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FUNDAMENTAL MATERIALS RESEARCH

NON-EQUILIBRIUM MATTER – THE NEXT DECADE AND BEYOND IN SPACE MATERIALS RESEARCH

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1. Background: Non-equilibrium processes are ubiquitous. Natural and synthetic materials are rarely the result of equilibrium processes. Numerous processes that occur in non-equilibrium conditions [1,2] have been exploited to achieve novel and often transformational technological advances in optical and aerospace materials, pharmaceuticals, foods and others [3]. Much of the underlying science about the relationships between non-equilibrium processing and the resulting properties, structure, and performance remains to be discovered. This paper develops a research theme to **identify, characterize and establish aspects of non-equilibrium processes that provide a foundation for transformational materials research**. "The need for a deeper understanding on non-equilibrium phenomena is nowhere greater than in materials science." [4]

Non-equilibrium processes can be used to develop novel functional materials *via* liquid and liquid-gas phase processing and solidification. **In contrast to equilibrium, the specific route determines the outcome of non-equilibrium processes**. Liquids can enter non-equilibrium states by supercooling below the melting point, supersaturation of solutes, and/or formation of structural or compositional heterogeneities on various length scales. Investigating these states is challenging because precise control of kinetic variables is essential in order to correlate processing with the properties (*e.g*. viscosity, diffusivity, density, thermal expansion, surface tension, interface kinetics, heat of transformation) and structure (*e.g*. atomic bonding, clustering, short-range and meso-scale ordering) as liquids evolve to the final product.

The central problem in many non-equilibrium studies is that process kinetics are strongly influenced by complex heat, momentum, and mass transport. In fluid systems – including molten phases, solutions and supercooled liquids – convection, stirring, fluid motion, sedimentation and flow-induced effects play critical roles in determining the nature of the resulting products. These processes are mediated by the fluid properties and structure and by gravity-induced transport. Microgravity experiments largely avoid the complications of kinetic variables by enabling processes to be performed in quiescent, diffusion-controlled transport conditions [5]. This enables synthesis and *in-situ* characterization of materials in ways that cannot be accomplished on Earth. Knowledge gained can help to advance materials processing on Earth both by optimizing processes and providing benchmark data to validate models used to develop new materials. Understanding how processes occur in different gravity levels is essential for development of space-based fabrication and manufacturing, *in-situ* resource utilization, materials re-use and in-flight servicing.

2. Benefits: Fundamental materials research underpins applied development and lays the foundation for technological innovation and transformational materials research both in space and on Earth. Non-equilibrium effects span all classes of materials and affect high temperature, ambient temperature, biological and electronic processes. Specific benefits of the research are:

- To achieve a fundamental understanding of:
    - Ways in which non-equilibrium liquid and liquid-gas phase processing can be controlled in the absence of fluid motion, sedimentation and buoyancy-driven convection.
    - How processing of multiphase fluids can be controlled to develop novel structures.
    - How freeze casting can be used to produce hierarchical materials with unique properties.
    - Fundamental non-equilibrium processes: glass formation, phase separation, metastable crystallization and bubble formation in supercooled liquids.
    - Fundamental non-equilibrium phenomena relating to morphological instability during solidification, electro-deposition, and precipitation.
    - Practical issues that affect the types of processing that can be accomplished in different gravity levels where transport rates can differ significantly from Earth-based conditions.

- Knowledge of material properties is essential for accurate computational modeling to reduce new materials development time/cost. Modeling areas span materials design (*e.g.*, CALPHAD) to molecular dynamics, multi-physics and multi-scale (*e.g*. for additive manufacturing processes).
- To develop and establish new technology skillsets needed in the workforce. A training pipeline and recruitment of diverse, talented personnel is essential to create innovation based on new knowledge and intellectual property that results from the research.
- To improve U.S. economic and technological leadership in amorphous, glassy and hierarchical materials used in optical, aerospace, infrastructure, energy conversion, and pharmaceutical technologies among others.

