

Chapter 1

INTRODUCTION

Colloidal suspensions are widely present in nature and in industry from biological fluids to advanced materials, with examples as diverse as cytoplasm, milk, and ink. They have attracted extensive research interests dating back to Einstein [1]. Despite almost 110 years of extensive experimental, computational, and theoretical investigations, the behaviors of dense colloidal suspensions remain poorly understood [2, 3]. Even the most elementary form—the hard-sphere colloidal suspensions that are mixtures of submicron rigid particles in a viscous solvent—exhibit rich and surprising behaviors such as glass and jamming transitions [4, 5], shear thinning and shear thickening, i.e., a decrease and increase of suspension viscosity with increasing strain rate [6], and particle migration [7, 8]. These behaviors arise from the complex interplay among interparticle forces, hydrodynamic interactions, and Brownian motion. A thorough understanding is critical for developing new materials and improving existing processes.

This thesis is a comprehensive computational investigation on the rheology of dense colloidal suspensions. By dense we refer to suspensions that exhibit flow-arrest transitions, i.e., that are unable to flow unless the imposed stress exceeds the yield stress. The volume fraction is therefore above the glass transition $\phi_G \approx 0.58$ but below the jamming transition $\phi_J \approx 0.64$ for hard-sphere systems. The current standard method for rheology simulations of colloidal suspensions is Stokesian Dynamics (SD) [9], which exploits both the mobility and the resistance formalism of Stokes flow to accurately capture the hydrodynamic interactions that are non-pairwise-additive and long-range in the far field and diverging in the near field. The monodisperse implementation of SD has been used to study suspension rheology up to the monodisperse fluid-solid transition $\phi_F \approx 0.494$ with fixed volume fraction ϕ and strain rate $\dot{\gamma}$ [10, 11]. However, we cannot directly use the standard SD or the Accelerated Stokesian Dynamics (ASD), the Particle-Mesh-Ewald (PME) variation of the SD [12], to study the rheology of dense suspensions for several reasons: (1) The monodisperse suspensions spontaneously crystallize when $\phi > \phi_F$. The crystallization process qualitatively alters the suspension behaviors compared to the amorphous state; (2) With constant imposed strain rate $\dot{\gamma}$ we implicitly assume the suspensions flow like a fluid, and therefore we are unable to accurately probe the

dynamics near the flow-arrest transitions; (3) We assume that the prescribed volume fraction ϕ is given and fixed. This assumption is valid for suspensions far from the jamming transitions. However, near the jamming point, the exact value of ϕ_J is strongly protocol dependent and therefore unknown, and the prescribed ϕ may not be reached.

The solution to the challenges above is the constant stress and pressure rheology of polydisperse suspensions. Introducing a small particle size polydispersity significantly suppresses the crystallization process [13]. This ensures that the suspensions are amorphous at least in the arrested state. Imposing a constant shear stress σ and measuring the resulting responses can probe both the flowing state, where the suspension continuously deforms with $\dot{\gamma} > 0$, and the arrested state, where the suspension behaves like a solid with $\dot{\gamma} = 0$. When the imposed stress is close to the yield stress, we can observe the dynamics of the flow-arrest transitions. Finally, imposing a constant pressure Π allows the suspension volume fractions to adjust accordingly, and to reach a maximum value in the $\Pi \rightarrow \infty$ limit. In this way, we can properly study the rheology of dense suspensions.

Introducing particle size polydispersity in colloidal suspensions not only suppresses the crystallization at ϕ_F , but also alters the hydrodynamic interactions among particles, and consequently, the suspension transport properties. Particle size differences can introduce qualitative changes in hydrodynamic interactions. For example, the trajectories of two sedimenting particles can become periodic if their sizes are different [14]. On the other hand, although there are extensive studies on the transport properties of hard-sphere and charge-stabilized monodisperse equilibrium colloidal suspensions [15–17], the influences of particle size differences have not been addressed. Here, the transport properties are measured at a time scale much smaller than the time scale of configuration change, and therefore they only depend on the instantaneous (equilibrium) configurations.

Experimentally, the constant stress and pressure rheology was first introduced by Prasad and Kytömaa [18] for non-Brownian suspensions using a concentric cylinder geometry with pressure control in the vorticity direction. They observed that ϕ changes with the imposed stress and pressure. Recently, Boyer et al. [19] introduced a different experimental setup based on the cone and plate geometry with pressure control in the velocity gradient direction. They successfully collapsed the results from different samples, and constructed the flow curve of non-Brownian suspensions. However, there is no corresponding computational investigations for

overdamped colloidal suspensions.

