Investigating dynamic stiffening and softening of a system of colloids cross-linked via polymers

Elisabeth Rennert
exr3935@rit.edu

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Investigating dynamic stiffening and softening of a system of colloids cross-linked via polymers

Elisabeth Rennert

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Materials Science and Engineering

School of Chemistry and Materials Science
College of Science
Rochester Institute of Technology
Rochester, NY
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Committee Approval

Approved: Dr. Michael Pierce, Ph.D. Date
Chair, Masters Program in Materials Science

Approved: Dr. Moumita Das, Ph.D. Date
Thesis Advisor, Committee Member

Approved: Dr. Scott Franklin, Ph.D. Date
Committee Member

Approved: Dr. Pratik Dholabhai, Ph.D. Date
Committee Member

Approved: Dr. John-David Rocha, Ph.D. Date
Committee Member

Approved: Dr. Poornima Padmanabhan, Ph.D. Date
Committee Member
Contents

0.1 Abstract ......................................................... 3
0.2 Introduction .................................................... 4
0.3 Model and Methods ............................................. 5
0.4 Results .......................................................... 12
  0.4.1 Packing Fraction .......................................... 12
  0.4.2 Rest Length ............................................... 15
  0.4.3 Energy Metrics ........................................... 18
  0.4.4 Decaying Probability of Attachment .................... 22
  0.4.5 Active Crosslinkers ...................................... 28
  0.4.6 Sinusoidal Attachment and Detachment Probabilities 31
0.5 Conclusions .................................................... 40
0.6 References ..................................................... 48
0.1 Abstract

With the goal of ultimately deciphering the design principles for biomimetic materials that can autonomously stiffen and soften, we investigate colloids as a model system that can dynamically transition from fluid-like (sol) to gel-like (gel) when crosslinked with polymers. The model was first developed with colloids only, interacting via a Lennard-Jones potential and undergoing Brownian dynamics, with experimentally relevant parameters, to test and refine the simulation. We then added polymer crosslinkers that connect the colloids via an attractive spring force, and investigate resulting collective properties, such as the time needed for the formation of system spanning networks and the elastic moduli, for various colloid densities, interaction strengths, and cross-linker rest lengths and densities. Using experimental parameters for polystyrene spheres and Bovine Serum Albumin (BSA) crosslinkers, we predicted the behavior of real systems. Finally, we replaced the passive, one-shot crosslinkers in our system by active cross-linkers that can dynamically attach and detach, and characterized how the degree of order and the mechanical response of the system change with time. Our results provide insights into the design of self-sustaining soft materials that can dynamically stiffen and soften, and how the properties of such materials can be tuned.
0.2 Introduction

Living systems have the ability to self-organize and autonomously generate coherent motion from molecular components. Over the past decades, humankind has been able to recapitulate some properties of living systems in active materials made by combining synthetic and biomaterials, including the ability to move and respond to local stimuli. However, the ability to autonomously self-organize and alter mechanical properties has proved difficult to engineer in such active materials. While many active systems have been developed and investigated, they either cause an irreversible organization or require external trigger to modulate behavior.

The goal of this project was to come up with predictive mathematical modeling that can guide experiments and provide insights into construction of active materials that can autonomously modulate their mechanical properties on a user-defined periodic schedule. Such materials will have wide reaching applications in self-healing materials, bio-robotics, sensors etc. To accomplish the above goal, we sought to develop a model of an autonomous active material that can dynamically and autonomously move through cycles of stiffening and softening. The coupling of biologically based oscillators with a mechanical system capable of sustaining forces can create an active system that can be tuned for the variety of applications mentioned above.

The KaiABC oscillator is a system of bacterial clock proteins that help regulate circadian rhythms in the photosynthetic cyanobacterium, Synechococcus...
cus Elongatus. It is formed from the interactions of three proteins, KaiA, KaiB and KaiC, and generates robust twenty four hour rhythms by linking and unlinking based on conformational changes caused by phosphorylation cycles. The KaiABC oscillator can be used to cross-link a system of colloids in solution, using biotinylated KaiB and NeutrAvadin-coated colloids. Due to the cyclic nature of the KaiABC, the resulting system will be able to continuously transition between states without external interference. The modeling and simulation of this system will be able to explore the parameter space and predict the mechanical properties of the resulting system as well as inform experiments. In what follows, I describe the model and method, the results, and my conclusions based on the results.

0.3 Model and Methods

The system we consider is a 2D system of interacting colloidal particles under diffusion that are linked by polymer crosslinkers. The particle motion is modeled by an overdamped Langevin equation

\[
\frac{dr}{dt} = D\beta(F_{LJ} + F_c) + \sqrt{2D}\eta
\]  

(1)

\(F_{LJ}\) is the interparticle interaction force defined by the 12-6 Lennard-
Figure 1: Sample system configuration for 30% packing fraction. Colloids are packed regularly in high density areas, but overall there are voids in the system, leading to a large number of edge particles.

