

Polymer Coated Superparamagnetic Beads Walking on Polymer Coated Surface

by

Stephanie E Moran

Submitted to the Department of Materials Science and Engineering in Partial Fulfillment of the Requirements for the Degree of

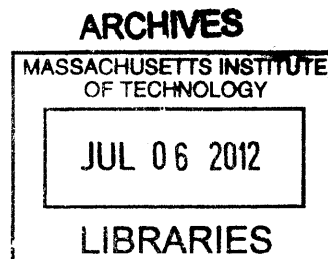
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Abstract

Biology has provided us with many organisms that are able to propel themselves through a fluid using cilia or flagella. This provides inspiration to create controllable systems that cannot only propel an organism or device through a fluid but can also create a fluid flow. Research has focused on how to mimic the mechanisms of these organisms for the use in microfluidic devices or drug delivery. This work examines walkers that are created using superparamagnetic beads placed in a rotating external magnetic field. Dipoles align in the beads so they assemble into rotors. These rotors follow the rotating magnetic field and are able to translate across a surface. This work looks at the effect of coating the beads and the surface with a polymer, Polyethylene Glycol(PEG). PEG has been shown to undergo a transition from an expanded state to a collapsed state under certain salt concentrations and temperature ranges. By looking at this transition we can see if the use of a polymer could affect the velocity of the rotors and if PEG could be used to control the velocity of the rotors or to initiate a transition. This transition is only seen by recording the velocity of the rotors, future research using other experimental procedures might be helpful in finalizing the transition of PEG in NaCl. It was unclear from these experiments whether the velocity of the rotors is dependent on the state of the polymer.

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1. Introduction

1.1 Problem Statement

Biology has provided many examples of mechanisms that allow organisms to propel through a liquid.¹ These biological systems provide an interesting source of inspiration for this research. Unfortunately we do not have the ability to precisely

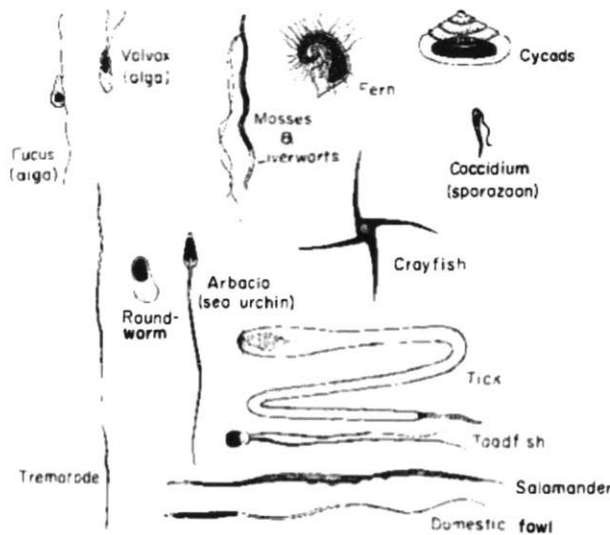


Figure 1. Organisms that use flagella and cilia to propel through a fluid (C. Brennen, Ann. Rev. Fluid Mech. (1977).)²

control the mechanics and behavior of most biological propulsion systems. We can only use these propulsion systems as a model for our own systems. There has been extensive research to understand how these organisms propel themselves using flagella and cilia. By using an oscillatory mechanism these organisms can translate in a fluid. These mechanisms have been used recently in biomimetic devices.^{3,4,5,6,7} It is important to understand how these systems function close to the surface when

we have a low Reynold's number condition. At low Reynolds number conditions there is only laminar flow, due to the dominance of the viscous forces.

This research focuses on the self assembly of superparamagnetic particles on a surface. These particles assemble into rotors in the presence of an external magnetic field. The magnetic field creates dipoles in each of the beads and as a result the beads align into a chain. By rotating the magnetic field these rotors follow the field and rotate. A no-slip boundary condition near the surface breaks the symmetry conditions and allows the chains to rotate.⁸ As the chains rotate they also create a controlled fluid flow. Altering the frequency and strength of the external magnetic field can precisely control these rotors. Previous research has shown that the surface interaction and frequency of these rotors plays a large role in the speed of the rotors.^{9,10} It was shown that with an increase in a downward force on the rotors resulted in a reversal motion of the rotors.⁹ The increase in the downward force could be interpreted as an increase in surface friction force between the beads and the surface. This research focuses on the surface interaction of these rotors. By coating the beads and surface in Polyethylene glycol (PEG) we observe how this affects the velocity of the rotors. The PEG provides a system where the beads are greatly slipping. We also look at how temperature affects the extension of the polymer and how this affects the velocity of the rotors. These rotors could potentially be used for drug delivery or to drive fluid flow in microfluidic devices.

1.2 Assembly of Rotors

We consider a single chain of a certain number of beads, N , in an external magnetic field with strength of B . The external magnetic field creates magnetic dipoles in each bead and then the beads assemble into rotors. The beads are superparamagnetic, which means that without a magnetic field they have an

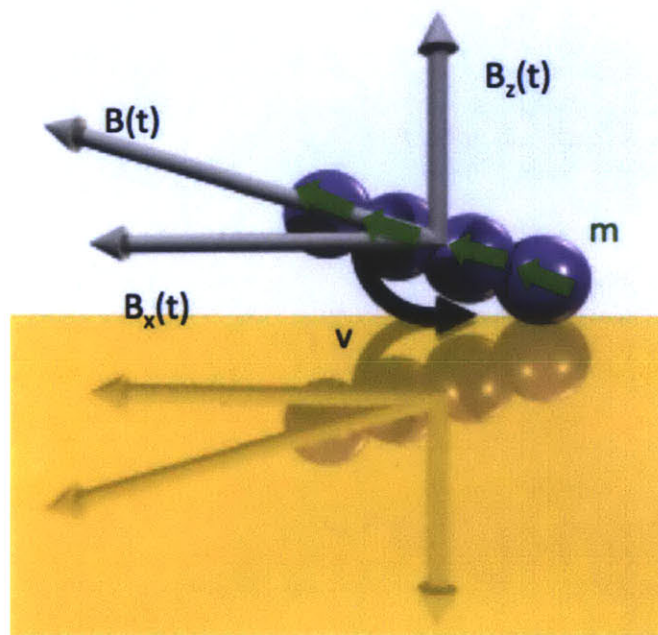


Figure 2. Diagram describing forces present during self assembly. Magnetic field applied, $B(t)$, frequency of magnetic field, ν , dipole moments present in the beads, m , and the two force components of the magnetic field, $B_x(t)$ and $B_z(t)$. The chain translates in the forward x direction.⁹

