# The Far-From-Equilibrium Behavior of Aggregating Colloids

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# I. INTRODUCTION

Colloidal aggregation is used extensively in industry for such products as paints<sup>1</sup> and gels.<sup>2</sup> There has been extensive experimental<sup>3</sup>, theoretical<sup>4</sup> and simulation<sup>5</sup> work to further our understanding of these complex systems. Within my own thesis research, we aim to produce a detailed understanding of the far-from-equilibrium behavior of specific colloid systems which have yet to be fully explained. We are working towards this goal using a combination of nonequilibrium statistical mechanics and computer simulations. On completion, this research will fill in several gaps in our current understanding of aggregating colloids in nonequilibrium applications and aid in the creation of new high tech materials through an application of colloidal science.

Simply put, colloids are particulate systems where mesoscopic (1 nm to 1  $\mu$ m) particles are dispersed in solution.<sup>4,6</sup> These particles can be composed of one of many materials ranging from clays<sup>7</sup> to synthetics polymers<sup>8</sup> and even complex biological macromolecules<sup>9</sup> and cells<sup>10</sup> can exhibit colloidal properties. While diverse in origin, all colloidal systems share some common characteristics which allows for the construction of theoretical frameworks based on the simple effects of solvent and colloid-colloid interactions.<sup>6</sup>

Aggregation in colloid systems is generally induced by a combination of van der Waals and hydrophobic forces,<sup>11</sup> although in binary mixtures it is possible for electrostatics to induce aggregation when the components have opposite net charges.<sup>12</sup> This is in contrast to the general effect of electrostatics in colloids, which is to create a repulsive interaction between like charged particles.<sup>4</sup> Such charged particle result from common industrial production methods used in creating latex particles,<sup>13</sup> and further casein colloids used in the food industry also contain a net charge.<sup>14</sup> The combination of repulsive and attractive interactions can either lead to aggregation or to a stable suspension based on which forces dominate.<sup>6</sup> To create the desired effect, these interactions can be modulated through such means as the addition of electrolytes to screen electrostatic interactions<sup>15</sup> or through addition of surfactants to compatibilize hydrophobic surfaces.<sup>16</sup> It is also possible for both attractive and repulsive interactions to coexist when they occur over different length scales.<sup>6</sup> This can lead to some very complex and interesting colloidal behavior.<sup>4,6</sup>

## **II. INTERACTIONS OF HAIRY COLLOIDS**

Within my first project, we were interested in rigorously calculating the interaction potentials between hairy colloids (Figure 1) with the intent of using the resulting potential of mean force for the dynamic simulation of hairy particle aggregation as occurs under certain solvent conditions.<sup>17</sup> Currently, this project is on hold until time and resources permit collection of additional results and the preparation of a publication, although we intend to complete this study on some time scale. What follows is a brief overview of the initial project.

The term hairy particle is used to describe colloidal particles whose surface is covered by a polymer layer and the interactions between particles are dominated by this layer.<sup>18</sup> Such a hair is common in synthetic polymer colloids where free ends protrude through the surface, although the layer is generally thin (< 1 nm) and sparse such that it is insignificant in colloidal interactions.<sup>8</sup> Layer interactions do become significant for small particles or when high molecular weight polymers produce thicker layers.<sup>8</sup> There has also been work aiming to construct such hairy layers through the grafting of long polymer chains to inorganic colloids.<sup>19</sup> Additionally, star polymers, where multiple polymer arms are joined in a common center, can behave as colloids when there are sufficient arms to create dense separable particles.<sup>20,21</sup>

There is existing theory<sup>22</sup> and simulation<sup>23</sup> investigating the compression energy for such hairy layers, although they assume the particle is sufficiently large to model the layer as flat, planar and infinite in directions parallel to the surface. Theory does exist for star polymer interactions, although many assumption are employed to produce simple expressions suitable for phase diagram construction and not for dynamical simulation.<sup>24</sup> More rigorous methods have been used to investigate the structure of individual star polymers<sup>25</sup> and more recently lattice Monte Carlo techniques have been used to study the equilibrium properties of ensembles of star polymers<sup>26</sup> as well as star and linear polymer blends.<sup>27</sup>

For our aim of calculating potentials of mean force between hairy colloids, we have constructed a simple model of a pair of hairy particles using the Bond-Fluctuation Model, which has proven successful in modeling the equilibrium properties of star polymer ensembles.<sup>26,27</sup> This coarse-grained bead model for polymers is based on a detailed lattice that allows for 108 different bonding vectors between bonded beads<sup>28</sup> and this high detail model



