Sedimentation of Colloidal Gels under different Gravity Conditions

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ABSTRACT

We are trying to understand different systems and their behavior under different gravity conditions. The systems are PMMA particles in suspension for model studies, model pastes made from silica particles, and real Colgate™ toothpastes. The main reason for these experiments is to understand the aging and gravitational effects on our samples: Do these samples age because of gravity? Are these effects coupled? Or are they different and independent effects? We do not yet have the answers for these questions, but our preliminary data can be a guide to the direction that these answers might take. We have used centrifugation to achieve low and high gravitational stresses. For the former we have constructed a device out of a simple sample rotator and for the latter we have used a commercial centrifuge. For the real toothpaste samples we used conventional centrifugation only, and compared two systems with different background fluids for the pastes: the first with glycerol and sorbitol and the second with glycerol alone. In parallel with all of these experiments at elevated (moderate and high) gravitational accelerations, we had the same samples sitting in earth's gravity and monitored via a CCD camera set up, for comparison.

INTRODUCTION

Sedimentation has been considered a problem for some marketing companies all over the world. Products based on weak colloidal gels tend to sediment over time under normal gravity conditions. This is certainly undesirable for the industries. In the gels that are used, the goal is to control characteristics including texture, flow and optical properties, among others. With our project we are investigating the effects of gravity and the aging effects in different types of gels. Our goal is to develop a deep understanding of the role of gravity in causing a delayed collapse in colloidal gels which are stable for some time before collapsing under their own weight in earth's gravity.

PROCEDURES AND RESULTS

Sedimentation under Normal Gravity (1g)

One of the samples that we have been working on during the summer is a sample with latex particles that have an index of refraction almost matched to that of the solvent in which they are suspended. This means that almost no light will be scattered on passing through the sample, and the particles will look almost invisible. We do this in samples for confocal microscopy so that we may look deep into the sample to gain truly three-dimensional information. We have observed and measured the sedimentation of the particles over time.

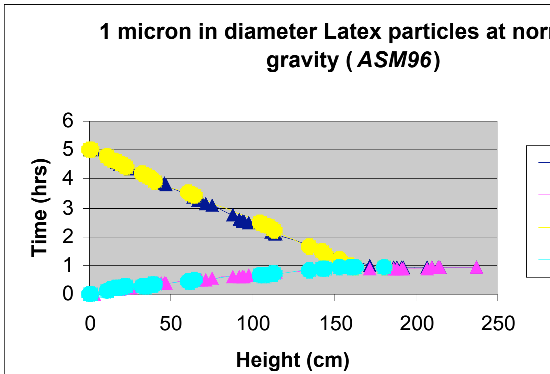

Fig. 1.1

Because the samples settle slowly under their own weight, we make measurements approximately every 2 hours or so until total sedimentation has occurred. Observations for this single sample are plotted in the Fig. 1.1, showing two sets of observations over time. The data for the first set is plotted with triangles (Δ) and the second one with circles (_). This graph shows the height of the sediment and the height of the interface over time. This sample takes approximately 12 days to settle completely. The similarity of the two sets of data seen in this that the particles settled the same way at two different times. The reproducibility of the data implies a predictability of the settling process.

Sedimentation under Low Gravity Conditions (~4g)

We also have been working in an apparatus that will apply a gravitational acceleration on the order of 10g (ten times normal gravity). The samples are the same colloidal gels that are stable for some time before collapsing under their own weight in earth's gravity. The design consists of a regular sample tumbler, which is used to rotate and mix samples at a fixed rate, modified to use for our purposes. We attached a metal bar of length 1.2 meters across the center of this tumbler in the horizontal position. A diagram of the set up is in the Fig. 1.2. Then we had the tumbler spin at maximum revolutions per minute (rpm).