observed average magnet moment of zero. When a magnetic field is applied to the superparamagnetic beads they align to the field creating a moment in each bead. The beads that we purchased for this experiment have some residual magnetism when the field is turned off but they still observe the properties needed when the field is applied to them. The chains rotate and translate across the surface when the

magnetic field is rotated in the x-z plane at a frequency, ν . Refer to figure 2 for the translation of the rotor and the force present due to the external magnetic field present. Chains rotating in a clockwise fashion translate in the forward x direction. It has been shown in previous research that the translational velocity is greatly dependent on N, B and ν . Due to this, in this research we keep at least two of these variables constant in order to isolate the surface interaction present. The magnet moment in each bead can be defined as:

$$m = \frac{V_c \Delta \chi}{\mu_0} B.^{9,10}$$

Where V_c is the effective volume of the bead defined as $V_c = \frac{4\pi a^3 f}{3}$ where f is the fraction of the bead that is paramagnetic, a is the diameter of the bead and $\Delta \chi$ is the difference in magnetic susceptibility between the bead and the medium it's placed in.

In this research we will be looking at a constant field of 10 mT, a frequency of 5 hz and 2 beads for the temperature variant experiments. We will also scan frequencies with a constant temperature and a constant field of 10 mT. This research will focus on this temperature and frequency change and how this affects the velocity of the rotors. The temperature change will allow us to see if the collapse of the polymer affects the interaction between the rotors and the surface.

1.3 Beads and Surface Interaction

The superparamagnetic beads are purchased from Solulink. The beads come already coated in streptavidin. The beads have a diameter of $2.8\mu\text{m}$ with a Polystyrene core that is encapsulated in an Iron magnetite central layer. The beads are put in a solution of Polyethylene Glycol-biotin. Polyethylene Glycol is polymer

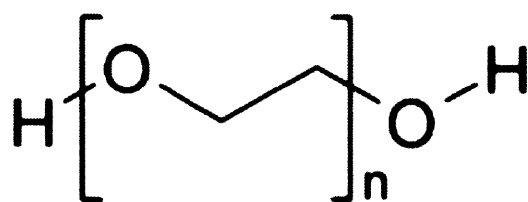


Figure 3. Polyethylene Glycol chemical structure.

that undergoes a transition from a collapsed state to an expanded state under certain temperature and salt concentrations. The structure of PEG is seen in figure 3 this unique structure is what allows this transition to occur. PEG is soluble in water and other polar solvents and is not soluble in nonpolar solvents. In this experiment we use PEG with a molecular weight of 5000. Other research has shown that block copolymers like PEG collapse under certain temperature and salt concentrations.^{11,12,13,14} In the extended condition there is a large separation seen between the colloid and the surface as displayed in figure 4.

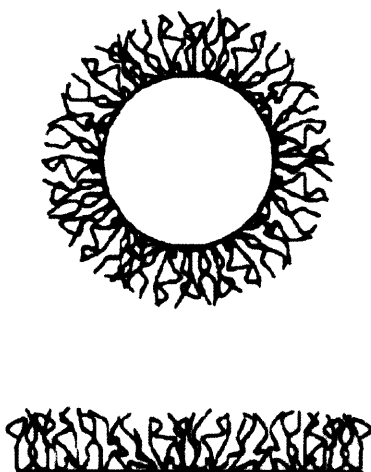


Figure 4. Illustration of Polymer extension state. Shows interaction between the surface and the colloid. The extended polymer repels itself(Fernades).¹¹

The other case is when the polymer is in it's collapsed state as see in figure 5. This indicates that the solvent is poor and the polymer prefers to be in its collapsed state.

We can examine this by the solubility parameter δ , which is defined as:

$$\delta = \left[\frac{\Delta H_v - RT}{V} \right]^{\frac{1}{2}}$$

Where ΔH_v is the molar enthalpy of vaporization and V is the molar volume.¹⁵

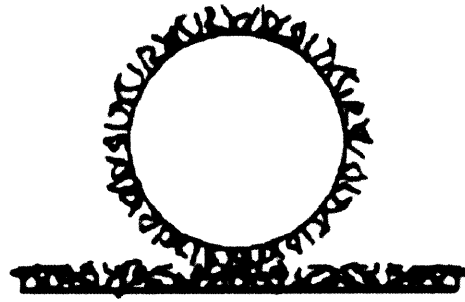


Figure 5. Collapsed state of polymer coated colloid and surface. Shows there is more interaction between the colloid and the surface which allows for more surface interaction(Fernades).¹¹

A biotin coated slide is purchased from Xenopore. The biotin coated slides are then coated with streptavidin. The mPEG-Biotin is attached to a biotin and has

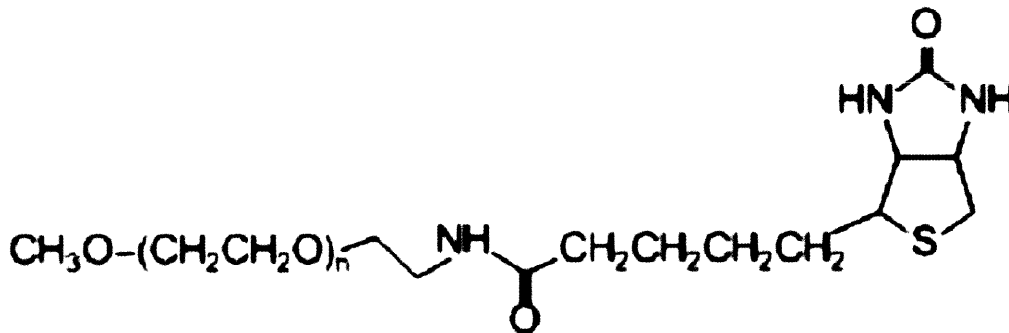


Figure 6. Methoxyl PEG Biotin. The structure on the right is the biotin and the $(\text{CH}_2\text{CH}_2\text{O})_n$ is the Polyethylene glycol. The biotin attaches itself to the streptavidin coated surface.