Jones Potential, based on the interparticle distance $r_{ij}$.

$$V_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] + \epsilon$$

Which is cut off at $r_{ij} = 2^{16}$ to make it a repulsive only force. $F_c$ is the elastic force on two particles connected via a polymeric crosslinker. It is modeled as a Hookean spring, such that

$$F_c = -K(r_{ij} - r_0),$$

where $r_0$ is the rest length of the crosslinker; thus for particle distance greater than this rest length, $F_c$ is an attractive force. The gaussian noise term,
drives the diffusive motion, where $D$ is the diffusion constant of the colloids and $\beta$ is a linking parameter equal to $\frac{1}{k_b T} = \frac{1}{\epsilon}$. The units of length and energy used to non-dimensionalize the equations in this simulation are the particle diameter $\sigma$ and $\epsilon$ respectively. The unit of time is defined as the time it takes for a particle to diffuse its own diameter; $\tau = \frac{\sigma^2}{D}$. When converting the dimensionless units to physical ones, values for experimental parameters were used to determine reasonable conversion values. The experimentally relevant diffusion constant for polystyrene beads of diameter 1 $\mu m$ was used, which gave a $\tau$ values of 4.14s. The formation of crosslinkers between a pair of colloids is limited primarily by the diffusion of the colloids. When the distance between them, $r_{ij}$, is less than the crosslinker rest length, they become coupled via a crosslinker with a certain probability. This probability is calculated at every timestep, so for different timesteps, it needs to be adjusted to maintain the same probability of attachment for beads in range for $1 \tau$.

The simulation was developed in C. Every timestep the interparticle forces were calculated for the system. Then the positions for each particle were updated based on the forces and diffusion values using Euler integration. The resulting position data was then further analyzed to produce the data seen throughout this thesis.

The simulation was originally developed using static crosslinkers that once attached, stay attached for the duration of the simulation. The experimental system is oversaturated with crosslinkers; in our model this implies a large
constant crosslinker concentration throughout the simulation. However, the number of attachment sites on a bead is limited, and can be taken up by self-attachment i.e. by a crosslinker both of whose ends are attached to the same bead. As a result the probability of crosslinking of two beads decays over time, which is incorporated in the model as:

\[ p_a = C p e^{-pt} \] (4)

where \( p \) is the base probability that a crosslinker will attach, and is proportional to the crosslinker concentration. The constant \( C \) is phenomenological parameter related to the concentration of initial available sites on the colloid. Note that as a result of the above, very low colloid concentrations do not lead to any noticeable crosslinking.

Next we implemented active crosslinkers with sinusoidally varying probabilities of attachment and detachment, to simulate the behavior of the KaiABC circadian oscillators which facilitate active crosslinking in the experimental system. The attachment and detachment probabilities are given by

\[ p_a = C p \sin^2 \left( \frac{\pi t}{T} \right) \]
\[ p_d = C p \cos^2 \left( \frac{\pi t}{T} \right) \] (5)

This mechanism allows the crosslinking polymers (bonds) to oscillate between attached and detached states on a timescale of a few timesteps, which is not the way the KaiABC driven crosslinking works experimentally. Hence, we
also investigated an alternate mechanism where the attachment probability $p_a$ still varies sinusoidally, but once attached, the bond has a fixed lifetime based on the period of the oscillation.

A major goal of the simulation was quantifying the level of order in the system to identify phase transitions between gel-like crosslinked states and liquid-like unlinked states. A variety of methods are used including the number of bonds per particle, the mean squared displacement (MSD), the radial distribution function (RDF), and the energy of the system under shear. The number of bonds in the system is a very rough measure of the level of interconnection in the system. In a perfectly connected hexagonal lattice, every particle would have six neighbors, but that would only be possible with systems so dense that they would not have a liquid phase. The MSD is a measure of how far the particles move. Under free diffusion it should be linear with a slope of $4D$ in two dimensions, however once networks form among the
particles, they have significantly reduced mobility, especially once a system spanning network forms. The RDF is the probability that two particles in the system are at a certain distance from each other. In a perfectly ordered lattice it has very sharp, regularly spaced peaks with constant amplitude. Given the diffusion and low density of the systems studied, the RDF for the most ordered cases has regular peaks, but they decay with distance.

![Figure 3: RDF for simulation system in the ordered phase. Peaks are regularly spaced at slightly more than 1 $\sigma$ due to the diffusion in the system. The spacing remains regular, even as the amplitude of the peaks decays over distance.](image)

We response of the networks to shear was calculated as follows. To apply shear to the system, and particles with connections that wrap around the top or bottom edges in the periodic boundary conditions were duplicated on the other side. This created a layer of edge particles with connections to the rest of the network. These edge particles were kept at a fixed $y$ value and sheared along the $x$. Once the system has been deformed by the shear, the difference
in energy densities can be found. The shearing is performed without the effects of diffusion to ascertain the energies of the specific configuration with more precision. However, this does result in energy values lower than with diffusion due to an inflation of average bond lengths by the diffusion. These energy density values provide a way to compare the mechanical properties across various configurations of the system. The 2d elastic modulus can be calculated by

\[ G = \frac{2E/A}{\gamma^2} \]  

(6)

Figure 4: Configuration image of system under shear. Red circles represent the fixed edge particles

Because the base energy level depends upon a variety of factors, primar-
ily the crosslinker spring constant and rest length, which can be defined a bit arbitrarily due to lack of experimental data, it is important to compare systems with the same $K$ and $r_0$ values. Since the energy unit for the system is defined by $\epsilon$, which is related to the temperature and thus the diffusion of the system, these values primarily determine the balance between energy contributions from interparticle $L - J$ interactions and Hookean elastic interactions due to the deformation of the crosslinkers. Practically there is a limit on how much one can be increased over the other before the simulation stops functioning. This means that the resulting shear modulus, $G$, value does not have much physical significance except as a comparison between simulated systems. However, this value can then be normalized by the value for a completely connected network, which we approximate with the results of a very high packing fraction system. This normalized value has more predictive power for experimental results.