FIG. 1: Schematic of model for hairy colloid interactions. The solid center of both particles is shown in blue and the polymer layer of the left particle is shown in red where as tan is used on the right on. Two different solvent conditions are shown with the upper schematic showing good solvent conditions and the lower one showing poorer solvent that induces aggregation to minimize solvent exposed surface.

is known to well reproduces polymer static properties.<sup>29</sup> Each particle is constructed as a solid core with grafted polymer chains creating the hair. A schematic of particles constructed in this model is shown in Figure 1

Solvent interactions are modeled by introducing a simple potential in terms of solvent exposed bead area as used commonly to model solvent effects in polymer lattice systems.<sup>30</sup> This potential is defined as

# $U = \mu_{\rm sol} n$

where *n* is the sum number of lattice bead faces exposed to solvent by not being in contact with another bead and  $\mu_{sol}$  is the solvent chemical potential.

To construct interaction potentials between particles, methods are developed to calculate the free energy of interaction between two particles at a specific separation distance relative to infinite separation. This is accomplished by making the beads composing the different hairy particles not perfectly volume excluding with each other, but instead introducing a finite energetic penalty  $E_{\rm ocp}$  for two beads from different particles occupying the same lattice site. By performing simulations over a range of  $E_{\rm ocp}$  values from 0 to a value sufficiently high to prevent any volume exclusion  $(E_{ocp} = 9kT \text{ in this case})$ and collecting the statistics on the number of overlaps at each  $E_{\text{ocp}}$  value, it is possible to calculate the interaction free energy energy. These calculations were performed using the free energy perturbation method the acceptance-ratio method, which is based on the probability for changing this fictitious potential.<sup>31</sup> These calculations are performed for a range of separation distances



FIG. 2: Free energy profiles between two hairy colloids as a function of their surface separation distance h, measured in lattice lengths a. Results shown for different solvent conditions as varied by solvent potential  $\mu_{sol}$  labeled on the plot. Points show numerical free energy calculation results and lines are smoothed curves as appropriate for dynamics simulation of these potentials of mean force.

to calculate an interaction profile.

Using this methods we have performed a proof of concept investigation where the interaction profiles for two hairy colloids were calculated under different solvent conditions. These initial results are shown in Figure 2 and here one observes how solvent effects can change the interaction between hairy particles from repulsive to attractive as solvent quality is decreased ( $\mu_{sol}$  increased). At some point in time we do intend to perform a more extensive investigation, looking at a collection of different hairy particle classes, to produce a rigorous study of hairy particle interaction under different solvent conditions. Additionally, we intend to use the calculated interaction profiles as potentials of mean force in the dynamic simulation of aggregation phenomena for such hairy colloids.

#### III. AGGREGATION DYNAMICS OF REACTIVE COLLOIDS

As mentioned in the introduction, very interesting colloid behavior can occur when the interaction between particles include both a repulsive and an attractive component at different length scales. The bulk of my current research focuses on the dynamics of such colloids when the resulting potentials includes an attractive well favoring aggregation between particles at close separation and an energetic barrier to entering this well at larger distances (Figure 3). These reactive colloid systems are particularly interesting, in that with a sufficiently high energetic barrier they can exhibit kinetic stability, de-



FIG. 3: Colloid particle pair-interaction potentials used in simulations where  $k_{\rm B}T$  is defined at T = 300 K. The dashed line shows the original Kostansek potential that diverges to  $-\infty$  at close separation. The black curve shows the modified potential where the close separation interaction is approximated by a parabola to simulate reversible surface adhesion between particles. The remaining curves are examples of linear scaling of the repulsive region of the base potential to modulate the barrier height independent of the attractive well. Shown curves correspond to scaling factors f = 0.7, 0.5, 0.3, and 0.1.

spite being far from from the thermodynamic equilibrium of aggregation.<sup>32</sup> Such reactive colloids are used in industrial products including modern latex paint.<sup>1,33</sup> In latex paints, this repulsive interaction prevent aggregation so as to keep the paint fluid and on evaporation of the water liquid component, aggregation proceeds and the paint cures. Additionally, shear forces, as occur in application with a brush, can result in partial aggregation and thickening to prevent running.<sup>34,35</sup> Therefore there is great interest in understanding this kinetic stability of reactive colloids and further learning more about how the energetic barrier can effect the formation of aggregation structures.