the following structure as shown in Figure 6. The biotin-streptavidin interaction is one of the strongest non-covalent interaction known. It is also resistant to most solvents and temperature ranges. We can assume that for these experiments that these linkages remain stable. During the experiment the PEG on the beads is interacting with the PEG on the surface and creating an interesting surface

chemistry as described earlier. From previous work it has been shown that the surface friction plays a significant role in the velocity and direction of the beads.⁹

1.4 Biotin-Streptavidin Interaction

This interaction was discovered in 1941 and is commonly regarded as the strongest non-covalent interaction present. Streptavidin is a bacterial homologous

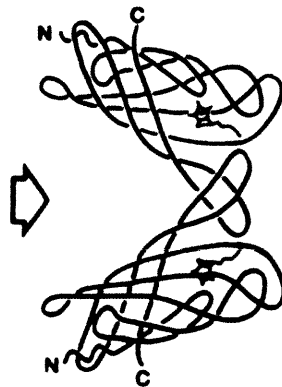


Figure 7. Structure of Streptavidin. Shows net-like structure of β barrels. (Weber)¹⁶

to the protein avidin and is isolated from *Streptomyces avidinii*. Biotin is a B complex vitamin.¹⁵ The structure of Streptavidin consists of eight sequential stranded anti-parallel β sheets.¹⁵ These β sheets interact with each other and form criss-crossed net like structure that create two β barrels as seen in Figure 3.¹⁵ Biotin binds in these barrels. The residues in the linings of the barrels are mostly aromatic or polar amino acids. When the streptavidin is placed in water, the water molecules fill the barrels.^{15,16} The biotin has to burry itself into the barrels and push the water out of the barrels. Once the biotin burries itself into the barrel there are multiple

hydrogen bonds created and even some hydrophobic interactions. The burrying mechanism of this interaction allows for a very strong interaction that can withstand most tempartures and pH values. The biotin-streptavidin has been observed to withstand temperatures as high as 70 degrees celcius. ^{5a,18}

2. Experimental Methods

2.1 Experimental Setup

The magnetic field of the rotors is created by applying a current through two

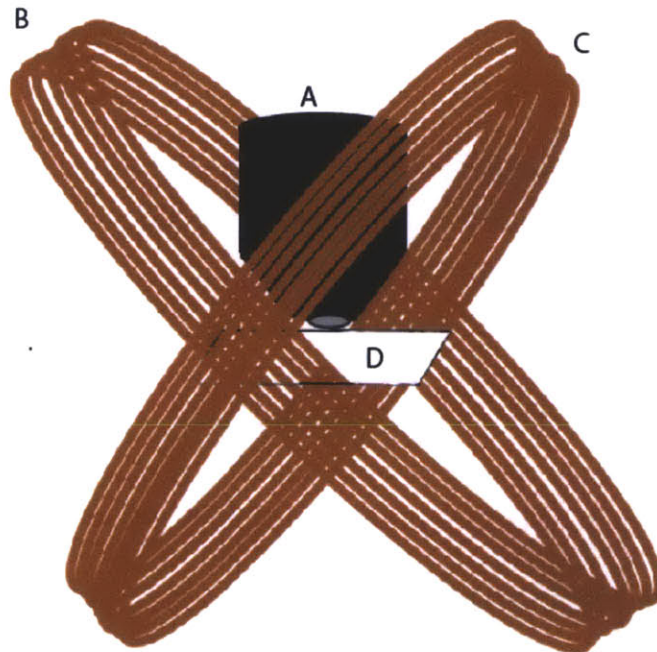


Figure 8. The experimental setup of the microscope with two concentric solenoids around a sample. The microscope lens is labeled A. A 40x microscope lens is used in all of the experiments. The outer solenoid is B, the inner Solenoid is C and the sample is D. The sample is placed on a stage that is separate from the microscope. The sample is lit from below.

concentric solenoids that are placed around the sample present as shown in figure 8.

The larger solenoid has an outer diameter of 4.75", an inner diameter of 3.625" and approximately 192 turns present. It has a sensitivity of 105 Oersted with 5 Amps DC. The smaller coil has an outer diameter of approximately 3.856", an inner diameter of 2.63" and approximately 235 turns. The small coil has a sensitivity of

170 Oersted with 5amps DC. The wire that the coils are constructed from is Teflon coated in order to ensure that they will be resistant to the heat that is produced from the current. A sinusoidal function is driven through the coils and is offset so that a rotating magnetic field is produced. This field rotates parallel to the sample allowing the rotors to walk in the horizontal direction of the microscope view.

The coils were constructed with help of Mike Tarkanian. Two plastic mandrels were made that were mounted onto a lathe where the coils were wrapped, then the mandrel could be disassembled and the coils removed. Winding the coils on the lathe allowed for the maximum turns per area. Mike also helped make Teflon bases to mount onto the microscope to ensure that the coils stay in place during experiments and do not conduct heat to the microscope.

The microscope slide is placed on a manufactured piece of plastic that is attached to a Newport MT Series XYZ mount. This allows for the microscope slide to be precisely moved in order to focus the sample. The mount is separate from the microscope in order to ensure that it doesn't affect the coils. The mount is attached to a Newport Optic grid and the microscope is placed on top of that as well. This is all placed on a nano-k Vibration Isolation stage by minus k Technology. This makes sure that there is no vibration in the sample from the table it is placed on. This vibration stage was borrowed from Matt Humbert.

The sinusoidal function is driven with a Quadrature Oscillator that was made for this experiment with the help of David Bono. This device controls the magnitude of the field and the frequency of the field produced. The device allows frequencies

ranging from hertz to kilohertz. The device also allows the magnitude of the two signals to be aligned accordingly in order to ensure that the two signals are of equal magnitude. The setup also allows the two signals to be offset, if that is what an experiment requires.

The signal is put through a HP 54601A Oscilloscope where the frequency of the field is measured. The current also goes through an analog oscilloscope that allows us to proportionally determine the approximate magnitude of the magnetic field present. The current is produced by a Crown DC-300A series II amplifier and then the current is driven through two 2 Ohm resistors in parallel that create a proportional 1 Ohm resistance. The current is driven through the oscillator and then the oscilloscope and then into the coils.

The sample is placed in the center of the two coils in order to assure that the sample has the strongest magnetic field. A 40x magnification is used for all of the experiments. The size of the beads is known and is used to calibrate the image. A multi-meter is placed on the sample in order to record the temperature. The multi-meter is placed as close to the sample as possible in order to get the most accurate temperature reading possible. The temperature is hand recorded along with the timestamp of the video in order assure the velocities are recorded with their corresponding temperature. The microscope feed is recorded through a computer. The video is then processed using tracking software to record the velocity of the rotors.

