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INVESTIGATOR(S):

Name: Minami Yoda
Email: minami@gatech.edu
Phone Number: 4048946838
Principal: Y

Organization: **Georgia Tech Applied Research Corporation**
Address: 505 Tenth St., NW, Atlanta, GA 303320001
Country: USA
DUNS Number: 364124651
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Submitted By: Minami Yoda
Email: minami@gatech.edu
Phone: (404) 894-6838
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Major Goals: As detailed in the attached report, this grant supported a workshop with the following objectives:
1) to identify the fundamental knowledge gaps in suspended particle dynamics and assembly subject to multiple physical, chemical, or electrical forces, including particle-particle, particle-fluid, and particle-boundary interactions;
2) to discuss and disseminate innovative approaches for controllable and continuous directed (self)assembly of colloidal structures from particle-laden microflows;
3) to identify priorities for defense-relevant applications for assembling functional structures with colloidal assemblies as building blocks using microflows, including heterostructures enabling local material property control, reconfigurable structures, and hierarchical structures with new functionality not available with individual materials.

Accomplishments: Please see the attached workshop report

Training Opportunities: About five graduate students and postdocs attended the workshop and learned about novel approaches using microfluidics and external stimuli to manipulate and assemble systems of suspended colloidal particles.

Results Dissemination: We are exploring archival journal venues for publishing an editorial or perspectives-type article on the workshop.

Honors and Awards: The co-PI, Dr. Shaurya Prakash, was a co-recipient of the Lumley Interdisciplinary Research Award from The Ohio State University College of Engineering.

Protocol Activity Status:

Technology Transfer: Nothing to Report

Partners

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I certify that the information in the report is complete and accurate:
Signature: Minami Yoda
Signature Date: 8/29/22   9:30AM

Workshop Report on:
Army Research Office (Hybrid) Sponsored Workshop on Many Particle Manipulation and Assembly in Continuous Flow Microfluidics

Held May 17-18, 2022

Scott Laboratory, the Ohio State University, Columbus, OH 43210

Organizers

Minami Yoda (minami@gatech.edu), *Georgia Institute of Technology*
Shaurya Prakash (prakash.31@osu.edu), *The Ohio State University*

Note: This workshop report is submitted as the Intermediate Progress Report for contract W911NF-22-1-0013

Executive Summary

A two-day hybrid workshop was held on novel approaches using microfluidics and external stimuli to manipulate and assemble systems of many suspended colloidal particles. This topic exploits recent advances in fabricating multistage microfluidic devices and actuators and designing patchy particles with various chemical functionalities. The primary question motivating the workshop was, "*Can we develop a general toolbox of flow+ approaches that combine microflows with external stimuli to continuously assemble suspended colloidal particles into micron-scale structures with a variety of functionalities?"*

This question and approach are innovative and novel because most existing methods assemble colloidal structures from quiescent suspensions, while the new toolbox would enable continuous extraction of pre-assembled microscale structures, as opposed to building a structure *via* layer-by-layer deposition. Pre-assembly in a flow+ configuration could: *i*) be used with smaller (≤ 1 μm) particles, *vs.* the larger (≥ 20 μm) particles used in current state-of-art assembly processes; *ii*) by using a variety of external stimuli, enable many-particle structures with tunable properties; and *iii*) reduce defects in these assembled structures *via* improved control over particle properties and diverse stimuli to actuate assembly. Flow+ could therefore provide a disruptive new method to manipulate nanomaterials.

Recent work on nanomaterials, colloidal assembly, and advanced manufacturing was presented and discussed. The participants concluded that flow+ approaches have great potential to provide a set of tools suitable for "real" (*e.g.*, non-spherical, polydisperse, heterogeneous material) particle systems. They also agreed that Federal agencies should, based on recent research discoveries and developments presented at the workshop, invest in these approaches. Investments should be made in both basic science and technological advancements on a variety of topics identified throughout this report. Given the complexity of this problem, overcoming these challenges requires a multidisciplinary "team science" effort.

