

Computer Simulation of the Expansion Mechanism of Osorb[®]

Brian Forrest Maddock

Physics Department, The College of Wooster, Wooster, Ohio 44691, USA

(Dated: May 9, 2014)

The goal of this project is to simulate the expansion mechanism of Osorb[®]. Data will be taken from this program and compared to physical data to test the accuracy of the theoretical expansion mechanism. The simulation models the Osorb[®] as a system of molecules connected by springs, which expand in the presence of a solvent (acetone). Several methods were tested as computational models for the expansion of Osorb[®]. The most promising of these methods would bifurcate an Osorb[®] molecule in the presence of a solvent, this new bifurcated molecule would be connected to the Osorb[®] structure via springs with a larger equilibrium length than the molecule it split from. However, due to inaccuracies in the code it was not possible to take data to compare to physical results.

I. INTRODUCTION

Osorb[®] is a swellable organically modified silica discovered at the College of Wooster by Dr. Paul Edmiston. Osorb[®] is a compound formed using the sol-gel process [1]. The sol-gel process involves developing “sols” or colloidal suspensions, and a cross-linked structure in the compound. These sols are then made into viscous gels and finally solid materials, mainly glass [2]. The final product of the sol-gel process has the capability to absorb a large range of biomolecules with varying chemical and physical properties.

Osorb[®] is exceptional due to its ability to absorb both polar and non-polar organic materials from aqueous solutions. The swelling that occurs during this time can increase the volume of the Osorb[®] sample by up to 800%. This exceeds the amount of swelling from most sol-gel materials which only swell to around 15% of their original size [3]. The swelling can vary depending on the sample. The difference in volume of the expanded and dried Osorb[®] is defined as the swelling capacity.

While this swelling occurs forces up to 500N/g are observed. This force exponentially decreases based on the compressed volume of the Osorb[®]. The rate of decay depends on the characteristic volume, V_c . It has been found that a higher swelling capacity correlates to a higher V_c [4]. This means that the forces that are exerted in a sample with a higher swelling capacity lead to the forces decreasing less rapidly with time.

The unique relationship between force and volume was first found by Theresa Albon [3]. Due to this research the relationship between volume and force is well understood. However, the underlying mechanism behind why Osorb[®] follows this relationship is not well understood.

Currently, it is theorized that Osorb[®] can be treated as a polymeric matrix. The matrix expands in the presence of organic molecules in order to provide more space to accommodate the absorbed molecules. The expansion is represented by void walls that are connected in a hierarchical manner. This expansion increases the void volume which allows molecules to fill the space. Once all the voids have been accessed and filled the will have reached Osorb[®] full capacity.

In order to test the accuracy of this theory a simulation was made to model the current expansion mechanism. This allows testing of the underlying mechanism, which can be compared to physical data. Ultimately, this research will bring a tool to refine and confirm the theory of the expansion of Osorb[®].

II. THEORY

A. Sol-Gel Process

Sol-gel materials is the term used to describe the range of materials that all share the sol-gel preparation technique. The sol-gel process allows for exact control over the final product. The sol-gel process consists of six steps. These steps are hydrolysis, condensation, gelation, aging, drying, and densification. The sol-gel procedure creates a colloidal suspension which is then dried into a gel and finally, densified to a glass. The main component of the sol-gel process is the creation of the colloidal suspension and the cross-linking that occurs[2].

B. Properties of Osorb[®]

After the creation of Osorb[®] through the sol-gel process it exhibits amazing properties. Osorb[®] has the ability to absorb non-polar and organic materials from aqueous solutions. During the absorption process, Osorb[®] can expand up to eight times its shrunken volume. An ordinary sol-gel material can only expand to around 115% of its shrunken volume. After absorbing materials the user will be left with swollen Osorb[®] as well as completely clean water. After this the Osorb[®] can be dehydrated to get out the solute in Osorb[®] in a state that is also reusable. For example, if oil was in water, Osorb[®] could absorb all the oil out of the water and then be dehydrated to yield: clean water, reusable oil, and reusable Osorb[®][4].

