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The Influence of Boundary Roughness on Dense Colloidal Suspensions

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An abstract of
a thesis submitted to the Faculty of Emory College of Arts and Sciences
of Emory University in partial fulfillment
of the requirements of the degree of
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Abstract

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We study the relationship between boundary conditions and particle motion in confined, concentrated colloidal suspensions. The study of glassy polymers in confinement has shown that changes in mobility are strongly dependent upon the polymer-surface interaction. We model this interaction by observing the effects of textured surfaces on colloidal particle mobility in confined dense suspensions (near the glass transition). We use confocal microscopy to directly image and track the colloidal particles in thin, wedge-shaped sample chambers made from textured glass. We texture the glass in a controlled, reproducible manner by spincoating and sintering colloidal suspensions onto glass slides. We found that our results were compromised by the presence of unintentional texture on the walls of our smooth slides. Both the mean squared displacement, and the particle distribution within the confining volume were found to be similar in both the textured and smooth walled chambers. Despite a measured volume fraction of $\varphi = 0.42$ we observed behavior indicative of a much lower φ in both samples. We did not observe layering within either sample, but we believe this is due to the effectively low φ rather than the textured boundary conditions. Although our results are inconclusive, we have developed a method to create controlled, reproducible textures. In the future, we hope to use these textures to study the dynamics of the glass transition and its dependence on interfacial dynamics versus finite size effects.

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I thank E. R. Weeks for overseeing this project. I thank K. V. Edmond for instructions on confocal microscopy, slide construction, the IDL programming language and helpful conversations. I thank C. B. Roth and W. A. Pahner for instructions on spincoating. Funding for this work was provided by the National Science Foundation (DMR-0804174).

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The Influence of Boundary Roughness on Dense Colloidal Suspensions

Daniel J. Real

April 19, 2011

1 Introduction

Some liquids, when cooled, smoothly but rapidly increase in viscosity, often by many orders of magnitude. While cool, these glass-forming liquids have similar properties to solids on the macroscopic scale. For instance, these materials retain their shape, are deformable, and can shatter much like a crystalline solid. However, microscopically they retain their amorphous liquid-like structure, i.e. they lack any crystalline structure.

We quantify the microscopic structural rearrangements of these liquid-like materials by measuring the time required for a deformed sample to return to equilibrium. Ideally the rate of return to equilibrium will decay exponentially, with the relaxation time τ giving the time required for the displacement from equilibrium to decay to $\frac{1}{e}$. Decreased particle mobility will result in an increased value of τ. With this definition we can relate the divergence in the macroscopic viscosity of a material to the divergence in the microscopic structural rearrangements, quantified by τ.

The relationship between structural rearrangements and viscosity has been described conceptually by the Adams and Gibbs hypothesis, which states that flow within supercooled liquids requires the cooperative motion of molecules [1]. As the size of these cooperatively rearranging regions (CRRs) diverges, so does the supercooled liquid's viscosity and relaxation time. We identify the temperature at which a liquid transitions into a glass by the dramatic increase in τ that accompanies the equally dramatic increase in viscosity. This temperature is called the glass transition temperature (T_g).

Computer simulations and experiments have probed the length-scales of these CRRs in glass-forming liquids by confining the liquid to small volumes, such as within thin films, nanocapillary tubes, or nanoporous materials [11, 5]. These studies have shown that a material confined to the length-scale of its CRRs in the bulk can exhibit an increased, decreased, or unchanged T_g, even for the same material [2]. Both simulation and experiment have suggested that the effect on T_g is strongly dependent upon the nature of the interaction between the sample and its confining boundaries [12, 19, 14, 22, 9, 8, 17]. In particular, studies of thin polymer films have shown that the difference between T_g in confinement and T_g in the bulk is strongly dependent upon the polymer-substate interactions[18, 9].

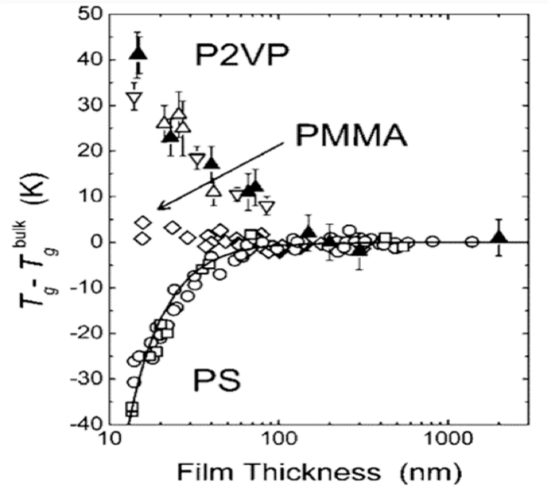


Figure 1: The difference in T_g from T_g^{bulk} in poly(2-vinylpyridine)(P2VP), poly(methyl methacrylate) (PMMA),and polystyrene (PS) as a function of film thickness supported on silica. Molecular dynamics are similar to the bulk for $T_g - T_g^{bulk} \approx 0$. We see the dynamics diverge below $\sim 100nm$. This change in dynamics is believed to be strongly dependent upon the polymer-substrate interactions. (Figure reproduced from Ref [18]