0.4 Results

0.4.1 Packing Fraction

The major goal of the simulation was to identify the phase transitions in a crosslinked colloidal system, and predict its mechanical properties. One of the primary parameters investigated was the packing fraction of the system. To establish phase transitions in the system, we first had to determine at what colloid density the system would be ordered without crosslinkers, and
thus not have a liquid-like to gel transition from. The threshold is around 40% packing, though the transition is not sharp, as is shown by the steadily declining MSD slopes in Fig 6. Most of the simulations discussed are at around 10-30% packing, to balance a distinct phase transition with the time necessary to reach system equilibrium.

Figure 5: Configuration images from 20 and 70% packing fractions. The high packing fraction case has ordering without any crosslinkers, while the lower one is more liquid-like

The packing fraction along with the diffusion constant, set the equilibrium time. The lower the packing fraction, the more time it takes for the particles to diffuse close enough together to attach, even if the probability of attachment itself is high. The preliminary testing and exploration of the parameter space used nondetaching crosslinkers with a constant, high probability of attachment. This case, called static, showed that smaller packing fractions reach saturation more slowly, but end up with a higher number of
Figure 6: RDF and MSD plots for a system with no crosslinkers at varying packing fractions. Around 40% packing the system begins to be in an ordered state without crosslinkers. Varying the packing fraction maintains diffusive behavior, but with an effective diffusion constant, $D_{eff}$, that decreases linearly with packing fraction.

bonds per particle after a sufficiently long time. This may be because for very low density systems, there aren’t enough particles to form a spanning system, so instead they pull together into very tightly connected smaller clusters. These tight clusters mean that lower density systems have much smaller average deformation of bonds, and thus have less energy despite having a higher number of bonds. They also had fewer bonds per area due to the number of particles being held constant across runs. This forced lower pack-
ing fractions to have a larger area, which was not overcome by the slightly elevated number of bonds. 20% packing fraction seems to be around the threshold where the particles can form spanning systems. This configurational difference indicates that the number of bonds in the system, while an indication of system formation, is not definitive of resulting mechanical behavior. This is supported by both the difference in MSD slopes between packing fraction as well as calculated shear energies.

![Figure 7: Bonds per particle over time for static crosslinkers. Initially the higher packing fractions have more bonds per particle, but at around 500 $\tau$ the lower packing fractions begin surpassing them, ending with a slightly higher number. The initial network formation is very fast, especially in higher density systems, followed by much slower growth as the final possible bonds are filled in. The 10% system is more gradual as it must diffuse farther to attach.](image)

### 0.4.2 Rest Length

In addition to packing fraction, the rest length of the crosslinker was also considered. It did not have any significant impact on the resulting configura-
Figure 8: The bonds per particle for the simple static case can be modeled by a logarithmic growth of the form $a + b \ln t$. A stretched exponential fit was also considered, and works well for lower packing fractions, but for higher it begins to diverge in the initial growth stage. For the 5000 $\tau$ time frame considered, the number of bonds shows continued growth. However, there is a maximum number of bonds per particle that can form in the hexagonal lattice that the ordered states reflect. This means that there has to be an eventual saturation in the system where it would diverge from the logarithmic model. For the system growth stage, the model fits very well, with less than 1% error for all fit parameters across packing fractions. Lower $b$ values indicate faster initial system growth, but a lower overall number of bonds. $b$ decreases with increasing packing fraction as would be expected. The increasing $a$ values compensate and keep all the packing fractions at similar numbers of bonds.

The rest lengths are defined as center-to-center distance of two connected particles, so the surface-to-surface distance is $r_0 - 1$. To keep the distance within reasonable dimensions for experimental crosslinkers the values used ranged from $r_0 = 1.01$ to 1.1. However, the actual length of the bonds in the simulation had very similar distributions across nominal rest lengths. The peak bond length was around 1.2, no matter the rest length, most likely a result of diffusion and the Lennard-Jones interparticle repulsive force counterbalancing the difference in spring forces from the
Figure 9: Configurations of system with static crosslinkers and constant probability after 5000 $\tau$. Packing fractions are 10, 20, and 30% (left to right). The 10% system has condensed into tight clusters, while the 30% formed a network spanning the space. This leaves 20% as an intermediate threshold between the two.

decreased rest length. The primary result of varying rest lengths was to modulate the effective spring constant $K_{eff}$, which additionally showed that the behavior of the system is insensitive to the specific value of $K_{eff}$ used. The second major observation on varying $r_0$ is concerning the distance at which particles are close enough to become coupled via bonds. Higher $r_0$ leads to more overall bonds in the system, with the effect most prominent in lower packing fraction systems, making it possible for them to surpass the higher packing fractions in terms of bonds per particle. However this likely implies the resulting clusters are more dense rather than system spanning, as they show no major differences in resulting configuration despite the difference in equilibrium number of bonds per particle.
Figure 10: MSD for static crosslinkers. The behavior is initially diffusive, with the $D_{eff}$ depending on the packing fraction. Once networks begin to form in the system, it becomes subdiffusive. The overall higher value of the lower packing fractions indicates higher mobility in the separated clusters than in the system spanning networks of the higher packing fractions.