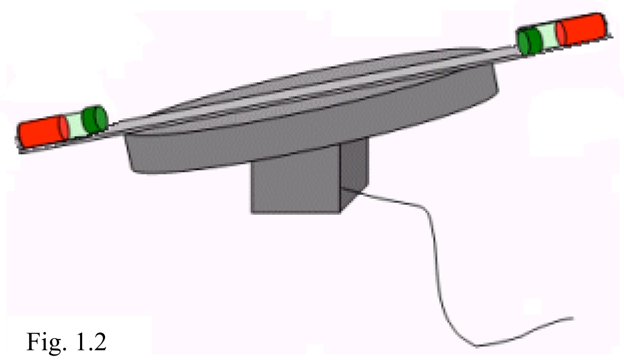

Fig. 1.2

We were able to achieve a force of approximately 4g, which was lower than the desired gravitational acceleration but it was acceptable as a starting point. Because the tangential velocity at this radius and rotational speed was too fast for real-time capture of images at normal video frame rate, we used a high-speed camera to observe the samples as they were subjected to the gravitational acceleration. The high-speed camera was placed on top of the array. We observed the sample for 5 hours and the results were just starting to occur. We also prepared the same samples to watch them at normal gravity. We have them standing and taking pictures with a CCD camera to compare the results with those for samples in which we change g. The experiment will be done again and we will watch the samples for a longer time, for 12 hours for example. This experiment together with the one with the centrifuge will give us a broader idea of the effects of gravity in the samples because we will have a wide range of different gravity conditions for the same colloidal gel.

Sedimentation with High-Value Gravity (~3000g-4500g)

It is also very important to understand the aging effects on our samples. Our goal is to begin to understand whether the samples age because of gravity or whether these two effects are independent. To the industries, not only important the appearance of the product is important, but also that the product will last with the desired properties. In order to make our samples "age" we centrifuge them which means that we subject them to elevated gravitational acceleration. We are working with samples that have Silica particles sitting in H_2O (□ = 0.115) and we mixed them with Xanthan polymer and Glycerol (0.18% w/w). We worked with different speeds and samples with different history.

Again we use a centrifuge to achieve higher gravity values. This centrifuge has different speeds of rotation to achieve different gravity conditions. The samples have different histories and we shake them to re-suspend the particles before we centrifuge them. These samples consist of equal weight mixtures of Xanthan polymer dispersed in glycerol, and silica particles in H_2O. The samples corresponding to the measurements of Fig. 1.3 had the following history:

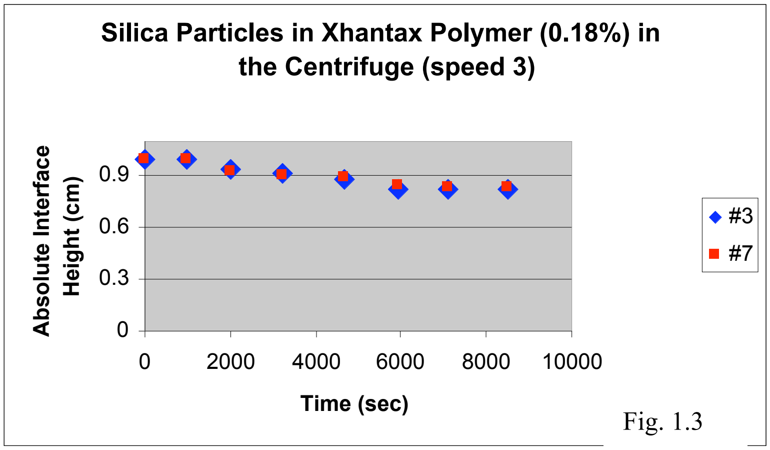

Fig. 1.3

July 7, 2003.	The samples were done.
July 9, 2003.	Samples were sitting at normal gravity for 2 days.
	Sample #3 was centrifuge in speed 3(~3000g) for ~2 hours.
	Sample #7 was centrifuge in speed 4(~4500g) for ~3 hours.
July 13, 2003.	Measurements completed.

The results were very similar and they look as we expect having the interface to go at certain steady value at the end. Even though the samples had different history, which could mean that technically they have different ages, they behave very similarly. The samples were done the same day, but one of them had been under a higher value of gravity and for a longer time as well. We will continue to study these systems to discover to what extent the age affects the properties of these types of samples.

Finding a Non-gravity Condition (0g)

We are also preparing some samples for confocal microscopy. Here, our goal is to match the density between our PMMA particles and the solvent in which they are suspended. These samples are fluorescently labeled (*ASM183*) for the confocal microscope to be able to scan them. With the ability to match the density in this system, we are able to eliminate gravitational effects and, study the aging effects in the absence of gravity, and by simultaneously matching the index of refraction of the solvent to that of the particles, we are able to use confocal microscopy to observe the structure and dynamics of the colloids. The solvents that we use are cyclobromohexane (CXB), tetralin and decalin, in weight ratios of 60.1% decalin to tetralin and 73.1% CXB to decalin + tetralin. This solvent mixture is very close to the density matching condition because the particles remain suspended for a long period of time. The preliminary data indicate that the samples that we prepared did not make a gel over the observation time of approximately 4 hours. This was something unexpected and we are trying to figure out what does this really means. We also prepared some samples that are not fluorescent (*ASM123*) and with them we will be able to observe with bright field microscopy to determine whether the particles are altered somehow because of this solvent mixture (e.g. change of size).

