Cover Page

<u>Topical White Paper</u> submitted to the Biological and Physical Sciences in Space Decadal Survey 2023-2032

MICRO/NANOMACHINES AND SOFT ACTIVE MATTER IN ZERO-GRAVITY: THE NEXT DECADE AND BEYOND IN-SPACE SMALL MACHINES, ROBOTS AND SOFT ACTIVE MATTER RESEARCH

Submitted by Donglei Emma Fan

Department of Mechanical Engineering, The University of Texas at Austin, Austin, TX, USA, email: dfan@austin.utexas.edu

Co-Authors:

Donglei Emma Fan

Department of Mechanical Engineering, The University of Texas at Austin, Austin, TX, USA

Peer Fischer

Max Planck Institute for Intelligent Systems; and Institute of Physical Chemistry, University of Stuttgart, Stuttgart, Germany

Alfred Crosby

Department of Polymer Science and Engineering, University of Massachusetts Amherst, MA, USA

Ayusman Sen

Departments of Chemistry & Chemical Engineering, Pennsylvania State University, University Park, PA, USA

Anna C Balazs

Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA, USA

Suman Sinha-Ray

Deputy Lead Discipline Scientist, University Space Research Association, NASA GRC, Cleveland, USA

Background and Challenges

The development of new forms of synthetic micro/nanomachines has moved closer to reality as witnessed by some remarkable progress in a field known as active matter. Current research activities in many labs around the world covering different disciplines are addressing the design, fabrication, and manipulation of individual active units as well as swarms of micro/nanoscale particles, machines, and robots.^{1,2}

One focus of the research in active matter is to understand and apply propulsion mechanisms in solution in designing versatile and efficient artificial micro/nanomotors that mimic their biological counterparts.¹ Significant advances have been made in synthetic and biohybrid micro/nanomotors that are either powered by chemical reactions³ or that are driven by external magnetic, electric, acoustic, osmotic, or optical fields.^{4–6} However, in several model systems it remains challenging to unravel the underlying mechanisms that govern the propulsion behaviors of either individual machines or their multi-body interactions. Often a number of effects are at play at once. It is therefore of fundamental interest to simplify the experimental conditions to fully understand the underlying propulsion principles and the interactions in both isolated and in swarms of micro/nanomachines.

Beyond propulsion, active matter offers significant promise in developing adaptable materials, which can dynamically change shape, morphology, and properties to meet new demands. For example, a material may be capable of 'draping' in one state to conform to complex geometries, and be 'rigid' or 'fixed' in a different state in order to provide conformal protection or stability. While such concepts can be applied to all materials in principle, particularly interesting results have been presented for soft materials. Here, surface interactions, based on electrostatic, van der Waals, or chemistry-specific forces, and elastic restoring forces can be designed to have similar strengths, thus enabling new structure and property modification routes that do not require pre-designed micro/nanostructures or the application of excessively large driving forces. While these mechanisms are promising and preliminary demonstrations are encouraging, they have mainly focused on smaller size scale systems due to the introduction of additional constraints in larger systems. 13,14

A major obstacle in the aforementioned studies are gravitational effects that invariably play a role in terrestrial experiments. The multi-unit active matter systems, sedimentation of individual units can affect electrostatic interactions, mechanical forces, local surface flows, and complex ionic distributions, which in turn often can conceal the intrinsic propulsion and interaction mechanism of the micro/nanomachines. Because of sedimentation, there are very few studies of active matter in a 3D environment away from walls, which would be possible in low gravity environments. The gravitational field also makes it extremely challenging to realize isotropic suspensions. In particular the assembly of micro/nanomachines (active building blocks) would greatly benefit from zero gravity conditions. Sedimentation after the intrinsic propulsion and interaction mechanism of the micro/nanomachines (active building blocks) would greatly benefit from zero gravity conditions.