Figure 11: Histogram of bond lengths for varying crosslinker rest lengths at 30% packing, and for varying packing fractions at $r_0 = 1.1$. All have similar peak bond lengths, but lower packing fractions have a narrower distribution of lengths, due to the tight clusters that form.

### 0.4.3 Energy Metrics

This leads into the relationship between the structural configurations, the number of bonds per particle, the shear modulus, and the degree of ordering
Figure 12: Bonds per particle for 30% packing and $r_0 = 1.1$ respectively. Longer rest lengths result in higher bonds per particle, with stronger effects on lower packing fraction systems.

Figure 13: Overlaid graphs of total energy density and bonds per particle. Despite having more bonds the lower density system has lower energy density. The total energy increases with the number of bonds, though not precisely with the same curve indicating higher energy (more stretched bonds) are forming later, to create a greater energy increase from a smaller number of added bonds. Alternately it might be due to conformational changes making the system stiffer as the later bonds are added after the initial burst of system formation.
in the system. As discussed above, the number of bonds is more a measure of the stage of system development than of the resulting shear. In the static case all the packing fractions reached equilibrium with approximately the same number of bonds per particle. Because of the larger area for lower packing fractions, the area density of bonds was lower over the entire space, though within the dense clusters it was slightly higher than in higher packing fraction systems. This on its own would result in a lower energy density, leading to lower ultimate $G$ values from Eq 6, but the disconnected clusters mean that the shear does not even affect parts of the system. Additionally, in cases where there are relatively few bonds wrapping in $y$, the results of the applied shear can be unreliable due to the manner in which the shear is applied. It leads to all of the stress being placed on a few of the bonds.

When the system is sheared, energies are calculated before and after the shear is applied. This leads to two metrics to describe the system. A $G/\tilde{G}$ value can be calculated using Eq 6, with $\tilde{G}$ being the value from a fully (very densely) connected network for the same number of beads. To obtain a quantity related to this ratio, we calculate the ratio of the corresponding total energies $E/\tilde{E}$ after shear is applied, for a given shear following the definition of shear modulus stated earlier. Note, however, unlike the above mentioned definition, $E/\tilde{E}$ may depend on the area of the system in the simulation.

To obtain an area independent measure, we also study the difference in energy before shearing, $E_0$, and after, $E$, i.e. the deformation energy. When normalized by the energy difference for a well connected system, this gives a
area independent measure of how much the system resists shear, given by

\[ \frac{E - E_0}{\bar{E} - \bar{E}_0} \]  

(7)

This value has a larger variance than \( G/\bar{G} \), but gives an interesting window into network formation and equilibrium. Because additional bonds increase the base energy of the system, this is a measure of how much bonds contribute to the overall structure of the network. Negative values can occur, especially in loosely connected systems with few bonds. This indicates that the shearing is only serving as settling influence on the system and allowing structures to slide into lower energy configurations. For low density systems, \( (E - }
$E_0)/E_0$ increases over time, indicating more strongly connected clusters. It is lower than high density systems even though it is not normalized by area, meaning that for the dense clusters commonly seen in low density systems, the shear is not affecting the entire system. However for high density systems it decreases slightly over time. The overall energy of the system is increasing over time, so the energy difference created by the shear is not increasing as much. This indicates that the later bonds are not as structurally relevant to the overall network, and that once a dense system reaches a certain threshold of bonds, further growth is not crucial to is mechanical properties. This contrasts with low density systems, where the dense cluster become even tighter with the addition of more bonds. This could impact the fluctuations in mechanical properties for the active system, making them more abrupt, despite the sinusoidal activity of the crosslinkers.

**0.4.4 Decaying Probability of Attachment**

With the updated model for static crosslinkers, using a decaying probability of attachment, there is similar behavior, especially in high density systems. The plateau in increasing numbers of bonds is more pronounced, as is expected from the decaying probability. There is a limited window before the probability drops so low no further bonds can form, and an equilibrium state results. Due to this it was not necessary to run the simulation for as long to reach an equilibrium state.

