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IN SITU CHARACTERIZATION OF VAPOR-DEPOSITED ORGANIC GLASSES

By

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Chapter 1

An introduction to vapor-deposited glasses for the non-scientist

1.1 Introduction

Humans have been making glasses for over 3000 years, yet many aspects of glass science are still not well understood. When asked to think of a glass, most people picture materials like windows or eye glasses. Most people do not know that glassy materials are even more prevalent in our everyday life; products such as smart phones, optical fibers used for communication, and even pharmaceuticals all utilize glassy materials. With that in mind, the need to thoroughly understand the basics of glasses has grown as technology has advanced. As a graduate student working for 5 years in the area of glass research, there are a lot of questions that I could choose to answer about glasses. In the text below you will see that I have taken a truly fundamental approach; I want to look at the building blocks of glasses, molecules, and see what I can learn from studying them. Specifically, a large part of my research has focused on *kinetic stability of vapor-deposited organic glasses.* After reading the following paragraphs, I hope that you will: 1) gain a better understanding of glass as a material, 2) understand a little bit about the materials we call "stable glasses," and 3) see how a simple system can be a good model for a complex system.

1.2 What are glasses?

Glasses have been around for a long time. There are many examples of "ancient" glasses dating back as far as the Egyptian Period (approximately 2500 years ago). Figure 1 shows how glasses have been used throughout history. Clockwise from the top left you can see arrowheads created from obsidian (volcanic) glass, small glass beads from the moon brought back by Apollo 15 astronauts, a glass jug from the ancient Egyptian age (about 2500 years old), and an insect encased in amber glass (about 20 million years old), another naturally occurring volcanic glass that can stay in the glassy state for 75 million years (you may have noticed insects encased in amber in Jurassic Park and Jurassic World movies!).

Figure 1. Examples of glasses used throughout history. Starting from the top left and going clockwise; obsidian arrowheads, glass beads from the moon, an ancient Egyptian glass jug, an insect encased in ancient amber glass. Reproduced from Ref [1].

The photographs in Figure 1 give you an idea of the versatility of glasses, but do not really define what a glass is. To answer this question, it is useful to first describe how a glass is typically prepared (a schematic illustrating this process is shown in Figure 2, which plots volume as a function of temperature). Starting at high temperatures with a liquid, a glass can be prepared by quickly cooling a liquid past its melting temperature (T_m), the temperature at which a liquid would typically crystallize (if it does crystallize). Although most materials can be made into a glass, not all can since they will crystallize too readily during the cooling process. There is no accurate way to predict if a material will crystallize or not, so it must be determined experimentally. After passing T_m, the system is now referred to as a supercooled liquid (since it is a liquid at a colder temperature than would normally exist). As the system is cooled to colder and colder temperatures, the volume continues to decrease and the components that make up the system are moving slower and slower. At a certain temperature, the components are moving so slowly that they cannot keep up with the rate at which the system is being cooled, so they will "fall off" the supercooled liquid line, thus becoming a glass. By this definition, a glass can be thought of as an extremely slow moving liquid. In fact, it is moving so slowly that it appears as a solid on an human timescale. The temperature at which the glass forms is called the glass transition temperature (T_g). You will notice that the glass has a lower volume than the liquid but does not have nearly as low of a volume as the crystal. It is useful to think about glasses as compared to crystals. Crystals are extremely organized on the molecular level. For example, think about table salt (crystalline sodium chloride). Salt crystals are like miniature cubes and that shape comes from the crystalline order. Conversely, you would never see a glass in the same type of cubic structure. Crystals are the optimal state for a system to be in; over very long periods of time (thousands of years) a glass will slowly evolve towards lower volumes. This process is called aging and is only possible because the components of the glass can still move (albeit on extremely long timescales).