Past research[3] has shown that the force during ex-



FIG. 1: Example of expansion. In the first panel the Osorb[®] is in its shrunken state. When the solvent is introduced in the second panel the Osorb[®] begins to adsorb the solvent. In the last panel The cross-linking structure is being broken down to allow for the absorption of the solvent by the Osorb[®]. [4]

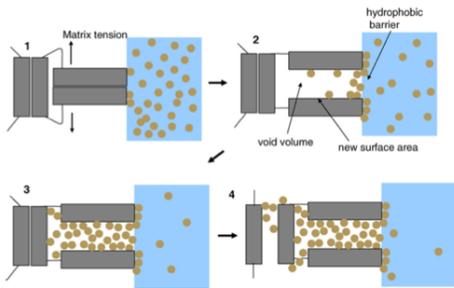


FIG. 2: Proposed model for absorption. 1) The solvent contacts the Osorb[®]. 2) The void walls expand to increase the Osorb[®]'s volume. 3) The molecules fill the new space until it is filled to capacity 4) New void space can be accessed further increase the total volume[1]

pansion follows the equation

$$F = F_0 e^{-\frac{V}{V_c}}, \quad (1)$$

where F_0 is the initial force, V is the volume, and V_c is the characteristic volume. The characteristic volume determines the rate of decay of the force and changes for different sample sizes and swelling capacities. The swelling capacity is a measure of how much an Osorb[®] sample can absorb. It is defined as the fractional change in mass from the dry to the swollen Osorb[®]. The exponential decrease in the force depending on the compressed volume of the Osorb[®] is a unique property of Osorb[®]. Dr. Paul Edmiston has theorized an expansion mechanism which leads to this relationship.

C. Swelling Mechanism

Currently, it is thought that during the sol-gel process the drying of the Osorb[®] causes a tensile stress in the compound. This stress is a result of the cross-linked structure of the Osorb[®]. This tensile stress is removed when a solvent is added to the Osorb[®] (Fig. 1). When this tensile stress is removed by the solvent it allows the Osorb[®] to expand, as the tensile force is no longer constricting the Osorb[®].

This swelling process is shown in Fig. 2. The tensile stress is held in a polymeric matrix as shown. When the solvent is added the polymeric matrix expands to form a void that the molecules can fill. Once the molecules fully occupy the new space in the matrix they can access trigger further void expansion to increase the available space. So, the expansion of one void space allows the expansion of others. This expansion continues until all the void space has been opened and filled. At this point the Osorb[®] can no longer expand.

This swelling mechanism can also be thought of as a system of springs. When the void walls are closed the spring is being compressed by a force. When a solvent interacts with the spring it eliminates this force which is compressing the spring. The spring then expands to its equilibrium length causing the Osorb[®] to expand as well.

III. COMPUTER SIMULATION

A. Overview of the Simulation

The goal of the computer simulation is to create a program which models the expansion mechanism proposed by Dr. Edmiston. The program was written in Obj-C/C++ using xCode. There are two types of simulations, *ab initio* and phenomenological. *Ab initio* is Latin for “from the beginning”. *Ab initio* programs simulate the physics from very small scales choosing to define interactions from an atomic level. The advantage of these programs is they tend to be quite accurate, but this accuracy comes at the expense of speed. In this simulation a phenomenological program is made. A phenomenological program uses the basis that a program need be as simple as possible, but not simpler. So, physics is represented phenomenologically. This means the depiction of the physics is accurate even though the underlying method may not be physical. This type of simulation acts physically without the rigor and computing power of an *ab initio* program.

In this program a series of Osorb[®] molecules are formed in a simple cubic lattice, as shown in Fig. 3. The molecules are connected by springs in the same pattern. During the simulation Osorb[®] molecules feel forces from the wall, lid, ground, and the springs which connect them to other molecules. These forces determine the structure of the Osorb[®] as well as keep it contained in the cylinder, as it would in the physical experiment. The solvent (acetone) is then put in the cylinder allowing the Osorb[®] to expand if an acetone molecule comes within a certain range of an Osorb[®] molecule. The Osorb[®] expands until it is restricted by the cylinder. From here the force on the lid is measured and recorded. This is done at multiple volumes for the cylinder in order to compare to the experiment.