The decaying bond probabilities help discover the varying rates of system
Figure 15: Energy difference over time for 20 and 30% packing fractions in the static case. Lower packing fractions have lower energy difference despite having slightly more bonds overall. There is more noise at the beginning due to fewer bonds causing less even shearing. The energy difference decreases toward the end as the higher energy, more stretched bonds are formed. These high energy bonds settle as the system is sheared, resulting in a reduction of the system energy. If this is not countered by the rest of the system increasing in energy, the resulting deformation energy can be negative. In either case it causes a lower deformation energy than earlier system configurations, causing the dip at the end of the plot.

formation for different packing fractions. The limited window to form bonds can create a packing fraction cutoff where a full network does not form higher than that for the static case. This can result in a large divide between the equilibrium number of bonds for these different packing fractions. Once a network has formed in a system, it then becomes easier for more bonds to form in it as the particles are held in proximity. As the half life of the probability decay decreases, the threshold for network formation gets higher. For $t_{1/2} = 100$ and 200 $\tau$, the threshold was around 10%, but for $t_{1/2} = 50$ $\tau$, 

23
Figure 16: The equilibrium number of bonds versus packing fraction in systems with decaying probabilities of attachment with varying half lives. The plateau at higher packing fractions indicates that the decaying probability is having relatively less impact as the packing fraction increases.

even the 20% packing couldn’t form a full network. The shorter half life cases favor higher packing fraction systems due to the lower amount of diffusion needed despite the higher initial probability.

The biggest impact on the high density systems was that the $G/\tilde{G}$ values were much higher, as they had time to make connections within the network to make it more complete. The $G/\tilde{G}$ for the low density systems were only slightly increased, and still very low, again supporting the claim that very low packing fraction systems cannot form spanning networks.

From Eq 4, we included a linking constant, $C$, to help tune the initial attachment probability in the system. Unless stated the, constant was set to 1, as it produced $p_0$ values around the level used in the static case. When $C$ was set to 10, the effects of the decaying probability were less noticeable,
Figure 17: bonds per particle and msd for a variety of packing fractions in the case of decaying probability with a half life of 50 $\tau$. The 4x line is what the MSD should be in 2 dimensions under free diffusion. Even in the 5% packing system, the MSD was still below that, showing the impact of even small clusters on the mobility of the system. Because of the decay in probability they never form into the tightly connected clusters observed in low packing systems with constant probability as the probability remained high enough to favor bond formation for much longer. As expected, this gave results closer to the static case, especially for lower packing fractions, which had time to form the tightly connected clusters that gave them higher bonds per particle than their more dense counterparts.

The systems with higher $C$ values also did not have the same cutoff behavior with respect to the equilibrium number of bonds. Instead it was again more similar to the static case with all the system ending up at around the same number of bonds. This suggests a $C$ value of around 1 as an optimal value to keep the base probabilities high enough that networks can form before the probability decays, but low enough that it has an effect.

This also leads into the question of competing timescales in the system.
Figure 18: configuration of the 5% packing for a decaying probability with a half life of 50 $\tau$. The dense clusters seen in previous low density systems did not have time to coalesce before the probability decayed. This result in even more scattered and liquid-like behavior than in configurations at similar packings for purely static crosslinkers.

The time it takes for a system to reach equilibrium is determined by the diffusion rate of the system as well as the probability. The effects of diffusion have been discussed earlier and is accounted for by the use of $\tau$ as a time unit, but the system formation can be suppressed by a low probability, as it takes many more interactions before the system can form. This will be useful for designing the active system with very timescales of oscillation much longer than the hundreds of $\tau$ that the fastest diffusive timescale requires (varying based on packing fraction). However, for a decaying probability a middle ground must be found that matches the timescale dictated by the
Figure 19: Bonds per particle with decaying attachment probability. For the lower density systems, longer half lives result in slightly higher equilibrium numbers of bonds. This suggests that systems that form more slowly result in more tightly connected structures.

probability with the half life of the decay. This would suggest that similar results could be achieved with a lower initial probability but longer half life. The linking constant of $C = 1$ would still be necessary as the $p$ value in the decay equation is also the rate constant and thus inversely proportional to the half life. This also suggests that a $C$ value in a physical system that is too low might suppress system formation in even higher packing fractions.

The results of runs with decaying probabilities suggest that networks will not form in systems with very low packing fractions. This extends the results from purely static crosslinkers to a much more dispersed and liquid-like end result. This agrees with experimental difficulty finding network formation for low volume fractions. Because the half life of the decay is related to the concentration of crosslinkers, it may be helpful to reduce the initial crosslinker
Figure 20: Shear metrics for decaying bond probability at varying half lives and packing fractions. For $G/\bar{G}$ the 50 half life goes down slightly because the bonds stopped forming earlier, so by the end it is just affected by diffusive motion and settling of any highly stretched bonds. For the $(E - E_0)/E_0$ plot, the lower packing fractions have much more variation to them as they have fewer wrapping connections. The 50 half life one in particular is especially mobile due to the previously discussed settling. Otherwise the energy differences are higher for the longer half lives, indicating a more stable network forms when the bonds form over a longer period of time.

centration as well as increase the density of colloids.

0.4.5 Active Crosslinkers

As was described above in Eq 5 the active crosslinkers were modeled using opposing sinusoidal probabilities of attachment and detachment. The parameter space was explored across a variety of packing fractions and base probabilities. Though the KaiABC oscillations are on a 24 hour cycle which is $20869 \tau$, oscillation periods of 100, 1000, and 10000 $\tau$ were primarily used to test the models examine the competing timescales inherent in the system.
Figure 21: Bonds per particle and energy metrics for decaying probability systems where $C = 10$. The bond behavior is similar to the static case, though with slightly lower equilibrium bonds, which also explains why it has slightly lower $G/\tilde{G}$ values as well. It, however, does have higher $G/\tilde{G}$ than the decaying case with lower $C$. 