Figure 1, reproduced from Ref [18], shows the change in T_g from the bulk as a function of film thickness for three different polymers supported on silica. We see that for polystyrene (PS) $T_g - T_g^{bulk} \approx 0$ for film thicknesses greater than 100nm. Below 100nm we see that T_g drops below T_g^{bulk}. This indicates that particles are actually moving *more quickly* in confinement than they were in the bulk. We see the opposite behavior in poly(2-

vinylpyridine)(P2VP), and almost no change in the behavior of poly(methyl methacrylate) (PMMA). The data from figure 1 shows the competition between two effects. The top free surface imparts excess mobility, leading to decreased T_g. The bottom interface with the silica substrate can have strong (P2VP), weak (PMMA) or no (PS) hydrogen bonding with the polymer. Interactions which arrest motion, such as these hydrogen bonds, typically result in $T_g - T_g^{bulk} > 0$, whereas interactions which facilitate motion, such as the free air boundary, tend to result in $T_g - T_g^{bulk} < 0$ [18, 9]. Ref [22] demonstrated that if PS is confined between two neutral surfaces, such as silica, then there is no change in T_g. This suggests that the intrinsic restriction of CRRs has no effect.

In an effort to observe the molecular dynamics of liquids approaching the glass transition scientists have studied model systems composed of small particles in a liquid [16, 23]. These particles are typically a few microns in diameter and are individually visible with optical microscopy. This model system, called a colloidal suspension, has one dominant control parameter, the volume fraction ϕ of the solid particles. By increasing ϕ we are able to simulate liquids of *lower* temperature. When $\phi > \phi_G \approx 0.58$, the sample appears glassy. Macroscopically, such samples lose their liquid-like qualities. They no longer flow, they can be deformed, and they can shatter like a crystalline solid. Microscopically particles in these samples are so closely packed that they are unable to move past their neighbors, and so no longer diffuse through the sample.

Confinement of these colloidal systems has been found to result in slower system dynamics, far more than would be simply due to hydrodynamic drag near a wall [15]. These experiments used either smooth glass walls, or walls with a few colloidal particles stuck to them[15, 7]. These boundary conditions resulted in two trends within the data. First, that smooth boundary conditions induced layering within the sample chamber. Second, that movement within layers was significantly more common than movement between layers. Edmond hypothesizes that "the infrequency of particle displacements between layers results in a hindrance of rearrangements within layers, resulting in an overall slowing of motion."[7].

Simulation has suggested that rough boundary conditions, like those created by stuck particles, will frustrate the formation of layers within a confined sample [19, 20, 13]. These simulations also predict that rough boundaries will slow the overall dynamics of the system. It is still unclear though if the slowing effect of the boundaries would be due to the frustration of layers or due to some other mechanism. Ref. [6] showed that texture created by the haphazard adhesion of particles to the walls of the confining chamber did decrease motion near the boundary, but these textures were created unintentionally, and their effect on particle dynamics remained localized to the boundary. In this work, we will expand upon the findings of Ref. [6] by creating reproducible, controllable textures. We then use these textures to study how roughness affects the formation of layers and the mobility of particles within the sample.

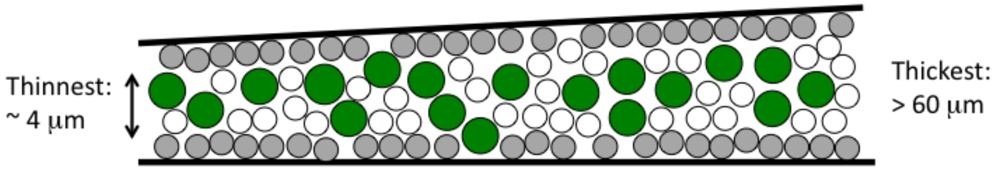


Figure 2: Diagram of sample chamber (not to scale). The large particles, in dark gray (green), and the texture particles along the wall, in light gray, are shaded to indicate their fluorescent dye. The small particles are drawn in white to indicate their lack of dye. making them invisible to the confocal microscope.