In addition to introducing physical boundaries, another way of keeping the pressure constant is to introduce a compressible solvent with a bulk viscosity κ_0 and adjust the uniform compressive flow in unconfined suspensions. In a compressible solvent, a rigid particle can not expand or contract with the uniform compressive flow and thus generates a flow disturbance satisfying the Stokes equation, which, in turn, generates a pressure moment [20, 21]. In this way, the normal stress of hard-sphere suspensions is proportional to the compressible flow. This approach eliminates the structural anisotropy due to confining boundaries.

The thesis consists of four parts. In the first part, we investigate the effects of particle size differences on the short-time transport properties of equilibrium colloidal suspensions. We extend the conventional SD method for infinite suspensions [22] to polydisperse systems. Since hydrodynamic interactions do not affect the equilibrium properties, these transport properties are computed using a Monte-Carlo approach. We address suspension properties including the short-time translational and rotational self-diffusivities, the instantaneous sedimentation velocity, the wavenumber-dependent partial hydrodynamic functions, and the high-frequency shear and bulk viscosities; and porous media properties including the permeability and the translational and rotational hindered diffusivities. The computational results are compared with existing theoretical and numerical results. For suspensions, we also explore the range of validity of various approximation schemes, notably the Pairwise Additive (PA) approximations with the Percus-Yevick structural input. We critically assess the strengths and weaknesses of the SD algorithm for various transport properties. For very dense systems, we discuss the interplay between the hydrodynamic interactions and the structures due to the presence of a second species of a different size.

In this part, we also develop an approximation scheme for the bidisperse partial hydrodynamic functions based on the $\delta\gamma$ -scheme for monodisperse suspensions [23, 24] with partial static structure factors as the input and a rescaling law for the mixture. The so-modified $\delta\gamma$ scheme predicts hydrodynamic functions in good agreement with the SD computations up to $\phi = 0.4$.

The polydisperse SD has an unfavorable $O(N^3)$ computation scaling, with N the number of particles in the system, which effectively restricts the algorithm to static computations of equilibrium systems, where hydrodynamic interactions do not affect the structural evolution, and to dynamic simulations with small N . This limitation

necessitates developing a new algorithm for dynamic simulations of dense suspensions.

The second part of the thesis is devoted to the development of a computational method designed for dynamic simulations of polydisperse suspensions with full hydrodynamic interactions, Spectral Ewald Accelerated Stokesian Dynamics (SEASD). Based on the framework of Stokesian Dynamics (SD) with extension to compressible solvents, the SEASD uses the Spectral Ewald (SE) method [25] for mobility computation, a far-field block-diagonal preconditioner for the iterative solver, and Graphic Processing Units (GPU) acceleration. For further speedup, we develop SEASD-nf, a polydisperse extension of the mean-field Brownian approximation of Banchio and Brady [26]. We extensively discuss implementation and parameter selection strategies in the SEASD, and demonstrate the spectral accuracy in the mobility evaluation and the overall $O(N \log N)$ computation scaling. The algorithm is rigorously validated using three computational examples in monodisperse and bidisperse suspensions: the short-time transport properties, the equilibrium osmotic pressure and viscoelastic moduli, and the steady shear Brownian rheology. The results show that the SEASD and SEASD-nf agree satisfactorily over a wide range of parameters, and provide insight to the dynamics of polydisperse colloidal suspensions.

The third part of the thesis shifts the attention from hydrodynamic interactions to the constant pressure constraint. We consider the structural and mechanical influences of the confining boundary motion if the constant pressure constraint is imposed. This problem is formulated as the film drying process by confining colloidal suspensions between a moving interface and a stationary substrate, with only excluded volume interactions among the particles and walls.

In this part, we develop a new variant of the Brownian Dynamics simulations, the Energy Minimization Potential-Free (EMPF) algorithm for confined systems and for stress profile measurement. The interface moves either at a constant velocity or with a constant imposed normal stress. For constant interface velocity U_w , comparing the rate of interface movement U_w/a to the rate of diffusion d_0/a^2 defines a Péclet number, $Pe_U = U_w a/d_0$, with a the particle radius and d_0 the single-particle diffusivity. In the $Pe_U \ll 1$ limit, Brownian motion dominates and the suspensions are driven by thermodynamics. In the $Pe_U \gg 1$ limit, a particle front emerges next to the moving interface and promotes localized, epitaxial crystallization. The stress profile becomes step-like and has a boundary layer next to the moving interface. The

most amorphous structures at a given gap width occur at moderate Pe_U . We also develop a continuum model for the drying process and compare the model prediction with the simulation results. With constant imposed normal stress, the suspension shows similar behaviors, except that the interface stops moving when the suspension osmotic pressure matches the imposed stress. This part shows the critical role of interface movement on the resulting suspension structures and mechanics.

