Computational and Theoretical Modeling of Complex Particulate Suspensions

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Overview

The objective of this work is to advance computational modeling capabilities for colloidal and non-colloidal particulate suspensions that more accurately and efficiently represent the complexity of real product formulations. Specifically, models will incorporate new algorithms for higher-fidelity representation of complex surface chemistry that leads to complex attractive and repulsive interactions including patchy electrostatic interactions, surface chemistry, and temperature-, salt-, or pH-sensitive attractive or repulsive forces that impact material phase transitions and flow behavior. Simulation of long-range many-body hydrodynamic and lubrication interactions endemic to these materials will be conducted with higher than ever efficiency for a million or more particles, owing to recently parallelized architecture of Stokesian dynamics simulations. In addition, our substantive expansions of the LAMMPS algorithm provide an important complement, with ultra-fast processing for suspensions in which hydrodynamic interactions are weak. Particle-scale interactions and motion will be interrogated at the microscopic level and connected to macroscopic material behavior and will provide a tool for iterative refinement of particle formulation and material performance. The advanced tools developed in the proposed research will be used to model and further the understanding of the impacts of complex composition on the gravitational collapse of colloidal gels, on the colloidal glass transition, and flow-induced changes in particulate microstructure. This work aims to synergize with the experimental investigations of Professor Jan Vermant (ETH) on the impact of complex surface conditions on suspension rheology. The outcome of this work will be an expansion of computational modeling capabilities available to industrial scientists for understanding and engineering particle interactions to control the flow of particulate suspensions, gels, and glasses.

Background

Colloidal gels, glasses, and suspensions form the vast majority of industrial-coating materials, most pharmaceutical fluids, over 95% of biological fluids, and are ubiquitous across personal-care and agricultural formulations. Despite the pervasiveness of these fluid-suspended, microscopically small particles (colloids), many of the behaviors of these materials have long defied explanation – such as the sudden collapse of colloidal gels, vitrification that thwarts crystallization, aggregation of therapeutic antibodies which can either destroy or enhance function, and discontinuous changes in viscosity as a few examples. A desired goal in the study of these materials is a direct predictive relationship between micro-particle formulation, suspension preparation, and macroscopic material performance. Progress in the last several decades has been substantial including

1. Advances in theoretical understanding of microscopic forces (electrostatic, hydrodynamic, Brownian, for example) and how these underlie dramatic changes in suspension behavior;
2. Development of model experimental systems; and
3. Modern computational algorithms and processors that enabled study of individual particles and their interactions, as a complement to experimental studies.

These developments answered many open questions in the behavior of dilute to moderately concentrated suspensions of spherical colloids – such as the origin of shear thinning, shear thickening, normal stress differences, and more recently, discontinuous shear thickening. These scientific advancements translated to impacts on industrial formulations science and engineering. However, wet particulate systems are typically more richly structured, including particles of varying size

and shape, with chemical and electrostatic interactions that lead to complex phase behavior, and systems that explore phase arrest such as gelation and vitrification. As a result, many of the basic science advances in understanding materials performance leave gaps in the understanding of e.g. impact of particle loading on 3D printing flow, vitrification during curing, gelation, gel collapse, and flow-induced aggregation and stability in the more complicated industrial systems. Understanding the particle-to-property relationships of these materials requires further advancements in computational modeling. The current frontier in the computational modeling of particulate suspensions resides in the incorporation of high-fidelity particle-particle interactions that faithfully mimic those in the real suspension, a challenge that requires deep connection between molecular-scale modeling, experiments, and colloidal-scale modeling. In addition, the high particle loadings endemic in these applications drive the need for very large-scale computational models capable of sampling the vast spectrum of structural self-assembly and relaxation modes.

