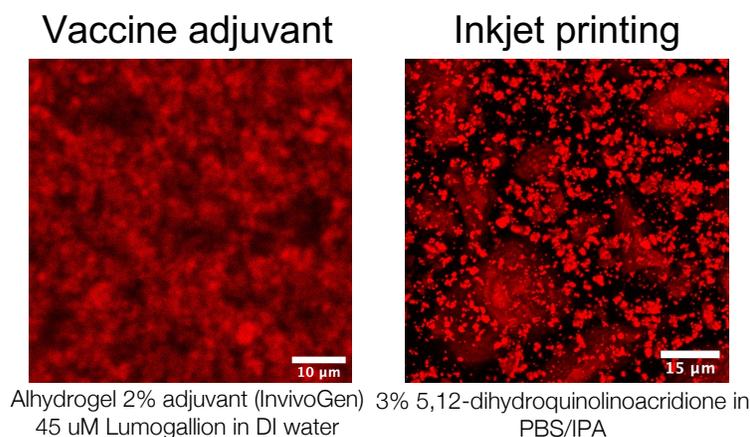




Q: Given that you plan to use confocal microscopy as an analytical tool, how do you plan to study (or apply your findings to) real industrial dispersions? Are there any non-model systems that can be analyzed with confocal microscopy?

A: We intend to work with simplified formulations that are representative of real industrial dispersions. There are plenty of industrial non-model systems that are compatible with confocal microscopy. **Fig. R2** shows two examples that were collected in our lab: (i) a 2 wt% aluminum hydrogel used in vaccine adjuvants for a pharmaceutical manufacturer, and (ii) a 3 wt% pigment dispersion used for inkjet printing onto plastic packaging. The samples shown in Fig. R2 contain aggregates that can coalesce over time due to thermodynamic incompatibilities that are stabilized kinetically. We note that certain materials such as fumed silica, carbon black, and titania may not be suitable for microscopy imaging due to their high refractive index mismatch with the solvent. Compatible systems are tagged with fluorescent dyes to enable microscopy, and are formulated after extensive discussions with company scientists to ensure that they are representative of the proprietary formulations used in commercial products.



**Figure R2.** Examples of non-model systems used by: (left) a pharmaceutical company as vaccine adjuvants and (right) an inkjet printing company as high brilliance pigments designed for plastic packaging materials.

Q: Finally, your proposal is actually two three-year proposals (which is fine, as long as you understand that renewal isn't automatic), and dispersion stability prediction isn't reached until year four. Given that the brief is for a three-year project, stability needs to be addressed in the first three years.

A: We have edited the timeline in p.5 of the main proposal to aim for stability prediction in year 3 (yellow highlights).

## Accelerated acoustic prediction of aging and failure

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Department of Chemical and Biomolecular Engineering, North Carolina State University

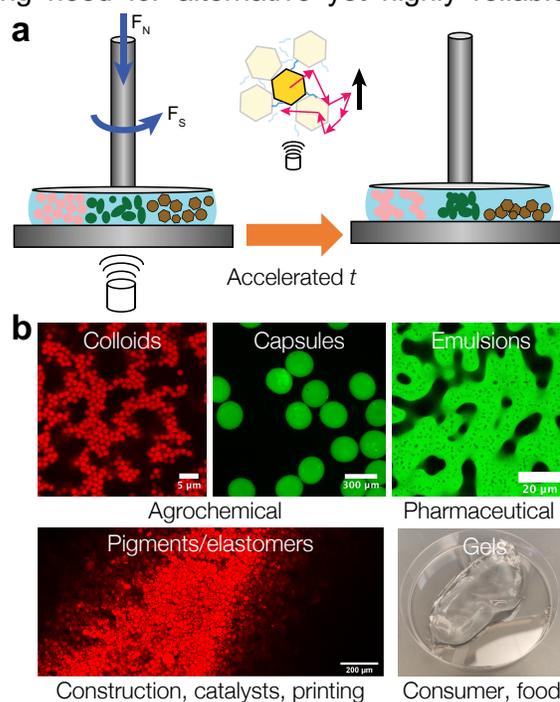
### 1. Overview

**Problem:** Aging assays have long been used to rank the stability and service life of materials when used normally. Although conventional methods exist to hasten the aging and failure of many colloidal dispersions (e.g.: ASTM D3342 or D7061), they rely on heating and are therefore not suitable for temperature-sensitive or bio-active materials. Centrifugation methods serve to enhance gravitational stresses in one direction; however, they do not speed up phase changes arising from thermodynamic and transport-related mechanisms such as flocculation, Ostwald ripening, and phase inversion.<sup>1</sup> There is a pressing need for alternative yet highly reliable protocols that can simulate dispersion stability without applying high temperatures, light, vacuum, or unidirectional stresses.<sup>2</sup>