Several critical knowledge gaps were identified, including (*a*) need for mechanistic theoretical and computational model development, (*b*) emerging and novel instabilities in microfluidics, (*c*) integration of models with experimental data, and (*d*) systematic approaches to enable team-based, application-focused research that meets Army needs. Given that most research efforts in this area consider specific (*vs.* general) particle systems and assembled structures, the participants recommended complementary experimental and modeling "benchmarking" studies for more general systems, and identified priority research areas. The discussions specified lists of desired target properties for the assembled structures, and several suspended particle effects and phenomena, that should be studied in a systematic fashion to control and engineer these target properties. An underlying sentiment prevailed in the breakout sessions that such investigations should also invest in high risk (and potentially high reward) development of novel multiscale measurement and fabrication approaches such as impedance spectroscopy, super-resolution microscopy, and advanced microfabrication techniques to enable further discoveries.

For a future "roadmap" for flow+ approaches, the workshop discussed how these colloidal structures could provide a modular system of "functional Legos" for designing and manufacturing functional nanomaterials or particle systems with a variety of functionalities, and noted that novel methods for assembling *O*(0.1–10 μm) particles into engineered microstructures would also bridge the technology gap between bottom-up assembly methods and top-down manufacturing methods.

Motivating Vision

The aim of this two-day workshop was to catalyze and inspire research on new microfluidics-based continuous and scalable approaches for dynamic assembly in flowing nano- and microparticle suspensions with tunable, hierarchical, and reconfigurable structure, and hence properties. The "big picture" question motivating this workshop was:

*Can we develop innovative and novel "**flow+**" approaches that combine microflows with external stimuli for general colloidal assembly approaches to dynamically and continuously assemble micron-scale heterostructures from suspended colloidal particles with a variety of functionalities*?

Our **motivating vision** is to develop a "toolbox" of flow+ approaches that are the basis for a system-level approach for manufacturing functional nanomaterials and nanomaterial systems based upon "functional Legos"[1] with different basic properties based upon charge, refractive index, and wettability, for example. These building blocks would then be assembled in various ways to form hierarchical and reconfigurable structures with tunable properties.

Objectives

The two-day workshop focused on flow+ approaches, where the combination of microfluidics and external stimuli (*i.e.*, forces) are used to engineer, assemble, and manufacture novel functional nanomaterial systems from colloidal particles of emerging materials (Fig. 1). Specifically, the **objectives** of the workshop were to:

- identify the fundamental knowledge gaps in suspended particle dynamics and assembly subject to multiple physical, chemical, or electrical forces, including particle-particle, particle-fluid, and particle-boundary interactions;
- discuss and disseminate innovative approaches for controllable and continuous directed (self-)assembly of colloidal structures from particle-laden microflows;
- identify priorities for defense-relevant applications for assembling functional structures with colloidal assemblies as building blocks using microflows, including heterostructures enabling local material property control, reconfigurable structures, and hierarchical structures with new functionality not available with individual materials.

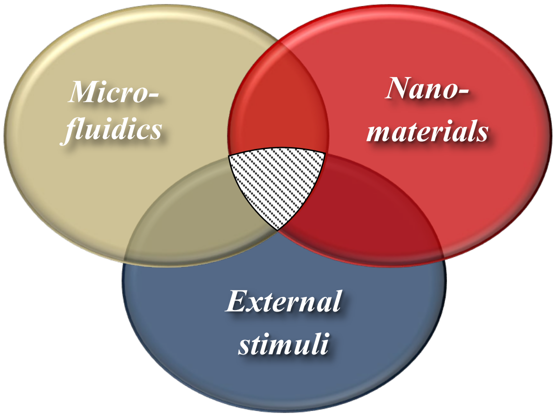

Figure 1 Flow+ approaches at the intersection of microfluidics, external stimuli and nanomaterials

In the long term, the **aim** of the workshop is to develop a "toolbox" of flow+ approaches for functional nanomaterials. Using these approaches will require design tools, namely a physically based modeling framework to guide which external stimuli (and flows) can be used to assemble

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[1] LEGO® is a system of universal plastic building blocks manufactured by The Lego Group (Billund, Denmark)

many-particle structures from a variety (*e.g.* dielectric, semiconducting, conducting, paramagnetic) of abiotic materials.