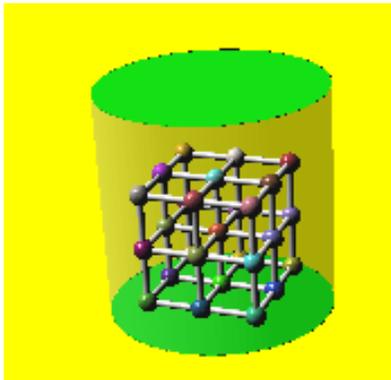


FIG. 3: Initial simple cubic structure. This figure shows the initial starting formation of the Osorb[®]. The multi-colored particles are the Osorb[®]. The connecting gray cylinders represent the spring connections.

B. Physics Behind the Simulation

This simulation employs basic Newtonian mechanics in driving the behavior of the rods. The forces that affect the Osorb[®] molecules are the wall, lid, ground, and spring forces. Using these forces we can obtain the velocity using

$$\vec{F} = m \frac{d\vec{v}}{dt}, \quad (2)$$

where \vec{F} is the translational force and \vec{v} is the translational velocity, and m is the mass. The mass m is set to one in order to simplify the expression. Once the velocity is found it is used to determine the position of the Osorb[®] molecule using

$$\vec{v} = \frac{d\vec{r}}{dt}. \quad (3)$$

The method of finding the force and velocity before updating position is called Euler-Cromer integration. This is a common method of numerical approximating derivatives. The Euler-Cromer integration method was chosen as the best balance of speed and accuracy.

C. Updating Osorb[®] and Acetone

In each iteration of the program the Osorb[®] and acetone updates over a time step, dt . For each time step the forces on the Osorb[®] and acetone are calculated. The acetone is updated such that the change in translational momentum and velocity are added to the current values. These calculations are made as follows:

$$\vec{p} \leftarrow \vec{p} + \vec{F}dt, \quad (4)$$

$$\vec{v} \leftarrow \frac{\vec{p}}{m}, \quad (5)$$

$$\vec{r} \leftarrow \vec{r} + \vec{v}dt. \quad (6)$$

The Osorb[®] molecules position and velocity are updated in a similar way. However, they do not maintain momentum after each step. Thus, the velocity is reset to zero before each iteration. This is modeled after a molecule in an extremely viscous fluid. Newtonian mechanics says

$$m\vec{a} = \vec{F} = \Sigma\vec{F} - \gamma\vec{v}. \quad (7)$$

However, when $\gamma\vec{v} \gg m\vec{a}$ then it is a valid approximation to let $m\vec{a} \rightarrow 0$. This is to say that at each step the Osorb[®] molecule does not maintain momentum. Thus, we redefine the momentum and the velocity completely at each point.

D. Expansion Mechanism

1. Method 1: Altering the Equilibrium Length

Altering the equilibrium length of the springs is the simplest method in which to model the expansion mechanism discussed previously. In this method the Osorb[®] molecules can absorb the acetone when the acetone comes within a certain radius of the Osorb[®] molecules. Upon absorption the acetone particle is removed from the program. At this point the equilibrium length of the springs which the Osorb[®] molecule is attached to are increased. This was done in several ways. One method was to only add a small value to the equilibrium length and allow the Osorb[®] to absorb many acetone particles. The second method was to limit the number of absorbable acetone particles but make the equilibrium length increase more drastically. For example, absorbing an acetone molecule would double the equilibrium length.

The advantage of this method is that it is simple to implement. Unlike the other methods you do not need to create additional Osorb[®] molecules. The new equilibrium length simply pushes the Osorb[®] molecules apart to replicate the expansion. This works well and allows the Osorb[®]s volume to drastically increase. However, this method fails to model the “pop” expansion that is suggested in the proposed mechanism. Instead, the molecules are slowly pushed apart. The other downfall of this method is that it contains no hierarchical structure.