2.2 Setup for Polymer Coated Surface

Biotinated slides are purchased from Xenopore. These slides are then coated with streptavidin. Cover slides are placed onto biotin coated slides with double sided tape and a horizontal channel is left on the slide. The streptavidin is purchased and diluted. The biotin and streptavidin interaction is one of the strongest non-covalent bonds present as described earlier. The slides are left with streptavidin for one hour. After an hour the streptavidin is removed and mPEG-Biotin is put onto the sample. The streptavidin is removed by placing a kimwipe on the edge of the cover slip and absorbing the streptavidin. The mPEG-Biotin creates another biotin-streptavidin interaction leaving the surface coated with PEG. The mPEG-Biotin is also left on the sample for one hour in order to assure that the surface is fully coated with PEG.

Streptavidin coated superparamagnetic beads that are purchased from Solulink are also coated with PEG. Equal parts Biotin-mPEG and streptavidin-coated beads are put together and then 1ml of water is also added. For these experiments 20 microliters of Biotin-mPEG and 20 microliters of diluted beads are placed in 1ml of water. The diluted beads are made from 10 microliters 10mg/ml solution with 1 ml of water. The PEG coated beads are then put onto the surface for one hour. This is in order to allow for the liquid to mostly evaporate leaving just the beads on the surface to make sure that the salt concentration is correct. Then the appropriate solution of NaCl is added to the surface. This is left for around 10 minutes to ensure that there isn't a concentration gradient present on the slide.

The sample is placed under the microscope and then attached to the stage to ensure the sample doesn't move during the experiment. This is usually done with electrical tape. The frequency of the field is set to 5hz and the strength of the field is maximized around 10 mT. The thermocouple is attached to the slide in order to record the temperature of the sample. A heat lamp is placed approximately 8" from the sample and put on it's lowest setting. The temperature is hand recorded during the experiments. A doublet is found and then recorded during the increase in

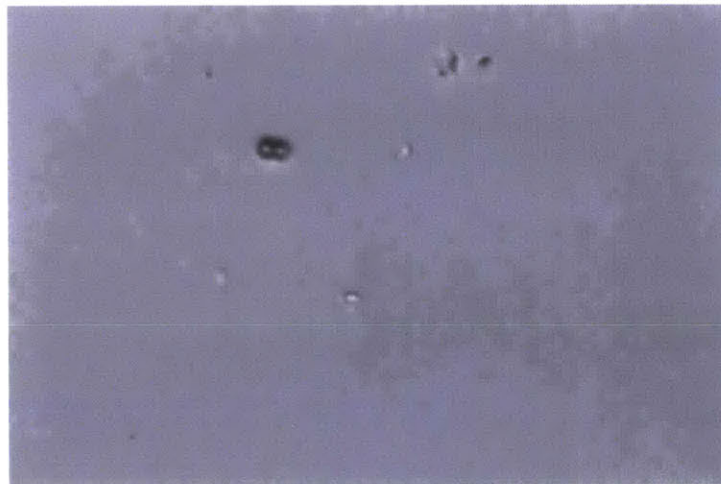


Figure 9. Image of a doublet of Solulink 2.8 micron streptavidin beads coated in mPEG-Biotin.

temperature. It is always the same doublet that is recorded for any of the results found in order to ensure the least amount of variance possible. Figure 9 shows an image of one of these doublets. The beads are 2.8 microns in diameter. The chains are reversed when they reach the end of the viewing area to ensure we are only recording the same sample. They are reversed back and forth during the entirety of the experiment.

The recording of the sample is then tracked using software called Tracker. The slope of this tracking is taken in the x direction and then averaged for each

temperature or frequency. Error bars are included in the final graphs. Error bars are the standard deviation of each point. The software also allows for calibration according to the diameter of the beads, $2.8 \mu m$. Figure 10 shows the results from

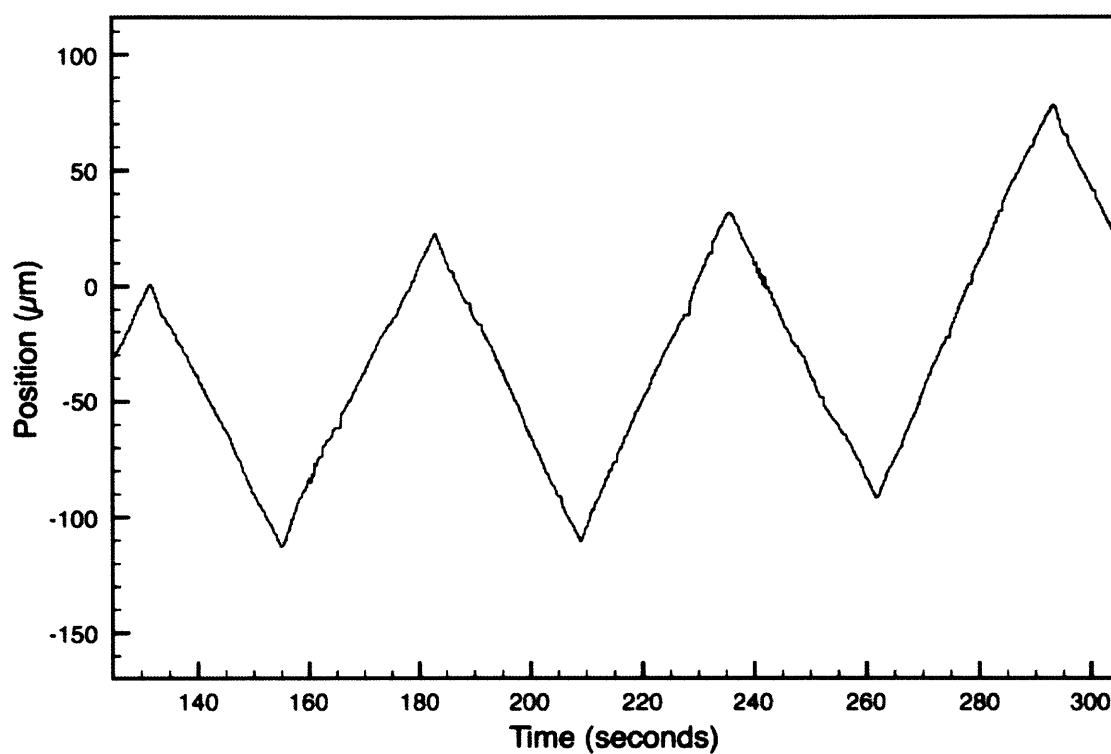


Figure 10: Raw Data of the Position of a doublet. This is tracking results for a rotor in 0.0M NaCl at 5hz in a magnetic field of 10mT.

the tracking software.