While such reactive colloids are used extensively, our current theoretical understanding of these systems is still rather incomplete. Our current theory of reactive colloids is based on calculating a simple potential of mean force between colloids pairs with the aim of determining the strength of the energetic barrier  $U_{\rm b}$ .<sup>6,36–38</sup> With this parameter, one classifies colloidal systems as either being aggregating  $U_{\rm b} \approx kT$  or stable  $U_{\rm b} \gg kT$ . There has been limited work using simulations to study the aggregation of reactive colloids, 39-42 although in all of these studies systems under high shear were investigated such that a strong driving force rendered the barrier insignificant and only the steady state rheology was studied. Colloid aggregation has been investigated through simulation for depletion force aggregating colloids where there is no energetic barrier to aggregation and interesting multiple phases of aggregation were observed.<sup>43,44</sup> An energetic barrier would be though to lead to even richer aggregation dynamics and study is needed.

Therefore we have undertaken a project to understand how the energetic barrier of reactive colloids influences aggregation dynamics. For this investigation, a simple model of reactive colloid aggregation has been constructed where the colloid interactions are taken to be pair separable and the reactive potential between two colloids is described in the formalism of Kostansek.<sup>38</sup> This potential extends conventional colloid theory, including repulsive electrostatics and attractive to van der Waals terms, to also include an attractive hydrophobic term. Terms within this model of colloid interaction were chosen to model latex spheres of diameter  $2R_p = 135$  nm in an electrolyte solution that results in an energetic barrier of  $U_{\rm b} = 10.3kT$  at T = 300K.<sup>6</sup>

## A. Simulation Model

This model of colloid interactions was augmented for numerical simulation. As the base Kostansek potential diverges to  $-\infty$  as colloid surfaces approach contact, the close distance attractive component has been approximated with a parabola as has been used in past simulation of reactive colloids.<sup>45</sup> Additionally, linear rescaling has been used to modulate the height of the repulsive barrier independent of well depth with scaling factor f, where the energetic barrier is given by  $U_{\rm b} = f10.3kT$  so that smaller barrier potentials can be constructed. Example potentials used in this study for different values of f are shown in Figure 3. To simulate the dynamics of reactive colloids with different barrier heights, the methods of Brownian Dynamics was used.<sup>46,47</sup> In this method, solvent effect is modeled by the Langevin equation in the Ohmic limit such that the colloid particles are inertialess and their motion is Brownian stochastic.<sup>47</sup> This description is appropriate for colloid particles<sup>6</sup> and used extensively in the simulation of many colloidal systems.<sup>39,43</sup> Hydrodynamics forces are not included as the solvent is not being driven and the random motion of colloids is insufficient to create a hydrodynamic field.<sup>48</sup>

Brownian Dynamics simulation of this model was performed following the algorithm developed by Ermak.<sup>49</sup> The physics of this method corresponds to the dynamics of the Langevin equation in the limit of inertialess particles in a fast relaxing solvent such that the dynamics of a colloid particle at any point in times can be described completely by the sum of pairwise forces, a viscous-solvent frictional force, and a stochastic term. With the condition of inertialess particles, a force balance equation can be used to solve for the instantaneous velocity of each particle that describes the particle's translation over a small interval of time.

The stochastic force is a mean field approximation of the the random fluctuations of solvent that couples to particle motion. This is a common simulation method in colloid science to average over the many degrees of freedom in solvent that have negligible effect individually due to their short time and length scale, but when summed and averaged result in a net diffusive drift of colloid particles with time.<sup>50–54</sup> In the Brownian Dynamics method, the resulting equation of motion for each particle coordinate  $\mathbf{r_i}$  over each finite time step of duration  $\Delta t$ , is

$$\Delta \mathbf{r}_i(t) = \mathbf{F}_i(t) \frac{\Delta t}{\gamma} + \Delta \mathbf{W}$$

where  $\mathbf{F}_i$  is the net pairwise force on particle *i* and  $\gamma$  is the drag coefficient of particles in solvent. For the spherical colloid particles in this model,  $\gamma$  is calculated from the particle radius  $R_p$  and solvent viscosity  $\eta$  ( $\eta_{\rm H_20} = 8.9 \times 10^{-4} \,\mathrm{Pa} \cdot \mathrm{s}$ ) by Stokes law  $\gamma = 6\pi \eta R_p$ .