In simple colloidal fluids for example, a competition between Brownian relaxation and imposed flow can produce pronounced shear thinning, and hydrodynamic forces can induce shear thickening[1,2] central to the flow behavior of foodstuffs such as mayonnaise[3–5] or industrial fluids such as polymeric solutions used for enhanced oil recovery[6]. Changes in concentration can increase viscosity and amplifies overall non-Newtonian shear-thickening and shear-thinning behavior. Increased interparticle repulsion can dramatically reduce hydrodynamic shear thickening[7] but direct frictional contact can lead to discontinuous shear thickening[8,9]. Thermodynamic phase change can also be triggered, such as crystallization by increasing colloid concentration[10], but even within one thermodynamic phase, changes in the interactions between particles can produce dramatically different microstructures and in turn, mechanical behaviors. This phase/property relation is extensively exploited in the processing of dairy products. A familiar example is milk, a special colloidal suspension that comprises fat droplets suspended in water, which forms an oil-in-water nano-emulsion. Processing techniques such as heating, acidification, and enzyme treatment control the size and interactions between the droplets to produce dairy products such as cream and yoghurt or imbue unique textures to cheese. Another broad colloidal material class is industrial coatings, which leverage particle attractions and phase transitions for curing and development of color and electronic properties. For example, phases of colloidal laponite[11,12], pigment[13,14], or metal oxide particles[15,16] can be fine-tuned to create colloidal films that impart corrosion resistant glazes, color, and magnetic properties for storage. Techniques such as attraction-driven self-assembly or evaporation-driven convective assembly that sculpt crystalline, glassy, or bi-continuous network structures have been developed for manufacturing paint[13,14], ceramics[17,18], magnetic storage[15,16], and biomedical devices[19,20]. Despite the sophistication of structural and rheological characterization methods, techniques for fine tuning structure and rheology of novel materials such as vegan dairy and meat products to mimic their traditional counterparts or industrial coatings with any color and desired selective permeability are typically empirical.

Overall, this ubiquity of applications of colloidal soft matter drive a need for predictive models that connect processing conditions with structure and properties to enhance and fine-tune performance. Hard-sphere colloids are the workhorse model system for colloidal phase behavior, where two parameters determine the thermo-dynamic/equilibrium state of the system: particle-scale interactions and colloid concentration. The potential of interaction between colloids in suspension can be modulated to trigger equilibrium phase transitions and formation of non-equilibrium "states" such as gels. Faithful representation of phase behavior in dynamic simulation requires analytical or numerical modeling of the potential that accurately mimics those in the experiment. Such high-fidelity representation is essential to realizing the power of simulations to interrogate microscopic detail.

Prior Approaches to Dynamic Simulation of Colloidal Systems

Simulating hydrodynamically-interacting colloids. Several methods bypass the difficulty of solving directly for fluid motion in dynamic simulation while accounting for hydrodynamic interactions between particles. These include primarily Fast Multipole Methods (FMM) and Stokesian Dynamics (SD). Originally developed for electrostatics[21], FMM has been applied to Stokes flow by expanding the surface integral for fluid velocity into a hierarchy of traction moments[22–27] and VSH developed recently by Corona *et. al*[28] can be leveraged to compute accurate value of boundary integral operators to accurately capture lubrication interactions[28,29]. Stokesian Dynamics overcomes this difficulty via a clever superposition of near-field and far-field behavior[30–33]. Fluid motion is bypassed by inserting the velocity into Faxén formulae to obtain particle motion, without ever having to explicitly compute disturbance flows. Fluid drag and hydrodynamic interactions are encoded directly into the fundamental couplings between surface tractions and particle motion: the surface integral is handled by Taylor-expanding the Green's function for Stokes flow about the center of the particles, which allows closure into a well-ordered series of multipole moments. When summed over all particles, this expression for the velocity gives the disturbance flow created by motion of any number of background particles. It is expressed compactly as a matrix equation relating particle motion to surface tractions, but is infinite in rank and must be truncated to a finite number of traction moments prior to inversion, ultimately producing a many-body coupling for particles separated by a few diameters or more. Because Stokes flow are linear, this far-field coupling can be superimposed with the near-field coupling, which at close separations has well known analytical solutions[34–37]. As a result, Stokesian Dynamics accurately models many-body hydrodynamic interactions, lubrication interactions, and correlated Brownian motion. Its primary challenges are the development of the coupling tensors and computationally handling the inversion of a dense matrix and taking its square root.