3. Results and Discussion

3.1 Variance of Temperature and Salt Concentration

As described earlier the PEG coated beads and surfaces were subject to

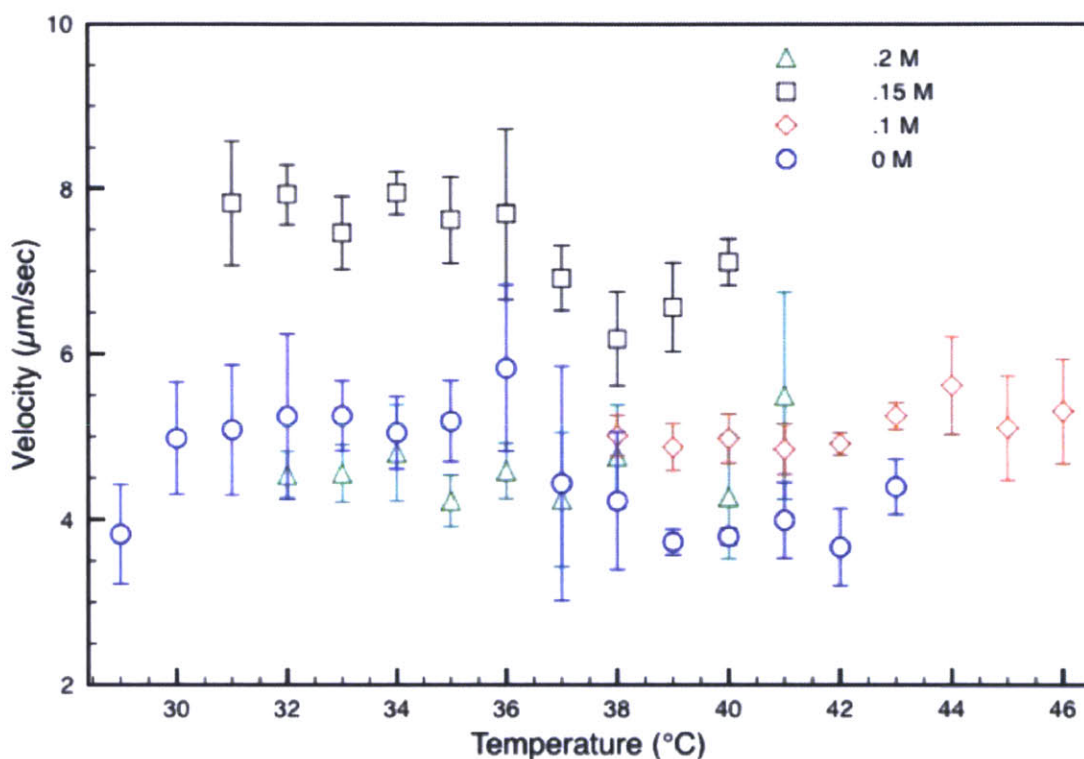


Figure 11. Velocity of doublets with varying NaCl Concentrations and temperature. The Beads and surface are coated in PEG.

increasing temperature and varying concentrations of NaCl. Figure 11 shows one set of results for this experiment. These are all tracking doublets and for every concentration there is only one doublet. The experiment for each run and each data point has anywhere for 2 to 9 velocities. Each velocity is the average speed across the microscope image. This experiment was ran at 5hz and with a field of 10mT.

From this set of data it was unclear what was occurring at the different NaCl concentrations so another set of data was ran to try to clarify the data. This set of concentrations so another set of data was ran to try to clarify the data. This set of

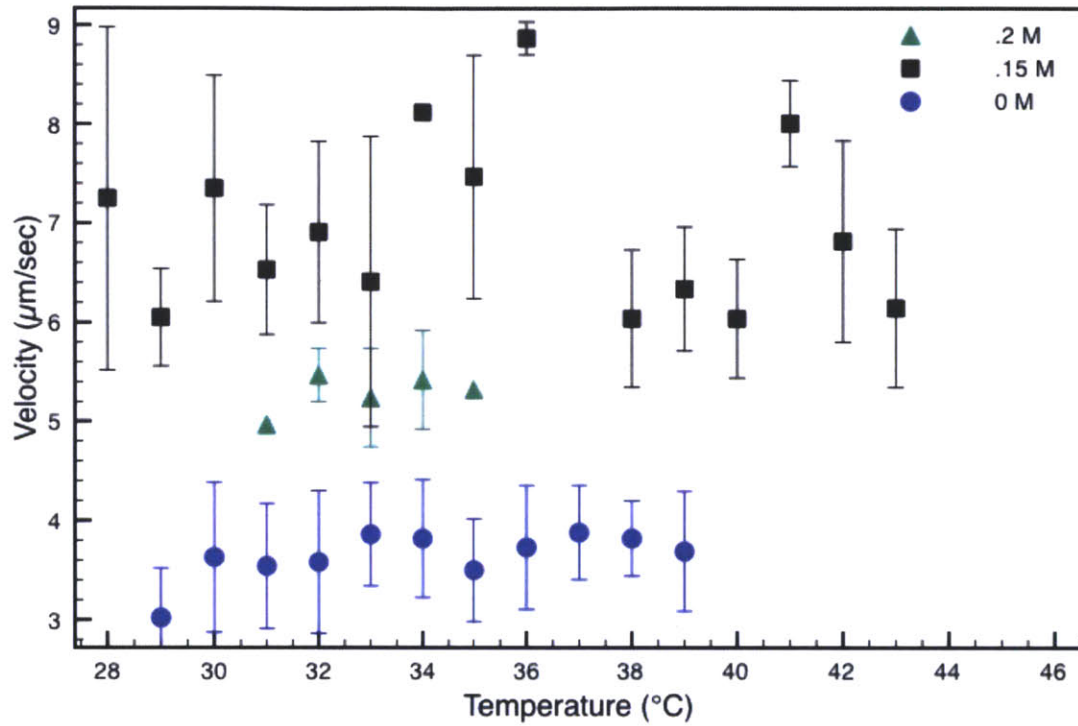


Figure 12. Second set of Data. Velocity of doublets with varying NaCl Concentrations and temperature. The Beads and surface are coated in PEG.

data can be seen in Figure 12. Figure 13 shows both of these data sets on the same graph for comparison.