The stochastic influence of solvent is introduced through the vector  $\Delta \mathbf{W}$ , every element of which is a random force characterized by a Gaussian distribution centered about zero with variance  $\langle \Delta W^2 \rangle = 2D\Delta t$ , where  $D = k_{\rm B}T/\gamma$  is the particle diffusion coefficient. This relationship between the extent of stochastic thermal fluctuation and solvent friction (coupling) follows naturally from the fluctuation dissipation theorem in the Markovian limit.

Using the Brownian equation of motion, simulations were performed in a cubic box with periodic boundary conditions. To limit sampling error and finite size effects, each simulation contained 1000 particles with the box size adjusted for the target volume fraction  $\phi$ . Due to the high volume fractions simulated and large forces, a rather small integration time step of duration  $\Delta t = 1$  ns was used. As simulations were used to investigate time scales on the orders of seconds, this implies billions of integration cycles for each investigated system and therefore computational efficiency was a high priority. To this end, common optimization techniques were used, including linear interpolation tables for the efficient evaluations of the analytically complex pair forces, neighbor tables to minimize unnecessary force evaluations, vectorized random number generation, and parallelization through the standard Message Passing Interface (MPI). Additionally, this high computational resources demand has limited the current investigation to a single ensemble trajectory per a system.

It was observed that occasionally particles would experience a pathologically high net forces due to the simulated potential that changes quickly over small distances; especially when such interactions are summed over multiple neighbors. This should necessitate an even smaller time step to preserve numerical stability and this would substantially impact computational efficiency for the handling of a chance event that occurred at low frequency. Instead, such high net forces particles were detected and their coordinate integrations were treated with a series of shorter integrations where the pair forces were reevaluated and a new stochastic force generated for each sub-cycle. As the stochastic contribution to the net force couldn't be known a priori, this detection was implemented as a recursive algorithm that attempted an exponentially increasing number of shorter sub-cycles until no individual sub-cycle had a change in energy greater than  $5 k_{\rm B}T$ . As larger magnitude thermal fluctuations were correlated with a greater number of sub-cycles, special care was taken to preserve the stochastic trajectory as additional sub-cycles were used. In contrast, a naive approach that discarded the previously seen thermal fluctuations when increasing the number of sub-cycles would introduce a bias in that larger magnitude fluctuations would be disproportionately discarded.

In our simulation studies, colloid suspensions with different colloid volume fractions  $\phi$  are initialized in a random structureless configuration and one then observes the onset of aggregation structure with different pair interaction potentials varying in barrier height. Aggregation is quantified by coordination number n or the number of neighboring particles within the attractive well r < 138 nm of a particle. The bulk aggregation dynamics is measured by the mean coordination number  $\langle n \rangle$  and this metric is shown in Figure 4 for the full barrier f = 1over a range of volume fractions. From these results it is seen that higher volume fractions aggregate faster and that significant aggregation of  $\langle n \rangle > 6$  is observed within 10 s for the barrier height of  $U_{\rm b} = 10.3kT$ .

Next, we investigated how aggregation dynamics changed when the barrier height was reduced to 1.03kTwith f = 0.1 and these results are shown in Figure 5. Here it is first observed that lowering barrier height accelerates aggregation dynamics as expected. Additionally, it is found that later stages of aggregation are ac-



FIG. 4: Bulk aggregation dynamics as quantified by the mean coordination number  $\langle n \rangle$  or average number of neighboring particles within the attractive well of each particle. Results for different volume fractions  $\phi$  with a pair potential having the full repulsive barrier, f = 1.

cessible in these simulations and very interesting aggregation behavior is observed in these later stages, including higher aggregation numbers approaching  $\langle n \rangle = 9$ . Further, aggregation dynamics can temporarily slow before a sudden increase in aggregation kinetics leads to a more aggregated system (this behavior is most obvious for  $\phi = 0.5, f = 0.1$ ). As will be discussed later, this later stage aggregation behavior is associated with reorganization and further study is needed.

One immediate question raised by the low barrier results, is will the higher barrier height systems exhibit this later stage behavior and on what time scale should it present? Rather than attempt to answer this question through further brute simulation, we have developed a kinetic scaling relationship which will allow a relation of low barrier dynamics to higher barrier heights. This is further useful as 10.3kT is only a moderate barrier height and barriers in excess of 100kT are used commonly in industry to create kinetically stable colloid suspensions.<sup>6</sup> Therefore we have investigated the kinetics of colloid aggregation with the goal of constructing a kinetic scaling relationship.

