Topical: Synthetic electrokinetically active colloids: a facile and versatile platform for microgravity investigations of collective behavior and interactions

Primary Author: Jarrod Schiffbauer, (304) 435-2525, Colorado Mesa University, jschiffbauer@coloradomesa.edu

Co-authors:
Alicia Boymelgreen, Florida International University
Sam Lohse, Central Washington University
Boris Khusid, New Jersey Institute of Technology

Introduction: In the past decade, the field of soft matter has grown exponentially as researchers focus on both biological and synthetic platforms as well as their intersection. The potential applications of soft matter are vast – from fundamental studies of non-equilibrium thermodynamics, including the basic principles of life, to the next generation of intelligent, environmentally responsive and/or self-repairing bio-inspired materials, active metamaterials, targeted drug delivery, theranostics, and environmental remediation. Any one of these markets represents trillions of dollars in revenue but maximizing the US edge in this emerging market will involve a multi-prong approach including international scientific collaboration while maintaining and increasing US technological competitiveness through the development of a skilled and diverse workforce. ***The development of a soft matter research program in space can be used to achieve both these goals by enabling scientific discovery that cannot be achieved terrestrially while providing a platform for a robust, domestic pipeline that channels underserved and underrepresented populations into STEAM fields and maximizes retention by supporting their development and providing a well-defined career path to research and industry.*** Specifically, the highly interdisciplinary nature of research in soft matter offers an opportunity to simultaneously attract and motivate a broad array of future scientists–physicists, chemists, biologists, materials scientists, mechanical and chemical engineers, and computer scientists—to develop the interactions which drive convergent research between disciplines. Here, we outline a proposed scientific research program that is uniquely enabled through long term microgravity conditions on the ISS, the broader aim of using this science to develop a domestic technology pipeline to maintain the US edge in this next generation research, its application, and commercialization. ***We believe such an integrated program will be crucial for the US to maintain a position of global scientific, technological, and economic leadership through the 21st century.***

Research Program: The umbrella of soft matter encompasses both synthetic[1–3] and biological systems[4]. The subset of active matter refers to non-equilibrium systems where energy is drawn from surroundings and converted to mechanical energy[5]. Among the vast array of synthetic active colloids, there exists a natural divide between those systems which are externally forced (moving under applied electric[6] or magnetic fields) and those where propulsion is obtained by interaction between the particle and suspended fluid – including catalytic reactions and self-electrophoresis[7]. However, ***in almost all terrestrial experiments, gravitational forces play an important role,*** conspiring to maintain colloids adjacent to the substrate so that the resulting motion is essentially 2D and can be significantly affected by particle-wall interactions which modulate the mobility of individual colloids through effects such as hydrodynamic and electrostatic attraction which in turn affect collective motion and phase separation**.** ***Key questions emerge from this gravitational constraint*** regarding how the particle-wall interaction affects observed collective phenomena such as clustering, mobile defects, motility induced phase separation (MIPS)[3,8,9], existence of effective temperature and apparent time-reversal symmetry (TRS)[8] and the translation to 3D under microgravity conditions[9]. Furthermore, how do these phenomena become modified in the presence of passive entities of varying surface properties, size, and shape? Looking beyond fundamentals to application, we question whether the inclusion of functionalization, including target-probe

DNA, or responsive biomolecules (proteins, enzymes,) be utilized in creating new active/responsive materials, e.g., nanofluids with variable rheologic properties.

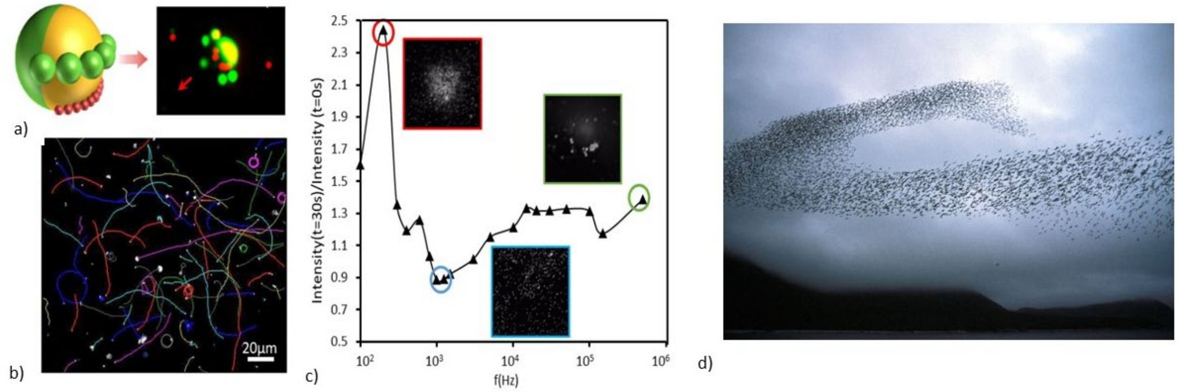

Figure 1a) dynamic self assembly of a complex active colloid b)independent pathlines of non-interacting active Janus particles driven by an electric field c)Plot of velocity of active Janus particle as a function of frequency d) Example of collective motion in nature among flocks of birds