3. Examples: Non-equilibrium states are pervasive across numerous scientific disciplines and classes of materials. Selected overlapping topics (see Fig. 1) are used to highlight high impact research problems in the context of advancing both basic and applied research areas in non-equilibrium materials science. **Emphasis is on liquid phase processes where transport properties largely determine the outcome**. Microgravity is needed to control transport effects that otherwise obfuscate the answers to research questions. High value research activities should be pursued in a combined flight- and ground-based program that leverages capabilities for characterization and modelling of materials. Work should be coordinated with needs for application development areas such as those cited earlier.

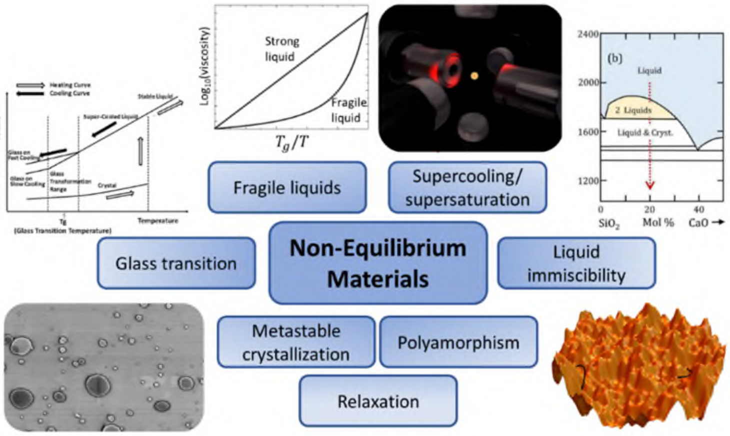

Fig. 1. Topic areas recommended for research on non-equilibrium materials. (image refs.: A-E)

Within these areas, there are pressing scientific questions where control of fluid motion and sedimentation can enable pioneering research. The use of models to both develop and test ideas and ultimately to establish predictive capabilities is an essential adjunct to the main experimental campaigns.

Glasses can be formed from all classes of materials [6-8]. Changes in thermophysical and thermochemical properties (*e.g*. viscosity, density, heat capacity), structural evolution, and energetics differ significantly among materials - polymerized and unpolymerized ionic materials, metals, and organic molecules. A unified model of glass formation encompassing these diverse materials would be a fundamental step forward in understanding the vitrification process. Toward this goal, measurements on supercooled liquids as they cool and form glass are important to answer questions about the mechanisms of vitrification. Understanding the extent to which glass forming behavior can be predicted from liquid properties and structure will help to guide the focus of experimental research efforts to improve functional glass properties. In soft materials, molecular conformality can be affected by fluid flow-induced stresses. Understanding how this influences the stability of glasses and their properties can help to improve pharmaceutical processing and development of functional soft materials. Glasses formed in a wide range of extreme thermal and chemical conditions occur throughout the Universe. Characterization of natural glass and amorphous materials is needed to evaluate them as resources. Studying the effects and behavior of radiation (*e.g*. cosmic rays) on glasses is important for development of reliable, long range flight hardware.

Fragile liquids exhibit varying degrees of non-Arrhenian behavior in the *ln. viscosity-inverse temperature* relationship [9,10]. The majority of liquids are fragile and many can form glass. These liquids provide a rich area for development of new non-equilibrium products in all classes of materials. Unveiling the temperature and composition dependence of viscosity, density and structure of supercooled liquids above the glass transition temperature is essential to understanding fragile liquids. The Stokes-Einstein relationship accurately relates viscosity and diffusion in some liquids but not others. Exploring the underlying differences between these cases can give valuable insight into structural evolution during processing and expected relaxation mechanisms. Some liquids can undergo strong-fragile transitions. A mechanistic understanding of this transition can provide the basis for developing new materials. For example, fragile liquids often require high cooling rates to avoid crystallization. Understanding effects of microgravity on the critical cooling rates for vitrification of fragile liquids made from heavy metal fluorides/chalcogenides is needed to produce high quality optical products from these materials. Thermal processing could be used to develop "fictive temperature gradients" to spatially tailor glass properties. Gradients form in many additive manufacturing processes. Understanding effects of flow on these processes is essential.