The Stokesian dynamics algorithm changed the landscape of the study of low-Re number particulate flows by making accessible the study of real systems where many-body effects and lubrication forces (e.g dense suspensions) play a role. It established dynamic simulation as an important complement to experiments, free of many of the assumptions made in dilute theories. The ability to monitor detailed particle positions and trajectories provided crucial insight inaccessible to experimentalists until decades later when microscopy methods advanced. This produced mechanistic understanding of key non-Newtonian behaviors of flowing Brownian suspensions, including the role of hydrodynamic interactions in shear thickening and verification that weakening Brownian motion, rather than a disorder-to-order structural transition produces shear thinning[38,39]. Stokesian Dynamics provided also a verification of theoretical models and insight into many other suspension phenomena[32,40,41]. More recent expansion of the Stokesian Dynamics algorithm includes modeling confined suspensions, which require deriving new Faxén relations and mobility functions[42–44]. Arbitrary geometries of the particles would require as well new Faxén relations and hydrodynamic functions, or to approximate the particle as an assembly of spherical particles[45,46]. The primary limitations of Stokesian dynamics center on matrix operations, where in conventional SD[31] the expensive step of inversion has $O(N^3)$ complexity (where N is the number of particles) and the expensive step of the construction of the dense far-field matrix has $O(N)$ complexity. These steps (inversion and construction) can now be avoided entirely in Accelerated Stokesian Dynamics (ASD). Here, based on the efficient scheme of Hasimoto for a periodic array of spheres in a Stokes flow[47], a judicious Ewald splitting[48] of the many-body far-field interaction into a real space contribution (with near- neighbor interactions only) and a wave space contribution permits

the use of Fast Fourier Transforms (FFT)[49] to obtain $O(N \log N)$ scaling[50,51]. Combining this strategy within a nested scheme with matrix-free iterative solvers such as GMRES[52] has reduced the simulation complexity from quadratic to linearithmic with the number of particles[40,50]. The $O(N \log N)$ scaling of ASD changed the game dramatically and enabled the accurate and fast study of $O(100)$ particles systems with many-body hydrodynamic interactions, by operating matrix free and thus bypassing the expense associated with inversion. However, Brownian motion requires the information in the now-unavailable mobility matrix; until recently, the far-field Brownian force has been computed either with a Chebychev approximation[51], an O.D.E technique[42,44,53] or a Krylov method[54]. A strategic choice of implementation can enhance performance significantly: serial computation is limited to $O(10)$[31] and $O(100)$ particles[50]. Recently Stokesian Dynamics was implemented on a single GPU on a shared memory architecture and is able to simulate from $O(10,000)$[53] to $O(100,000)$ particles[46], where efficient algorithms were designed to account for the GPU architecture.

Simulating other microscopic forces. Progress in the last several years in the computational modeling of colloidal gels and glasses has permitted unprecedented particle-scale interrogation that has shed light on long-standing issues such as gel collapse and delayed shear yield, as well as mechanistic understanding of the colloidal glass transition. However, detailed quantitative matching between simulation and experiments even in simple hard-sphere systems has been challenging. One of the key requirements for constructing computational models that accurately represent the real laboratory material is a means by which to match particle-scale interactions between colloids *in silico* to those in the experimental system. The typical approach in simulations is to select one of several standard analytical potentials with a nominal strength and range that matches those reported in the experimental literature. However, the experimental measurements typically rely on indirectly inferring the pair-level interparticle potential using a combination of measurements of microstructure – in dilute suspensions obtained via scattering techniques such as small angle x-ray or neutron scattering (SAXS or SANS). These techniques require diluteness and equilibrium conditions to avoid complex data analysis of measured scattering data[55]. Thus, it is typically assumed that the interparticle potential in dilute conditions is sufficient to describe interactions for dense samples, and that measurements of equilibrium structure alone can be utilized to construct a potential model that can accurately represent attractive forces between particles in simulation. However, these assumptions fail when the attractive forces are long-ranged and potentials developed from these techniques fail to accurately predict equilibrium and non-equilibrium phase boundaries as the detailed interaction profile influence the location of such boundaries[56].