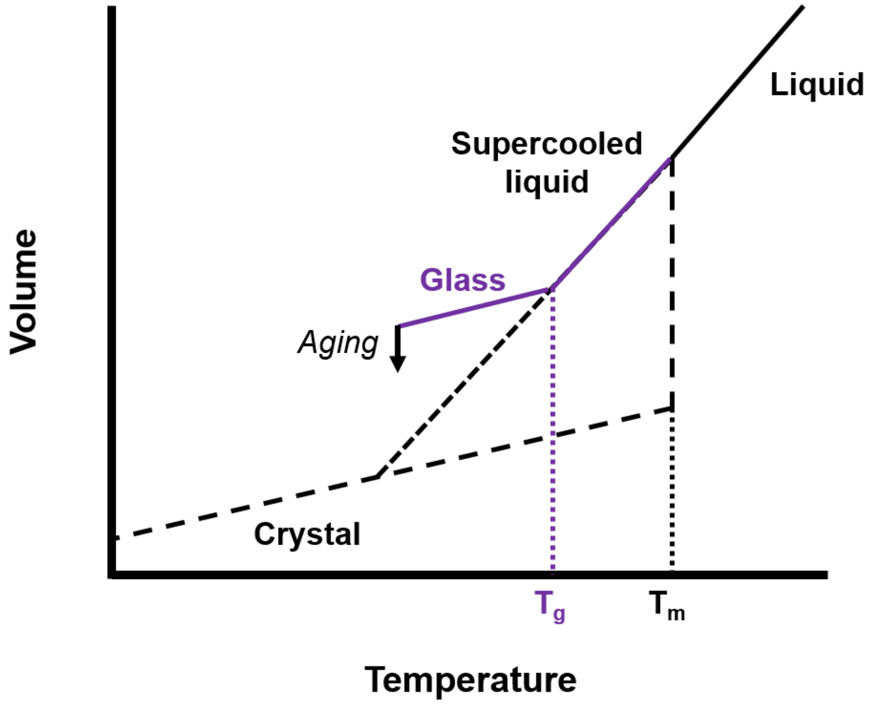


Figure 2. Volume as a function of temperature illustrating how a glass is typically prepared. The arrow indicates aging, as the glass is continually trying to reduce its volume.

1.3 Stable glasses prepared by physical vapor deposition

In looking at this title there are probably two questions that pop up: 1) What are stable glasses? And 2) What is physical vapor deposition? In this section I will answer both questions, starting with the second. Physical vapor deposition is another preparation method that can be used to create glasses. In physical vapor deposition, as schematically illustrated in Figure 3, a material is released into a vacuum (low pressure) chamber. In the vacuum chamber the released material is in a gaseous state, so it can move freely and frequently in the chamber. After bouncing around a little, the material will hit a substrate (solid surface that we prepare our glass on) that is held at a particular temperature. Once the material is stuck to the substrate it cannot leave and continued deposition results in the growth of a thin film of material. In the case of my research I am using a liquid as my source of material (although it turns into a gas once introduced into the low pressure chamber) and controlling the deposition of molecules of that material onto the substrate.

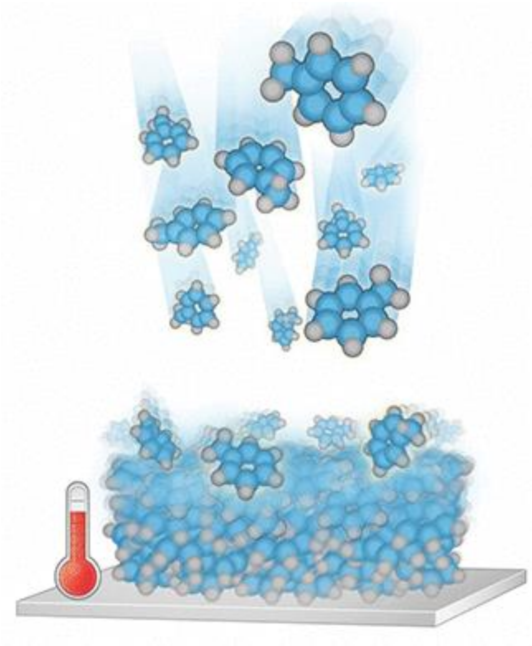
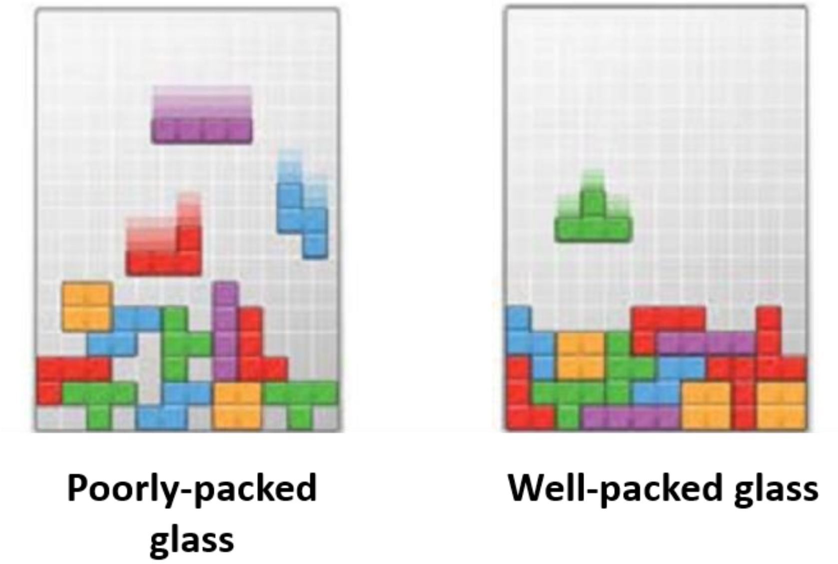


Figure 3. A schematic illustration of physical vapor deposition. After the gaseous molecules bounce around inside the vacuum chamber they will eventually find the substrate held at a particular temperature. With continued deposition a thin film made up of the deposited molecules will eventually form. Reproduced with permission from Ref. [1].