Introduction and Identification of Knowledge Gaps

Nanomaterials are an especially promising class of functional materials because their chemical, electromagnetic, and optical (for example) properties can be designed and engineered *in situ*. We propose a system-level approach for designing and manufacturing functional nanomaterials based upon functional Legos—building blocks with a variety of basic functionalities (*i.e.*, properties) that can be assembled in various configurations to form hierarchical structures with tunable properties. These Legos will be assemblies of many nano- and microparticles designed with a variety of functionalities, including surface properties such as wettability and charge and bulk properties such as refractive index, electrical conductivity and luminescence.

The dynamics of suspended colloidal particles near a solid surface is a problem fundamental to colloid and interfacial science, multiphase fluid dynamics, and recently, microfluidics. In our vision, it is also the basis of a new approach, flow+, that combines fluid flow and external stimuli for scalable and continuous colloidal assembly of nanomaterials.

Our vision has two distinct parts, and is inspired by the promise of the Materials Genome Initiative of an integrated computational and experimental approach that enables rapid fundamental advances in: (*i*) novel nanomaterials tailored to have specific properties and (*ii*) a continuous flow+ method integrated with materials design to build functional structures with these materials. This vision, however, is based on combining and assembling larger $O(10-100\text{ nm})$ particles of a variety of materials, instead of molecules or monomers, into micron-scale structures with a variety of functionalities—functional Legos—that can in turn form hierarchical structures that can be interfaced with micro- to millimeter scale devices and interconnections. Consequently, functional Legos are envisioned as a modular systematic way to "bridge" the gap between molecular and macroscale structures—and, with appropriate modeling tools, mitigate some of the entropic challenges that cause manufacturing defects and/or slow (assembly) kinetics encountered at the molecular scale.

A number of Federal agencies (*e.g.*, NSF, DARPA) have invested previously in advanced manufacturing and nanomanufacturing. These investments have led to significant advances in 3D printing, as the most prominent example of advanced manufacturing, as well as advanced control systems and process engineering. For example, the main objective of a DARPA program launched in 2015, the Atoms-to-Product (A2P) effort was to develop an engineered approach to develop printers that allow use of molecular materials to products utilizing assembly rules similar to natural (biological) systems while improving upon the slow growth and kinetics typical of biological systems. As noted by DARPA, the "…program aims to bring the benefits of microelectronic-style miniaturization to systems and products that combine mechanical, electrical, and chemical processes." Moreover, "the program calls for closing the assembly gap in two steps: From atoms to microns and from microns to millimeters." All of the three program thrusts—assembly of optical metamaterials, nanometer to millimeter in a single system, and flexible, general purpose assembly—focused upon advances in layer-by-layer assembly.

These, and other past efforts, as discussed during the workshop also laid out key unanswered fundamental questions at the *interface of flow+ and materials science*. For instance, as new nanomaterials continue to be developed, are there specific properties that can be tailored to allow tuning of particle assemblies by using a flow+ approach? If so, what would be the physical limits on (a) materials design, and (b) extent to which flow+ can manipulate engineered nanomaterials for specific particle structures and subsequent assemblies? Similarly, questions about flow instabilities in microfluidics were raised as described in the summary sections below. Additional questions asked related to fluid properties, the range and types of external stimuli that can be coupled to continuous flows with particles in microchannels, and the understanding of such flows. Clearly, the workshop identified both fundamental and technological challenges that still remain in flow+ interactions with colloidal nanomaterials, despite a rich history of progress in both fluid mechanics and nanomaterial sciences.

Therefore, we also note that the systems-level approach proposed here, and discussed at the workshop, is innovative and novel because it combines colloidal assembly, where functionalized (*e.g.,* "patchy") particles are assembled by external stimuli from a (usually quiescent) suspension [Ravaine and Duguet 2017; Ben Zion *et al.* 2017; Han *et al.* 2022], with the actuation and sensing technologies developed in microfluidics to enable continuous scalable and "on demand" assembly—and subsequent inspection and extraction of many-particle structures. Unlike previous efforts, this assembly approach integrates not only homogeneous, but also <u>heterogeneous</u>, materials within a single structure, and may therefore provide a new way to control local properties <u>within</u> a given structure, such as an anisotropic solid-state thermal interface (*i.e.*, heat transfer) material tailored for a specific set of extreme conditions.