**Solution:** This IFPRI project will address the critical gap in colloid and dispersion screening through an **accurate, accessible, and translatable testing platform that accelerates aging by imparting controlled bursts of energy to increase particle mobility.** The method works by exciting microscopic constituents using high frequency ultrasound. The excited particles collide more frequently and with greater energy, which dramatically increase the occurrence of local slip events that ultimately cause large-scale failure such as syneresis, yielding, and collapse<sup>3,4</sup> (**Fig. 1a**). Predictive correlations obtained from the accelerated platform will be **validated against real-aged and commercial samples.** While this project will involve particle-level structural measurements, a significant benefit of this project is that **the microstructural data will not be necessary for field deployment of the method.** *In situ* particle-level measurements are important in understanding how local cracks or fractures lead to rare but catastrophic material failure. They enable the development of micromechanical correlations to slow the aging and failure of a broad class of dispersions through local interaction design.

**Commercial and scientific samples:** Acoustic and real-time aging will be performed on a set of formulations developed with input from IFPRI members (**Fig. 1b**). The PI will also obtain commercial samples from industry partners where possible. Formulations of interest include:

- Dense, weakly attractive colloidal gels in density and refractive index-matched solvents (Sterically stabilized PMMA colloids with depletants in organic media)
- Microcapsule suspensions of gel vesicles enclosing organic compounds (Alginate capsules containing clomazone or similar)



**Figure 1.** This project will develop an acoustic platform to accelerate aging in wet systems by at least 100 fold. (a) The method works by increasing the activity of particles through pulses of high frequency ultrasound, which increases the rate of collision and thus kinetic destabilization. (b) The PI will test this method on five kinds of formulations that best represent the technological sectors of the IFPRI member base.

- Oil-in-water nanoemulsions with adsorbed co-surfactants (PDMS oil in water containing anionic and non-ionic surfactants such as AOT and Span 80)
- Concentrated silicone-based elastomer composites (PMMA microbeads in PDMS matrix)
- Synergetic polymer gels containing rheology modifiers (Caseinate with gum arabic)

**Rationale:** Prior studies have shown that ultrasound pulses induce softening of different colloidal gels.<sup>5</sup> Studies have also used acoustic perturbations to reduce the viscosity of shear thickening suspensions by disrupting the stress-bearing networks.<sup>6</sup> Gibaud *et al.* (ref. 5) showed that ultrasound waves of higher intensities lead to greater softening of diffusion limited cluster aggregation (DLCA)-type gels, including those made from calcite, silica, and carbon black. Recent studies on granular and dense colloidal materials suggest that prior to yielding, microscopic "hot spots" grow into larger regions that undergo irreversible slip deformation.<sup>7,8</sup> These collective rearrangements ultimately pass a critical strain energy threshold and become precursors to material failure. Unlike aging, failure and avalanche events are non-Arrhenius in nature and are similar to crack initiation in brittle materials.<sup>9</sup> Avalanches in wet dispersions, just like avalanches on snow-capped mountains, are thought to be catalyzed by vibrations that rarely but suddenly lead to strain localization and subsequent large-scale fluidization of compacted solids (for a demonstration, see the opening scene of the movie "Ice Age 1").

The core idea is that an external energy input of suitable power and frequency will increase the rates of coarsening, flocculation, and densification of dispersions. These will increase the probability of failure precursors appearing in the microstructure.

**Impact:** Establishing an alternative aging protocol greatly expands new tools for the analytical characterization and molecular design of advanced dispersions. The project will also advance science by enabling direct particle-level visualization of aging materials in a reasonable experimental timeframe, without intricate machining required for high temperature or centrifugation accessories on a microscope. Furthermore, the proposed acoustic protocol specifically stimulates destabilization modes associated with thermal fluctuations. Data from this project are therefore valuable in pinpointing the thermodynamic interactions that lead to flocculation and syneresis, which address persistent challenges in extending dispersion shelf life.