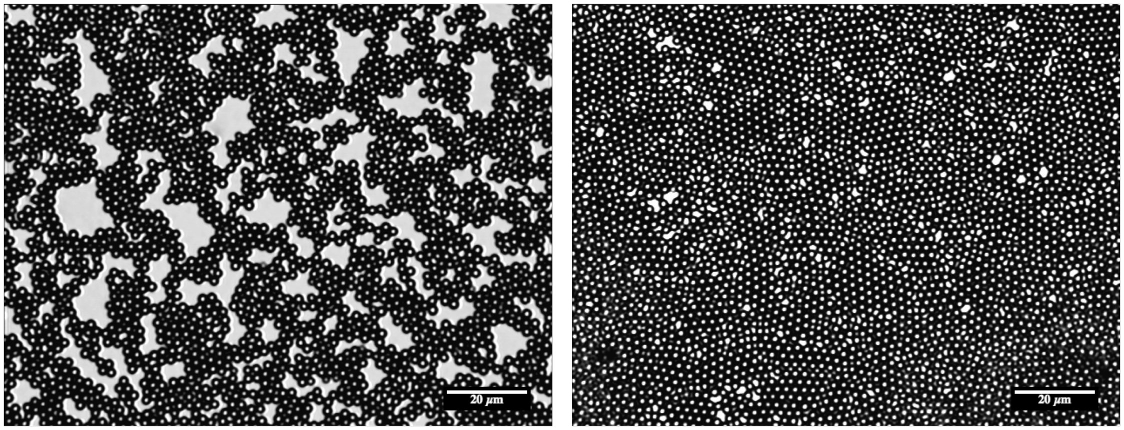
2 Experimental Methods

To create my samples I chemically synthesized two species of poly-methyl-methacrylate (PMMA) particles with the assistance of Kazem Edmond. These particles are sterically stabilized with a short polymer layer of poly-12-hydroxystearic acid (PHSA), which prevents them from aggregating [16, 4]. In an ideal mixture of solvents these particles behave as good approximations of hard spheres, with interactions only when they are close enough for the PHSA polymers to overlap [16]. Our solvent mixture is composed of cyclohexylbromide, and cis- and trans-decalin, chosen to match the index of refraction and the density of the PMMA particles[4]. In this mixture, the particles acquire a charge. The addition of tetrabutylammonium chloride to the solution masks the particle's charge, thereby minimizing any charge effects.

To frustrate crystallization in our samples, we use a mixture of two particle sizes. A small, undyed species with mean radius $a_S = 1.23\mu m$, and a larger, dyed species with mean radius a$_L = 2.16\mu m$. The polydispersity of each species is approximately 5%, and the individual volume fractions are approximately $\phi_S \approx \phi_L = 0.21$, creating an overall volume fraction of $\phi = 0.42 \pm 0.05$. In order to insure that each species was of equal volume fraction we first sediment each closely density matched sample in a centrifuge at 3500rpm for a time sufficient to create hard packed pellets at the bottom of the vial. This ensured that each sample was at the random-close packed volume fraction. It is known that this packing fraction is independent of the radius of the spheres, and so should be the same for both samples [21, 10]. Supernatant was then removed and each sample was massed on a Mettler-Toledo model AB204-S milligram scale. To achieve the desired volume fraction we calculated the necessary volume of solvent based on the mass of the solution assuming an initial volume faction of $\phi = 0.6$. The solvent was then added by mass assuming standard temperature and pressure densities. Finally, the two samples were combined in equal volume, again measured by mass. There is, however, still uncertainty in determining the precise volume fraction of the sample. This uncertainty arises from difficulties in determining the precise size of each particle species, and from the polydispersity of particle sizes within a species.

To image our particles we use a fast-scanning confocal microscope (VT-Eye from Visitech, International) with a 63× air objective (N.A. 0.70) [15]. We then use a 2× optical magnification implemented within the confocal. This additional magnification aids in identifying and tracking particles. We capture 2-Dimensional movies at 40 frames per minute. The field of view is $\sim 33\mu m \times 33\mu m$ and particle positions are resolved to within 50nm in x and y. To aid in image analysis only large particles are dyed, and thus we cannot observe the behavior of the small particles using confocal microscopy.

We place the colloidal solution in wedge-shaped sample chambers (fig. 2), with a wedge



(a)

(b)

Figure 3: Examples of texture created using the spincoating techniques described. **(a)** Deposition of a lower ϕ solution creates patchy textures. **(b)** High ϕ solutions create uniform textures. By controlling ϕ we are able to make many types of textures with consistent results.

angle of $< 0.2°$. This gradient allows us to study small sections of the same sample at a variety of thicknesses H, down to $H = 4\mu m$, yet is so slight as to have no observable effect at any particular thickness [15, 7]. Each of our two types of confining chamber are constructed from untreated glass (a glass cover slip on one side, a glass microscope slide on the other).

