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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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Space Biology Special Category:	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 Changed email 3/30/2009 (chaikin@princeton.edu no longer valid).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
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
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Flight Program:	ISS		
Flight Assignment:			
Key Personnel Changes/Previous PI:			
COI Name (Institution):	Hollingsworth, Andrew (New York University)		
Grant/Contract No.:	NNX13AR67G		
Performance Goal No.:			
Performance Goal Text:	<p>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.</p> <p>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</p>		

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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.

DNA coated colloids

We have previously reported how DNA-functionalized colloids can be used to perform self-assembly protocols with specific particle-particle recognition and association. In our experiments, micron and sub-micron scale particles are designed to recognize and selectively interact with each other by DNA-sequence encoded coatings. Using cinnamate functionalization in the DNA fabrication, even more sophisticated colloidal assembly has been realized. This is achieved by a UV-light initiated crosslinking step. After particles or structures are assembled by the specific binding of complementary strands of DNA, certain bonds are made permanent by shining on UV, allowing flexibility in design and construction.

During this research period, two US patents were assigned to New York University (Chaikin, et al.; Lang and Chaikin) regarding "Self-replicating materials" and "DNA photolithography with cinnamate crosslinkers." Success in creating a self-replicating system with polystyrene colloid can be translated to a wide range of materials such as metals and ceramics, semiconductors and plastics. Such composite, microscopically-designed materials should find wide application as sensors, solar cells, battery and fuel cell components, as well as new materials for personal products and pharmaceuticals.

The upcoming Advanced Colloid Experiment (ACE)-T and ACE-E experiments will involve DNA-coated colloidal spheres, patchy particles, and emulsion droplets, which will be manipulated by applied electric fields and thermal gradients to produce 3D micron scale structures. Confocal microscopy is key to the observation and tracking of the constituent particles in real time and real space.

Colloidal Swimmers

During this period, we continued our study of light-activated colloidal "swimmers" propelled by a combination of osmotic and phoretic effects. Motility is a basic feature of living microorganisms, and how it works is often determined by environmental cues. Recent efforts have focused on developing artificial systems that can mimic microorganisms, in particular their self-propulsion. We have reported on the design and characterization of synthetic self-propelled particles that migrate upstream, known as positive rheotaxis. This phenomenon results from a purely physical mechanism involving the interplay between the polarity of the particles and their alignment by a viscous torque. We show quantitative agreement between experimental data and a simple model of an overdamped Brownian pendulum. The model notably predicts the existence of a stagnation point in a diverging flow. Taking advantage of this property, we demonstrated that our active particles can sense and predictably organize in an imposed flow. Our colloidal system represents an important step toward the realization of biomimetic microsystems with the ability to sense and respond to environmental changes.

Colloidal interactions in low polar fluids

We performed high-resolution measurements of the pair interactions between dielectric spheres (PMMA colloid) dispersed in a fluid medium with a low dielectric constant. Despite the absence of charge control agents or added organic salts, these measurements revealed strong and long-ranged repulsions consistent with substantial charges on the particles whose interactions are screened by trace concentrations of mobile ions in solution. The dependence of the estimated charge on the particles' radii is consistent with charge renormalization theory and, thus, offers insights into the charging mechanism in this interesting class of model systems. The measurement technique, based on optical-tweezer manipulation and artifact-free particle tracking, makes use of optimal statistical methods to reduce measurement errors to the femtonewton frontier while covering an extremely wide range of interaction energies.

Charged colloids at an oil-water interface

Our poly(methyl methacrylate) (PMMA) colloidal particles have nonionogenic surfaces that are sterically stabilized with poly(12-hydroxystearic acid) (PHS). These spheres can be rendered nearly neutrally buoyant through the addition of

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density-matching cosolvents such as tetrachloroethylene (TCE) without affecting their long-ranged interactions, although TCE is a good solvent for PMMA. When dispersed in cyclohexyl bromide (CHB), however, these particles can display extremely long-ranged repulsions that are strong enough to stabilize colloidal crystals at volume fractions below 0.001. These repulsions arise from positive surface charges that are believed to be built up by association of positively charged species in solution with the particles' surfaces, or with the PHS layer covering the surfaces, or both. These positive species, in turn, are believed to arise from hydrolysis of CHB leading to dehydrobromination. The resulting hydrogen bromide then dissociates slightly in the moderately polar oil to produce protons that contribute to the spheres' charges and Br⁻ ions that remain in solution.

In the presence of an interface with a conducting aqueous phase, image-charge effects lead to strong binding of the hydrophobic colloidal particles to the interface, even though the particles are wetted very little by the aqueous phase. We studied both the behavior of individual colloidal particles as they approach the interface and the interactions between particles that are already interfacially bound. We demonstrated that using particles which are minimally wetted by the aqueous phase allows us to isolate and study those interactions which are due solely to charging of the particle surface in oil. Finally, we showed that these interactions can be understood by a simple image-charge model in which the particle charge q is the sole fitting parameter.

ACE-E Science Concept Review (SCR) October 19–20, 2015 NASA Glenn Research Center (GRC). PM Chaikin attended and presented the New York University (NYU) SCR.

ACE particle development

Throughout and into the next reporting period, AD Hollingsworth (NYU Colloid Synthesis Facility) is preparing colloid samples for LMM (Light Microscopy Module) confocal microscope performance testing. We synthesized a cyanine-based reactive dye (Cy3-MMA), which will be incorporated into PMMA spheres, in addition to the traditional rhodamine fluorophore.

Bibliography Type:	Description: (Last Updated: 05/21/2019)
Articles in Peer-reviewed Journals	Palacci J, Sacanna S, Abramian A, Barral J, Hanson K, Grosberg AY, Pine DJ, Chaikin PM. "Artificial rheotaxis." <i>Science Advances</i> . 2015 May 1;1(4):e1400214. eCollection 2015 May. http://dx.doi.org/ ; PubMed PMID: 26601175 ; PubMed Central PMCID: PMC4640647 , May-2015
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