Moreover, the combination of microscale flows and external stimuli could enable novel dynamic and non-equilibrium assembly processes, as well as multi-stage manipulation of colloidal particles in an integrated "microreactor", where reaction types and rates can be controlled both in space and time, to produce functional nanomaterials on demand. The enhanced advection due to the small volumes typical of microreactors result in rapid mixing and reaction. Adding flow+; however, broadens the capabilities of microreactors—for example, by using local actuation to deliver materials (*e.g.*, nanoparticles) in preferred orientations, or to locally and specifically catalyze reactions. These additional "knobs" could significantly enhance our ability to control and <u>sequence</u> "simple" single-step chemical reactions and processes beyond the current state of the art. Furthermore, as discussed during the breakout sessions, the flow+ approach could provide new drivers beyond convection and diffusion for assembly mediated by chemical reactions *via* non-inertial forces (*e.g.*, those due to electric fields).

The flow+ "toolbox" approach is also timely. First, the field of microfluidics has moved beyond single-stage and single-purpose devices to flexible multi-stage <u>systems</u>—*e.g.*, microreactors [McMullen and Jensen 2010]—that integrate a variety of microfluidic actuators and sensors, including functional nanomaterials [Wongkaew *et al.* 2018]. To date, the major applications of microfluidics (*e.g.*, medical diagnostics tests) are "passive", relying upon capillary forces and diffusion. Microreactors are instead "active" devices that require, and exploit recent innovations in, microscale pumping, valving and mixing.

Second, a variety of abiotic and biotic nanomaterials based on carbon, semiconductors, proteins, and nucleic acids, for example, have demonstrated remarkable properties and functionality where the whole is greater than the sum of the parts [Busseron *et al.* 2013; Dinsmore *et al.* 2002; Mak and Shan 2022]. Nanomaterials are unique because these are inherently functional materials with electromagnetic, optical, or acoustic properties [Kim *et al.* 2022; Koman *et al.* 2018; Yang *et al.* 2022]. The research and practice communities have also developed various computational tools to "design" a variety of anisotropic nano- and microparticles—the building blocks for these nanomaterials—with specific surface functionalities [Glotzer and Solomon 2007; Keys *et al.* 2011]. However, it has also become clear that fully realizing the potential of such functional nanomaterials requires integrating (*e.g.*, assembling) and interfacing a variety of materials to create micro- to mesoscale hierarchical structures.

Many of the field-defining leaders from academia and government that participated in this workshop (complete list of attendees and affiliation appended to this report) recognized that ***flow+ technologies can provide entirely new ways to envision particle assembly***. The breakout sessions briefly discussed reconfigurable materials for truly functional and hierarchical structures. Such structures could be assembled by a specific flow+ method, but could also potentially be designed so that the assembled structures could be ***disassembled*** with a different combination flow+ parameters i.e., a tool for assembly and a potentially different tool for disassembly within the same technology "toolbox". For example, the (admittedly incomplete) observations of colloidal band assembly reported by Yoda and Prakash [*e.g.*, Yee and Yoda 2018; Lochab *et al.* 2018] are reversible—bands only form above a threshold electric field (at a given shear rate), and the bands disassemble on timescales of a few minutes once the electric field is turned off. To our knowledge, ***there are no existing methods that can generate reversible structures***—*i.e.*, particles assembled into a functional structure, which can be controllably broken back down to individual particles and recycled into new structures.

As pointed out during the workshop, the transport of suspended nano- and microparticles, even in the very low Reynolds number Re (and low Peclet number Pe) flows typical of microfluidics, is surprisingly complex and poorly understood, especially when the symmetry of the creeping ($Re \leq 1$) flow is broken by an additional external stimulus, and/or a solid surface. For the most part, serendipitous experimental discoveries (including those by the workshop organizers enabled by the Army Research Office [Yee and Yoda 2018, 2021, 2022; Lochab *et al.* 2018; Lochab and Prakash 2021]) of a rich variety of colloidal structures further support the need for continued investigations to realize the vision of flow+. These discoveries are also starting to inspire related modeling and analysis, but there remain several knowledge gaps that must be overcome to develop a robust physically based modeling framework to design and guide flow+ approaches. Furthermore, there remains a significant gap in integrating physical, flow-based computational models with materials design and development, and using these tools for controlled assembly and subsequently scalable manufacturing of colloidal structures.

