Final Report

PRF# 56719-DN19: The Dynamics of Colloidal Healing: Restoration of Visco-plasticity in Dispersions of Attractive Colloids

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Colloidal dispersions are commonplace in the oil and gas industry. The colloidal scale features of these multiphase materials are engineered to express mission critical mechanical properties. Drilling muds, for instance, must possess a yield stress sufficient to support cuttings and shear thin enough to minimize the cost of pumping. Muds inherit these properties from attractive colloids – clay particles – which form percolating, arrested networks with visco-elastic and visco-plastic character prevalent in a number of industries and everyday applications. Important questions exist about the lifetime and recovery of the mechanical properties in the presence of an external forcing field. For example, deformation of flowing mud breaks the physical bonds between the attractive colloids and leads to fluidization. Proppants used in fracturing conformance control my fail catastrophically and unpredictably under extreme weight. How quickly are properties such as the yield stress restored after large deformations? What is the reliable lifetime of a gel network under gravitational compression? The answers to these question have broad implications for the stability of attractive colloidal dispersions and their application to industrial processes and are the topic of this project.

Computer simulations are one useful tool to investigate the dispersion microstructure and correlate local particle dynamics to the global material failure. However, models for microstructural evolution during colloidal gelation of attractive dispersions have often struggled to match experimental observations. The dynamics of these kinetically arrested particle networks are controlled by the solvent-mediated interactions between particles, which are called hydrodynamic interactions (HIs) and are dictated by the viscous fluid response, and the stochastic motions associated with Brownian diffusion. Recently, we have demonstrated the necessity of long-ranged hydrodynamic forces in discrete element simulations of heterogeneous gelation at the colloidal scale. Computational models neglecting long-ranged HI will inevitable fail to predict the correct phase behavior of colloidal dispersions[5].

Motivated by these findings, we investigated the role of HI in setting the dynamic response of the microstructure. In particular, to understand the viscoelastic response we computed the relaxation rates of weak colloidal gels employing different models of the hydrodynamic interactions between the suspended particles in a normal mode analysis of a harmonic network representing the gel. We developed a simple phenomenological model of the internal elastic response to normal mode fluctuations, which shows that long-ranged hydrodynamic interactions play a central role in the viscoelasticity of the gel network because they fundamentally alter the collectivity and energy dissipation in the microstructure. We have conducted dynamic simulations with long-ranged HI of the stress decay to confirm the normal mode predictions and the phenomenological model at moderate particle concentrations. Analogous to the Zimm model in polymer physics, our results indicate that long-ranged hydrodynamic interactions play a crucial role in determining the microscopic dynamics and macroscopic properties of the colloidal dispersions. A computational model neglecting hydrodynamic interactions will yield erroneous estimates of $G(t)$, $G^*(\omega)$ and other related viscoelastic and mechanical properties.

Having analyzed the formation and dynamics of arrested colloidal dispersions, we have also studied the breakdown of the network microstructure in colloidal gels. When subjected to external stresses the percolating network can become unstable leading to the formation of vorticity aligned flocs[6]. The origins of this instability remain a mystery, and discrete element simulations have to date, failed to reproduce the phenomena. We use new Brownian Dynamics simulations with HI to show that this instability is fluid mechanical in origin[1]. Squeeze flows between vorticity aligned flocs prevent collisions and realignment under flow, thus promoting stability of large-scale, vorticity aligned density fluctuations. We identify the uniquely controlling parameter in the problem, a Mason number Mn^*, describing the ratio of the strength of shear flow to the most probable rupture force, that collapses the microstructural and rheological data. We find two distinct regimes of the shear response critical to both computational

and experimental studies: dynamic yield and steady-shear flow. The nonlinear rheology and measures of their structural anisotropy seen in simulations agree well with a wide variety of experiments and are independent of the regime of steady-state response. Characterizing experimental systems in terms of Mn^* will aid in identifying regimes of intact gels and network breakdown as well as describe the onset and evolution of nonlinear flow instabilities allowing to better deign the microstructure suitable for a given engineering application.