**Biography:** Hsiao is assistant professor of Chemical and Biomolecular Engineering at North Carolina State University in Raleigh, NC, USA. She received her B.S. in Chemical Engineering from the University of Wisconsin-Madison in 2008 and her Ph.D. in Chemical Engineering from the University of Michigan in 2014, working with Michael Solomon on the microstructure of colloidal suspensions in flowing systems. Her postdoctoral training at the Massachusetts Institute of Technology with Patrick Doyle was on colloidal nanoemulsions and 3D printing. Her group at NC State University is recognized for advancing the fields of suspension rheology and colloidal materials, through the Camille Dreyfus Teacher-Scholar Award, Sloan Research Fellowship, ACS Unilever Award for Outstanding Young Investigator in Soft Matter, NSF CAREER award, and AAAS Marion Milligan Mason Award.

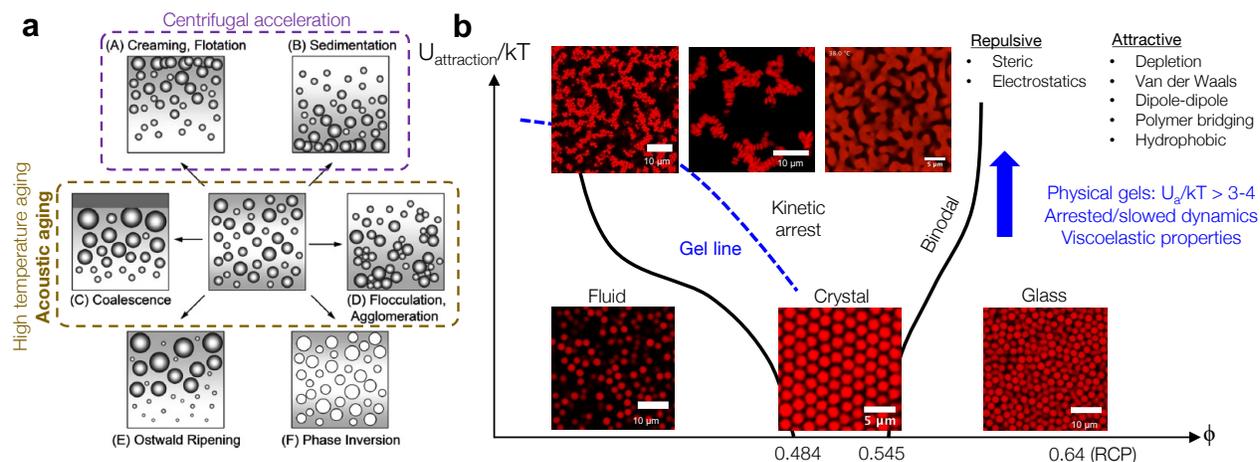
**Track record + IFPRI history:** PI Hsiao has long-standing expertise in shear-induced visualization of colloidal microstructure (PI's Ph.D. work was funded by a 2009 IFPRI project awarded to Solomon and Furst),<sup>4,10-12</sup> modeling rheological structure-property correlations,<sup>13,14</sup> and meaningful interactions with industry members spanning different technological areas<sup>15,16</sup> (2019 IFPRI collaboration grant with Vermant on simplified industrial formulations). Previously, the PI helped set up the 2009 IFPRI AGM in Michigan, and actively participated in the 2022 IFPRI meeting in Brussels. The PI has also engaged in proposals, papers, or scientific discussions with many IFPRI members as well as past and present grant holders (E. Furst, K. Daniels, J. Vermant, J. Brady, W. Poon, N. Wagner, P. Nott, amongst others).

## 2. Background and Preliminary Results

**Patent case study:** There are very few patents on aging acceleration in dispersions. Some do exist, for example in patents filed by LUM GmbH, an analytical equipment company that specializes in centrifugal aging protocols.<sup>17</sup> The method is far more commonly embedded in formulation patents that claim an improvement in colloidal stability over prior art. This is expected since methods-based patents tend to be challenging to enforce. Accelerated stability characterization is mentioned in patents that protect the chemical or polymeric modification of ink pigments,<sup>18,19</sup> color-sensitive resins,<sup>20</sup> elastomer composites,<sup>21</sup> therapeutic pharmaceuticals,<sup>22</sup> coatings,<sup>23</sup> cosmetics,<sup>24</sup> catalysts,<sup>25</sup> cement,<sup>26</sup> herbicides and pesticides<sup>27-29</sup> and many other formulation products that are of direct interest to IFPRI members.