Key Ideas and Overview of Presentations and Break-out Sessions

The hybrid workshop was organized into three half-day sessions based upon the themes of nanomaterials, colloidal assembly, and advanced manufacturing. Each of these sessions opened with descriptions of research needs and priorities for a Federal agency (*e.g.* ARO, NSF), followed by three presentations on research innovations in microfluidics-related colloidal assembly and nanomaterials. Together, these nine research presentations highlighted the breadth and depth of the field. Each session ended with extensive discussions during moderated in-person and hybrid breakout sessions identifying the major research issues requiring further study and barriers to making flow+ approaches feasible.

Overall, the use of flow+ to engineer material systems relevant to the needs of the Army (and the Department of Defense) is an area that requires further investment. The research presented at the workshop described, and inspired, novel and innovative ideas that should translate to high impact research.

This section summarizes the main ideas from the presentations, then describes the key ideas expressed and reinforced by multiple speakers. The breakout session discussions also identified some specific “destinations” to guide a roadmap for developing flow+ approaches. Only the main points are highlighted in this brief report, in part because the presentation slides have already been shared with the workshop sponsors.

The first session on nanomaterials was opened by Dr. Ralph Anthenien of the Army Research Office (ARO), who gave a brief introduction to Army needs and challenges related to nanomaterials. Dr. Shunji Egusa of University of North Carolina, Charlotte showed how suspended gold nanoparticles could be assembled into patterns (*i.e.*, 2D structures) by heating, and evaporating, the liquid phase—and although the exact mechanisms underlying this type of pattern formation were unknown, temperature differences of less than 5 °C were sufficient to change the pattern. Dr. Lilian Hsiao of North Carolina State University (NCSU) then described her group’s unexpected discoveries on particle material-property relationships, specifically the rheology (*e.g.*, shear thickening behavior) of concentrated suspensions, and presented experimental results demonstrating that two suspensions at the same particle concentration φ, but with different particle shapes, exhibit very different behaviors. Finally, Dr. Orlin Velev of NCSU presented a variety of reconfigurable and responsive structures assembled from magnetic nanoparticles and Janus polymer-metal microcubes actuated by capillary forces and external magnetic fields.

In the second session on colloidal assembly, Dr. Evan Runnerstrom of ARO gave a brief introduction to Army research interests in hierarchical and reconfigurable nanomaterials. Dr. Sharon Glotzer of the University of Michigan gave a comprehensive introduction to modeling tools for predicting the behavior and dynamics of “patchy” particles, or large programmable atoms, that can dynamically assemble into functional materials with prescribed properties. She identified a number of outstanding issues, including the inability to model heterogeneous assembly, *i.e.*, predict the interactions between particles with different properties. Next, Dr. Minami Yoda of the Georgia Institute of Technology described experimental observations from her group of flow+ assembly of very elongated band-like structures driven by (shear) flow + a dc electric field, and measurements demonstrating that the particle dynamics contradict current electrokinetic theory. The third speaker, Dr. Kripa Varanasi of the Massachusetts Institute of Technology (MIT), gave an overview of hierarchical “heterointerfaces” (*i.e.*, heterogeneous in spatial scales, surface chemistry, morphology, for example) and how they could be designed to reduce friction as well as enhance heat transfer and chemical reactions. A number of commercial applications were presented, as well as the challenges in scaling up to large-scale production of heterointerfaces.

In the last session, Dr. Khershed Cooper of the National Science Foundation (NSF) gave an overview on the NSF Advanced Manufacturing program. Dr. Jaime Juarez of Iowa State University presented results on using acoustophoresis to assemble a heterogeneous fiber which achieves superior mechanical properties by concentrating particles on one side in a ultraviolet-cured polymer matrix. Dr. Shaurya Prakash of The Ohio State University described a novel method for extracting and preserving band-like structures (discussed by Dr. Yoda in the colloidal assembly session) by printing these bands suspended in a liquid bridge from a nozzle onto a porous membrane, and the optimization of this extraction method. The last talk by Dr. John Hart of MIT presented a unique layer-by-layer advanced manufacturing approach for printing "tall" particle assemblies using particle suspensions issuing from a nozzle. Although it took a few hours to print $O(0.1\text{ m})$ structures consisting of many millions of particles, these structures were noteworthy because they were solely supported by capillary forces after the liquid evaporated.