Another concern for the long-term stability of the colloidal microstructure is mechanical compression due to gravity. The gel can exist in a mode of free settling when the network weight exceeds its compressive yield stress and where hydrodynamic instabilities leading to loss of network integrity occur. Insight into the collapse process was provided by experiments that have shown that the loss of integrity is associated with the formation of eroded channels, so-called streamers, through which the fluid flows rapidly[4]. However, understanding how this nucleation and growth is related to microstructural parameters remained elusive. We have developed a phenomenological model that describes dynamically the radial growth of a streamer due to erosion of the network by rapid fluid back flow. The model exhibits a finite-time blowup – the onset of catastrophic failure in the gel – due to activated breaking of the inter-colloid bonds. We again employed dynamic simulations to examine the initiation and propagation of this instability, which is shown to be in good agreement with the theory. We have also validated our model predictions by comparing it to measurements of streamer growth in two different experimental systems[3, 4]. Ultimately we find that engineering strategies for avoiding settling instabilities in networks meant to have long shelf-lives have to focus on the competition of two time scales. Over the time scale of poroelastic collapse the gel compacts and appears stable. If however the blow-up time for the given gel falls before the completion of poroelastic collapse the network is destined to fail catastrophically.

Finally, we have investigated the role of boundaries in controlling the structure of colloidal gels under flow. We found that anisotropic density fluctuations couple to the flow through the boundaries to produce large scale ordered patterns with the fluid. In a parallel plate geometry, these patterns are logs of colloidal aligned with the vorticity direction of the flow and spaced periodically. The wave length selection mechanism is a hydrodynamic one, in which an initial density fluctuation acts as a Rotlet between the parallel plates and produces a periodic pattern of counter rotating vortices that decay exponentially in intensity. These vortices collect attractive particles while the stagnation points between the vortices clear particles out of the interstices resulting in a periodic array of log-like aggregates. Such pattern formation can be used to self-assembly striped patterns at any scale for which such flows and geometries are feasible. With collaborators, we are looking at the possibility of freezing such patterns using a cross-linkable solvent in order to produce well defined micro-wire arrays from dispersions of attractive colloids such as carbon black. The resulting arrays (if generated at the right scale) have applications in microelectronic devices including flexible touch displays.

Our findings on the dynamics and breakdown of colloidal microstructure are consequential for future computational models and experimental studies of attractive colloidal dispersions. Dynamic simulation of colloidal gels must include hydrodynamic interactions to recover the flow phenomena and mechanical processes observed in reality.

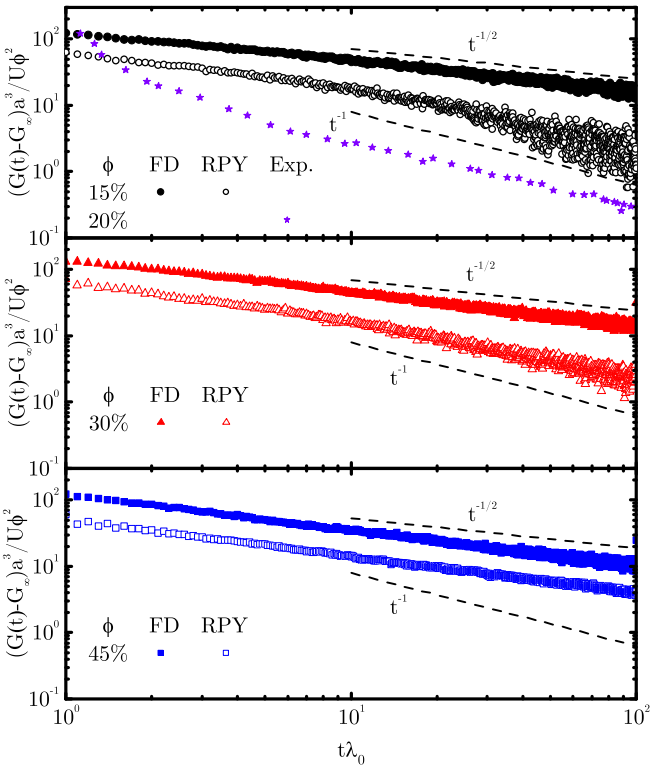

Figure 1: The time-dependent shear modulus $G(t)$ is strongly affected by the presence of long-ranged HI in dynamic simulations. $G(t)$ is plotted as a function of lag time after an instantaneous strain increase of $\gamma_0 = 1\%$ as measured for the three different volume fractions for both hydrodynamic models. Measurements were averaged over 500 realizations for each data set to reduce thermal noise. We estimate the single particle relaxation λ_0 based on the depletion well depth $U = -10k_BT$ and range of $0.1a$. Also shown (violet stars) are results from an instantaneous stress relaxation experiment of a colloidal gel with $\phi = 20\%$[2].