Gravitational effects are especially important in soft, active matter systems, such as those used in new adaptive materials concepts. In these systems, gravity is known to

play a significant role in limiting the size of the materials components because of settling and wall interactions. However, the full impact of gravitational effects has not been studied, and thus there may be many unknown factors that need to be considered. Eliminating walls, sedimentation, and density effects are therefore expected to permit for the first time experiments that are essential for a fundamental understanding and at the same time allow emergent behaviors of several artificial and biological active matter systems to be observed across a larger range of size scales. ^{22–27}

New Opportunities Endowed by Zero (or Micro-) Gravity Conditions:

The following research questions are expected to benefit from zero (or micro-) gravity conditions:

1. <u>Unraveling the propulsion mechanisms of synthetic active matter systems:</u> Minimizing the interactions between micro/nanomachines and substrates (walls) will help in the understanding of complex propulsion mechanisms. Eliminating or reducing the influence of gravity will be of interest in all types of active propulsion systems, including those that utilize physical fields or those that are based on chemical reactions. For instance, when manipulating micro/nanoparticles with electric fields, surface charges can easily alter the motion direction due to local electroosmotic flows, which conceal the actual forces and torques exerted on the micro/nanomachine.²⁸ Rotating a magnetic motor near a substrate can give rise to rolling and walking and thus complicate matters as the surface causes symmetry breaking, something which is of importance in low Reynolds number fluid environments.²⁹ The problem is even more complex for catalytic micro/nanomotors, where ion flows are substantially altered near a surface, which in turn causes changes in speed and even the orientation of a Janus swimmer near a substrate.^{30,31}

Catalytic reactions can also pump fluid flows.³² Eliminating the influence of gravity reduces the density effects and thus the density-driven generation of gradients in the chemical species and ions.³³ Both density and phoretic forces play a role, but in zero-gravity one could easily distinguish these processes. Since the active motors won't sediment it also eliminates the introduction of torques that arise because of altered fluid flows near a substrate.^{34,35}

The examples above highlight only a few effects that complicate the study of micro/nanomachines on Earth. Zero-gravity conditions will eliminate many of these complications and offer valuable control settings and provide new insights in active-matter research. New propulsion principles that have been masked by surface interactions due to sedimentation could be revealed.

2. <u>Interactions and 3D assembly of matter (under non-equilibrium conditions):</u> The assembly of active matter in a regime far from thermodynamic equilibrium is of importance as nearly all assembly processes in living systems also arise under non-equilibrium conditions, *i.e.*, enabled by chemical reactions, enzymes, or cellular processes.^{36–38} Since artificial micro and nanomotors are

typically much larger than their biomolecular counterparts, they are affected by gravity. Maintaining an active system that is uniformly distributed in a volume for long periods of time is nearly impossible in a gravitational field. Since the assembly of active matter in 3D is dynamic and evolves with time, one would constantly need to adjust the conditions to maintain the suspension. Obtaining more sophisticated structures is likely to require longer times, which further complicates studies of self-assembling systems. Experiments in space eliminates the influence of gravity and hence buoyancy effects in active suspensions of micro/nanomotors: Zero-gravity conditions that last for longer times would permit an in-depth study of non-equilibrium interactions and assembly processes.

Wall-effects can drive assembly through both density driven and phoretic flows. Experiments under zero-gravity conditions can easily distinguish between the two and lead to new understanding of forces that drive self-assembly under non-equilibrium conditions.

- 3. Reconfigurable rheology of soft matter: The zero-gravity condition also provides a simple, clean system for shedding light on the basic physics of (reconfigurable) rheological systems enabled by active matter. Recently, it was demonstrated that high-density light-driven chemical motors dispersed in bulk suspension could exhibit as high as 10-fold enhancement of viscous coefficient that can be reversibly switched by controlling light conditions. Controlling rheology of fluids "on the fly" has important technological implications. In order to prepare active material systems for bulk rheological measurements, stable dispersions are needed. This is difficult to realize under gravity.
- 4. Surface driven soft adaptable materials: Surface interactions between neighboring components or with a surrounding environment can be used to control the shape and assembly of soft materials systems, where the elastic restoring forces can be small. However, gravitational forces often limit the size scales where can be utilized. Demonstrating surface-driven these concepts transformations and associated assemblies in zero-gravity conditions will lead to new understanding of how complex structures can be created autonomously using programmed surface-elastic interactions within single components or between multiple components.^{8,10} Additionally, many material systems, such as filamentous assemblies like rope and textiles, have properties that are greatly impacted by their own weight due to the enhanced inter-filament frictional forces in gravitational fields.⁷ Fundamental understanding of properties of soft, filamentous based materials systems in zero-gravity conditions will create new pathways for taking advantage of controlled inter-filament interactions for property and shape transformations. 11,15,39-41 This understanding may also provide insight into changes of mechanical properties of biological tissues, which are often composed of filamentous assemblies.