Real Toothpaste Samples under Normal & Elevated Gravity Conditions

Finally, we have been working with some samples sent by the Company Colgate-Palmolive; these samples are prototypes of Colgate™ toothpastes. We also subject these samples to elevated gravity with centrifugation methods. For these samples we have used different concentrations of dentifrice (white paste that contains the silica particles) and polymer solution as a diluting phase. We used 50/50,

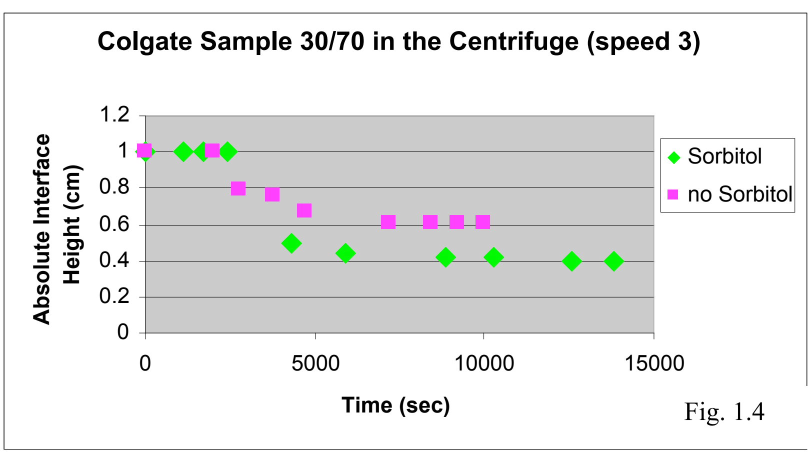

Fig. 1.4

30/70, 10/90, 5/95 and 0.05/99.05 ratios of the particulate and diluting phases, and different speeds in the centrifuge to study gravitational effects on stability. We also prepared corresponding samples for observation under earth's gravity in the CCD camera to compare the effects of normal and elevated gravity on the stability of pastes. We received two types of material one with Glycerin/Water continuous phase and the other one Water/Sorbitol/Glycerin continuous phase. In Fig. 1.4 we see the interface of two samples as a function of centrifuge rotation speed. The sample that contains sorbitol collapses to a greater degree, and has a lower final height as a result. We have found this in every one of the samples we have studied in this comparison. The time scale seems to be shifted to shorter times at higher values of gravity.

CONCLUSIONS

In conclusion, to study samples under normal gravity conditions, we may wait a long time for any effects as the timescale is very long for real pastes to become unstable and settle under gravity. A concentrated suspension of latex particles (*ASM96*) under earth's gravity takes approximately 12 days to come to its final state under sedimentation. For two sets of data on the same sample over time, the data superimpose and the sedimentation profiles are reproducible. The next step will be to observe the sample for a longer time (e.g. +30 days) and observe whether the sediment stays at the final height that we have recorded or whether it will again become unstable and sediment still further. Ideally this would involve comparing many different sets of data to see whether the sedimentation profile of suspended particles alone changes with time.

With the preliminary data that we have for xanthan system, it appears that these systems do not age because of gravity. However, this data is very preliminary and further tests need to be carried out. Our observations could be simply an exception to the typical behavior specific to this concentration (50/50). We have already started collecting some data with the low *g* experiment and further test will be done on this matter.

We have been able to simultaneously match the density and the index of refraction of a suspension of fluorescently labeled PMMA particles. The percentages that optimize these two conditions are 39.9% weight ratio of tetralin to decalin and 73.1% weight ratio of CXB to decalin and tetralin. This net solvent ratio apparently can impart to the sample with PMMA particles a density match which neutralizes gravity, and at the same time an index match which neutralizes scattering and allows for imaging deep into the sample. Having both conditions matched we can get three-dimensional information and decouple aging effects from gravitational effects.

Further work needs to be carried out on the real toothpaste system to reproduce this data. With the data we have up to this point we can say that the samples with sorbitol are apparently less mechanically stable than those without. We have observed that at elevated gravity this difference is more apparent. We see that the timescale for stability scales with g, which means that at higher gravity the samples destabilize and collapse earlier. Further centrifugation on different concentrations is required to truly understand the difference between these two systems and their sedimentation properties, and most importantly, to develop a physical relationship between the age of the sample and the sedimentation properties.

REFERENCES

"Dynamics of Weakly Aggregated Colloidal Particles". Maria L. Kilfoil, Eugene E. Pashkovski, James A. Masters, and D.A. Weitz. Philosophical Transactions: Mathematical, Physical & Engineering Sciences **361** 753 (2003).