Supercooling and supersaturation are frequently means by which a system enters non-equilibrium. The degree to which this occurs depends on avoiding nucleation of new phases. Supercooling/supersaturation is essential to form glass from liquid precursors. Containerless processing can enable deep supercooling of liquids by eliminating extrinsic heterogenous nucleation [11-13]. This process enables investigation of supercooled liquids and often formation of glass or amorphous materials that cannot be made by other methods. Levitation techniques can help reveal the structural pathways through a variety of cooling routes [4]. These "extreme" glasses can serve as benchmarks for glass discovery. Understanding the ways that thermophysical properties and structure of liquids change as a function of supercooling will help to support models of liquids. For example, correlation of melt and solution properties and structure with process parameters can provide needed data for machine learning based design of functional materials. Understanding how the properties of supercooled/supersaturated molecular liquids behave in response to fluid flow is important for development of non-equilibrium phases in soft materials. Terrestrially, practical issues of fluid motion and dissolved gases affect the degree to which liquids can be supercooled. In microgravity, supersaturation of dissolved gases in "quiescent" liquids can be explored and exploited to develop new structural materials. Freeze casting can transform polymeric aqueous solutions and colloidal suspensions into complex hierarchical glassy and composite materials, such as those mimicking nacre and other bioinspired materials with superior mechanical behavior and other unique properties [14,15]. Controlled freezing experiments in a microgravity environment combined with multiscale modeling provides a powerful means to develop a fundamental understanding of the combined effects of fluid flow on complex reorganization of matter outside of thermal and chemical equilibrium.

Fluid immiscibility, or phase separation, results in formation of coexisting liquids with different chemical composition and usually different density [16]. In addition to diffusion, the morphology of such mixtures depends on convective transport and density driven sedimentation. Precise measurements of diffusion coefficients can play a significant role in the developing realistic models of convective dissolution in CO_2 sequestration techniques [17]. Inhomogeneities or phase separation may be useful if they can be introduced into a liquid or glass in a controlled manner to develop periodic differences in density, composition, refractive index or hardness. The degree to which fluid motion affects phase separation and the morphology of resulting products will be crucial for space-based materials processing. The behavior of dissolved and exsolved gases can result in a two phase mixture. Flow and buoyancy can move gas bubbles in liquids. The magnitude of motion affects the ability to remove unwanted gases (fining). Understanding how phase separation affects the stability of glasses that are prone to surface (interface) crystallization is needed for future *in-situ* resource utilization.

Polyamorphism is the transformation of an amorphous phase into a different phase with the same chemical composition and different density (High and Low Density Amorphous, HDA and LDA) [18]. New high performance optical glasses can be explored with better knowledge of how polyamorphism is related to glass formation, fragile-strong transitions and incongruent phase separation. Investigation of the properties, structure and energetics of HDA/LDA phases *in-situ* can provide data on complex systems undergoing metastable transformations.

Metastable Crystallization frequently occurs from a vapor or a liquid *via* formation of nanosized and often disordered nuclei, or phases with different structure from the stable bulk form [19]. The crystallization pathway typically proceeds *via* metastable phases with incremental changes in structure and free energy occurring until the stable material forms. Kinetic stabilization of novel metastable materials can be enabled by understanding the thermodynamics of phases at the nanoscale. Thermodynamics and kinetics of crystallization are both relevant to glass production. Quantifying the heat released when supercooled liquids and metastable materials crystallize is important for modeling radiative heat transfer and hydrodynamics of deep space environments. Morphological instability can result from positive feedback between diffusional gradients and interface motion during solidification, electrodeposition and precipitation. Surface and interfacial energy can isolate the patterns of instability. Avoidance of natural convection is essential to investigate and characterize these phenomena that will be important in space based materials processing and fabrication.

Relaxation decreases the free energy of a non-equilibrium state, usually *via* activated processes that transition between minima in the energy landscape. When a glass is “trapped” in a low energy state, it may persist indefinitely due to large activation barriers [20,21]. Understanding the origins of primary and secondary relaxation modes will help guide discovery of more stable non-equilibrium phases. This is important in both hard and soft matter glasses where different degrees of stability occur. Flow can affect relaxation, particularly in molecular liquids where conformality changes can alter non-equilibrium processes and kinetics. Shear-induced flows and mechanical excitations of the liquid change chemical trajectories through the energetic landscape, resulting in unexpected reaction selectivity [22-24].