An exemplary case study from a L'Oréal patent<sup>24</sup> shines light on the need for alternative aging tests. This patent incorporates tocopherol, resveratrol, and baicalin as low solubility active ingredients into a water-based cosmetic formulation. The inventors attempted shelf life testing by comparing one formulation at room temperature and one heated gently at 45°C for two months to simulate shelf life. Although the inventors claimed that this composition will theoretically be stable over 3 years, the heated-aging data showed that there was a 12% loss in resveratrol, 7% loss in tocopherol, and 7% loss in baicalin concentration over 2 months. The losses were a little less significant at room temperature. [The use of an acoustic aging test here would have allowed these researchers to decouple the mechanisms associated with stability, and to ultimately claim newer compositions with increased stability based on fundamental interactions between components.](#)

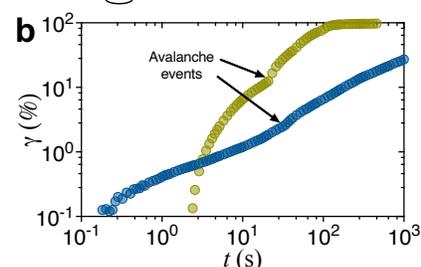
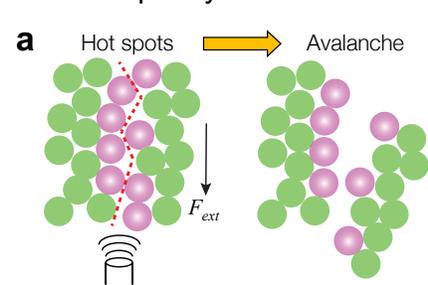
**Why dispersions age:** Wet dispersions containing multiphase components, such as solids or liquids suspended in another solvent, can either stay thermodynamically stable or become unstable over a period of time due to incompatibility. The degree to which components separate from each other is mostly due to the interplay between thermal motion, external stresses, and interaction energy.<sup>30</sup> Thermal motion refers to the amount of vibrational energy possessed by individual component, which is intrinsically dictated by temperature as well as particle size. External stresses often exist in the form of gravity, but can also be introduced as shear or electromagnetic fields. Finally, the interaction energy between the components in the formulation is responsible for the thermodynamic landscape as particles explore their surroundings through thermal motion. These three fundamental mechanisms are responsible for nearly all of the destabilization phenomena in dispersions.<sup>31</sup> Syneresis, for instance, results from an expulsion of water from hydrophobic polymers,<sup>32</sup> while coarsening in gels arises from attractive interactions between components<sup>33</sup> (**Fig. 2a**). Rheology modifiers and attractive interactions are popular ways



**Figure 2.** (a) Different types of accelerated aging tests target different destabilization mechanisms. (b) Rheological and microstructural modification of a dispersion can be achieved by adding repulsion or attraction, or by adding modifiers that increase the viscoelasticity and slow aging processes.

to kinetically arrest destabilization without resorting to high particle concentrations (**Fig. 2b**). Both methods lead to an increase in viscosity and reduce the chances of thermal collision between particles. Nevertheless, all unstable dispersions eventually age and phase separate, causing a loss in product quality and consumer acceptance.

**Microscopic hot spots as failure precursors:** Failure in dispersions is observed macroscopically as a reversible or irreversible loss of product consistency, including syneresis,



**Figure 3.** (a) It is possible to use external energy to increase the activity of microscopic hot spots (pink), regions of highly mobile components that develop into slip planes and avalanches. (b) Preliminary results of rare avalanches in a colloidal hard sphere suspension sheared below the bulk yield stress.

sedimentation, and phase separation. They can also be detected as avalanche or stick-slip events in creep testing, and as transient slip bands in optical imaging or scattering experiments. Although the connection between failure and microstructure is not well established for wet systems, previous studies found microscopic hot spots in sheared granules, which manifest as localized regions of ballistic particle mobility (**Fig. 3a**). When these hot spots appear in suspensions under creeping flow, experiments show that they are correlated with intermittent stick-slip events and large stress fluctuations. Preliminary experiments on colloidal suspensions sheared below the bulk yield stress show avalanche behavior (**Fig. 3b**) which are likely due to the appearance of hot spots that grow into slip planes that enable collective rearrangements of large clusters. This class of non-local failure mechanism is expected to be similar to polymeric materials undergoing brittle fracture, with a probability distribution function for the time to failure,  $t$ , that scales as  $p(t) = (\alpha\beta)(t/\beta)^{\alpha-1}e^{-(t/\beta)^\alpha}$ , where  $\alpha$  and  $\beta$  are fitting parameters.<sup>34</sup> The addition of external fields, including acoustic perturbations, will skew  $p(t)$  to shorter times depending on the magnitude and frequency of the applied force.

