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. The long-term goal is construction of models that incorporate new algorithms for higher-fidelity representation of sophisticated chemical and physical interactions including patchy interactions (physical valency), size and shape polydispersity, chemical reactions, bumpy surface topography, and temperature-, salt-, or pH-sensitive attractive or repulsive forces that impact material phase transitions and flow behavior. **The nearer-term focus of this proposal focuses on representing size polydispersity, detailed matching of interactions between particles to experimental systems, and modeling bumpy particle shapes.** Long-range many-body hydrodynamic and lubrication interactions are important in some industrial suspensions and unimportant in others; to address both regimes, the stated objectives will be carried out in our two primary simulation platforms. For suspensions in which particles experience strong hydrodynamic interactions, we will implement the new algorithms into our Parallel Accelerated Stokesian Dynamics with Brownian Motion (PASD-B). For freely-draining systems, we will implement the new algorithms into our adaptation of the LAMMPS algorithm. In both platforms, massive parallelization provide high computational efficiency. Microscopic particle and interaction detail will be connected to macroscopic material behavior and will provide a tool for iterative refinement of particle formulation and material performance, using our existing suite of post-processing codes. The advanced tools developed in the proposed research will be used to model and further the understanding of the impacts of size and shape polydispersity as well as sophisticated surface attraction and repulsion on suspension flow, gelation and vitrification, with options to study impact on gravitational collapse of colloidal gels. This work aims to synergize with the experimental investigations of Professor Jan Vermant (ETH) and Matthew Helgeson (UCSB). 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.

SCIENCE 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 primary goal in the study of these materials is direct predictive relationships 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. 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.

Phase/property relations are extensively exploited in the processing of food and industrial 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, because computational models lack much of the details of particle attributes in these more complex but very common systems.

Modeling Challenges

Hard-sphere colloids have been 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. However, as noted above, most industrial suspensions involve colloidal particles that are irregular in shape, polydisperse in size distribution, squishy, soft, or porous, and which experience short- and long-range attractions and repulsions that can shift with changing temperature or other environmental triggers, and thus dramatically alter flow rheology, phase behavior, curing, and long-term stability. Predictive modeling of such behavior in dynamic simulation requires advances in algorithms to accurately mimic particle interactions and the impact of real processing conditions. While molecular-dynamics simulations is capable of representing such detailed interactions between pairs of particles, predictive models of entire suspension behavior requires representation of these interactions between hundreds of thousands of particles in large-scale models — and such large-scale modeling capability lags far behind.

Advancement requires multi-scale connection between molecular-scale modeling (which can explicitly represent individual solvent and other molecules that give rise to interactions between colloids, but are severely limited in duration and system size owing to the extremely high resolution of molecular modeling) and meso-scale modeling such as Stokesian dynamics or Brownian dynamics, which can simulate very large suspensions but coarse-grains particle interactions. In addition, verification that a computational model produces the same material behavior as the experimental system (effective viscosity, viscoelastic moduli, osmotic pressure, phase and gel lines) is essential, and this requires algorithms to iteratively refine computational models to experimental systems. Together, these three — molecular-scale modeling, colloidal-scale modeling, and experiment are the three legs required to support a comprehensive modeling effort.

Dynamic Simulation of Colloidal Systems

Colloids are microscopically small particles suspended in a continuum fluid. Colloids range in size from a few nanometers to a few microns can be spherical, rod-like, or irregularly shaped; they can be slippery, sticky, squishy, porous, or solid; and can exist in dilute conditions like a gas of particles, dense liquid-like suspensions, or concentrated enough to form crystals or glasses. Continuum mechanics describe the flow of the suspending medium, but because colloids are Brownian, their motion and distribution are stochastic. The competition between Brownian, hydrodynamic, and external forces that determines the arrangement of particles in space, which in turn affects the bulk material properties. There are three primary ingredients required to model colloidal suspensions[21]: detailed models of the microscopic forces between the colloids; a systematic way to connect these forces to the distribution of particles in space and time; and statistical models to predict bulk suspension properties as volume or configuration averages over all phases. Of these, the representation of microscopic forces is the center of advancement in modeling suspensions.