29
Figure 22: A comparison of the bond behavior across many of the system parameters for the simple active case. For all of the combinations considered, the number of bonds changes in a sharp peak instead of a sinusoidal variation. For the top figure, three decades of oscillation period were compressed to the same timescale to compare the number of bonds at the same point in the oscillation cycle. Longer periods only increased the maximum number of bonds, as would be expected for a longer system formation time, and made the peak slightly sharper. Increasing both the packing fraction and the base probability had a similar effect, though lower packing fractions had both narrower and lower peaks, due to the increased system formation time.
Figure 23: As has been previously seen, the energy level follows the number of bonds in activity. However, the $G/\tilde{G}$ peak value is lower than it would be for a static system of the same packing and bonds per particle. The sharp peak in the number of bonds means that once a spanning network forms it does not have time to develop fully before the bonds break again.

0.4.6 Sinusoidal Attachment and Detachment Probabilities

The simple model using competing probabilities unfortunately did not produce an ultimately sinusoidal behavior, but instead sharp peaks of bond activity. These peaks were found across two decades of oscillation periods, so it is not due to competition with the system's diffusive timescale. The reason for these peaks is based on the nature of the probability calculations themselves. Attachment probability is calculated only when particles diffuse into range, but detachment is calculated every timestep. This effectively increases the detachment probability over attachment, explaining why the regions of bond activity were so narrow. The peaks occurred at $t = T/2$, which from Eq
Figure 24: MSD values for the $T = 1000$ active case. The behavior is primarily diffusive, with vary $D_\text{eff}$ values based on packing fraction. There are periodic small plateaus in the slope corresponding to the brief windows of bond formation. The MSD follows the trend reflected by other methods of analysis that the system spends most of the time in a disconnected, mostly diffusive state instead of forming detectable system spanning networks.

5 is the maximum of $p_a$, as would be expected. Expanding from that, one would expect the balance to tip in favor of growth at $t = T/4$, when the two probabilities are equal, but due to the advantage held by $p_d$, the peak edges are pushed in. The sharpness of the peaks is caused by the system reaching a critical number of bonds where the colloids are held in place by the existing bonds, and thus boosting further bond formations, a process which the happens in reverse during the sharp drop in number of bonds. This explanation also covers why lower packing fractions have narrower peaks whereas lower base probabilities have lower maxima but the same peak width. In the lower packing fraction systems, the critical amount of bonds takes longer to form, causing the rapid system growth to occur later.
An adjusted model was developed to counteract the advantage detachment had in the basic model and create an activity more sinusoidal and similar to the KaiABC activity. This was to simply suppress the base probability of \( p_d \). The base probability was divided by a quarter of the period, a number chosen due to the fact that the systems spends around a quarter of the period in a well connected state where they are almost constantly within range for attachment. In this case there is variation in the shape of the curve across timescales, indicating that the diffusion/equilibrium timescale for the system has come into play, instead of being dominated by the detachment probability. For a base probability of \( p_0 = 0.01 \), the \( T = 1000 \) system has almost perfectly sinusoidal bond activity, while the lower and higher periods are skewed towards detachment and attachment respectively. A reduction in the base probability results in slightly higher oscillation amplitude, but lower maximum value.

The \( T = 10000 \) case has very similar number of bonds across all packing fractions, indicating that it gets near a saturated state, as opposed to the spread of bond numbers across packing fractions found in the decaying model. While all of the systems go to 0, or very near it, at the bottom of the oscillation, the higher period cases spend much less time in the very low bond states. The fact that they do hit 0 means that the configurations that form each time are different, so all the repeating units can be averaged together for greater accuracy of measurement.

From the oscillations in bond activity and energy metrics, the system can
Figure 25: Bonds per particle and MSD at varying periods of oscillation with $p_f = .3$ and $p_0 = .01$ in the suppressed $p_d$ model. While are at least roughly sinusoidal, the higher period cases spend less time in the diffusive state. The $T = 1000$ and 10000 cases reach a high enough number of bonds that they might form system spanning networks, as is indicated by the sharp changes in MSD slope every cycle.

be seen to transition between a stiff, gel-like state and a liquid-like state. However, as was discussed earlier, due to the diffusive constraints of the model, the $T = 100$ did not have a strong distinction between the states, as it did not have time for the system to fully form, even at higher packing fractions. The packing fraction was also an important factor in determining system formation. These active systems reflected the cutoffs mentioned earlier in that systems with packing fractions of 10% or below did not form spanning networks, but instead formed clusters of varying size.