To answer these questions, here we propose developing a series of experiments and simulations which focus on synthetic, electrically driven active colloids and mixtures of active-passive colloidal systems. ***Due to their versatility and external programmability, these systems permit a broad range of effects to be discovered on a versatile experimental platform. This capability is critical when considering the expense of adapting experiments to space conditions, sending them to the ISS and executing them there.*** It is now well established that direction and speed can be controlled by the magnitude and frequency of the externally applied electric field[6] which also alter the states of collective motion[2]. Additionally, replacing DI water with electrolytes[2] or surface functionalization can be used to increase observed behavioral modes. Active and passive colloids of different density can be combined in microgravity, and magnetic materials/cores may be employed as well, all free from sedimentation/buoyancy effects. These permit additional fields to be imposed, providing more avenues for manipulation of the system. Experiments are to be complemented by theoretical and numerical studies, used both in predictive down-selection of experimental design as well as an aid in understanding experimental results.

Key fundamental research questions: Electrokinetically driven active colloids and hybrid active-passive mixtures with tunable interactions permit the investigation of several important research questions concerning non equilibrium systems, active matter, confinement, and the role of various forces. The understanding gained from studying the EK system can be generalized to other active matter platforms. Five categories of research question emerge which are readily addressed with electrically driven colloids:

1) How do phenomena like MIPS and other active phase-segregation/aggregation behave in 2D “confined” systems vs. 3D “unconfined” systems? Do wall effects/confinement affect the stability of these systems?

2) What are the limitations of TRS and effective equilibrium theories? Are there viable non-equilibrium thermodynamic phase-field theories (with appropriate energy and entropy densities) which describe the dynamics of these systems? Can one pass between these theories in some limit?

3) What happens when there are (at least) two kinds of passive bath particles; big, slow ones, and fast, little ones? What about responsive macromolecules (proteins)?

4) What kinds of structures form in active-passive systems? The terrestrial 2D vs.microgravity 3D pictures should be very different; one might anticipate both ordered and disordered phases, and that the 3D stability of any such structures may be more precarious.

5) Can the various and subtle surface-particle and particle-particle interactions be disentangled experimentally in microgravity? For example, how important a role do Casimir effects play[10]in particle-wall or particle-particle interactions?

Approach: Three basic experimental approaches are proposed to provide additional flexibility and control: (1) Using mixed active and passive systems with differing radii (2) Employing steady biased fields in addition to the active AC driving field (and/or magnetic fields.) (3) Including biomolecular components to enable specific binding and responsive properties. These approaches may offer interesting insights into TRS and effective equilibrium, as well as leading to some novel and as-yet unimagined applications. The fact that sedimentation will still affect the NPs, but on a much slower timescale than the JPs is itself interesting and relevant to the questions about effective equilibrium temperatures and TRS. Understanding the behavior of systems composed of these basic building blocks of active, passive, and responsive elements is expected to help pave the way to for the development of tunable/active materials, programmable materials, or even materials that can compute.

Accompanying theoretical/numerical studies will employ a combination of multiparticle dissipative particle dynamics (DPD) simulations[11,12], continuum hydrodynamics approaches (including both non-equilibrium and effective equilibrium), and machine learning methods[13,14]. Multiparticle DPD is a well-developed technique which can be used both to directly model the system, to provide parameters for mesoscale hydrodynamics models[15]and to further develop phase-field or other hydrodynamics models[15–17]. The models can be used in conjunction fruitfully with experiments. Additionally, machine learning (ML) methods have been employed both to analyze data and obtain model-free predictions[13]. Coupling these approaches is an important step in developing robust, hybrid approaches which incorporate physics-based models into ML, which will lessen the 'reality gap' between ML predictive simulation and experiments.

Applications: The fundamental knowledge has direct translation into a variety of potential applications such as active fluids with tunable properties, self- and directed- assembly/active metamaterials, drug/molecule delivery, or even active materials repair. By including specific binding functionality (e.g., target-probe DNA or antibody-antigen proteins) one can envision active probe-functionalized Janus micro-carriers which can search out, retrieve, and transport smaller cargo NP that is target-functionalized, or mobile components which can be transported to a region and prompted (by environmental/external cues) to assemble into some pre-programmed structure.