Mature computational techniques: hydrodynamic interactions. In dilute suspensions, robust theory exists to explain the fundamental physics of hydrodynamic interactions and Brownian motion, and how their interplay under various flow conditions leads to non-Newtonian rheology and phase transitions. However, many-body interactions become important in moderately concentrated and dense suspensions, requiring the computational solution of the detailed momentum balance on either the fluid or on each individual colloidal particle. In contrast to Molecular Dynamics modeling, most meso-scale modeling approaches (like Stokesian dynamics, Brownian dynamics, and Immersed Boundary Methods, among others) represent the suspending fluid implicitly, treating it as a continuum solvent with specified viscosity ad density. Dissipative Particle Dynamics (DPD) straddles both limits. The continuum approach makes it possible to follow suspension behavior over seconds, minutes, even hours or days – as compared with nano-seconds in MD approaches.**There are two primary approaches for mesoscale computational modeling colloidal suspensions: those in which the Navier-Stokes equations are solved, subject to boundary conditions on each particle; and those in which detailed solution of fluid motion are bypassed and instead the microhydrodynamics are encoded into mobility and resistance tensors that dictate how particles move.** Each approach has its strengths and weaknesses. Approaches such as Immersed Boundary Methods are powerful for representing complex flow and container geometries, as well as non-Newtonian suspending solvents, but are challenging beyond a small number of particles. Approaches such as Fast Multipole Methods (FMM) and Stokesian Dynamics (SD) bypass solution of the Navier-Stokes equations, but must overcome two key challenges: representing lubrication interactions between nearly-contacting colloids, which are singular; and representing many-body interactions for other particles. Stokesian Dynamics overcomes both challenges using an efficient and accurate superposition technique[22–25].

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[23]. 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[26,27]. Stokesian Dynamics also provided a verification of theoretical models and insight into many other suspension phenomena[24,28,29]. More recent expansion of the Stokesian Dynamics algorithm includes modeling confined suspensions[30–32].

The primary limitations of Stokesian dynamics center on matrix operations where, for a system of N particles, required initially $O(N^3)$ operations and limited early simulations to fewer than 30 particles. However, several algorithmic advances in the last 20 years have resulted in dramatic efficient gains. The $O(N \log N)$ scaling of Accelerated Stokesian Dynamics (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 matrix inversions. Despite this progress, computation of far-field coupling due to Brownian disturbance flows remained an Achilles' heel of Stokesian dynamics. The computations involved in Brownian motion were not accelerated in the version of ASD with Brownian motion[33]; an approximation used as a workaround sufficed for many years of study of flowing suspensions but can introduce questionable error into study of phase behavior, where Brownian motion is a central factor in system dynamics. Until recently, the far-field Brownian force has been computed either with a Chebychev approximation[33] or other techniques[30,32,34].

Moreover, serial versus parallel implementation can enhance performance significantly: serial computation is limited to $O(100)$ particles[35]. Recently Stokesian Dynamics was implemented on a single GPU on a shared memory architecture and is able to simulate from $O(10,000)$[34] to $O(100,000)$ particles[36], where efficient algorithms were designed to account for the GPU architecture, along with implementations of new methods to efficiently handle the complexities of Brownian disturbance flows. We recently developed a suite of scalable algorithms to simulate large-scale colloidal systems amenable for modeling dense colloidal suspensions, glasses and gels with full hydrodynamics[37]. To handle the large number of particles and consequent many-body interactions present in such systems, we developed a novel parallel implementation of Accelerated Stokesian Dynamics (ASD) a distributed memory architecture. We demonstrated good scaling 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 interactions. Our straightforward and flexible approach reduces the computational time of the Brownian far- field force construction from $O(N \log N) + |\alpha|$ to $O(N \log N)$[37]. More recently, 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. **Overall, representation of strong hydrodynamic interactions and Brownian forces in large suspensions is now robust.**