Research Approach

Overall, the proposed research that can benefit from studies in zero-gravity conditions requires extensive experimentation. However, space stations can only offer limited resources and research time. Therefore, a more efficient, realistic, and economical approach could start with studies in drop-towers with customized sensing and imaging capabilities at variable gravity before progressing to free flyer and low-earth orbital (LEO) facilities.⁴²

Summary:

In summary, the study of active matter in space will provide many opportunities to add new knowledge to the fundamental science of both artificial and biological active matter, including isolated swimmers, swarms, and adaptive soft materials. Effects of surfaces and density can be eliminated and thus the governing mechanisms underlying propulsion in active systems can be revealed. In addition, bulk suspensions with long-term stability could be realized that would for the first time offer the opportunity to realize the experimental conditions required to study non-equilibrium assembly processes. We expect that zero-gravity will enable new effects, phenomena, materials, and behaviors of active systems to be discovered. This will substantially advance our understanding of active matter.

References:

- 1. Palagi, S. & Fischer, P. Bioinspired microrobots. *Nat. Rev. Mater.* **3,** 113–124 (2018). DOI: 10.1038/s41578-018-0016-9
- 2. Joh, H. & Fan, D. Materials and Schemes of Multimodal Reconfigurable Micro/Nanomachines and Robots: Review and Perspective. *Adv. Mater.* **2101965**, 1–17 (2021). DOI: 10.1002/adma.202101965
- 3. Balazs, A. C., Fischer, P. & Sen, A. Intelligent Nano/Micromotors: Using Free Energy to Fabricate Organized Systems Driven Far from Equilibrium. *Acc. Chem. Res.* **51**, 2979 (2018). DOI: 10.1021/acs.accounts.8b00511
- 4. Kim, K., Guo, J., Xu, X. & Fan, D. Recent Progress on Man-Made Inorganic Nanomachines. *Small* **11**, 4037–4057 (2015). DOI: 10.1002/smll.201500407
- 5. Kim, Y., van den Berg, J. & Crosby, A. J. Autonomous snapping and jumping polymer gels. *Nat. Mater.* (2021). DOI: 10.1038/s41563-020-00909-w
- 6. Li, J., Rozen, I. & Wang, J. Rocket Science at the Nanoscale. *ACS Nano* **10**, 6, 5619–5634 (2016). DOI: 10.1021/acsnano.6b02518
- 7. Cerda, E., Mahadevan, L. & Pasini, J. M. The elements of draping. *Proc. Natl. Acad. Sci. U. S. A.* **101**, 1806–10 (2004). DOI: 10.1073/pnas.0307160101
- 8. Barber, D. M., Crosby, A. J. & Emrick, T. Mesoscale Block Copolymers. *Adv. Mater.* **30**, 2–7 (2018). DOI: 10.1002/adma.201706118
- 9. de Pablo, J. J., Jackson, N. E., Webb, M. A., Chen, L. Q., Moore, J. E., Morgan, D., Jacobs, R., Pollock, T., Schlom, D. G., Toberer, E. S., Analytis, J., Dabo, I., DeLongchamp, D. M., Fiete, G. A., Grason, G. M., Hautier, G., Mo, Y., Rajan, K., Reed, E. J., Rodriguez, E., Stevanovic, V., Suntivich, J., Thornton, K. & Zhao, J. C. New frontiers for the materials genome initiative. *npj Comput. Mater.* **5**, (2019). DOI: 10.1038/s41524-019-0173-4
- 10. Barber, D. M., Yang, Z., Prévost, L., du Roure, O., Lindner, A., Emrick, T. & Crosby, A. J. Programmed Wrapping and Assembly of Droplets with Mesoscale Polymers. *Adv. Funct. Mater.* **30**, 1–9 (2020). DOI: 10.1002/adfm.202002704
- 11. Pham, J. T., Lawrence, J., Lee, D. Y., Grason, G. M., Emrick, T. & Crosby, A. J. Highly stretchable nanoparticle helices through geometric asymmetry and surface forces. *Adv. Mater.* **25**, 6703–8 (2013). DOI: 10.1002/adma.201302817
- 12. Lee, D. Y., Pham, J. T., Lawrence, J., Lee, C. H., Parkos, C., Emrick, T. & Crosby, A. J. Macroscopic nanoparticle ribbons and fabrics. *Adv. Mater.* **25**, 1248–53 (2013). DOI: 10.1002/adma.201203719
- Mora, S., Maurini, C., Phou, T., Fromental, J.-M., Audoly, B. & Pomeau, Y. Solid Drops: Large Capillary Deformations of Immersed Elastic Rods. *Phys. Rev. Lett.* 111, 114301 (2013). DOI: 10.1103/PhysRevLett.111.114301
- 14. Jeon, S. J., Hauser, A. W. & Hayward, R. C. Shape-Morphing Materials from Stimuli-Responsive Hydrogel Hybrids. *Acc. Chem. Res.* **50**, 161–169 (2017). DOI: 10.1021/acs.accounts.6b00570
- 15. Grason, G. M. Perspective: Geometrically frustrated assemblies. *J. Chem. Phys.* **145**, (2016). DOI: 10.1063/1.4962629
- Sydney Gladman, A., Matsumoto, E. A., Nuzzo, R. G., Mahadevan, L. & Lewis, J. A. Biomimetic 4D printing. *Nat. Mater.* 15, 413–418 (2016). DOI: 10.1038/nmat4544
- 17. Chaikin, P., Clark, N. & Nagel, S. Grand Challenges in Soft Matter Science:

- Prospects for Microgravity Research. No. E-19904 (2021). DOI: None found
- 18. Wang, W., Duan, W., Ahmed, S., Sen, A. & Mallouk, T. E. From one to many: Dynamic assembly and collective behavior of self-propelled colloidal motors. *Acc. Chem. Res.* **48,** 1938–1946 (2015). DOI: 10.1021/acs.accounts.5b00025
- 19. Singh, D. P., Choudhury, U., Fischer, P. & Mark, A. G. Non-Equilibrium Assembly of Light-Activated Colloidal Mixtures. *Adv. Mater.* **29**, 1–7 (2017). DOI: 10.1002/adma.201701328
- 20. Choudhury, U., Singh, D. P., Qiu, T. & Fischer, P. Chemical Nanomotors at the Gram Scale Form a Dense Active Optorheological Medium. *Adv. Mater.* **31**, 1–7 (2019).). DOI: 10.1002/adma.201807382
- 21. Kassuga, T. D. & Rothstein, J. P. Buckling of particle-laden interfaces. *J. Colloid Interface Sci.* **448**, 287–296 (2015). DOI: 10.1016/j.jcis.2015.02.012
- 22. Liu, C., Xu, T., Xu, L. P. & Zhang, X. Controllable swarming and assembly of micro/nanomachines. *Micromachines* **9**, (2017). DOI: 10.1126/science.1230020
- 23. Howard, D., Eiben, A. E., Kennedy, D. F., Mouret, J. B., Valencia, P. & Winkler, D. Evolving embodied intelligence from materials to machines. *Nat. Mach. Intell.* **1**, 12–19 (2019). DOI: 10.1038/s42256-018-0009-9
- 24. Asfahl, K. L. & Schuster, M. Social interactions in bacterial cell-cell signaling. *FEMS Microbiol. Rev.* **41,** 92–107 (2017). DOI: 10.1093/femsre/fuw038
- 25. Yan, J., Monaco, H. & Xavier, J. B. The ultimate guide to bacterial swarming: An experimental model to study the evolution of cooperative behavior. *Annu. Rev. Microbiol.* **73**, 293–312 (2019). DOI: 10.1146/annurev-micro-020518-120033
- 26. Dey, K. K. & Sen, A. Chemically Propelled Molecules and Machines. *J. Am. Chem. Soc.* **139**, 7666–7676 (2017). DOI: 10.1021/jacs.7b02347
- 27. Gentile, K., Somasundar, A., Bhide, A. & Sen, A. Chemically Powered Synthetic "Living" Systems. *Chem* **6**, 2174–2185 (2020). DOI: 10.1016/j.chempr.2020.08.010
- 28. Guo, J., Gallegos, J. J., Tom, A. R. & Fan, D. Electric-Field-Guided Precision Manipulation of Catalytic Nanomotors for Cargo Delivery and Powering Nanoelectromechanical Devices. *ACS Nano* **12**, 1179–1187 (2018). DOI: 10.1021/acsnano.7b06824
- 29. Zhang, L., Petit, T., Peyer, K. E. & Nelson, B. J. Targeted cargo delivery using a rotating nickel nanowire. *Nanomedicine Nanotechnology, Biol. Med.* **8,** 1074–1080 (2012). DOI: 10.1016/j.nano.2012.03.002
- 30. Popescu, M. N., Uspal, W. E., Domínguez, A. & Dietrich, S. Effective Interactions between Chemically Active Colloids and Interfaces. *Acc. Chem. Res.* **51,** 2991–2997 (2018). DOI: 10.1016/j.nano.2012.03.002
- 31. Liu, C., Zhou, C., Wang, W. & Zhang, H. P. Bimetallic Microswimmers Speed Up in Confining Channels. *Phys. Rev. Lett.* **117**, 1–6 (2016). DOI: 10.1103/PhysRevLett.117.198001
- 32. Sengupta, S., Patra, D., Ortiz-Rivera, I., Agrawal, A., Shklyaev, S., Dey, K. K., Córdova-Figueroa, U., Mallouk, T. E. & Sen, A. Self-powered enzyme micropumps. *Nat. Chem.* **6**, 415–422 (2014). DOI: 10.1038/nchem.1895
- 33. Yu, T., Athanassiadis, A. G., Popescu, M. N., Chikkadi, V., Güth, A., Singh, D. P., Qiu, T. & Fischer, P. Microchannels with self-pumping walls. *ACS Nano* **14**, 13673–13680 (2020). DOI: 10.1021/acsnano.0c05826