The fourth part of the thesis focuses on the constant stress and pressure rheology of colloidal suspensions without and with hydrodynamic interactions. We use the Potential-Free Brownian Dynamics (PFBD) [27] for computations without hydrodynamic interactions, and use SEASD-nf for hydrodynamic simulations. As the confinement strongly affects the suspension behaviors even without hydrodynamic interactions, we impose the constant pressure constraint by introducing a compressible solvent.

We first study the flow behaviors using PFBD. Expressing the flow behavior in terms of the macroscopic friction coefficient $\mu = \sigma/\Pi$, with σ the shear stress and Π the osmotic pressure, reveals a Shear Arrest Point (SAP) from the collapse of the rheological data in the non-Brownian limit. The flow curves agree quantitatively (when scaled) with the experiments of Boyer et al. [19]. Near suspension arrest, both the shear and the incremental normal viscosities display a universal power law divergence, demonstrating the important role of jamming on the arrest of colloidal suspensions and illustrating the care needed when conducting and analyzing experiments and simulations near the flow-arrest transition.

We then investigate the constant stress and pressure rheology with and without hydrodynamic interactions by focusing on the rheological, structural, and dynamical characteristics of the flowing suspensions. Hydrodynamic interactions, for example, lead to the preferential alignment of particles in the vorticity direction at high imposed stresses, and the shear-melting of the string-order structures at moderate stresses.

For suspensions without hydrodynamic interactions, we also explore the suspension instability near flow-arrest transitions. Through temporal coarse graining, the stationary strain rate distribution near flow-arrest transitions shows two peaks, with one in the arrested state and one in the flowing state. The stress-scaled self-diffusivities at different stresses collapse, and depend only on Π and $\dot{\gamma}$. The results lead to a diffusion-rheology flow map for Brownian suspensions. Spatially, the fast-moving particles move collectively when the suspensions change from an arrested state to a

flowing state.

Adopting a granular perspective that characterizes the suspension dynamics using the viscous number $I_v = \eta_0 \dot{\gamma} / \Pi$ with η_0 the solvent viscosity, we find that the rheology, the structural features, and the diffusive dynamics collapse in the high pressure limit. For glassy suspensions, μ and ϕ approach the arrest point (ϕ_m, μ_m) as $I_v \rightarrow 0$, which approaches the SAP in the $\Pi \rightarrow \infty$ limit. Away from the flow-arrest transitions, $\delta\phi = \phi_m - \phi$ and $\delta\mu = \mu - \mu_m$ exhibit universal power law behavior with respect to I_v , suggesting that the jamming physics dominates the flow behavior, and that thermal fluctuations only change the arrest locations. With this insight, we also develop a simple rheology model that accurately captures the behaviors of glassy suspensions. Hydrodynamic interactions only quantitatively alter this behavior. Moreover, the results from hydrodynamic simulations in the non-Brownian limit agrees quantitatively with the experiments of Boyer et al. [19] with a shift in ϕ .

In addition, the interaction friction coefficient $\mu^I = \mu - (1 + \frac{5}{2}\phi)I_v$ collapse for *all* flowing suspensions as functions of $\dot{\gamma}a^2/d_\infty^s$, with d_∞^s the long-time self-diffusivity, as $\mu^I \propto \dot{\gamma}a^2/d_\infty^s$. The data collapse suggests a generalized Stokes-Einstein-Sutherland relation with an effective temperature proportional to the imposed pressure. The structural distortions also collapse with $\dot{\gamma}a^2/d_\infty^s$ for all the flowing suspensions, suggesting that the shear stresses are only proportional to the product of structural distortion and osmotic pressure near flow-arrest transitions. These universal behaviors are valid regardless of hydrodynamic interactions, suggesting that a mean-field description is possible for the diffusion and rheology of Brownian suspensions.

The thesis is arranged as follows: the first part contains Chapters 2 and 3, with Chapter 2 focusing on the short-time transport properties and Chapter 3 on the modified $\delta\gamma$ -scheme for approximating the bidisperse diffusion properties. The second part is Chapter 4, presenting details of the SEASD algorithm. The third part is presented in Chapter 5 as the structure and mechanical properties in the colloidal film drying process. The fourth part is in Chapters 6, 7, and 8. Chapter 6 presents a short study on the mechanical aspects of the constant stress and pressure rheology of colloidal suspensions without hydrodynamic interactions. Chapter 7 significantly expands the previous chapter with additional focus on the dynamical and structural aspects. Chapter 8 thoroughly investigate the influences of hydrodynamic interactions. We finish this thesis with a conclusion and outlook in Chapter 9.

Finally, we note that Chapters 2–8 are presented in a form suitable for publication, with Chapters 2, 3, 4, and 6 already published.

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