Opportunities in computational techniques: complex interparticle forces. Progress in the last several years in the computational modeling of of interparticle forces in suspensions has shed light on several long-standing open questions in industrial colloidal materials. For example, recent efforts to represent frictional forces in computational models now recovers discontinuous shear

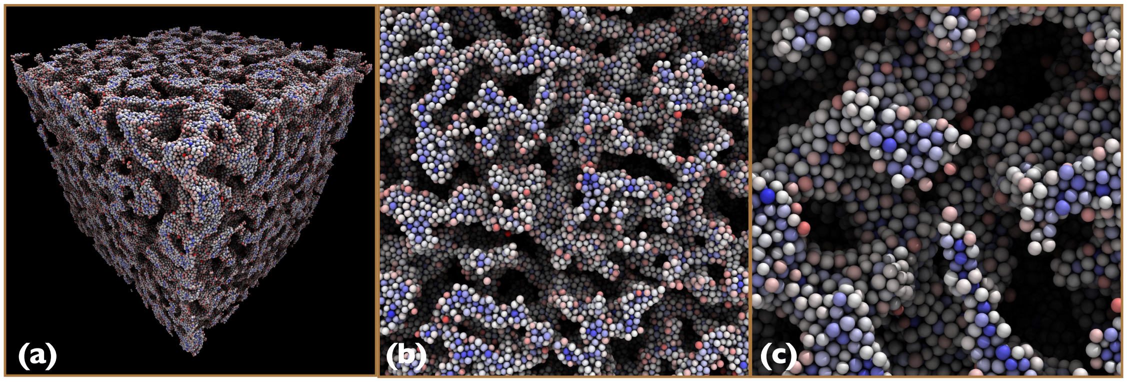

Figure 1: Snapshots of a colloidal gel from dynamic simulation. (a) One periodic cell. (b) 2x magnification. (c) 4x magnification. Number of contacts per particle indicated by color, ranging from red (few) to blue (many).[40] Cross sections of gel strands reveal high-contact number interior particles and glassy interior morphology.

thickening long observed in industrial suspensions but was the subject of contentious disagreement until theoretical and computational modeling interrogated the detailed influence of surface friction and contact. Another example is the representation of reversible attractive physico-chemical forces in colloids that led to the first studies of age-evolution of structure and rheology in colloidal gels, which led in turn to explaining the origins of gravitational collapse and delayed shear yield. Vitrification is another area of progress in computational study, where recent work has been able to interrogate particle dynamics deep into the glassy region inaccessible to experiments. **While these advances provide fundamental mechanistic insight and particle/structure/property relationships for general phase and non-Newtonian behavior, current models are still relatively simple in terms of particle attributes and interactions.**

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[38]. 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[39]. As a result, current computational methods cannot accurately *match* interparticle potentials to laboratory systems that predict gelation, vitrification, and percolation lines except in very simple cases.

Our progress in simulating laboratory conditions for particle interactions. We 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[40–43]. 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

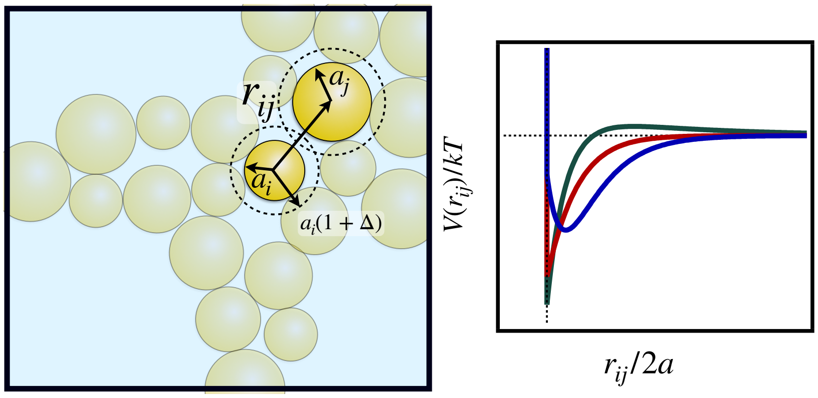

Figure 2: Our algorithm can predict experimentally-derived particle interactions that mimic equilibrium and non-equilibrium phase transitions in laboratory samples.[44] The computational model constructed in our expanded LAMMPS can represent this interparticle interaction, that can take any range or detailed shape.