4. Conclusions and Recommendations: Microgravity research in the area of liquid phase processing, properties and structure of non-equilibrium materials is a high value activity that is central to NASA’s mission. The research will develop and underpin: (i) cutting edge fundamental science uniquely enabled by microgravity, (ii) applied materials and processes needed for future space exploration, and (iii) discovery and characterization of new materials that can ultimately impact Earth-based manufacturing. Fundamental research is an essential bedrock for applied research and development of next-generation products.

Performing experiments in microgravity can achieve near-ideal diffusion-controlled heat and mass transport in liquids. These conditions enable fundamental research on the evolution of properties and structure for non-equilibrium liquids and solutions that cannot be accomplished in ground-based experiments.

The research is crosscutting and impacts multiple basic and applied areas. The scope of materials and the disciplines needed to develop a comprehensive research program is broad and overlaps major Biological and Physical Sciences program areas. It includes molten ionic materials, metals, soft matter and solutions over a range of temperatures and in a variety of flow conditions. In some cases, multi-disciplinary teams are needed to achieve maximum output from the research. Adopting a high-risk/high-payoff approach with rapid funding in areas that demand urgent attention can enable advances in applied materials that are seeded *via* the fundamental research program [25].

To achieve maximum impact, the research should include both flight- and ground-based elements. Flight experiments exploit the unique capabilities available on rockets, orbiters and potentially planetary-based facilities to control gravity level, fluid flow, sedimentation and convection. Augmenting this work with ground-based characterization and experiment development can significantly extend the reach and impact in a cost effective way. Ground-based research can both optimize experiment design and provide a control to isolate effects of gravity. These requirements can be met *via* ground-based use of: (i) specialized NASA facilities, (ii) specialized national facilities such as the Advanced Photon Source and Spallation Neutron Source to measure atomic structure and dynamics, (iii) powerful computational modelling for analysis and efficient development of new materials, and (iv) collaborative research programs that combine a diverse range of knowledge and skillsets needed to solve complex problems.

Containerless techniques (levitation) are versatile and enabling tools that can avoid extrinsic heterogeneous nucleation to access highly non-equilibrium states and high purity, pristine liquids even at extreme temperatures. While some of this can be done on the ground, control of fluid motion is required to obtain *in-situ* measurements of liquid transport properties and explore processes that involve sedimentation or convective transport. In order to realize the full potential of these techniques, integration of: (i) high resolution imaging at selected rates from 30 to 1000 frames per second, (ii) measurement and control of thermal gradients, (iii) control of oxidation potential from highly oxidizing to redox and inert atmospheres, and (iv) better ways to control sample rotation (*e.g.* to avoid induced gravity to minimize phase segregation and to control bubble migration) [26] are needed.

Modelling can accelerate transfer of new knowledge to applications development, particularly when benchmark data can be used for validation. Modelling approaches range from empirical machine learning-based methods to those which capture the detailed electronic- or atomic-level physics of the non-equilibrium systems. A combination of modelling approaches typically provides the most comprehensive understanding of the system. This can include models at different length scales or time scales, or models focusing on different types of properties. Density Functional Theory (DFT) is being combined with both machine and active learning. This approach enables DFT methods to provide large scale simulations with quantum accuracy and quench rates of 0.1K/ps [27,28]. Close connection between models, experimental research and benchmark data are essential.

Flight hardware development is expensive and relatively high risk. Evaluation of existing NASA and international flight hardware is recommended. NASA should analyze the benefits of: (i) upgrade/re-use versus development of new hardware, and (ii) teaming with other US agencies, international space agencies and commercial providers to share costs/know-how for hardware development and operation. Limited access to microgravity is one of the largest inhibitors to progress. More frequent down-mass is needed to accelerate science and technology development. Eliminating loss of signal due to incomplete satellite coverage would increase utilization of available experiment time in space-based work.

Fundamental research can generate potentially high value Intellectual Property (IP). NASA needs to have clear and easily implemented policies to identify, distribute rights and exploit new IP that can result from the research program.

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