2. Method 2: Bifurcating Molecules

In the bifurcating molecule method when enough acetone is absorbed into a single Osorb[®] molecule the molecule bifurcates, producing a new molecule and retaining the original. This bifurcation process continues until the acetone is exhausted or the maximum number of bifurcations have occurred. There are two methods

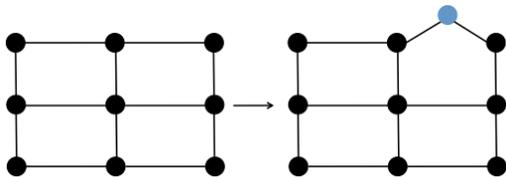


FIG. 4: Picture of the random bifurcation method. The new particle, drawn in blue, is randomly created within a radius of the original particle. The connections originally held by the parent molecule are split between the parent and the new molecule, one of them being given to the new molecule. The second being the connection formed between the parent molecule and the newly formed molecule.

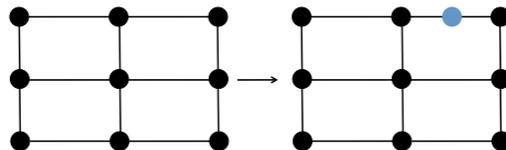


FIG. 5: Picture of the Split distance bifurcation method. The new particle, drawn in blue, is placed in between the two already established particles.

for the placement of the bifurcated molecules. The first, shown in Fig. 4, randomly places the bifurcated molecule within a certain radius of the parent molecule, this will be called the random bifurcation method. The second method is the split distance bifurcation method. As the name implies this method places the new molecule half way between the parent molecule and one of the molecules which it is connected to, as depicted in Fig. 5. The molecule which it is placed between is randomly chosen, from all the Osorb[®] molecules connected to the parent.

The advantages of the bifurcating molecule method is that it more accurately portrays the sudden expansion that is described in the physical mechanism. In this model the closed matrix are represented as single molecules. The expansion of the a closed matrix to an open matrix is replicated by a single single molecule bifurcating with each molecule acting as a “wall” after the bifurcation. The difficulty of this method is distributing the connections of the the original molecules among the parent molecule and the bifurcated molecule.

Determining the connections for the split distance bifurcation method is the simpler of the two cases. We can see these connections in Fig. 5. The new molecule is placed between two current molecules so the original connection between the molecules is broken. The two molecules than each gain a connection with the newly formed molecule. The randomly bifurcated molecule has many choices for removing or keeping connections. The difficulty is maintaining enough connections to keep the Osorb[®] structurally intact while not creating so many

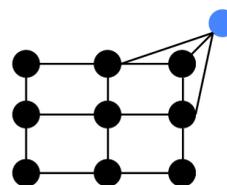


FIG. 6: Picture of the combination method. The bifurcated molecule shown in blue is placed away from the structure. It also maintains the two connections the original Osorb[®] molecule had while both the parent molecule and the bifurcated molecule gain a connection between each other.

that the expansion of the Osorb[®] is restricted. The best method to maintain this balance is to randomly split the connections of the original molecule, as shown in Fig. 4. The broken connections are then assigned as connections to the newly formed molecule.

3. Method 3: Combination

The final method combines the ideas behind the previous two methods. In this model the acetone is absorbed by an Osorb[®] molecule and the molecule bifurcates randomly within a radius of the parent molecule. As scene in Fig. 6, this is similar to the random bifurcation method, but the molecule only expands away from the structure. The new molecule is connected to the structure via springs with an increased equilibrium length. The equilibrium length of the new molecule has twice the equilibrium length of the parent molecule.

This is advantageous because this method allows for a sudden expansion of the matrix. However, because of the increased equilibrium length of the new particles are naturally pushed away from the larger Osorb[®] structure. The newly formed molecule can keep all the connections of the original molecule, while still being able to expand and keep a strong structure. Each molecule can bifurcate one time, except the molecules who have expanded to a point where their equilibrium length is eight times the initial value. At this point that molecule can no longer expand.