We need to find out if the PEG is in it's collapsed or extended state in the

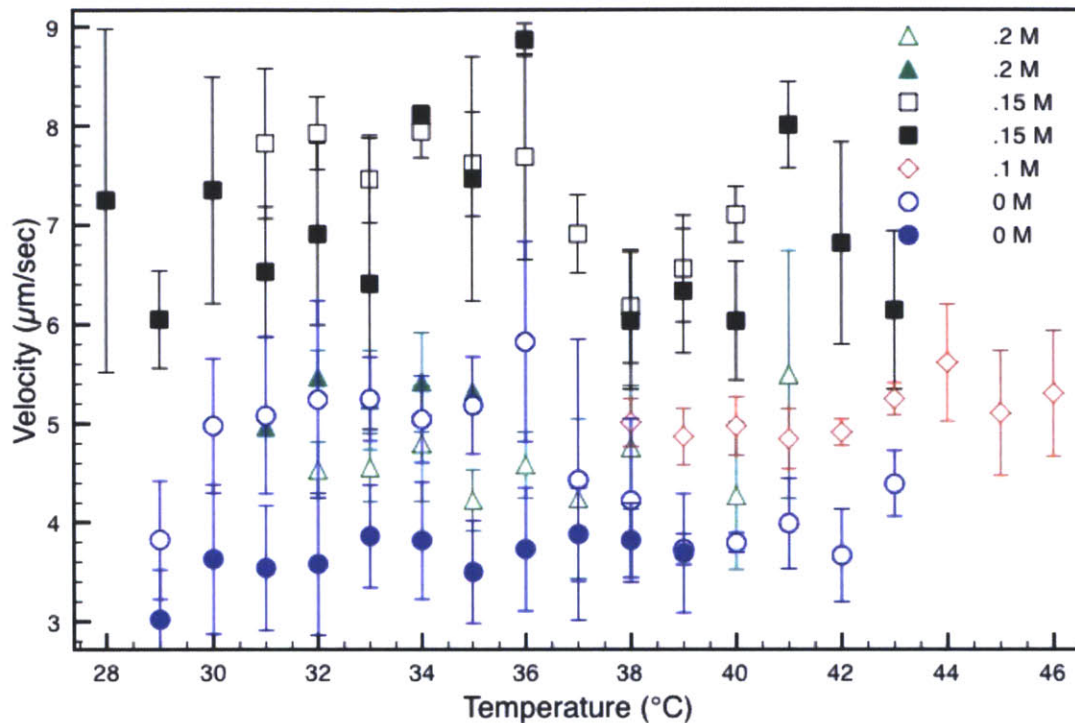


Figure 13. Combined graph of figure 9 and figure 10. Velocity of doublets with varying NaCl Concentrations and temperature. The Beads and surface are coated in PEG.

various temperatures and NaCl concentrations. In other research by Fernandes and Bevan they indicate for a PEO-PPO-PEO block copolymer that as they increase the $MgSO_4$ concentration, the temperature at which the polymer collapses decrease as seen in figure 13.^{11,12} If we assume that this is true for this case as well, then most likely the .15 M is in the extended state. However this is inconsistent with the velocity data because we would expect to see similar velocity results for .2M state as well. This makes it unclear if PEG continues to stay in its collapsed state as the concentration of salt increases. What the data seems to suggest is that there is no

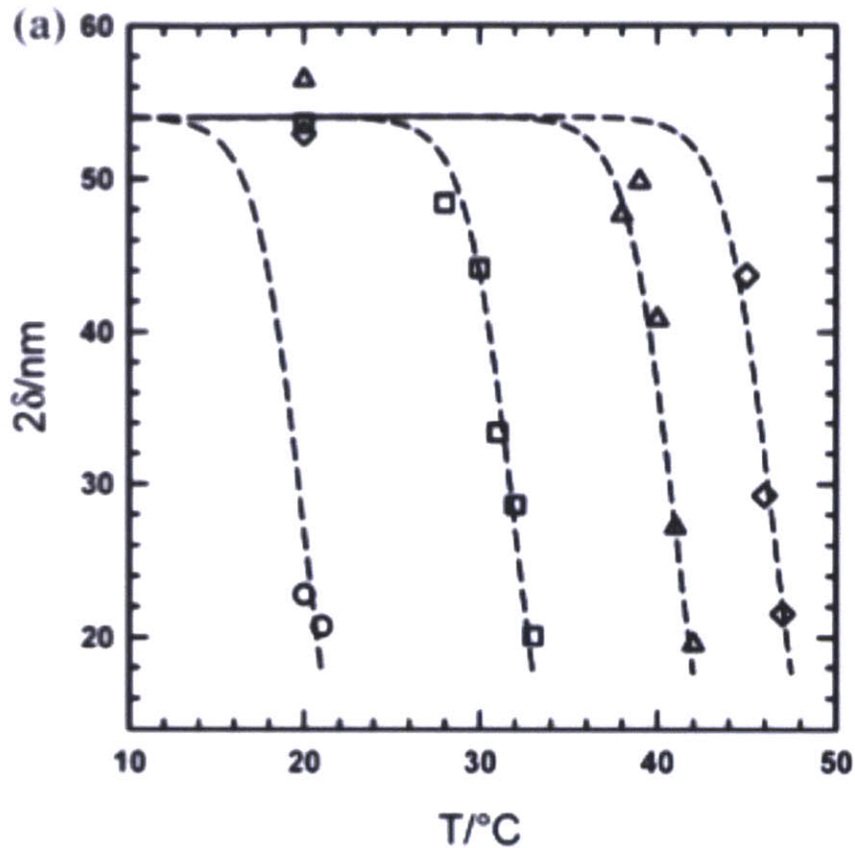


Figure 14. Graph from Fernandes of PEO-PPO-PEO coated colloid and surface. The symbols indicate the concentration of $MgSO_4$ present in the solution: .2 M (◇), 0.3 M (△), 0.4 M (□), and 0.5 M (○). The y axis indicates the energy density of the polymer and the drop indicates the collapse of the polymer(Fernades).¹¹

correlation between the velocity of the rotors and the state of the PEG. It is also unclear due to the inconsistent data. There are fairly large error bars on most of the data points, which makes it unclear if there is a significant change in velocity for the .15M states.