Our Approaches

Simulating Hydrodynamics: "Parallelized Stokesian Dynamics with Brownian Fluctuations" [Ouaknin, Su & Zia, J. Comp. Phys., 2021][57] We recently developed a suite of scalable algorithms to simulate large-scale stochastic particle systems amenable for modeling dense colloidal suspensions, glasses and gels with full hydrodynamics. To handle the large number of particles and consequent many-body interactions present in such systems, we leverage an Accelerated Stokesian Dynamics (ASD) approach, for which we developed parallel algorithms in a distributed memory architecture. We parallelized the sparse near-field (including singular lubrication) interactions, and the matrix-free many- body far-field interactions, along with a strategy for communicating and mapping the distributed data structures between the near- and far field. We demonstrated good scaling to for a million particles distributed over tens of thousands of processors. In addition, we developed a novel algorithm to efficiently simulate correlated Brownian motion with hydrodynamic

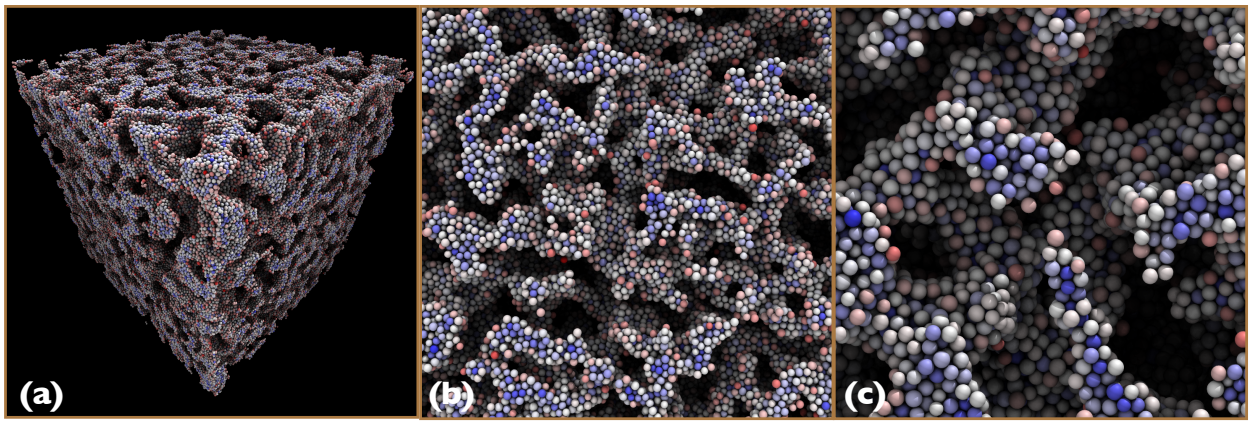

Figure 1: Snapshots of a colloidal gel from dynamic simulation. (a) One periodic cell. (b) 2x magnification. (c) 4x magnification. Number of contacts per particle indicated by color, ranging from red (few) to blue (many).[58] Cross sections of gel strands reveal high-contact number interior particles and glassy interior morphology.

interactions. The original Accelerated Stokesian Dynamics approach requires the separate computation of far-field and near-field Brownian forces. Recent advancements propose computation of a far-field velocity using positive spectral Ewald decomposition, but we constructed an alternative approach for calculating the far-field Brownian velocity by implementing the fluctuating force coupling method and embedding it using a nested scheme into ASD. This straightforward and flexible approach reduces the computational time of the Brownian far- field force construction from $O(N \log N) + |\alpha|$ to $O(N \log N)$. Details of our method can be found in Ouaknin et al., J. Comp. Phys. (2021)[57]. We have implemented an interparticle interactions algorithm that represents a basic isotropic attraction and repulsion between particles, and demonstrated phase separation, gelation, and vitrification behavior.