To determine the chamber height we take a 3D image of the volume and identify those particles stuck to the glass walls. The chamber height is measured from center to center of these stuck particles. Using this method the chamber height can be determined to an accuracy of $\pm$ 0.1 μm. Some samples required visually measuring the chamber height; however, the inaccuracy in these samples ($\pm$ $0.5\mu m$) did not affect our findings.

2.1 Texture Creation

Several methods were attempted to create texturing on glass slides. We first allowed colloidal suspensions of various volumes and volume fractions to dry onto a glass slide at room temperature. This method created large areas of monolayer particles at the center of the droplet, but resulted in the “coffee ring” effect which occurs when a solution of solid particles is allowed to dry on the substrate. This effect, caused by the capillary flow of particles in suspension to the edge of a droplet, creates “ring-like” deposits along the perimeter[3]. These deposits were often dozens of microns in height, and would span the width of our thin confining chambers. We then attempted drying the colloidal suspensions quickly in ovens at ∼60℃. While this reduced the size of deposits along the perimeter, it also prevented the desirable monolayers seen in air drying.

We briefly considered creating textures by imprinting the ridges of an astronomical diffraction grating into a polymer film that had been spincoated onto glass. We experienced difficulties from particulate matter creating imperfections in the polymer film. We were also concerned that the ridges of an astronomical diffraction grating would be destroyed in the imprinting process, although experiments never advanced to that stage.

Instead, we have found that the best way to add texture to the confining walls of our sample was to spin coat a high volume fraction ($\phi \approx 0.50$) colloidal suspension onto glass slides cleaned with toluene. We found that the most evenly distributed textures are created at a spinspeed of $\sim 3500 rpm$. A successfully coated glass slide should create diffraction patterns when viewed under oblique illumination. Spin coating is a procedure commonly used to apply uniform thin films to flat substrates. Typically an excess amount of solution is placed on the substrate, which is then spun to high speeds, causing the fluid to be spread by centrifugal force.

We break from standard procedure by depositing solution onto an already spinning substrate. Depositing the sample onto an already rotating substrate improves the uniformity of deposition by preventing the natural, haphazard adhesion of particles to the glass surface, and minimizes the “coffee ring” effect which occurs as the sample rests on the surface of the unmoving slide. These mountainous rings disrupt the formation of uniform textures across the glass. Once the desired texture is created it is sintered onto the surface at ~90°C for up to two minutes, this slight melting process ensures that the colloidal particles are strongly adhered to the glass. Figure 3 shows two types of textures that we are able to create using this method.

3 Results

For all of our experiments we quantify the average particle motion within a sample by calculating the mean square displacement (MSD) as

$$\langle \Delta x^2 \rangle = \langle [x_i(t + \Delta t) - x_i(t)]^2 \rangle_{i,t} \qquad (1)$$

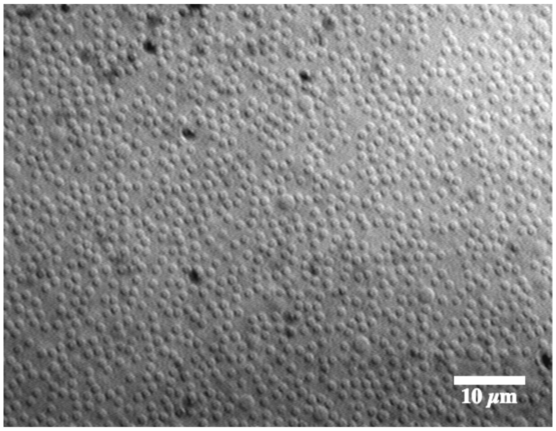


Figure 6: This image clearly shows a large number of small, undyed particles stuck to the boundaries of our "smooth" chamber. These particles are invisible to confocal microscopy, so their presence went unnoticed until recently. This image was taken using differential interference contrast (DIC) microscopy.