Dr. Anthenien noted the need to evaluate instabilities in fluid flow, especially in presence of particles. Although there has been significant work on hydrodynamic flow instabilities for canonical single-phase flows, instabilities in multiphase, *e.g.*, particle suspension flows, especially in the presence of multiple forces or stimuli, are largely unexplored. The additional stimulus/stimuli inherent in flow+ approaches break the symmetry of creeping flows and introduce novel flow instabilities in low *Re* flows (unlike hydrodynamic instabilities), such as electrokinetic instabilities. There is therefore a major "gap" in, and need for, experimental studies of instabilities in microscale flows—and how such instabilities contribute to the flow+ toolbox.

There is also a knowledge gap in modeling and analyses of flow+ microfluidics in terms of flow instabilities that go beyond the standard hydrodynamic or electrokinetic flow instabilities in the literature. Preliminary analyses by the workshop organizers as part of their (2016–19) ARO-sponsored research suggested that there may be significant local gradients in the conductivity and permittivity of the suspending fluid for particle-laden flows in confined microfluidic channels beyond the gradients inherent to the particles themselves. The effects of such local gradients — and their impact on fluid and particle dynamics—remains largely unknown and is therefore a major knowledge gap.

Notably, the length scales for these local gradients vary over three orders of magnitude, namely from the thickness of the electrical double layer (nm) to a few particle diameters (μm). Moreover, these gradients are driven by phenomena with orders of magnitude variation in temporal scales, from charge polarization (μs) to (flow) convection (ms). There are few experimental methods at present that can resolve and probe these flows given that these orders of magnitude variations in spatial and temporal scales exist within a single microchannel with an overall critical dimension of <100 μm. Hence, there is a need to pioneer and develop new experimental techniques to measure and resolve fluid flow, particle dynamics, and local gradients within such microfluidic devices. Given that experimental discoveries inspired flow+, such techniques will likely lead to further discoveries that challenge and test our understanding. This multiscale problem also presents a unique opportunity to develop and test new modeling and computational approaches, including machine learning-based tools.

Moreover, current theories and models of particle-fluid mixtures, or suspensions, are almost exclusively based on ideal systems consisting of monodisperse, spherical and neutrally buoyant particles. This work needs to be extended to "non-ideal" polydisperse particle-fluid mixtures, where the particles are also comprised of a variety of (*e.g.*, semiconducting or conducting) materials relevant to the Army needs, some of which were mentioned during the workshop.

Summary of Breakout Sessions

Discussions during the breakout sessions, intended to expand on the presentations by individual researchers, identified a number of challenges for translating flow+ approaches using existing particles to manufacture engineered material systems. One such challenge is the significant knowledge gaps in fluid and particle material-property relationships, as illustrated by Dr. Hsiao's rheology results. These experimental observations suggest that current models of suspension rheology that only depend on φ, such as the generalized Einstein equation for viscosity and its extensions, are inadequate for suspensions of particles of different shapes. A fundamental understanding of how particle shape and orientation impact the rheology, and hence the dynamics, of suspended particles would be a useful flow+ tool in engineering and assembling functional nanomaterials.

One common theme over the research presentations and breakout sessions was the complexity and breadth of this topic in terms of the broad variety of assemblies and particle materials, as well as the need to resolve and understand phenomena across multiple spatial and temporal scales to control assembly and "manufacturing" defects. The vision of flow+ was supported by the vast majority of the workshop participants because they, and the broader research community, recognize that the tremendous advances realized by layer-by-layer assembly and manufacturing processes are limited to "coarse" (20−100 μm diameter) powders or particles.

At present, there are no reliable methods for manipulating and assembling smaller particles, let alone colloidal or even smaller nanoparticles of sizes approaching larger molecular length scales of ~10 nm. In short, there is a technology gap between the bottom-up assembly methods (which work well at molecular length scales, albeit slowly because they are largely driven by equilibrium thermodynamics) and top-down manufacturing methods (which have led to many advances, including fabrication of semiconductor and MEMS devices), where flow+ approaches can provide a much-needed bridge. Several presentations highlighted how each research group has developed their own modeling and experimental methods optimized for specific particle materials and assembled structures with no uniform metrics to compare performance across the literature.