E. Forces

1. Wall, Lid, Ground Forces

As the Osorb[®] molecule expands it eventually reaches the wall, lid, or ground of the cylinder which surrounds it. When this happens the Osorb[®] molecule must not penetrate through the surface it encounters. So, a force must stop the interpenetration. This force is a phenomenological force, with the properties that it is strong close to the wall, lid, and ground but zero when molecules are not close to these surfaces. The phenomenological force

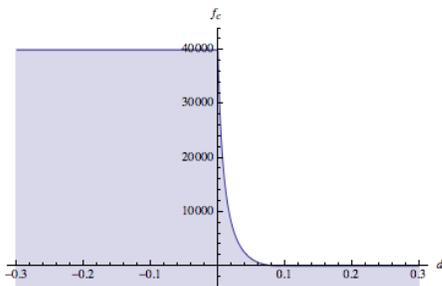


FIG. 7: Graph of the force law. This graph depicts the force law with the $f_s = 40000$, the maximum value. The force quickly drops to zero as the distance from the surface grows.

function takes three parameters: f_s , r_m , and r . These represent the force scale, the maximum radius, and the radius between the molecule and the surface, respectively. The force function takes these parameters and puts them into the following function which returns the force:

$$force = f_s \frac{r_m - r_{min}}{r + r_{min}}. \quad (8)$$

The force scale determines the proportional strength that is returned, and r_m determines the maximum radius by which a force may be returned. If the radius is larger than r_m then the force is set to return zero. If the radius is smaller than r_{min} then the force function returns f_{scale} . The force function follows the curve in Fig. 7.

When interacting with the lid or ground the force returned is applied in the opposite direction of the z -axis motion of the particle. This ensures that the particle will be kept within the bounds of the cylinder. However, the wall force must be broken down into components. This is done by finding the coordinates of the Osorb[®] molecule interacting with the wall. The x and y coordinates are normalized, and the force is in the direction towards the center of the cylinder with the magnitude of the force in each direction determined by the normalized coordinates.

2. Spring Forces

The spring force is modeled as a classic spring using the equation

$$F_x = -k(x - l_e)[5], \quad (9)$$

where k is the spring constant, and l_e is the equilibrium length of the spring. Similarly to the wall force, the spring force is broken down into the x , y , and z components. Each component has a magnitude that is determined by the total force and the separation in the corresponding direction of that component. This force pushes the Osorb[®] molecules apart when it is shorter than the equilibrium length and pulls the Osorb[®] molecules together when it is longer.

F. Data Measurement

The data measurement is made to mirror the approach taken in the physical experiment. The Osorb[®] is initialized inside the cylinder, and the acetone is initialized from the bottom of the cylinder with a random velocity in the x and y direction and a random positive velocity in the z direction. This mimics the injection of acetone into the bottom of the cylinder as done in the physical experiment. The Osorb[®] then absorbs the acetone and expands. It continues to expand until it reaches the edges of the cylinder.

When the Osorb[®] is finished expanding, it will be contained in the cylinder by the Osorb[®]. The containment leads to a force being exerted upon the lid of the cylinder. The sum of all the spring forces acting on the lid is taken and recorded. Two methods were tested for determining the force on the lid due to springs. The first was to take the distance from each molecule and the lid and input the value into the force function as the radius, and then pass the total spring force on the molecule as the f_s . This returns a value of the force on the lid scaled based on the spring force pushing up on the particle and the distance the particle is from the lid. The force function still has a maximum radius for the return of any force so a particle that is far from the lid will return a force of zero. The second method was to find all the molecules within a certain distance of the lid and sum together the total spring forces on each of these molecules. The main difference between these methods is that the first weights the forces based on how close the Osorb[®] molecules are and the second method does not. This process is done several times for varying cylinder volumes.

IV. RESULTS AND ANALYSIS

A. Method 1: Altering Equilibrium Length

Altering the equilibrium length produced unphysical results, such as in Fig. 8 and Fig. 9. As the system expanded to fill the cylinder the Osorb[®] molecules arranged in the lowest energy state, as expected. However, due to the lack of connections between molecules the Osorb[®] lined up such that the Osorb[®] molecules would clump together in the corners of the cylinder. This resulted in no force being applied to the lid of the cylinder. In Fig. 8 it is possible to see the diagonal lining up of the Osorb[®] structure. In Fig. 9, the way in which the Osorb[®] molecules clump in the corners, ignoring the presence of each other is obvious.