where the average is taken over all particles i and all initial times t. An analogous formula applies for $\langle \Delta y^2 \rangle$. We find that $\langle \Delta x^2 \rangle \approx \langle \Delta y^2 \rangle$ for all our experiments, so we have chosen instead to show $\langle \Delta r^2 \rangle = \langle \Delta x^2 + \Delta y^2 \rangle$. Figure 4(a) shows the motion of particles in $\langle \Delta r^2 \rangle$ for $\Delta t < 100$s at multiple confinement heights within the smooth walled chamber. We see the mobility of the particles decrease with confinement. Note that each line is relatively linear below $\Delta t = 75$s. If our sample were exhibiting the dynamics of a "supercooled" liquid we would expect to see a plateau in the MSD curve beginning at $\Delta t \approx 10$s [15, 7]. Before the plateau, particles have not encountered their confining neighbors, once their local free volume has been explored they are trapped within a cage created by the neighboring particles. The plateau ends when particles begin to break out of these cages by means of cooperative rearrangements [24, 25]. The lack of such a plateau indicates that particles are not being trapped by their neighbors. This, in addition to other evidence we will see latter, suggests that our sample is at a relatively low volume fraction ϕ. Fluctuations above $\Delta t = 75$s are due to poor statistics. The top two lines indicate the bulk dynamics of the sample, and were taken at $80\mu m$ and $20\mu m$. We see that slowing has begun by $H \approx 10\mu m$ (3^{rd} curve from the top). Figure 4(b) shows the same plot this time for textured chambers constructed from textures similar to figure 3(b). Surprisingly, we do not see a significant difference in the behavior of the two systems.

We can gain a better sense of the confinement effect by plotting the MSD at a particular time ($\Delta t = 21$s) against the height of the confining chamber (Figure 5). The circles indicate points where data was taken, the size of each circle is comparable to the statistical error in the MSD and the measurement error in height. The time interval $\Delta t = 21$s was chosen for its accurate statistics, and for its clear demonstration of the observed behavior across multiple timescales, there is nothing else particularly significant about this time interval. We see that both samples seem to behave as if they were in the bulk for $H > 20\mu m$, this is indicated by the plateau in the MSD. We also see that the drop-off in the MSD curve has roughly the same nature with both smooth (dark gray or blue line) and textured (light gray or red line) boundary conditions. On its own this would contradict the findings of numerous simulations [12, 19, 14, 22, 9, 8, 17, 11]; however, we now know that the smooth walled chambers are in fact not smooth at all. We believe the small peak in the textured MSD at $H = 7.4$ microns is within the uncertainty of our measurements.

We see in Figure 6 an image taken at the coverslip of a smooth walled chamber. This image, taken using differential interference contrast (DIC) microscopy, clearly shows a large number of small, undyed particles stuck to the glass surface. We belive that this unintentional texture is having the same effect as the artificially create texture. This would explain the similarity in the MSD curves for both samples.

We are still unsure of the cause behind the diffusive behavior of our sample. If we compare our MSD curves to those of previous experiments, we find that our sample behaves much like the low ϕ samples of similar papers using smooth boundary conditions. Figure 7 shows the results of Ref [15]. We see four samples at three volume fractions, $\phi = 0.23, \phi = 0.42, \text{and} \phi = 0.46$. These volume fractions are reported as the total volume fraction of both species, and are comparable to $\phi = 0.42$ calculated for our own samples. The uppermost line of Figure 7 showing the behavior for $\phi = 0.23$ is remarkably similar to the behavior seen from our own results in Figure 5. Both samples show bulk dynamics above $20\mu m$ and neither exhibit the order of magnitude decrease in $\langle r^2 \rangle$ that the high ϕ samples from Figure 7 exhibit. The colloids used in this experiment had not been used in previous experiments. As such their size ratio is unique to this experiment. Furthermore, it is possible that the particle interactions of these new species differs from the interactions of older species. Although the inherent mechanics behind the behavior we observed is certainly more complicated it is possible that the large difference in particle diameter is leaving the larger species less affected by the presence of the smaller species then expected. This could explain why the effective volume fraction we observe from dynamics is similar to the measured volume fraction of the larger species alone.

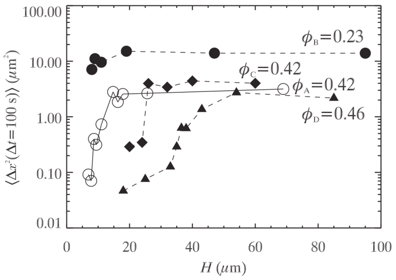


Figure 7: Value of $\langle \Delta r^2 \rangle$ at $\Delta\ t = 100\ s$, as a function of thickness H, for samples with ϕ as indicated. The $\phi_B = 0.23$ curve (solid circles) has very similar dynamics to our own sample. Both exhibit bulk behavior above $H > 20\mu m$, and neither decay by orders of magnitude as is seen in the other three samples.