STEAM pipeline: The proposed soft matter research offers a unique opportunity to foster the domestic pipeline for several reasons. Strong interdisciplinarity carries a broad appeal and can motivate a wider range of scientific interest. Space science is popular and exciting across socio-cultural and political boundaries in the US. This is evidenced by the number of NASA logos and t-shirts which can be observed on public college campuses and at high schools across the US. Because of the broad and cooperative nature of space research, through implementation partners, flight providers, and eventually even commercial LEO platforms, this research program provides a natural mechanism for academia-industry-government partnership that serves to both innovate and educate—moreover, one which emphasizes the critical connection between innovation and education.

Concerning strengthening the participation of underserved and underrepresented groups, before reaching the "leaky pipeline," we must first funnel non-traditional students into STEAM. This involves outreach to local high schools along with early recruitment and consistent mentorship in undergraduate research and beyond. These efforts can begin with hands-on activities, school visits to university facilities or space agencies, etc. as high school students, and continue through undergraduate research, industry, or other REU/summer internships. The program would include networking assistance, the creation of a domestic undergraduate-to-graduate pipeline, and 360 mentorship programs to help develop career trajectory. The breadth of such an effort will make it necessary to collaborate with social scientists, educators, industry leaders, and government agencies.

Critical infrastructure:

Research Program: In the past 10 years, the Light Microscopy Module was used to execute an immensely successful research program on passive colloids which revealed new insight on crystal structure[18] towards the manufacture of precise nanostructured materials and interactions of foams and emulsions[19]– notably supported previously by companies such as Proctor and Gamble.

To achieve the goals of the next generation of soft matter research into active, non- equilibrium systems will require significantly improved visualization and characterization capabilities – higher resolution in time and space, multi-dimensional visualization and integrated external control systems to probe and drive the active colloids. As has been the legacy of the space program since its inception, it is anticipated that the development of this infrastructure will also advance terrestrial research capabilities. The ideal visualization system would offer 3D imaging with micro to nanometer scale resolution using technologies including the spinning disc confocal and TIRF for sub nanometer resolution. To probe the system and manipulate individual colloids, auxiliary systems including optical tweezer arrays and AFM would enable research into a wide variety of effects including the influence of particle-wall interactions and surface functionalization that inform both the fundamental physical understanding and optimization towards terrestrial application.

Finally, to fully exploit the rich array of active mobilities and interactions, the capability of external forcing modes should be accessible. Previously, the LMM was able to accommodate uniform thermal heating. Here, we are looking to extend this capability to including AC and DC electric fields, rotating electric and magnetic fields and acoustic forcing.

In the interest of reducing crew time, a focus should be placed as well on the integration of automated control systems and data interpretation. Here again, there is a distinct and novel role for ML[13]. This certainly would enhance terrestrial capabilities by increasing efficiency and output and maximizing human and material resources. This combined setup will represent the next generation of research platform for terrestrial research as well.

Domestic Pipeline: There is broad inter-agency support for inter university programs such as the one being described herein. These programs provide as an invaluable service the recruitment, retention, training, and placement/networking assistance to establish domestic pipelines for highly skilled workers in what will undoubtedly be transformative in terms of both fundamental science and technological application in the coming century. Because of the nature of microgravity science, there will be numerous opportunities for internships and mentorship with industry providers as well as academic advisers. Moreover, a formalized domestic STEAM pipelines as part of a concerted research effort can facilitate the convergence of disciplines beyond STEAM; scientists can work with social scientists to develop broad programs to meet the needs of students

Necessity of LEO/microgravity: The ISS and its commercial successors offer a unique long-term microgravity environment that is critical for the many of the proposed experiments. The formation of 3D non-equilibrium structures and the comprehensive study of approach to possible non-equilibrium steady states require long times in microgravity. Where possible, or for developmental experiments, terrestrial zero-g simulations and/or suborbital flights will be utilized. Additionally, the excitement of space research and the potential to collaborate with both national labs – towards a research career – or industry through partners, such as SpaceX, Blue Origin, Axiom, Space Tango, and a growing list of others, provides multiple opportunities for the development of the STEAM pipeline.

Conclusions: A broad and comprehensive research and training program has been proposed which builds upon the critical issues of the Grand Challenges in Soft Matter. The program not only addresses key scientific and technical issues but aims to fortify national economic security by building a dedicated STEAM pipeline to recruit, train, and retain scientists and engineers. We again emphasize the comparison between of terrestrial systems, confined to quasi-2D motion and fully 3D systems, which are only possible in microgravity. Thus, LEO access is a critical component of such a program.

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