Simulating Complex Surface & Processing Conditions: Expanded LAMMPS. We have recently developed a new algorithm that combines experiments and simulations that accurately predicts not only equilibrium phase transitions in colloids, but also gelation, vitrification, and self-assembly into complex structures[58–61]. We expanded the existing LAMMPS software package to implement time-dependent adjustment of pairwise-interaction forces that can mimic laboratory "quenches" in temperature, pH, or concentrations that change interparticle interactions over time. The novel framework includes an iterative process for analyzing scattering measurements data to construct an interparticle potential. The framework is agnostic to the size, shape, or topology (e.g. patchy interactions) of particles and interactions and is thus suitable for a wide range of particulate systems found in natural, biological, and industrial samples. To streamline the analysis of large simulation outputs, our group also developed a suite of post-processing code that can quickly assess the microscopic and macroscopic structure, rheology, and tortuosity of suspensions and solids formed in our simulations. Thus, our framework for extracting potentials, simulation tools, and post-processing code can be pipelined to interrogate in vitro samples to construct a computational model that can be subjected to simulations that replicate laboratory samples. In our current work, we demonstrated an application of our tools to extract an interparticle potential from a laboratory model thermoresponsive nanoemulsion system and implement it simulation. The resultant simulations produce a close match in equilibrium and non-equilibrium phase transitions.

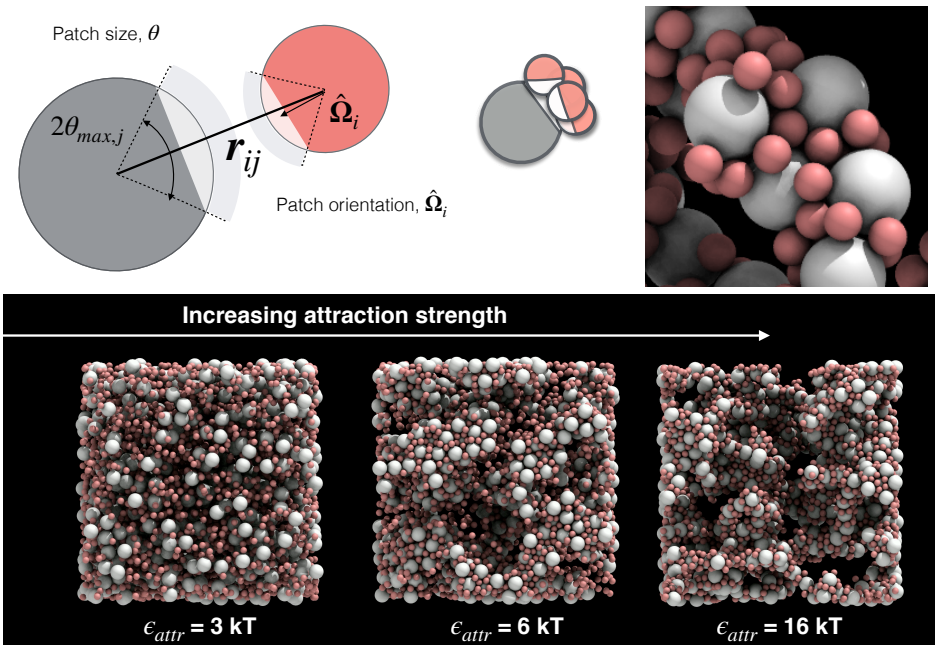

Figure 2: (Top) Patchy colloidal interaction model in which surface patches (light colored regions), characterized by patch size θ attract, represent charged surface patches. Implementation of patchy surfaces result in orientation-dependent bonding *in silico* that. (Bottom) Simulation snapshots of size-polydiseprse colloids with patchy interactions of various attraction strength. Increasing attraction strength produces distinct morphology. [62]

Proposed Work

We propose to advance the modeling of industrially-relevant complex particle systems by expanding our current models beyond smooth hard-sphere colloids. To do so, we propose to systematically incorporate a set of physico-chemical surface conditions into our models, interacting with experiments and molecular-dynamics simulations to refine the detailed representation of interactions. We will then apply our models to the study of three important problems in colloidal systems: colloidal gelation; gravitational collapse of colloidal gels; and flow-dependent rheology of dense suspensions.