**Fixed Bond Lifetime**

Another model proposed also has a sinusoidal probability of attachment, but once attached has a fixed lifetime after which it detaches. The lifetime is
Figure 26: RDFs for the active model with suppressed $p_d$, calculated at the peak and trough of the crosslinker activity. This illustrates both the relative order between the liquid and gelled states as well as the amount of ordering the system achieves. The lower period systems have more noise due to a smaller time window to average over at a specific point in the cycle. While the $T = 10000$ system has more ordering overall, the 1000 system has greater differentiation between the states.
Figure 27: The energy values for different T values, averaged over all available periods, for a 30% packing fraction in the suppressed $p_d$ model. The $T = 10000$ case has a peak $G/\tilde{G}$ value of 0.4. While that is not as high as the equilibrium values of the static linkers, it is comparable to the decaying probability value for the same packing fraction. This indicates a discernible change in the mechanical properties of the system as it goes through its oscillation cycle. The $(E - E_0)$ plot also reflects oscillations in the system. While there is the expected noise at low bond levels, both the higher $T$ system showed a peak, indicating a development of the network with added bonds as opposed to small clusters being formed. The $T = 100$ system remains negative for most of the time, as would be expected from its overall low $G/\tilde{G}$ values, indicating low levels of bond formation and less reliable shearing results.

set to be $T/2$, with the addition of gaussian noise with a variance of $T/8$. The fixed lifetime is to ensure that bonds do not flip back and forth between attached and detached due to the competing probabilities, especially when they are near equal, as that is not reasonable behavior for the physical system in question. We also considered a further expansion of this model which also had a fixed cooldown time where a bond could not be reformed, but that resulted in increasingly minor oscillations as the bonds became more and more out of phase with each other. The previous models are still valid because
Figure 28: Configuration images for all T values in the in the suppressed $p_d$ model. Top left is a representative configuration for the low bond level for all the systems, with periods of 100 for top right, 1000 for bottom left, and 10000 for bottom right. The impact of the oscillation period on the system development is clear, and as was seen in the other metrics considered, the 1000 and 10000 system are much closer to each other than 100. Again a clear transition between states can be seen in the active system.
during the peaks of bond formation the effect is minor, so the timestep-scale bond oscillations act as a sort of gradiated check on bond formation. However, the fixed lifetime model exhibits some interesting behaviors due to the fact that it prevents all the bonds from breaking at the same time, as in the other model when the detachment probability rises, and producing the peak-like behavior seen in the basic active model. This model also causes some out of phase bonds that, due to being formed late, remain connected even during the low attachment probability regions. To maintain the state transition, the system parameters need to be tuned to allow for a distinct transition. For initial runs with $p_0 = 0.005$, there were sinusoidal oscillations in bonds, but due to the number of out of phase bonds, especially in the longer period runs, there was a much less distinct transition between states. The oscillations are still sinusoidal, but the minimum bond values do not drop to around 0, indicating the network does not completely dissolve each period. However, we have previously discussed systems with low numbers of bonds that still exhibit liquid-like behavior, with only small clusters formed. While the low density system had larger fluctuations in its number of bonds and distinct changes in slope in its MSD, it had barely any variation in its $G/\tilde{G}$ values. In contrast the high density system appeared not to vary much over the course of the oscillation, except in the $G/\tilde{G}$ values, which are arguably the most important measure as they correspond to the system stiffness, which can actually be measured. This highlights the different regimes these metrics cover. The former are focused on whether or not a network has formed in the
Figure 29: Plots of the bonds per particle over time in a fixed bond lifetime system with 30% packing and $p_0 = 0.005$. The second plot is at $T = 1000$, with varying packing fractions. As has been seen in other active systems, the $T = 1000$ and 10000 systems are closer to each other than the 100. The variations are sinusoidal, though higher periods are heavily skewed toward bond formation, with only a sharp dip during the low probability phase. For the $T = 100$ system, the bonds per particle never gets above 2, indicating a very weak system at the peak, and a gel-like system at the trough. This system may have the most distinction between states as the other two stay at a high enough number of bonds that the variation will be more akin to a formed network that becomes slightly softer.

The main goal is to create a phase transition, so if the maximum bond value is high enough, it may provide enough of a difference. If the bonds were the only factor determining the system properties, the amplitude of the oscillation would provide a cutoff. However, especially with higher density systems, once the bonds are above a certain threshold, additional bonds have lessened effect on the development of the mechanical properties of the network. It may be beneficial to use a higher initial probability, so that the bonds form more rapidly and thus stay in sync. In that vein a higher
Figure 30: Mean Squared Displacements for the varying periods of oscillation. The $T = 100$ system is the only one with any variation in the slope. That variation means that it actually transitions back into a more liquid-like state that allows the particles to diffuse. For the other two, the particles remain locked in a network despite the variation in numbers of bonds.

packing fraction than the 30% one primarily explored, again to boost the initial formation of bonds.