In previous experiments, smooth walls were seen to induce layering throughout the sample volume [15, 7]. Figure 8(a) shows the layering seen in Ref. [7]. This plot of particle number per μm^3 as a function of distance from the bottom glass slide shows clear layering within the volume of the sample at a confinement height of $H = 8.06\mu m$. We, however have not observed clear layering effects above $H = 6\mu m$. Figure 8(b), shows the distribution of particles in a chamber of $H = 8.9\mu m$. We see two sets of clear peaks, the first at $z = 0\mu m$ and $z = 8.9\mu m$, the second at $z = 1\mu m$ and $z = 7.7\mu m$. The first set of peaks indicates the location of the applied texture. The second set of peaks indicates where particles have layered along the texture boundary [15, 7]; however, layers do not seem to propagate throughout the volume. We believe that the absence of layering within the sample is indicative of an effectively low volume fraction ϕ, and is not the result of texture frustrating the formation of layers. The difference in the magnitude of n between the graphs is proportional to the ratio of particle sizes. If the volume of each particle is accounted for this discrepancy disappears.

4 Conclusion

We find our results to be inconclusive on the effects of boundary conditions on the dynamics of confined, concentrated colloidal suspensions. Our results were compromised by the presence of unintentional texture on the walls of our smooth slides, and we still lack a satisfactory explanation of the dilute behavior we observed. We observed that both the mean squared displacement, and the particle distribution within the confining volume were similar for both the textured and smooth walled chambers. Despite a measured volume fraction of $\phi = 0.42$ we observed behavior indicative of a much lower ϕ in both samples [15]. We did not observe layering within either sample, but believe this is due to the effectively low ϕ rather than a result of the textured boundary conditions. Further research is necessary to make a definitive claim on the effects of texture on the dynamics of dense colloidal suspensions in confinement.

We have however been able to develop a method to create controlled, reproducible textures on glass slides. This method can be used to create many types of textures by varying the volume fraction of the colloidal sample deposited on the slide. We also believe new textures could be created from samples of polydisperse particle size. In the future, we hope to use these different types of texture to determine how the dynamics of the glass transition are influenced by the interaction of particles with the boundary versus the restriction of possible CRRs due to confinement effects. Such an understanding will provide insight into the mechanism behind the altered dynamics of glass-forming systems in confinement.

5 Acknowledgements

I thank E. R. Weeks for overseeing this project. I thank K. V. Edmond for instructions on confocal microscopy, slide construction, the IDL programming language and helpful conversations. I thank C. B. Roth and W. A. Pahner for instructions on spincoating. Funding for this work was provided by the National Science Foundation (DMR-0804174).

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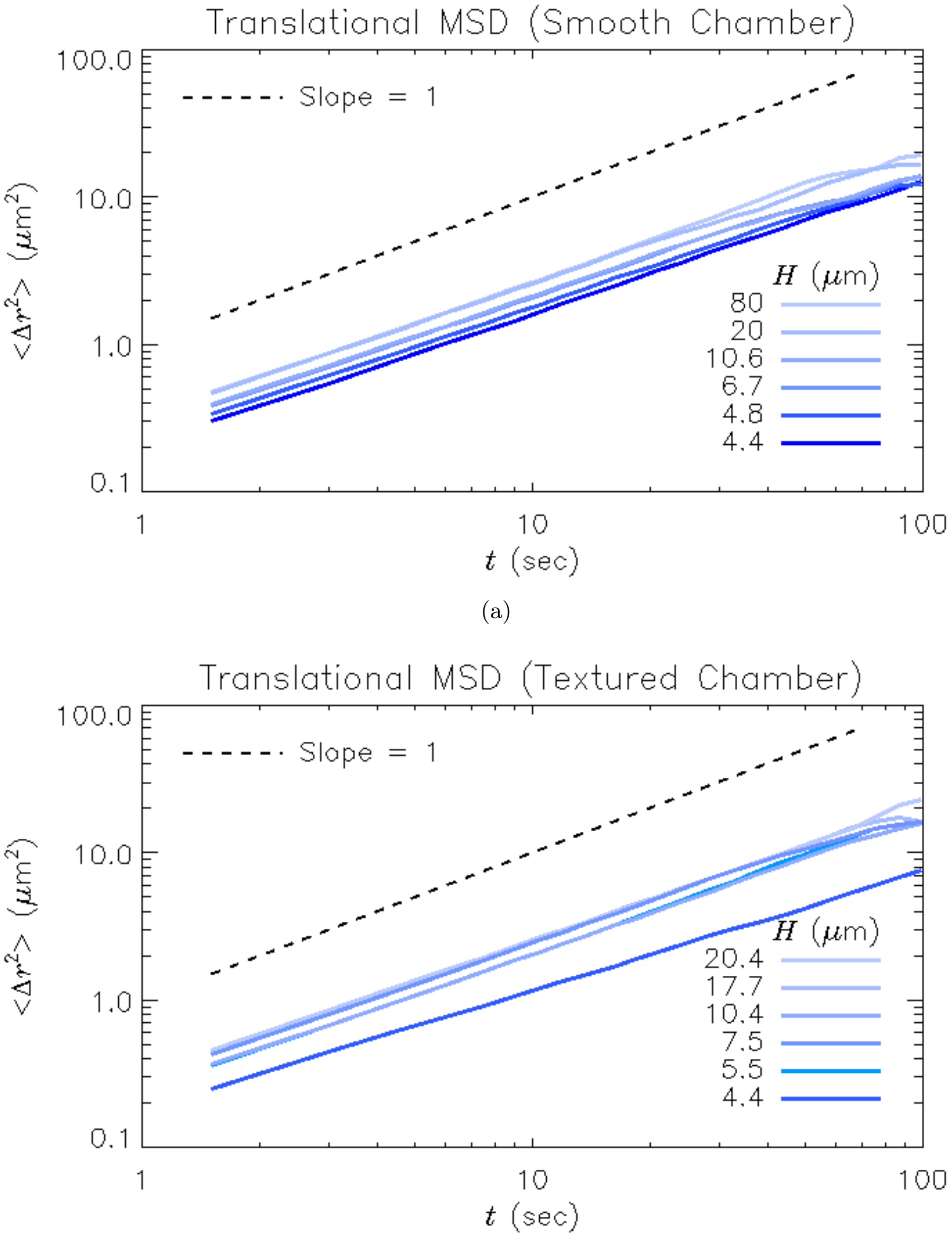