Aim 1. We will expand our LAMMPS models to incorporate surface roughness, bumpiness, and thermo-sensitivity of size and hardness.

Specific Objective 1: Represent more complex particle interactions.

We will construct new particle-interaction algorithms, and utilize collaboration with experimentalists and molecular-dynamics level simulations to refine the detailed interactions between particles.

(a) Patchy interactions: Attraction and Repulsion Valency: We will make use of and adapt existing functionality within LAMMPS to model patchy distribution of surface charge on particles. Our initial model was recently validated [Figure 2] [62,63].

(b) Orientation of surface patches: We plan to utilize an existing framework in LAMMPS, previously used for representing ellipsoidal particles, to track the orientation of patchy particles via quaternions. The use of quaternions, rather than unit orientation vectors in Euclidean space, allows for rapid computation of orientation-dependent attractions and rotational diffusivity. This framework can be applied to simulation of particles with additional shape anisotropy.

(c) Chemical reactions: Reactive networks in dense inorganic systems require a complex coupling of chemistry and physics, involving diffusive transport, entropic exclusion, detailed particle interactions, and combinatoric matching between reacting components. Both the detailed colloidal-scale physics and interaction chemistry must be represented with detailed kinetic parameters and spatial representation of proximity at which reaction proceeds. We will incorporate our recently developed

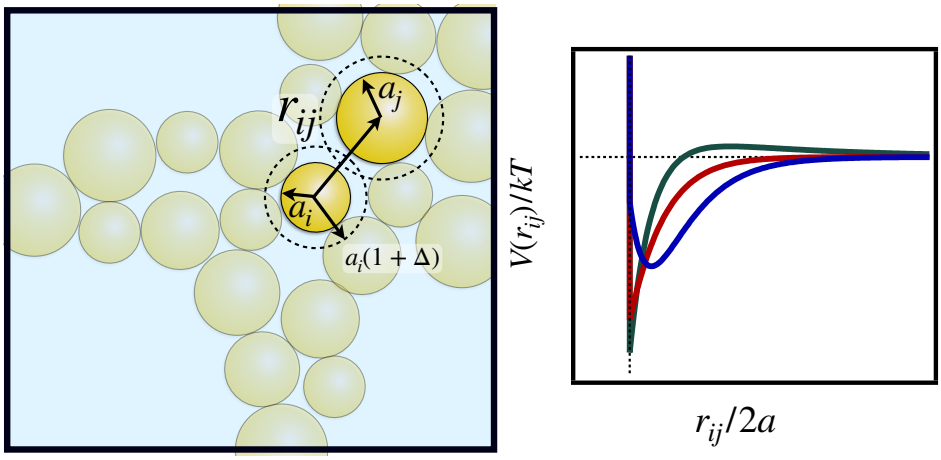

Figure 3: Our recent algorithm can develop experimentally-derived particle interactions that mimic equilibrium and non-equilibrium phase transitions in laboratory samples.[65] The computational model constructed in our expanded LAMMPS can represent this interparticle interaction, that can take any range or detailed shape.

reactive combinatoric chemistry framework into LAMMPS, because it is well-suited to model large system sizes of dense, interacting particles. While the physics of particles and their interactions will be represented in the robust LAMMPS framework, we will adapt an existing chemical reaction framework, SRSim[64], to model combinatoric chemistry occurring between macromolecules.

Specific Objective 2: Increase computational efficiency. We will implement a hybrid-style pair potential in order to selectively add patchy attractions to desired particle pairs in a system. Use of such a hybrid approach can be up to an order-of-magnitude more efficient than conventional approaches, particularly when scaling to large system sizes of dense, heterogeneous systems. Practically, it would also allows the user to easily tune the model's microscopic interaction characteristics to match experimental systems, including the valency and specificity of each type of patchy particle.

Specific Objective 3: Validate and refine the model against other colloidal models. We will first validate our patchy dynamic model in well-studied limits: purely repulsive hard spheres, isotropic attractions where the patch covers the entire surface, and Janus particles.