#### B. Analytic Model of Reactive Colloid Aggregation

To this end, a analytic theory of colloid aggregation is constructed based around a kinetic master equation of the following form



FIG. 5: Bulk aggregation dynamics for one-tenth barrier height f = 0.1 (solid lines) for different colloid volume fractions  $\phi$ . For comparison, dynamics are also shown for the full barrier f = 1 as dashed lines.

$$\frac{d}{dt}P_n(t) = -(k_n^{\rm f} + k_n^{\rm b})P_n + k_{n-1}^{\rm f}P_{n-1} + k_{n+1}^{\rm b}P_{n+1} \quad (1)$$

where  $k_n^{\rm f}$  and  $k_n^{\rm b}$  are the forward (association) and backward (dissociation) rates respectively and  $P_n(t)$  denotes the probability for a colloid to have *n* neighbor particles.

In accordance with Kramer's theory,  $^{55}$  the backward rate can be estimated as

$$k_n^{\rm b} \approx \frac{\omega_0 \omega_{\rm b}}{2\pi \gamma/m} \exp\left(-E_{\rm b}/k_{\rm B}T\right)$$
 (2)

where *m* is the mass of a colloidal particle;  $\omega_0$  is the frequency of oscillations near the potential minimum;  $\omega_{\rm b} \equiv -U''_{\rm kos}(h_{\rm max})/m$  is that for the top of the potential barrier;  $E_{\rm b} = U_{\rm b} + 5.3 k_{\rm B}T$  is the height of the potential as is seen from the point of the potential minimum.

The forward rate is proportional to the number of collisions and thus to the overall concentration C of particles,

$$k_n^{\rm f} = Ck_a \tag{3}$$

where the association constant  $k_a$  in dense systems ( $l \ll R_p$  or  $\phi > 0.05$ ) can also be evaluated with the help of Kramer's theory:

$$k_a \approx V \frac{\omega_1 \omega_{\rm b}}{2\pi\gamma/m} \exp\left(-U_{\rm b}/k_{\rm B}T\right)$$
 (4)

Here  $V \approx 4\pi (R_p + R_p)^2 l$  is the "reaction" volume in the vicinity of the potential barrier and  $\omega_1$  represents the effective oscillation frequency outside the barrier. In

TABLE I: The values of  $k_a$  calculated from Equation 4 at different volume fractions  $\phi$  and barrier heights  $U_{\rm b} = f \cdot U_{\rm b, full}$ . The line corresponding to the low concentration limit ( $\phi = 0.05$ ) can be only interpreted as a result of extrapolation.

$\phi$	f = 0.1	f = 1
( 0.05	$5.9\cdot 10^{-6}$	$4.6 \cdot 10^{-9}$ )
0.20	$3.1 \cdot 10^{-5}$	$2.4 \cdot 10^{-8}$
0.35	$6.5\cdot 10^{-5}$	$5.1 \cdot 10^{-8}$
0.50	$2.4\cdot 10^{-4}$	$1.9 \cdot 10^{-7}$

crowded systems such oscillations are always present due to permanent collisions with particles from the second solvation shell.  $\omega_1$  has the value of the same order as  $\tau_D^{-1}$ . For the full energy barrier  $(U_{\rm b,full} = 10.3 k_{\rm B}T)$  we derive the association constant  $k_a$  to be in the range from  $10^{-8}$  to  $10^{-7}$  cm<sup>3</sup>/s, and around  $k_a \sim 10^{-5}...10^{-4}$  cm<sup>3</sup>/s for the smallest energy barrier  $(0.1 U_{\rm b,full})$  used in the simulations (see Table I).

As for the forward rate in the case of dilute systems  $(l \sim R_p \text{ or } \phi = 0.05)$ , when the diffusional flow of particles plays the crucial role, the theory of diffusion-controlled reactions in the steady-state predicts

$$k_n^{\rm f} \approx \frac{Ck_a k_D}{k_a + k_D} \tag{5}$$

where  $k_D \approx 4\pi (R_p + R_p)D_{\rm m}$  is the diffusion rate which is proportional to the number of collisions per unit concentration. We found  $k_D$  to be about  $10^{-11}$  cm<sup>3</sup>/s. Although Equation 4 is not suitable for defining the values of  $k_a$  in the low concentration limit, it can be used as a rough prediction which is shown in the first line of Table I. Because its estimation is larger than  $10^{-10}$  cm<sup>3</sup>/s, the aggregation mechanism for the dilute colloidal suspension is always in the diffusion-controlled regime.