**Existing aging tests:** Aging tests are used to monitor the mechanism of failure in dispersions and to (re)-design formulations for extended shelf life. The aging rate also plays

a critical role in dispersion design. Centrifugal or tilt tests increase the sedimentation and creaming velocities of density mismatched formulations,<sup>35</sup> while elevated temperature<sup>36</sup> and the proposed acoustic tests increase the coalescence and flocculation rates (**Fig. 2a**). Complexities arise from inherent nonlinear changes in the material's mechanical and microstructural properties with real time, which may or may not track linearly with accelerated tests. Generally speaking, because aging is an activated process, the kinetic rate of change scales with temperature up to a point where there is a phase change in the microstructure (e.g.: near the glass transition point in polymers<sup>37</sup>). The pathway of change could obey zeroth, first, or second order kinetics, and there may be an induction time before any change occurs.<sup>38</sup>

### 3. Research Plan

The goal of this project is to develop an easy-to-use, scalable, and potentially translatable acoustic platform that can be used to rapidly age various industrial dispersions. The acoustic setup will be made compatible with optical microscopy and rheometry setups such that predictive structure-property relationships can be extracted. Experimental validation will be conducted using a select set of real-aged and heated colloidal gel samples. The acoustic aging method represents a paradigm shift from standard temperature and centrifugation methods because it allows for the testing of sensitive formulations, for example those that contain biologics and lipid particles.

The proposal is written based on a 6-year timeframe: Phase I of the project will generate predictions of dispersion stability based on age-accelerated and real-aged samples. The acoustic platform will be supported with bulk rheometry and optical microscopy analysis. Phase II will build upon the prior results from acoustic aging tests to increase the shelf life of IFPRI formulations.

The goal of Phase I is to use acoustic aging to predict how dispersions destabilize, by following changes in their rheology and structure over time.

The goal of Phase II is to intelligently design formulations with improved resilience.

### **Years 1-3 (Phase I)**

#### 1) *Refine aging formulations based on IFPRI membership needs*

- Incorporate polymer and small molecules relevant to industry base (Y1, Q1)
- Ensure the use of well-established material parameters (e.g.: size, fluorescence, interaction potential) that are within specification limits (Y1, Q1)

#### 2) *Compare rheology of dispersions with and without acoustic stimulation*

- Install and validate acoustic transducers on stress-controlled rheometer (Y1, Q2)
- Measure viscosity and viscoelasticity of stimulated gels over time (Y1, Q3-4)
- Quantify creep, recovery, and avalanche behavior for IFPRI samples (Y2, Q1-4)
- Check differences between acoustically stimulated samples and heated samples (Y2, Q1)

#### 3) *Visualize hot spots in accelerated, commercial, and real-aged samples*

- Identify microscopic "hot spots" in real-aged colloidal gels using structure-dynamics correlations at single particle level (Y2-3)
- Conduct similar imaging analysis of for acoustic-aged and heat-aged gels (Y3, Q1-2)

#### 4) *Generate stability phase diagrams*

- Demonstrate correlation of aging in accelerated and normal conditions (Y1-3)
- Generate phase diagrams for different dispersions as a function of acoustic power and frequency, focusing on points where the rate has increased by >100x (Y1-3)
- Obtain physical understanding of relationship between acoustic power, frequency, interaction potential, and diffusion time (Y2-3)

#### 5) *Obtain predictive correlations for aging and failure*

- Correlate destabilization rate with interaction parameters (e.g.: solubility index, interfacial energy, volume fraction, attraction range and strength) (Y3-5)
- Rank dispersion parameters based on probability of failure (Y3-6)

### **Years 4-6 (Phase II, if funded)**

#### 6) *Prototype and test acoustic transducers on confocal rheometer*

- Translate acoustic setup to confocal rheometer for simultaneous aging, microstructural, and rheological measurements (Y5-6)
- Ensure that results are reproducible with respect to Phase I (Y5-6)