Physical vapor deposition is a unique process because it creates a film in an almost layer-by-layer fashion. This type of thin film growth means that, during deposition, each molecule gets a chance to be a part of the surface layer of the growing film. It has been shown that molecules on the surface of a film are moving us much as 100 million times faster than the molecules in the rest of the film. This huge increase in mobility for the molecules at the surface is due to the fact that they have fewer neighbors than the molecules in the film. Within the film each molecule is surrounded and packed in place by other molecules on all sides, but the molecules at the surface of the film have one side free of neighbors keeping them stuck in place. The result of this increased mobility is that molecules on the surface are able to move around to find favorable positions in the film. Even more so, since each molecule is part of the surface layer at some point during the deposition, all of the molecules are in extremely preferred positions. This means that a glass prepared by physical vapor deposition is a lot more organized than a glass prepared by the typical method of cooling a liquid, since the molecules have some chance to organize themselves in a way that would be more like a crystal (since that is the ultimate preferred state). The difference between an ordinary glass prepared by cooling a liquid and a glass prepared by physical vapor deposition can be easily visualized by thinking of a game of Tetris, as shown in Figure 4. Just as the Tetris pieces are the building blocks for completing the game board, molecules are the building blocks for glasses. The liquid-cooled glass results in molecules basically freezing into place since they are just cooled from a randomly oriented liquid; this gives rise to a poorly packed glass. The glass prepared by physical vapor deposition has a density more that is more like the crystal, since the molecules are packed well together.



Poorly-packed glass

Well-packed glass

Figure 4. Tetris games are a convenient analogy for the difference between a glass prepared by cooling a liquid and a glass prepared by physical vapor deposition. In a liquid-cooled glass the molecules are essentially stuck in their random structure inherited from the liquid, resulting in a poorly-packed glass (left). On the other hand, a glass prepared by physical vapor deposition has the ability to try to be more like a crystal, resulting in a well-packed glass (right). Reproduced with permission from Ref. [1].

Since glasses prepared by physical vapor deposition are organized differently than glasses prepared by cooling a liquid, you might expect that the vapor-deposited glasses have different properties than the liquid-cooled glasses; you would be correct! In fact, vapor-deposited glasses can have a lot of extraordinary properties. Of the many I will only be focusing on one for the purpose of this chapter; kinetic stability. Simply put, a kinetically stable glass is a glass that can be heated to temperatures higher than its ordinary glass transition temperature (the temperature at which the supercooled liquid becomes a glass). The reason for this increased ability to withstand heating comes from the physical vapor deposition process. Since the molecules are much better organized and more tightly packed, more energy (in the form of heat) is required to loosen the molecules out of their structure, meaning that a higher temperature is required to transform the glass back into the liquid state. This temperature indicates the onset of transformation from a glass to a liquid, so it is called the onset temperature; a high onset temperature is one indication of kinetic stability. The onset temperature of a vapor-deposited glass compared to a liquid-cooled glass of the same material is illustrated in Figure 5. This experiment shows film thickness data collected at a range of different temperatures. The as-deposited glass (bottom curve) is thinner and thus denser than the liquid-cooled glass (since it is more well-packed). Additionally, upon heating the onset temperature of the as-deposited glass is much higher than the liquid-cooled glass. Thus this vapor-deposited glass can be classified as kinetically stable.

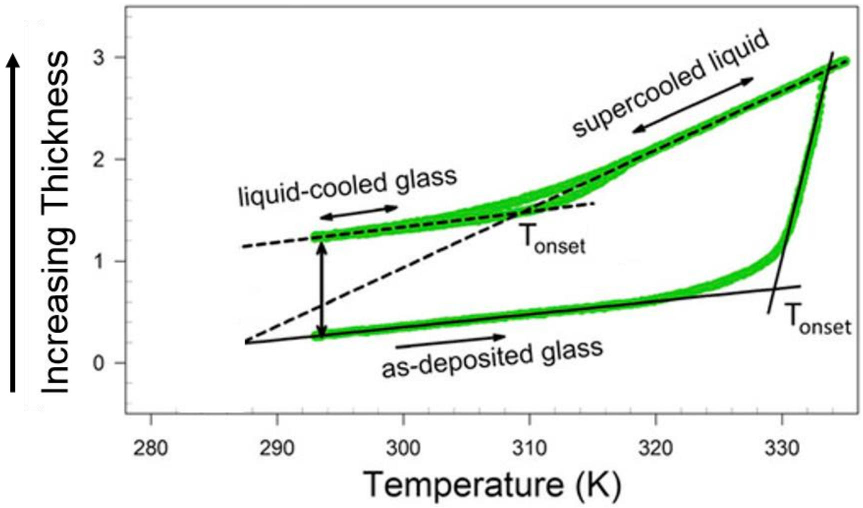


Figure 5. Percent thickness change upon heating of a vapor-deposited glass (bottom curve) and a liquid-cooled glass (top curve). Note that the onset temperature of the as-deposited glass is significantly higher than the onset temperature of the liquid-cooled glass. Reproduced with permission from Ref. [2].