B. Method 2: Bifurcating Molecules

The bifurcating molecule method also produced unphysical results, due to the lack a strong structure. Similarly to the first method, in the bifurcating molecule

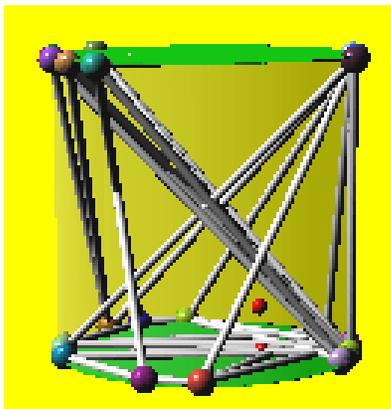


FIG. 8: A side example of the failed equilibrium length. The molecules tend to line up on one side of the cylinder while the molecules they are connected to line up diagonal to them. This figure shows the diagonal structure of the Osorb[®] after expansion. This drastically reduces the force that can be felt by the lid.



FIG. 9: An example from the front of the failed equilibrium length. This figure shows the clustering of the molecules in the corners. It also illustrates the problem with interpenetration between Osorb[®] molecules.

method the structure was not stiff enough to be able to apply force to the lid. In Fig. 10, one can see that the addition of extra molecules succeeded only in allowing the Osorb[®] molecule to be able to fold in upon itself when it encountering forces due to the wall.

C. Method 3: Combination

The combination method produced a strong enough structure to not collapse like previous methods. The structure was stiff and exerted a force on the lid, as shown in Fig. 11. The force versus volume data is shown in Fig. 12. The force did not decrease exponentially as expected. The force versus volume graph was interpreted in two ways. The first was with an exponential fit The ex-

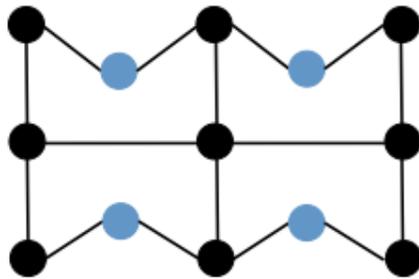


FIG. 10: Figure of the inward collapsing of bifurcated molecules. The failure of the bifurcation methods occurs when they structures collapse in upon themselves. The newly bifurcated molecules, shown in blue, have add additional connections. However, the connections they have broken allow them to collapse inward and cause no force to be applied to the constricting cylinder.



FIG. 11: Figure of the fully expanded structure via the combination method. The structure of the fully expanded molecule is stable and when compressed pushes with a force on the lid.

ponential was used in order to try and connect the graph to the physical data previously found. However, due to a small range of volumes tested, the fit value for V_c was uncertain. The second fit was linear. This yielded a slope of 156 ± 24 . It is interesting to note that there is a swift drop of the force around a volume of 5000.

A major flaw was discovered at a volume of about 8000. When the volume was increased to this value the Osorb[®] could no longer expand to a volume large enough to fill the entire cylinder. At this point the Osorb[®] would remain floating roughly in the center of the cylinder. However, given enough time it would begin to drift upwards and make contact with the lid of the cylinder. As the Osorb[®] drifted up it would exert a force on the lid. This force would increase up to values as high as 80.

The reason for this drifting is unknown. This drifting affect doesn't occur when the volume is lower. If the same

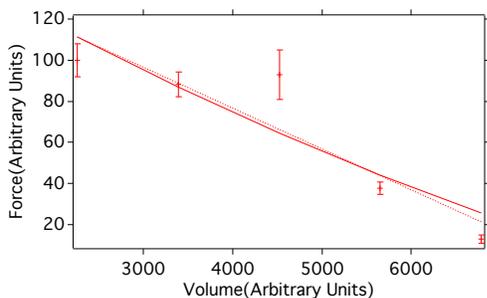


FIG. 12: Graph of the force versus volume. A. The exponential fit is shown in the solid line, and the linear fit is shown in the dashed line. As you can see the exponential fit is not very drastic. The linear fit was chosen as the best fit for the data. The data seems to have a sharp drop off after a height of 40. This shows a decrease in force as the volume increases but not in the way we expect.

drifting still occurred the Osorb[®] structure should still tend to be pressed against the lid creating a stronger force against the lid. The data shows this does not happen and the force drops down to around 10, for the largest cylinder in which the Osorb[®] can fully fill. The reason for this issue and the associated inconsistency based on the volume are unknown, but must be fixed before reliable data can be produced.

