dimensions and three dimensions." Proc Natl Acad Sci US A. 2017 Feb 21;114(8):1850-5. https://doi.org/10.1073/pnas.1607226113 ; PubMed PMID: 28137847; PubMed Central PMCID: PMC5338427 , Feb-2017
Articles in Peer-reviewed Journals	Driscoll M, Delmotte B, Youssef M, Sacanna S, Donev A, Chaikin PM. "Unstable fronts and motile structures formed by microrollers." Nature Physics. 2017 Apr;13(4):375–9. https://doi.org/10.1038/nphys3970 , Apr-2017
Articles in Peer-reviewed Journals	Kelleher CP, Guerra RE, Hollingsworth AD, Chaikin PM. "Phase behavior of charged colloids at a fluid interface." Phys Rev E. 2017 Feb;95(2-1):022602. https://doi.org/10.1103/PhysRevE.95.022602 ; PubMed PMID: 28297978 , Feb-2017
Articles in Peer-reviewed Journals	van der Wel C, Bhan RK, Verweij RW, Frijters HC, Gong Z, Hollingsworth AD, Sacanna S, Kraft DJ. "Preparation of colloidal organosilica spheres through spontaneous emulsification." Langmuir. 2017 Aug 22;33(33):8174-8180. https://doi.org/10.1021/acs.langmuir.7b01398 ; PubMed PMID: 28731356; PubMed Central PMCID: PMC5569361 , Aug-2017