The following analysis is mainly carried out for the cases of high volume fractions, where the overall scaling behavior can be deduced from the Kramer's' law Equations (2-4). Dilute systems have been widely investigated in literature and remain out of the scope of this paper, although we present the results of our simulations of such systems for comparison.

When the potential barrier  $U_{\rm b}$  changes, the values of  $E_{\rm b}$  and  $\omega_{\rm b}$  change proportionally to it. Other parameters remain unaltered. Thus, if the barrier is multiplied by factor f, then new values of the rates become

1. 1

$$k_n^{\mathrm{D}}\big|_f = \chi k_n^{\mathrm{D}}\big|_{f=1}$$
$$k_n^{\mathrm{f}}\big|_f = \chi k_n^{\mathrm{f}}\big|_{f=1}$$

1. 1

where

$$\chi = f \exp\left[\left(1 - f\right) U_{\rm b, full} / k_{\rm B} T\right]$$

Changing all the rates in Equation (1) in accordance with the same law is equivalent to rescaling time by the factor  $\chi$ . The results of this procedure are shown in Fig. 6. It is seen that all curves show similar initial kinetics except in the low concentration limit,  $\phi = 0.05$ . In this case, the curves coincide only at very small time when the coordination number is less than one: the clusters have not been formed yet in this "bimolecular" limit. At moderately longer time scales it is seen that this scaling relationship works well for higher volume fraction with larger deviations observed as volume fraction is decreased. Lastly, there is a significant difference in the longest investigated times between different barrier heights at the same volume fraction. These deviations are investigated further to explain the effect of barrier height on aggregation kinetics.



FIG. 6: Scaled coordination number dynamics plotted by scaled time  $\chi t$  where  $\chi = f \exp [\beta (1 - f) U_{\rm b}]$  with f being the barrier height scaling factor and  $U_{\rm b}$  being the barrier height of the unscaled potential. Different barrier heights are denoted by the symbols:  $f = 1 (\triangleright), f = 0.7 (\diamond), f = 0.5 (\Box), f = 0.3 (\triangle), f = 0.1 (\bigcirc)$ . Additionally, different volumes fractions are identified by curve color as labeled on plot.

The short time deviation from the expected kinetic scaling relationship observed at lower volume fractions can be explained by the importance of spatial diffusion at lower densities. This was studied by observing the distribution of particle coordination number at short time scales (results not shown). Even at the earliest of time scales, it was found that aggregation in the reduced barrier case lags behind the full barrier when time is scaled following the relationship based upon barrier height. At these initial time scales there is minimal existing structure and aggregation proceeds largely through the formation of dimers. The scaling relationship accounts for the difference in times scales for dimer reaction involving the potential barrier height and therefore the only dif-



FIG. 7: Snapshots of simulation configurations for  $\phi = 0.35$  and f = 0.1 through out time. Particles are color coded by coordination number, n, with  $0 \le n \le 3$  - blue,  $4 \le n \le 6$  - green,  $7 \le n \le 8$  - red,  $9 \le n \le 10$  - pink,  $11 \le n \le 12$  - orange. In the later two snapshots particles with  $n \le 10$  are rendered partially transparent to better show the highly aggregated crystalline domains.

ference is spatial diffusion. Additionally, investigation of root mean square diffusion distances support this theory with the high barrier height simulation showing a much longer diffusion length,  $3\mu m$  vs.  $0.2\mu m$  at  $\chi t = 1$ s, than the tenth-barrier simulation.

As previously noted, the later stages of aggregation warrant further investigation as different aggregation dynamics are observed and such are not explained by the kinetics scaling relationship. In studying this phenomena, the distribution of coordination numbers among individual particles was investigated at different volume fractions for the lowest barrier f = 0.1 where such anomalous behavior is most prevalent (results not shown). In comparing these distributions with Figure 5 it was found that the later stages of aggregation are associated with a population of highly coordinated particles with individual coordination numbers n > 11. Further, on visual inspection of simulation configurations, it was found that these highly coordinated particles are associated with crystalline domains interspersed throughout the colloid system. Example snapshots of such configurations are shown in Figure 7 for  $\phi = 0.35$ .

Correlated with these highly coordinated crystalline domains are void zones with few particles such that the late stage colloid aggregation structure is highly heterogeneous. These structures explain the failure of the kinetic scaling relationships to model the late stages of aggregation as this theory models a simple 1-dimensional potential energy landscape considering only the scaling of a single barrier. In contrast, the process associated with reorganizing an already aggregated colloidal gel into crystalline domains likely involves a much more complex potential energy surface with contributions from many pairwise interactions. Therefore it is possible that with different barrier heights the mechanism of reorganization may change with different intermediate structures and hence the controlling potential energy surface at one barrier height is not simply a linear rescaling of the potential energy surface of a different barrier height system with the same mean coordination number.