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.

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 can then optionally 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 develop new potential interactions via collaboration with experimentalists and molecular dynamics simulations towards detailed matching of interactions between particles to experimental systems.

Specific Objective 1: Develop the bumpy-surface model. We will utilize two approaches for building the ‘raspberry’ particle model as defined by the Vermant group at ETH. First we will construct the algorithm in our LAMMPS model using valency model recently developed in our group. We will explore the impact of the bumpy shape on diffusion, viscosity, osmotic pressure, and packing. We will then conduct an evaluation of how this portion of the algorithm can be incorporated into our Accelerated Stokesian dynamics model.

Specific Objective 2: Match to molecular dynamics simulations. Insight from MD simulations will be leveraged model the details of contour interactions, to determine if the colloidal-scale model can be simplified for efficiency, and to provide a baseline for refinement during experimental matching.

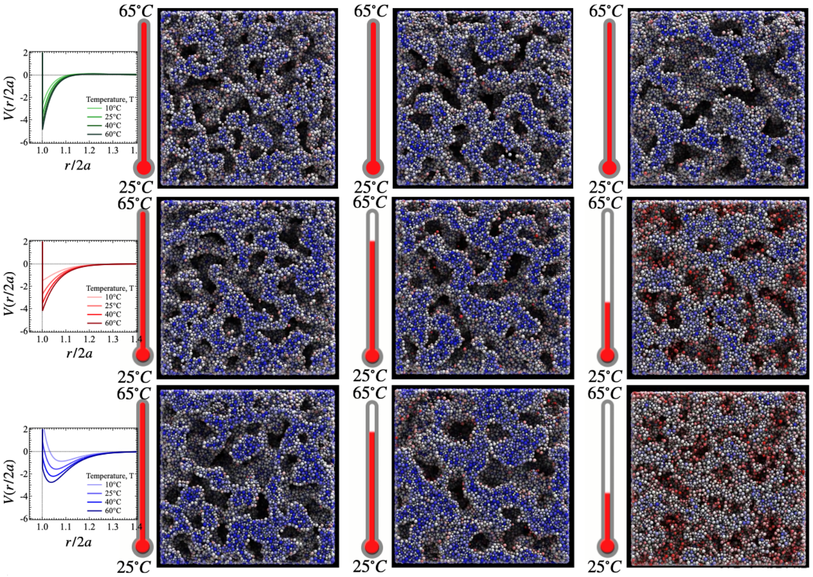

Figure 3: Our interactive algorithm accurately predicts qualitative changes in gelation and vitrification when attractive forces that are identical at equilibrium are involved in phase arrest.[44] In the proposed work, we can expand this model for other laboratory conditions besides temperature changes, or other particle surface conditions.

Specific Objective 3: 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][44,45]. We will expand this algorithm with additional models of the interactive potential to simulate the bumpy-surface 'raspberry' particles synthesized in the research laboratories of Prof. Dr. Jan Vermant and Prof. Dr. Lucio Isa at ETH. We will then carry out the matching process via iterative refinement with experiments to select best representative potential.

Aim 2. Incorporate the new particle interaction algorithms and size polydispersity 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. This will involve merging spectral or other methods for distributing size into our parallel computing platform. This work can occur alongside Aim 1.

Specific Objective 2: Validation testing. In collaboration with experimentalists, we will verify the impact of size polydispersity on packing, diffusion, osmotic pressure, and vitrification.

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