Dr. Velev's presentation featured stimuli-responsive materials, as summarized above. The breakout sessions (and the speakers themselves) recognized that realizing the promise of these remarkable materials requires improving their sensitivity and response to external stimuli (*i.e.*, better sensing), and increasing the actuation forces delivered by these materials. There is also a need to develop and use physically-based models, validated by experiments, to develop and improve stimuli-responsive materials.

The workshop made clear that there is a need for a more general systematic approach to facilitate application-based research and "benchmarking" studies to identify and establish fundamental physically based rules to exploit and control fluid-particle interactions to drive particle assembly into (eventually) stable structures (*e.g.*, functional Legos). Developing and using machine learning (ML) models to optimize known processes by identifying general assembly methods and approaches from already existing large datasets was also discussed. It was noted, however, that ML approaches require large volumes of training data—and there may a need to obtain such sets of reliable and accurate experimental data to develop artificial intelligence models that provide useful predictions.

The breakout session discussions developed a list of "target" properties for assembled structures including:

- structural properties (*e.g.* porosity, defects density)
- electromagnetic properties (*e.g.* conductivity, polarizability)
- optical properties (*e.g.* refractive index)
- thermal properties

The workshop participants also developed a (partial) list of suspended particle effects and phenomena that should be studied in a systematic way to learn how to control and engineer these target properties for engineering applications relevant to Army needs, as well as under extreme operating, assembly, or manufacturing conditions. The list included:

1) The effects of (fluid and differential particle-fluid) inertia
2) The effect of particle shape
3) (Electric, magnetic, acoustic, etc.) "field" effects
4) Dielectric or polarization effects
5) Interparticle forces
6) Heterogeneous suspensions of particles with different chemical and physical properties
7) Bubble and capillary effects to drive flow
8) Bubble-(*vs.* particle-)laden suspensions
9) Non-Newtonian effects

Finally, a number of experimental and modeling techniques for studying these effects require further development:

- advanced super-resolution (*e.g.*, confocal) optical microscopy techniques and imaging techniques suitable for chemically reacting and opaque microscale flows
- holographic optical traps (*e.g.*, optical tweezers)
- robust and reliable ways to generate spatially and temporally structured (*e.g.* electric, acoustic) fields and actuation appropriate for nano- and microparticles of various shapes and materials
- machine learning approaches for optimizing assembly and manufacturing conditions
- advanced 3D printing techniques that go beyond current layer-by-layer or direct write methods and minimize nanomaterial defects

In summary, the workshop participants recognized the complexity, broad scope and potential of flow+ approaches. They identified several knowledge gaps, including model development and novel instabilities in microfluidics, as well as a number of effects that should be investigated systematically with complementary experimental and modeling "benchmarking" studies to identify and establish the fundamental phenomena governing flow+ approaches.

Recommendations and Outcomes

The workshop brought together leading researchers and government participants and showcased the state-of-art in science and technology for use of flow+ methods for suspensions of micro- and nano-particles in microfluidic channels. The participants agreed that recent research discoveries and developments should inspire Federal (*e.g.*, ARO, NSF) research investment to "seed" new flow+ approaches that combine microfluidics and external stimuli to assemble novel functional nanomaterial systems—and in the long term, functional Legos—from colloidal particles of emerging materials. Given the cross-disciplinary nature of this topic, these investments should engage a multidisciplinary coordinated team of researchers.

The presentations, discussions, break-out sessions, and collective knowledge sharing prioritized the following areas:

(1) Flow+ technologies to provide a "toolbox" of approaches that integrate computational modeling and experimental methods to enable novel forms of particle assembly. These tools should:
   a. Emphasize "real" particle systems—*e.g.*, many irregular, non-spherical particles with a size distribution—*vs.* ideal systems of a few monodisperse spherical particles
   b. Include improved models of fluid-property-structure-function relationships for such "real" particle systems

(2) Heterogeneous assembly of multiple particle materials, shapes, sizes, fluid-particle combinations, and other (*e.g.* electromagnetic) properties. These assembly methods should explore:
   a. Using flow parameters and complex microchannel geometries to enable templating and/or controlled manipulation of particle assembly characteristics, including assembled structure properties, should be developed
   b. Heterogeneous assembly of patchy particles into stimuli responsive and reconfigurable materials. Here, reconfigurable materials involve the reversible assembly of constituent particles into a functional structure, that can then be disassembled into constituent particles and, ideally, reused in another structure.