- 34. Arfken, G. B., Griffing, D. F., Kelly, D. C. & Priest, J. in *Int. Ed. Univ. Phys.* 306–325 (Elsevier, 1984). DOI: 10.1016/B978-0-12-059858-8.50021-2
- 35. Das, S., Garg, A., Campbell, A. I., Howse, J., Sen, A., Velegol, D., Golestanian, R. & Ebbens, S. J. Boundaries can steer active Janus spheres. *Nat. Commun.* **6**, 1–10 (2015). DOI: 10.1038/ncomms9999
- 36. Needleman, D. & Dogic, Z. Active matter at the interface between materials science and cell biology. *Nat. Rev. Mater.* **2**, 1–14 (2017). DOI: 10.1038/natrevmats.2017.48
- 37. Gnesotto, F. S., Mura, F., Gladrow, J. & Broedersz, C. P. Broken detailed balance and non-equilibrium dynamics in living systems: A review. *Reports Prog. Phys.* **81,** 066601 (2018). DOI: 10.1088/1361-6633/aab3ed
- 38. Turlier, H., Fedosov, D. A., Audoly, B., Auth, T., Gov, N. S., Sykes, C., Joanny, J. F., Gompper, G. & Betz, T. Equilibrium physics breakdown reveals the active nature of red blood cell flickering. *Nat. Phys.* **12,** 513–519 (2016). DOI: 10.1038/nphys3621
- 39. Grason, G. M. Frustration and packing in curved-filament assemblies: from isometric to isomorphic bundles. *Soft Matter* **9**, 6761 (2013). DOI: 10.1039/C3SM50229E
- Grason, G. Braided bundles and compact coils: The structure and thermodynamics of hexagonally packed chiral filament assemblies. *Phys. Rev. E* 79, 041919 (2009). DOI: 10.1103/PhysRevE.79.041919
- 41. Chandra, D. & Yang, S. Stability of high-aspect-ratio micropillar arrays against adhesive and capillary forces. *Acc. Chem. Res.* **43**, 1080–1091 (2010). DOI: 10.1021/ar100001a
- 42. Gabriel Dumy, Nathan Jeger-Madiot, Xavier Benoit-Gonin, Thomas E. Mallouk, Mauricio Hoyos, Jean-Luc Aider, "Acoustic Manipulation of Dense Nanorods in Microgravity", *Microgravity Science and Technology*, 32,1159–1174 (2020). DOI: 10.1007/s12217-020-09835-7