V. FUTURE WORK

This is the first research being done into a simulation of the expansion of Osorb[®]. Extending this program in the future will be important to making good use of this base program. There are several alterations that can be made in order to improve the current state of the simulation.

An important flaw in the program is that Osorb[®] molecules that are not connected ignore the existence of each other. This leads to the stacking of Osorb[®] molecules and it allows the structure to collapse such as in the bifurcation methods. This problem can be addressed by implementing a force which keeps Osorb[®] molecules from interpenetrating, similar to the force function used for surface interactions.

The current method of measuring the force causes problems as the lid applies a force down on the Osorb[®] molecules. However, the force from the springs acting on the Osorb[®] molecules exerts a force on the lid when the lid cannot move. In order to fix this the lid must be made a component of the simulation. The lid can be acted on by a gravitational force. The lid will then be given a mass that is alterable. By making the mass changeable one could allow the Osorb[®] to build up and then by increasing the mass compress the structure again. By doing this it is possible to control the downward force on the Osorb[®] molecule, and data can be taken on the volume

of the Osorb[®] depending on the downward force.

Other expansion methods may also be implemented. Initially, the structure could be fully expanded. The fully expanded structure could then be shrunk down to create various random connections that cause the Osorb[®] to maintain its shrunken state. The cylinder can then be created around the shrunken structure, and the acetone introduced. In this method the acetone can break the connections allowing the molecule to expand into the cylinder.

It is also essential to fix the upward drift that occurs when the Osorb[®] is put in a cylinder of larger volume than the Osorb[®] can expand to. The reason for this error is unknown, but no accurate data can be taken until this issue is fixed. The other major flaw in the code that needs to be addressed is measuring the force on the lid. The Osorb[®] structure expands as intended, implying that the expansion mechanism is working. Thus, the problem with the force on the lid lies within the method that we are using to calculate the force on the lid, and not with the expansion mechanism. So, creating a more accurate way to quantify the force on the lid will need to be implemented to produce reliable data.

Aside from major changes that can be made to the program it is important to make additions to the Graphical User Interface (GUI) in order to improve the user friendliness of the program. Currently, the only available option to the user is the input of the desired lid height. The user can also start the experiment, pause, and reset the program. However, it would be ideal for the user to be able to switch between different expansion methods and change constants such as the spring force or equilibrium length from the GUI.

VI. CONCLUSION

This research has succeeded in discovering several methods which do not accurately portray the expansion and force of Osorb[®]. It has also discovered one which visually behaves as desired, but the associated force does not follow the exponential as expected. However, this is believed to be a problem with the code and not a problem with the method of simulating the expansion mechanism. The program that has been created is a strong framework for the beginning of this project. With further improvements this program will be a valuable tool in understanding the expansion mechanism of Osorb[®].

Acknowledgments

I would like to thank my advisors Dr. Lehman, Dr. Lindner, and finally all the members of our Junior I.S. class for all helping in various ways.

-
- [1] Laura A. Underwood and Paul L. Edmiston , *Adsorption of dissolved organic species from water using organically modified silica that swells*. Separation and Purification Technology **66** (2009), 532-540
- [2] John D. Wright, Nico A.J.M. Sommerdijk , *Sol-Gel Materials: Chemistry and Applications* (Overseas Publishers Association N.V, 2001)
- [3] Albon Theresa, *Expansion Forces Within Swellable Organically Modified Silica*, Summer Research Report (The College Of Wooster, 2011),
- [4] Axe Daniel, *Effects of Temperature on the Expansion Force of Osorb[®]*, Senior Independent Thesis (The College of Wooster 2013)
- [5] Duane E. Roller, Ronald Blum, *Physics: Mechanics, Waves, and Thermodynamics*, (Holden-Day, Inc. San Francisco, CA, 1981)