(3) Developing and optimizing tools for extracting (*vs.* assembling) a variety of colloidal structures. In other words, what are the best ways to extract 1D, 2D, or 3D structures with well-defined properties so that their properties are preserved?

(4) Flow instabilities in microscale colloidal particle suspensions: unlike "traditional" hydrodynamic instabilities, or even electrokinetic instabilities, there is surprisingly little known about how local microscale property gradients affect flow stability and particle dynamics.

(5) Developing techniques for probing confined microscale flows, especially in flow+ configurations. This should emphasize non-traditional techniques (*vs.* optical microscopy, for

example) such as electrical impedance spectroscopy, X-ray imaging, ultrasound imaging, and magnetic resonance imaging to characterize chemically reacting and optically opaque flows.

Future Plans

In the five months remaining in this workshop grant, which ends on January 31, 2023, the remaining funds will be used for travel by the PI and co-PI to further develop and support the recommendations from this workshop. Building upon discussions with the workshop speakers and participants, we plan to visit and meet with researchers in nanomaterials and advanced manufacturing at:

- Army Research Office in Cary, NC
- Army Research Laboratory in Aberdeen, MD
- Air Force Research Laboratory in Dayton, OH
- National Science Foundation in Alexandria, VA

The objective of these visits will be to discuss research efforts and needs in these areas, and determine how the emerging research areas discussed during the workshop address these needs and complement current efforts. This will further focus the priority research areas recommended by the workshop and ensure that future research inspired by this workshop will be attuned to Army and DoD needs.

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Workshop Attendees and Affiliations

** = attended via Zoom*

- Igor Aronson*, *Pennsylvania State University*
- Luke Baldwin, *Air Force Research Laboratory*
- Ralph Anthenien*, *Army Research Office*
- Tommie Blackledge, *The Ohio State University*
- Paul Bohn, *University of Notre Dame*
- Suncica Canic*, *University of California, Berkeley*
- Carlos Castro, *The Ohio State University*
- Khershed Cooper*, *National Science Foundation*
- Christopher Crouse, *Air Force Research Laboratory*
- Fraser Daniel, *The Ohio State University*
- Shunji Egusa, *University of North Carolina, Charlotte*
- Daniel Ewim, *The Ohio State University*
- Placid Ferreira*, *University of Illinois at Urbana-Champaign*
- Johnathon Gales*, *New York University*
- Udita Ghosh*, *Indian Institute of Technology, Varanasi*
- Sharon Glotzer*, *University of Michigan*
- Yoav Green*, *Ben Gurion University of the Negev*
- John Hart*, *Massachusetts Institute of Technology*
- David Hoelzle, *The Ohio State University*
- Lilian Hsiao, *North Carolina State University*
- Safa Jamali*, *Northeastern University*
- Jaime Juarez, *Iowa State University*
- Shashi Karna*, *Army Research Laboratory*
- Aditya Khair, *Carnegie Mellon University*
- Parisa Mirbod, *University of Illinois, Chicago*
- Matthew Munson*, *Air Force Academy*
- William Olbricht*, *National Science Foundation*
- Rahul Panat*, *Carnegie Mellon University*
- Shaurya Prakash, *The Ohio State University*
- Ramadan Abu Rjal*, *Ben Gurion University of the Negev*
- Evan Runnerstrom, *Army Research Office*
- Stefanno Saccana*, *New York University*
- John Sebastian*, *Ben Gurion University of the Negev*
- Alexey Snezhko*, *Argonne National Laboratory*
- Peter Stevenson, *Air Force Research Laboratory*
- Kripa Varanasi*, *Massachusetts Institute of Technology*
- Pani Varanasi*, *Army Research Office*
- Orlin Velev*, *North Carolina State University*
- Xiangchun Xuan*, *Clemson University*
- Minami Yoda, *Georgia Institute of Technology*
- Junghoon Yeom*, *Naval Research Laboratory*