(a)

(b)

Figure 4: The mean square displacement for our samples over a range of thicknesses. The dashed line has a slope of 1.0. Both samples exhibit behavior indicative of low ϕ. We find that the behavior of both samples to be similar due to roughness on the boundaries of the "smooth" chamber. Because this texture was created by the small, undyed species, it's presence went unnoticed until shortly before this writing.

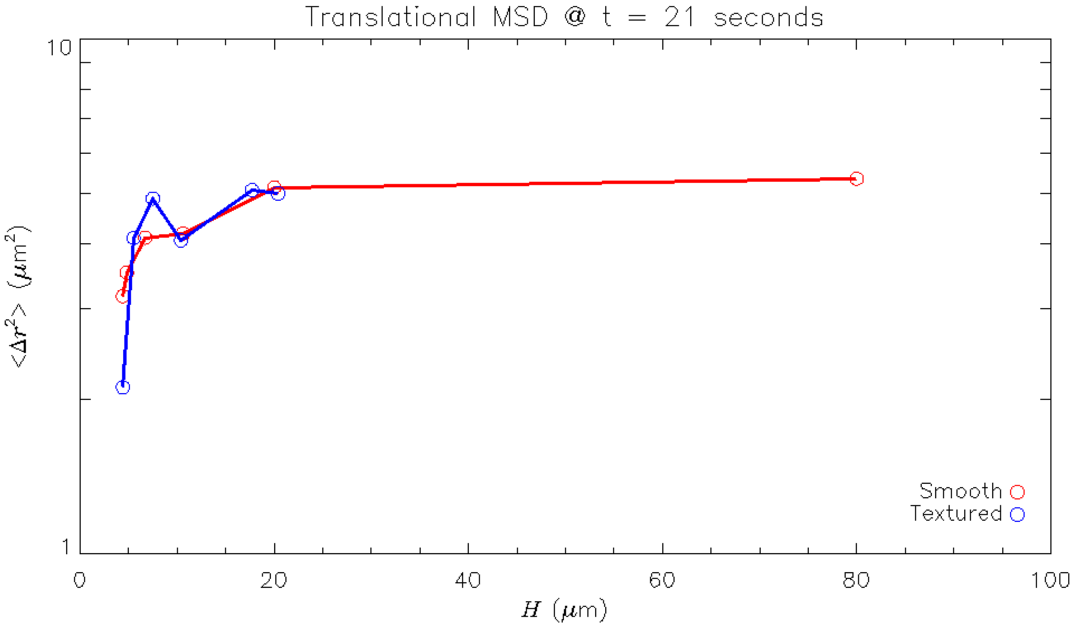
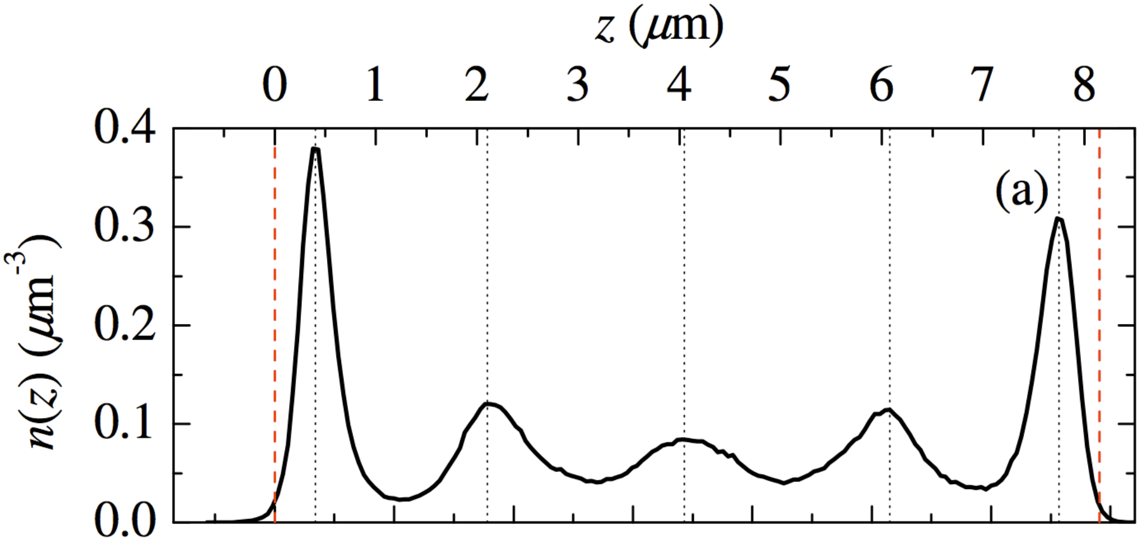
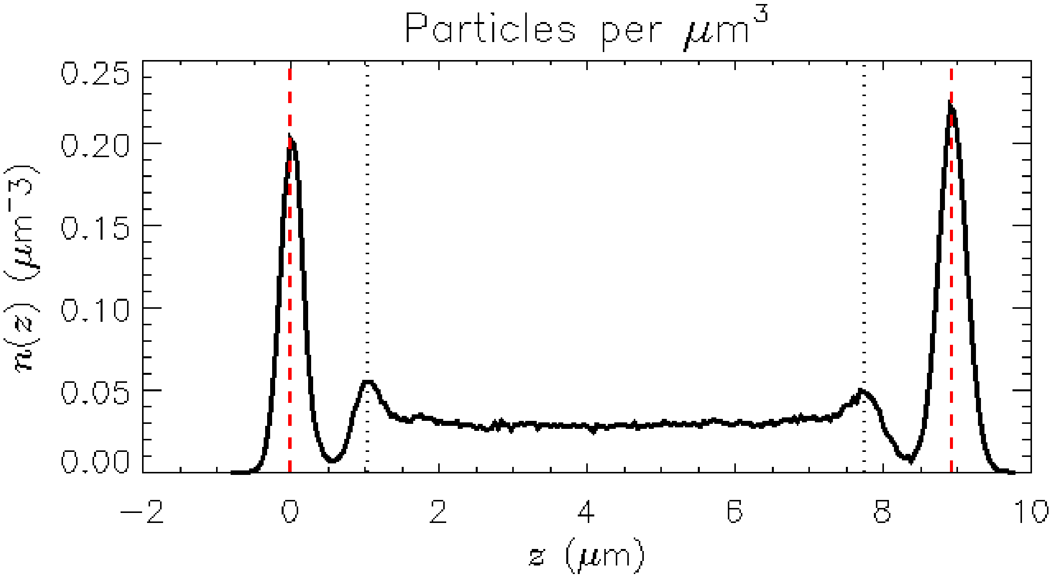


Figure 5: Value of $\langle \Delta r^2 \rangle$ at $\Delta t = 21s$, as a function of thickness H, for samples with measured $\phi = 0.42$. The plateau for $H > 20\mu m$ indicates bulk behavior. The downturn at $H = 20\mu m$ indicates the onset of confinement effects. This height is much lower than would be expected from previous studies of samples at $\phi = 0.42$. The time interval $\Delta t = 21s$ was chosen for it's accurate representation of the dynamics across multiple timescales, there is nothing else particular to that value.



(a)



(b)

Figure 8: Number density n as a function of the distance z between the walls. **(a)** Data taken by Edmond shows clear evidence of layering. **(b)** The lack of variation in n from $2 - 7\mu m$ indicates that layers did not form in our samples.