Previous simulation research shows that with increased friction on the surface we see an increase in velocity as seen in Figure 15.⁹ The data from Figure 15 was obtained from a simulation of various sized rotors with a term, f_0 , that increases the friction with the surface on the rotors. If there were a difference in surface friction due to the change in state of the PEG there would be a noticeable difference in the velocity of the rotors.

The .15M concentrations does seem to have a slight increase in velocity when compared

to the other salt concentration, but if it was due to the state of the PEG then we would see this in the .2M state as well. This seems to indicate that the increase in velocity of the rotors is due some other factor. The friction between the beads and the surface is what ultimately allows the beads to translate in the x direction. This demonstrates that by coating the beads with PEG and closer examination of the PEG at NaCl concentrations

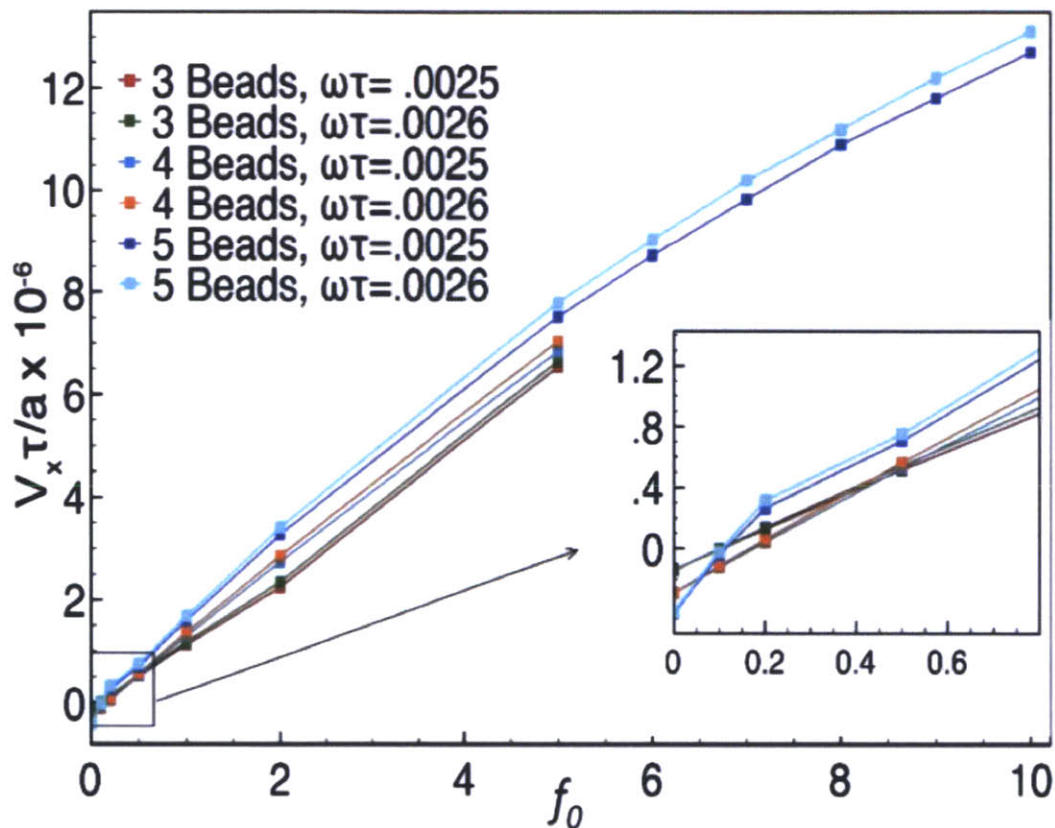


Figure 15: Average velocity of rotors, $V_x \tau / a$, versus the frictional constant f_0 with varying frequency, $\omega\tau$. See a steady increase in velocity with an increase in the friction on the surface(Moran).⁹

there isn't any correlation between the surface coating and the velocity of the rotors. With the use of other experiments like a surface force apparatus we could clearly define the friction that is occurring between the beads and the surface and examine what state the PEG is in.¹⁹

3.2 Frequency Dependence

Another experiment was run to determine the effect of frequency on the interaction between the coated bead and the coated surface. The experiment was ran with no salt present in the system and as a comparison the same experiment was ran with uncoated beads on just a glass surface. Figure 16 shows the results of this experiment. The PEG coated bead and surface tends to indicate more of linear relationships between velocity and frequency where the uncoated bead and surface has more of an exponential response to the frequency. From figure 17, which are the results from previous simulation data with an increase in a downward force, we see this same transition from a linear response to velocity to a more exponential response.⁹ The exponential response is seen with an increase in the downward force on the rotors. This indicates that the PEG coated surface is mimicking a situation with very little downward force present while the glass surface indicates more of a downward force present. This is due to the fact that at zero salt concentration we are at the collapsed state of the polymer where we have seen earlier that we have a heavily slipping system, which is more similar to no downward force on the beads. The downward force or increase in A can be correlated to more surface interaction between the beads. So the collapsed stated of the polymer has very little surface

interaction stated compared to non-coated beads.