Aim 2. We will iteratively refine our potential interactions via collaboration with experimentalists and molecular dynamics simulations.

Specific Objective 1: Match to experiments. We recently developed an algorithm for detailed matching of the interactive potential of an experimental system to both equilibrium and non-equilibrium phase transitions and complex self-assembly [Figure 3][65,66]. We will expand this algorithm with additional models of the interactive potential for anisotropic interactions. We will then carry out the matching process via iterative refinement with experiments to select best representative potential.

Specific Objective 2: Match to molecular dynamics simulations. Insight from MD simulations will also be leveraged to improve bio-fidelity of coarse-grained models, which can evolve systems of hundreds of thousands of polydisperse macromolecules over milliseconds[58] while retaining both spatial and temporal resolution of individual particle dynamics. Such resolution enables interrogation of the coupled spatio-temporal impacts of transient interactions that can operate and drive behavior over disparate length- (nm to μm) and timescales (ns to ms). Through our advances in modeling biological fluids, we can simulate highly polydisperse suspensions (e.g. tridisperse size ratios of 1:3:6) in LAMMPS with millions of particles. Even systems with moderate to strong inter-particle attractions can be evolved over millisecond timescales in reasonable compute times.

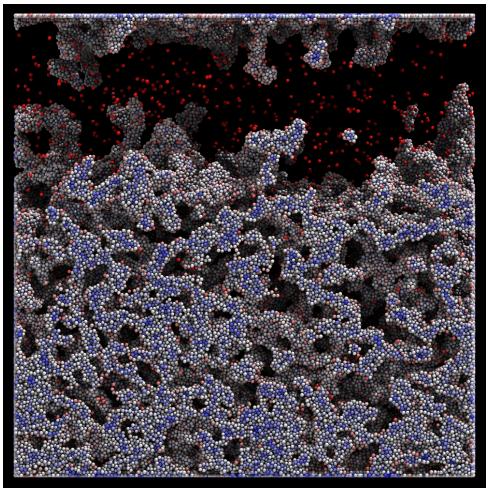

Figure 4: Simulation snapshot of an *in silico* gravitational collapse of a colloidal gel that replicates delayed gravitational yield observed in experiments.[59] We find that gravitational collapse is activated phase separation, driven by negative osmotic pressure and assisted by gravitational forces.

Aim 3. Incorporate the new particle interaction algorithms into our Parallelized ASD model.
Specific Objective 1: Represent size polydispersity in ASD. Representing size polydispersity in the ASD environment requires adapting new spectral methods into the domain discretization. We will incorporate these changes into our model during the first two years of the project. Incorporating the other representations of particle surface conditions and interactions is far simpler, and can occur alongside this development.
Specific Objective 2: Represent patchy and other interactions already validated in LAMMPS in ASD. These pairwise interactions involve non-hydrodynamic modules in the ASD algorithm that must be modified separately.

Aim 4. Explore the impact of complex surface conditions on rheological behavior.
We will utilize our existing tools for measuring structure (static structure factor; pair distribution function, contact-number distribution, crystal fraction, local volume fraction distribution),[58,59] dynamics (diffusion via mean-square displacement, dynamic structure factor, bulk flow),[67–69] and rheology (osmotic pressure, shear stress, viscosity, normal stress differences, linear viscoelasticity, etc.)[70]. We can impart linear oscillatory shear, sudden startup of shear flow, gravitational forcing, imposed step stress and more and connect these in detail to changes in particle conditions such as interactive potential, or changes in sample preparation such as condensation, gelation or vitrification conditions. We can also track bond orientation, bond stretching and compression, cluster size distribution, as well as a host of other particle- and mesoscale structural effects of changes in particle interactions and processing conditions. Moreover, we can track each of these metrics during phase transitions, flow, and response to imposed fields and forces, as during aging of arrested states of the material. We will explore the impacts of complex colloid surface conditions on gravitational collapse [Figure 4],[59] the colloidal glass transition, and non-Newtonian rheology in dense suspensions.

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