#### 7) *Model microstructure, failure precursors, and aging*

- Compute structural and resilience properties using network science models (Y4-5)
- Conduct statistical analysis of failure probability based on network parameters (Y5-6)

#### 8) *Targeted design of IFPRI formulations for extended shelf life*

- Inverse design dispersions to arrest aging and reduce fragility (Y6)

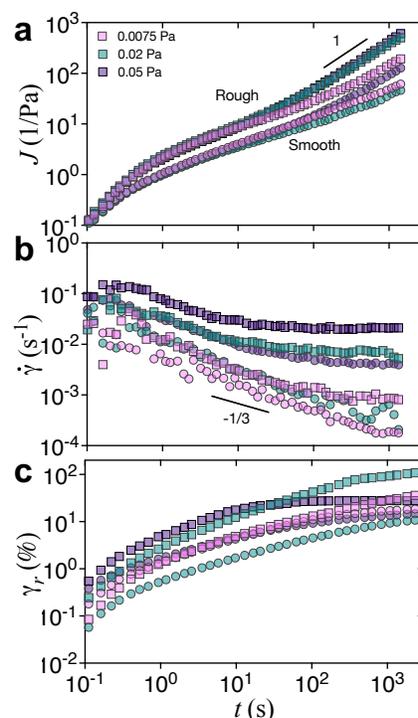
**Budget:** The PI's National Science Foundation grants will be used in parallel with IFPRI funds to support 2-3 Ph.D. students working on this area. [The PI is interested in collaborating with industrial partners to write NSF and DOE grants to advance manufacturing readiness \(early 2023\).](#)

## Methodology

**Creep and avalanche rheology:** All IFPRI dispersions will be characterized using creep and recovery protocols, where the compliance scaling with time reflects solid-to-fluid transitions and intermittent yielding, and the recovery data indicate the degree of non-affine plastic deformation in the material. The plan is to subject the dispersions to stresses on the order of gravity or below the bulk yield stress to represent the storage of products in realistic environments. High quality results at low stresses are possible in the PI's lab because of a customized rheometry protocol that eliminates preshear history effects and minimizes axial force variations, such that the effects of particle interactions on rheology are measured rather than extraneous effects such as meniscus surface variations, osmotic pressure differences, sample aging, or other instrument errors. Bulk rheological measurements will be performed on a TA Instruments DHR-2 stress controlled rheometer, with sandblasted geometries for slip reduction, temperature ramping capabilities, and solvent evaporation reduction. Preliminary creep and recovery studies performed on a set of smooth and rough colloids at maximum packing are shown in **Fig. 4**. The results indicate easier fluidization of rough colloids possibly due to collective motion in shear.

**Acoustic transducer setup:** To enable acoustic aging, a piezoelectric ultrasound transducer will be installed on the TA DHR-2 and Anton Paar MCR 302 rheometers in the PI's lab. The transducer will be purchased from commercial vendors such as Imasonic or Sofranel. The vibration frequency and amplitude of the transducers will be adjusted using a power amplifier and an oscillatory function generator. These transducers are known to be compatible with rheometer bottom geometries.<sup>5</sup> The magnitude of the acoustic pressure will be kept below the yield stress of the dispersion so as not to introduce nonlinear deformations, while the frequency will be varied with respect to Brownian diffusion time scales. The frequency of the acoustic perturbations could also be an added way to decouple physical mechanisms of aging: higher frequencies target hydrodynamic interactions, while lower frequencies target the mobility of particles in the dispersion.