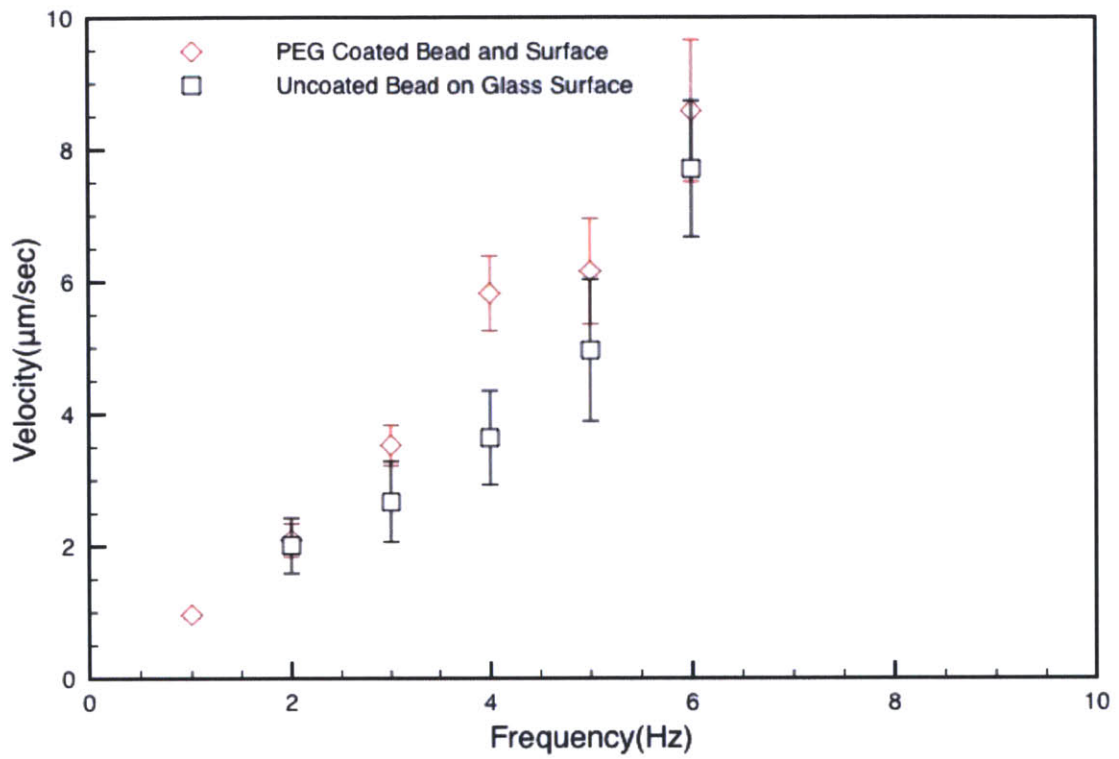


Figure 16: Velocity response to frequency for uncoated beads and surface as well as PEG coated beads and surface. Experiment is run at room temperature with a 10mT magnetic field.

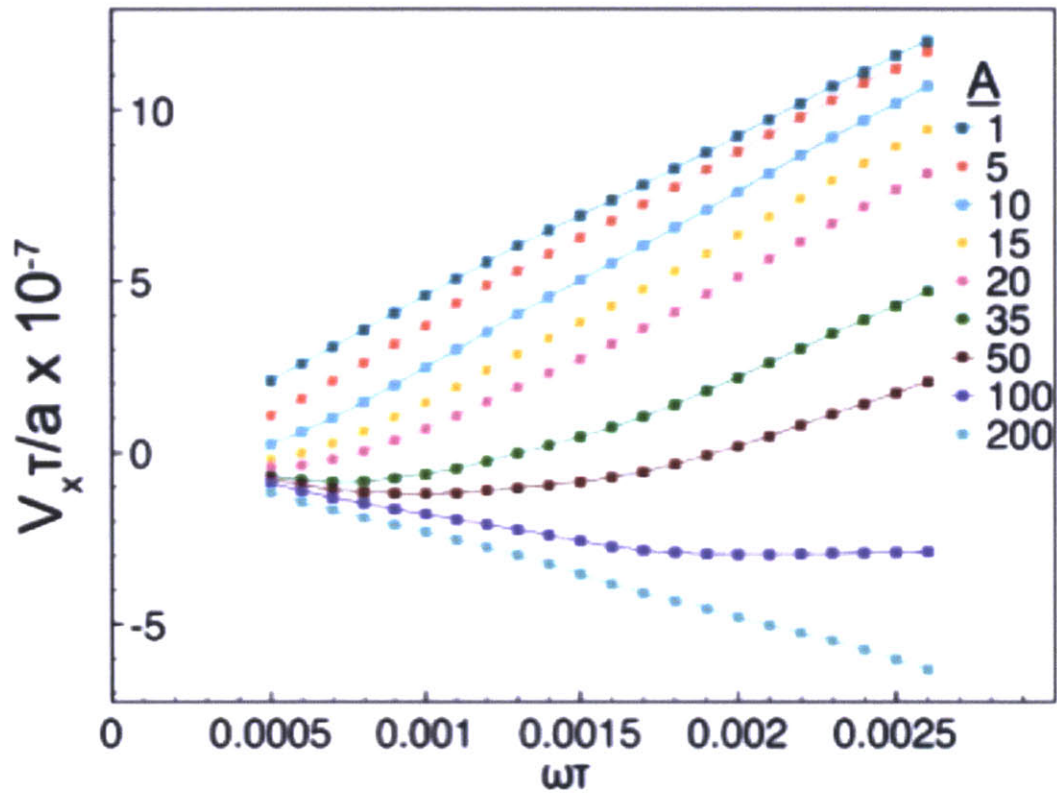


Figure 17: Graph from previous simulation with increasing downward force on rotors where the factor of the downward force is represented by A(Moran).⁹

4. Conclusions and Future Work

From these results we see no direct correlation between the state of the PEG and the velocity of the rotors; however with more experimentation it might be apparent that there is correlation. It would be more beneficial to do an in depth analysis of the collapse and expansion of the PEG that we had purchased using experiments like surface force apparatus.¹⁹ If the experiment was ran where we could see the rotors from the side rather than the top one could measure the size of the beads to correlate that to the state of the PEG on the surface and the beads. This would allow us to pin point when the collapse occurs so it could potentially be correlated to a velocity change in the rotors. In a microfluidic device the flow could be increased by either an increase in temperature or the injection of a certain salt concentration into the system, if this system did provide a controllable correlation between the collapse state of the PEG and the velocity of the rotors.

This research leads itself to some interesting possibilities that could be explored with the use of new equipment. With the current experimental setup that our lab has it is unlikely to find exactly where the transition of the PEG occurs. Our results do suggest that there is a possible correlation between the state of the PEG and the velocity of the rotors, but currently it's inconclusive. It would be helpful to run the same experiment with different salts like KCl, to make sure that there isn't a problem with the NaCl.

Some experiments that we have ran show that by attaching magnetic beads on the surface it is possible to increase the speed of the rotors significantly. As the rotors walk across attached beads there is a slight increase in velocity. It would be interesting to create different magnetic surfaces and see how one could control not only the velocity of the rotors but also the path of the rotors. By making magnetic channels with a turn it could be possible to steer the rotors. This would be especially useful in understanding how to steer the rotors for drug delivery applications.

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