Evidence for this is found by analyzing the static structure factor when the mean coordination number is  $\langle n \rangle = 6$  for systems with  $\phi = 0.2$  at different barrier heights as shown in Figure 8. Here it is observed that the microstructure of these systems are substantially different despite having the same bulk extent of aggregation. In general, it is seen that the lower barrier height cases have more structure than the higher barrier cases, although f = 1 is something of an exception. This additional structure may hinder reorganization into crystalline domains which would explain why the scaled kinetics of the low barrier cases reorganize faster than that of the higher barrier cases when the theory predicts identical scaled results. The relationship between barrier height and intermediate structures and how this affects aggregation dynamics is obviously rather complex and warrants further investigation in future work.

#### C. Conclusions

Within this study, we have provided a first characterization of the aggregation dynamics of reactive colloids including the effect of barrier height at different



FIG. 8: Static structure factor as calculated for the first configuration of each trajectory where the bulk coordination number is  $\langle n \rangle \geq 6$ . Time of configuration shown in parenthesis within legend. Shown for different barrier heights f at a volume fraction of  $\phi = 0.2$  and calculated over the distribution of particle centered separation distances, plotted by wave vector scaled by particle diameter (twice particle radius  $R_p$ ). Results show how an aggregating configurations of the lower barrier heights system generally has more structure than higher barrier height systems with comparable extents of bulk aggregation.

colloid volume fractions. These results form the core of a manuscript that we have prepared for publication and are currently finalizing with our industrial collaborators. It was found that the early to intermediate stages of aggregation are well described by a kinetics model based upon Kramer's theory. Later stages of aggregation involve reorganization with a dependency on the intermediate aggregation structures that change with barrier height in a manner not captured by this simple analytic theory. Therefore more complex behavior is observed in these later stages and further study is needed to provide a theory of reactive colloid structural reorganization.

## IV. INTERMEDIATE STRUCTURES IN REACTIVE COLLOID AGGREGATION

The reorganization of structure in reactive colloids, as observed in the later stages of aggregation, has been found to be non-trivially related to barrier height and we are currently working to develop a theory of this process. The intermediate aggregation structures preceding reorganization have been identified as important in controlling the dynamics of this process and further investigation of these structures is needed. In a visual analysis of intermediate aggregation structures, we have identified several different classes of structures, including isolated clusters, infinite heterogeneous networks of clusters, and infinite homogeneous networks. (Figure 9) We hypothesize that within each of these classes, reorganization will proceed through different mechanisms, and therefore it would be useful to understand the conditions under which each structure will be formed.

As part of this investigation, we are developing more rigorous criteria to classify these intermediate structures through analysis of aggregation graphs. These graphs encode the network structures of colloid aggregation with each particle as a node and edges denoting pairwise aggregation (Figure 10). In analyzing these graphs, we have explored various stochastic algorithms with the aim of determining the length scales of highly interconnected clusters and the strength of connections between clusters. An optimal method is still in progress, although we are close to creating a rigorous criteria to classify intermediate structures in terms of cluster sizes and strength of interaction between clusters.

# V. REVERSIBLE VS. IRREVERSIBLE AGGREGATION IN REACTIVE COLLOIDS

We have also began investigating the effect of well depth on aggregation dynamics, particularly with regard to reversible vs. irreversible aggregation. Beyond theoretical interest, this property of colloids is an important design parameter for aggregating colloid products, with the strength of aggregation modulated through such means as addition of surfactants to reduce the hydrophobic component of attraction.<sup>6,16</sup>

The effect of well depth  $U_{\rm w}$  was modulated through linear rescaling of the well region of the pair potential between colloids to vary well depth independently of barrier height. From this the original well depth of  $U_{\rm w} = 5.3kT$  was rescaled to two values of  $U_{\rm w} = 0.53kT$ and  $U_{\rm w} = 53kT$  to create wells with insignificant interaction and very strong irreversible aggregation respectively. Using these new potentials, we have simulated colloid aggregation over the range of investigated volume fractions to determine the importance of well depth on reactive colloid aggregation dynamics.