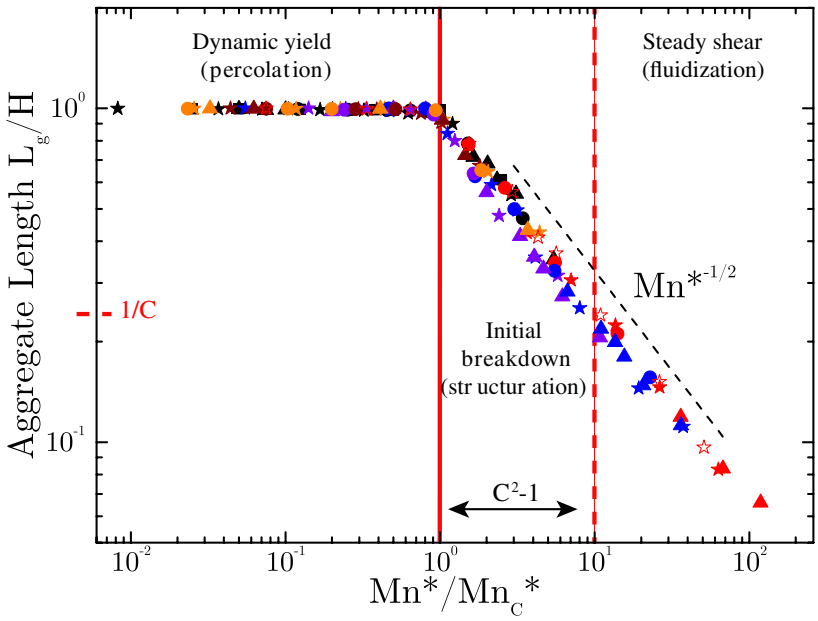

Figure 2: The stable aggregate length scale L_g at a given shear strength Mn^* reveals three different regimes of shear response of a colloidal gel under confinement: Dynamic yield, initial breakdown and steady-shear. L_g is measured relative to the length scale of confinement H and the Mason number is scaled on the critical value for network breakdown, Mn_c^*. The threshold $C = H/L_g$, required for statistically significant sampling of the bulk steady-shear response, sets the width of the initial breakdown region. **??**.

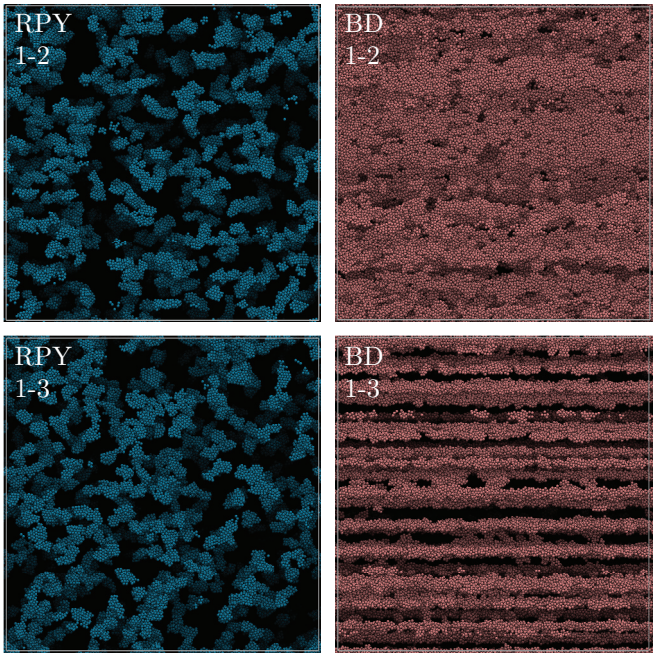

Figure 3: The final structure of the colloidal dispersion after 500 strain units($\gamma = 500$) in the flow-gradient plane (1–2, top) and flow-vorticity plane (1–3, bottom) using the RPY approximation for long-ranged HI(left) and simple Brownian Dynamics (BD) with HI turned off(right). The effect of correctly accounting for long-ranged HI is striking - in simple BD the particles arrange themselves into sheets in the 1–2 plane, orthogonal to what is observed in experiments. In contrast, with long-ranged HI we observe anisotropic density fluctuations in the 1–3 plane and shear alignment along the extensional and compressional axes in the 1–2 plane.

References

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