0.5 Conclusions

In this project, I constructed and simulated a model to study the dynamic stiffening and softening of a system of colloids crosslinked via polymers. The simulation achieved its goal of finding a regime in which there is an autonomous transition between liquid-like and gel-like states for colloid area fractions that would be liquid-like in the absence of crosslinkers. For highly ordered systems there is a fixed number and arrangement of neighbors. This ordering might be enhanced if the biotinylation of the beads themselves was patterned for those specific structures using patchy colloid methods.
Figure 31: The energy metrics for the varying $T$ values, averaged over all available periods. The $T = 10000$ system has a significant increase in energy above the other two, with a peak approaching 1. These levels are around what the static linkers achieved after reaching equilibrium, indicating a very stiff network. There is a discernible variation in the network stiffness, though it never goes low enough to be fully liquid-like. In contrast the $T = 100$ system has relatively low variations, given that in previous models it has been closer to the high period system that the low. The $T = 100$ system never reaches a $G/\tilde{G}$ level that would indicate a gel-like network, with the variation so low it would likely not be discernible. In the $(E - E_0)/E_0$, the values were predictably negative for the lower period systems that did not form spanning network, but for the high density system, the value remained fairly steady. Because the number of bonds remained so high, as soon as they broke, they were held in place long enough to quickly form again. This means that the new bonds were continually strengthening the network in opposition to the detachments, which should result in a constant value.
Figure 32: Low (left) and high (right) configuration images for $T = 1000$ (top) and 10000 (bottom). Both systems have clear shifts in configuration, but they display different points in the network formation process. The low density system is the initial formation, encompassing a purely liquid state and a very sparse network. In contrast the high density system is the final stages of development as the network contracts and refines, increasing the number of particles in a highly ordered chunk.
Figure 33: RDFs for the fixed lifetime model, calculated for the minimum and maximum ppoints of crosslinker activity. There is still a distinction between the two states, but as other metrics have shown, it is not as strong a distinction as in other cases. The systems get more ordered as the oscillation period increases. At the lower end, the $T = 100$ case has low levels of order and almost no distinction between the states, indicating that no system formation occurred. Interestingly, the highest period seems to have the most distinction between the states, though it never reaches a fully disordered liquid like point.
Figure 34: Comparison of bond behavior in the fixed lifetime model across varying base probabilities. While a lower probability results in slightly more sinusoidal behavior, it also causes a lower maximum value. The fact that the probability still affects the maximum indicates that, while it plateauning due to reaching bond saturation, the saturation value is being modulated by the probability as was seen in the static case.

With this phase transition in mind, we investigated systems where the packing fraction of the colloids was approximately between 20% and 40%. We studied a wide range to facilitate predictions to inform experiments that would be carried out by our collaborators. In preliminary models with static crosslinkers it was found that a gel-like state occurred when a spanning network formed in the system. This state transition from the original liquid-like to the gel state was examined by a number of methods, including calculations of a measure for shear modulus, radial distribution function, and mean squared displacements. The number of bonds, while used as a shorthand for linker activity did not have a direct correlation to the relevant material properties. The maximum value of the packing fraction range reflects ordering
occurring in the system at very high packing fractions due to crowding inter-
actions. The lower limit is more variable and depends on the specific model
being considered. The absolute minimum limit is for the simple static case
with time to reach equilibrium. In that case at very low packing fractions,
spanning systems never form, and instead coalesce into dense disconnected
clusters of varying size. The other models all involve some degree of limita-
tion on bond formation, so there is no way for a spanning network to form
in them if it couldn’t in the static case.

For the case where probability of attachment of crosslinkers to colloids de-
cays with time, the minimum colloidal packing fraction for network formation
is increased for very short half lives. Despite the higher initial probability,
colloids could not diffuse close enough before the probability decayed to a
point where attachment was no longer possible. This introduced competing
timescales into the system, in the form of a diffusion timescale and a bond
decay timescale, with the smaller of the two determining the limits to net-
work formation. This suggests we can enhance the possibility of network
formation in experiments on systems with low colloidal packing fractions by
reducing the crosslinker concentration, which would correspond to a longer
half life.

The competing timescales in the decaying model then informed the in-
vestigation of active crosslinkers which can dynamically attach to and detach
from the colloids. The timescales are in terms of $\tau$, which is the nondimen-
sionalized time unit of the system, which is the time it takes a colloid to
diffuse its own diameter. The diffusion timescale is on the order of hundreds of $\tau$, but the KaiABC oscillation period is much longer ($20000 \tau$). The simplest model with opposite probabilities for attachment and detachment did not result in sinusoidal bond activity, the models with suppressed detachment probability and fixed bond lifetime did. While the former gave sinusoidal bond activity across all values of the oscillation period studied, the latter allowed more variation. The primary difference was that the fixed bond lifetime model did not return to a completely disconnected state at the minimum and reached bond saturation at the maximum. While that lead to overall smaller amplitude in the oscillation, it had a much higher maximum shear modulus value. While the parameters used are phenomenological, they can be related back to experimentally obtainable quantities. For example, the base probability of attachment is related to the crosslinker concentration, and the 2D packing fraction of colloids can be obtained from their 3D volume fraction. These parameters can be varied. Even the period of linker activity can be tuned. Though the KaiABC oscillation period is fixed at approximately 24 hours, the conversion into $\tau$ can be tuned by modifying the diffusion constant of the system. The simulation predicts the conditions for an active system with autonomous transitions in material properties.

Finally, in our study, the full surfaces of the colloidal particles are accessible for attachment by crosslinkers, and it would be interesting to explore how the results would be modified for colloids that are patterned with patches of specific shapes carrying a finite number of attachment sites and arranged in
precise geometries. Such patchy colloids will allow for anisotropic interactions and provide an additional mechanism for regulating self-assembly and gel formation, and will be explored in future work.
0.6 References