Currently, we have collected complete results for systems with a low barrier to aggregation of  $U_{\rm b} = 1.03kT$  (f = 0.1) and these are shown in Figure 11. These results provide a good picture of how well depth factors into reactive colloid aggregation. In the insignificant well case  $U_{\rm w} = 0.53kT$ , one observes a small extent of aggregation resulting from jamming, where volume exclusion constraints force a certain extent of nearest neighbor interaction. For the irreversibly aggregation wells  $U_{\rm w} = 53kT$ , the importance of dissociation in aggregation is found. Specifically, the irreversible well slightly accelerate aggregation in the early stages while quenching to the ini-



FIG. 9: Examples of the three classes of intermediate structures observed in reactive colloid reorganization: isolated clusters, a network of clusters, and a homogeneous network. The same coloring scheme as Figure 7 is used in showing these simulation snapshots.



FIG. 10: Examples of aggregation graphs that encode network structure. Shown for the three examples from Figure 9 and a closeup of one of the graphs is included to show the particles as nodes with edges as pairwise aggregation.

tially formed structures and this prevents reorganization to higher extents of aggregation. Visual analysis shows that the resulting structures are highly homogeneous and lack any highly aggregated domains. Therefore further investigation of reversible vs. irreversible aggregation will be closely tied to our work analyzing reorganization and intermediate aggregation structures.

## VI. EFFECT OF SHEAR FORCES ON REACTIVE COLLOIDS

Lastly, it is known that shearing forces can drastically alter the aggregation dynamics of reactive colloid systems by providing a driving force to overcome energetic barriers.<sup>56</sup> We are very interested in investigating this driven phenomena at the same high level of detail as we have applied to stationary systems. A challenge in such an investigation, is the proper handling of the multibody hydrodynamic forces in a computationally tractable fashion, without over simplification of important terms.<sup>57</sup> Multiple methods have been developed for simulating hydrodynamics in sheared colloidal systems and we are still determining which methods will be optimal for reactive colloids, although methods will require substantially more computing power.<sup>57–60</sup>

In anticipation of this future large-scale computational need, we have recently completed a proposal for 3 million hours of Teragrid cluster computing time. In support of this proposal, we have performed a preliminary investigation of shear forces in colloid aggregation, without the modeling of shear forces. While these results are highly suspect with this omission, they are included here to show the possibility of interesting effects from shear forces (Figure 12). It is found that shear accelerates aggregation at the early stages by providing energy to overcome the reaction barriers, while at later times aggregation is limited by shear forces breaking up long range structures and thereby inhibiting higher levels of aggregation. Details of such results will change with proper modeling of hydrodynamics interactions, although these initial results are indicative of interesting shear induced behavior.





FIG. 11: Current results investigating effects of different well depths  $U_{\rm w}$  on the aggregation dynamics of reactive colloids. Results shown for a low reaction barrier of  $U_{\rm b} = 1.03kT$  (f = 0.1) at different volume fractions as denoted by color:  $\phi = 0.5$  - magenta,  $\phi = 0.35$  - green,  $\phi = 0.2$  - blue, and  $\phi = 0.05$  - red. Three different well depths are investigated for each volume fraction and the aggregation dynamics for each are shown as different markers:  $U_{\rm w} = 0.53kT \bigcirc$ ,  $U_{\rm w} = 5.3kT$  (original value)  $\triangle$ , and  $U_{\rm w} = 53kT \square$ .

# VII. THE PATH FORWARD

As discussed in the last few sections, we are currently investigating several phenomena in reactive colloid aggregation: the reorganization of colloidal structures as important in the later stages of aggregation; different well depths leading to reversible or irreversible aggregation; and the effects of shear. As of current, these projects will be the future focus of my research. On completion, each will extend our knowledge of reactive colloid aggregation beyond the basic characterization provided in our first study. Additionally, we are also investigating other aggregating colloidal systems, such as the bicolored Janus particles that are gaining interest in nanoscale assembly,<sup>61</sup> and if time and resources permits we hope to further investigate the nonequilibrium behavior of additional aggregating colloidal systems.

FIG. 12: Preliminary results for shear dependent aggregation dynamics, as measured by average particle coordination number as a function of time. Results shown for three different shear rates  $\dot{\gamma} = 0s^{-1}$   $\bigcirc$ ,  $\dot{\gamma} = 100s^{-1}$   $\triangle$ , and  $\dot{\gamma} = 1000s^{-1}$   $\diamond$  for volume fractions of  $\phi = 0.5$  - magenta,  $\phi = 0.35$  - green,  $\phi = 0.2$  - blue, and  $\phi = 0.05$  - red.

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