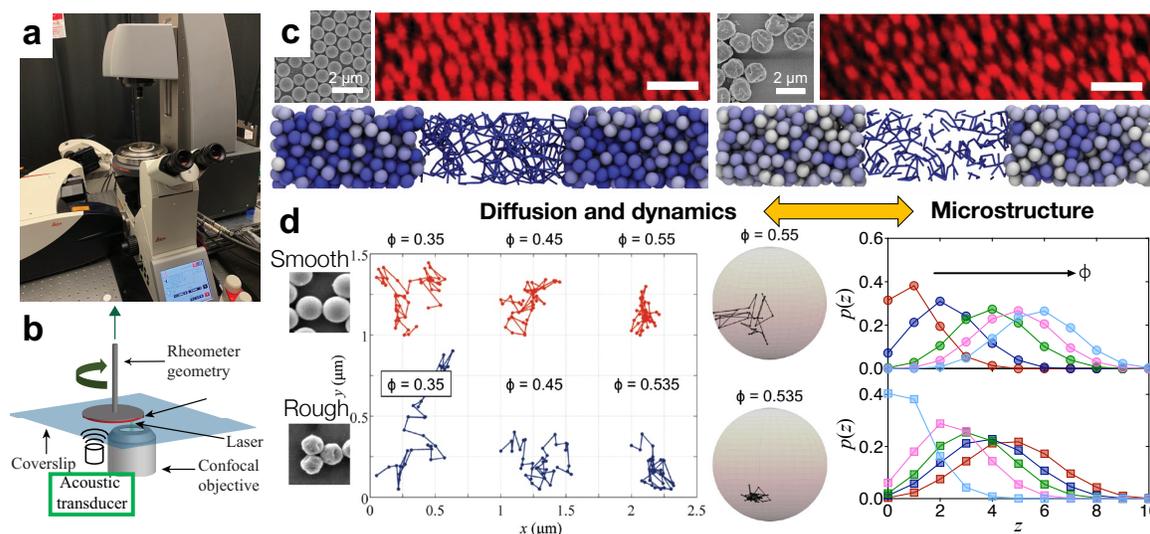
**Direct visualization with confocal rheometry:** The presence of hot spots, or "plastic centers", will be tracked using the PI's confocal rheometer setup (**Fig. 5**). This instrument captures particle-level rearrangements in sheared materials, for instance in the PI's recent work on shear thickening suspensions.<sup>13</sup> First, the experiments will be conducted with real-aged, density mismatched colloidal gels containing fluorescent particles that allow the simultaneous measurement of creep compliance with microstructural changes. Measurements with and without an applied shear stress. The data will be benchmarked against results obtained from the stand-alone rheometer. Second, microstructural evolution of the gels will be tracked without the application of a shear stress. The dispersions will be placed in a separate glass vial equipped with a thin glass coverslip such that microscopy visualization can take place over months or even years. Once the image processing parameters are optimized for a model colloidal system, concurrent measurements of the translational and rotational diffusion and the contact network distribution will be made (**Fig. 5d**). Network parameters that provide excellent distinction of the local microstructure will be obtained using the Gaussian mixture model and graph theories.<sup>39</sup> This connection between particle-level dynamics and structure will enable the identification of hot spots, defined as particles that have



**Figure 4.** Preliminary (a) creep, (b) strain rate, and (c) recoverable strain data collected for smooth and rough colloids at concentrations just below the maximum jamming fraction. They show that dispersions near or below the yield stress show intermittent flow related to failure precursors.

few connections to nearest neighbors and with the highest mobility. After this point, acoustic transducers will be installed on the confocal rheometer to accelerate aging.

**Models of aging and failure:** In addition to ongoing collaborations with computational experts on simulations that incorporate hydrodynamic lubrication and particle shape effects, the PI will explore ways to model failure based on Ising models and soft glassy rheology. The Ising model is applicable for jammed states with and without frictional frustration, and has been well correlated to the contact mechanics scalings of packed granules.<sup>40 41</sup> This model may be especially appropriate for non-Arrhenius states that lead to failure. Soft glassy rheology is useful for activated processes such as stress relaxation<sup>42</sup> and aging<sup>43</sup> of colloidal gels, and may provide guidelines associated with the energy required for hopping. This energy barrier is important in designing particle interactions that will increase microstructural uniformity and reduce the occurrence of hot spots. Modeling aspects will be studied more fully in Phase II of the project.



**Figure 5.** The knowledge creation portion of this project is to locate microscopic precursors to failure in dispersions. This information is not only important scientifically, but is also crucial to the inverse design of IFPRI formulations. (a, b) A confocal rheometer platform in the PI's lab will be outfitted with acoustic transducers to track hot spots in creeping dispersions. (c) This instrument has previously resulted in a clear picture of the networks formed by shear thickening suspensions of smooth and rough colloids.<sup>13</sup> (d) The proposed method to identify microscopic hot spots is to locate particles that have very high diffusivity and few nearest neighbors. This can be done with image processing algorithms that track the particle trajectories and microstructure.<sup>4,10</sup>

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