1.4 Using small molecules to study kinetically stable glasses

Kinetically stable glasses have a wide variety of potential uses given that ordinary glasses are utilized in a range of applications. These include technological applications such as display layers in organic light emitting diode phone screens, like the iPhone 10, and optical fibers for telecommunication. Glasses can also be used in pharmaceuticals, since glasses of some drugs have higher effectiveness and are more soluble compared to crystals (an example of this is Itraconazole, an anti-fungal medicine). Glasses can even be made of the same molecules that make plastics (polymers) and these polymer glasses are used in airplane fuselages. Although there is a lot of research focused on studying the exact molecules that would be used in some of these applications, my doctoral research has focused on studying simple, small molecules that can serve as model systems for answering fundamental questions about stable glasses. There is a need to study the simple molecules because there are still many features of stable glasses that are not completely understood. For example, my research has focused on answering questions like: What kinds of molecules can make stable glasses? Are stable glasses a good model for studying a low-temperature, stable liquid? And, can vapor-deposited glasses be used to access new kinds of liquids? The details in answering these questions are beyond the scope of this chapter, but reaching conclusions about each question posed was much easier when using a simple molecule.

1.5 How can you study something inside a vacuum chamber?

Although it may be easier to understand a complex phenomenon when studying simple molecules, the simplicity of the molecules does pose an additional experimental challenge. All of the molecules that I used throughout my thesis work have glass transition temperatures below room temperature. This means that at room temperature, the molecules cannot be in the glassy state; they can only exist in the liquid state because room temperature is too hot. The challenge that comes from this is that all of my characterization and analysis of the glasses I make has to be done inside the vacuum chamber (which we keep at cold temperatures) or *in situ*, as it is called technically. For all of the work presented in my dissertation, there were three techniques that I used to study my glasses. For ease, I will only explain one technique in detail here: AC nanocalorimetry.

Let's take the name of the technique and break it down into components, I think this will be the best way to explain how the technique works. AC *nano***calorimetry**. Let's start with "nano" as it is the simplest to explain. This refers to the amount of material that we are working with. The devices for this technique are extremely small. In Figure 6 you can see that the devices themselves are smaller than a dime. Even more so, there is a small active area where we actually perform the measurement, which is about a 30 micron square (one micron is one millionth of a meter). For reference, a human hair can be anywhere between 20 – 180 microns in diameter. Since the area we are actually using for the measurement is so small, we only need nanograms (one nanogram is one billionth of a gram) of a material in order to effectively analyze it. This is where the “nano” part of the technique name comes from.

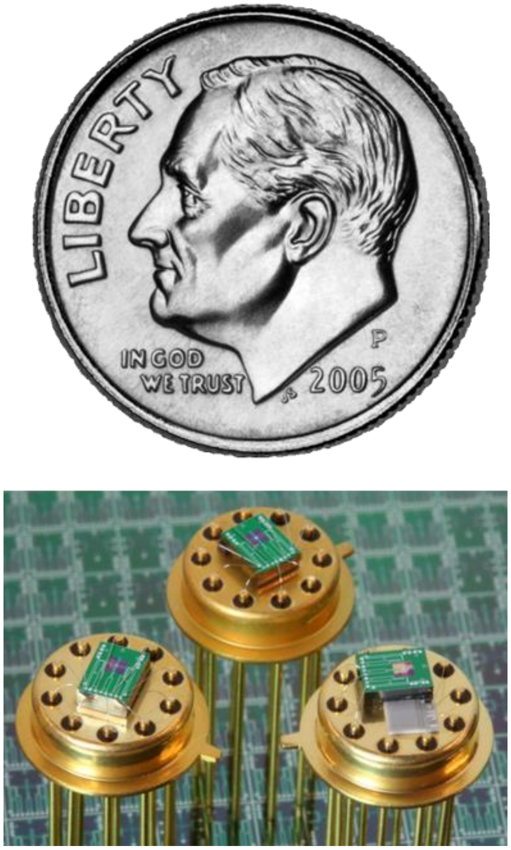


Figure 6. Nanocalorimeter devices shown against a dime for scale. The green chip on the top of the device contains the 30 micron square active area that is actually used for a measurement. The width of the active area is equivalent to the diameter of a thin human hair and requires only nanograms (one nanogram = one billionth of a gram) of material for analysis. Figure courtesy of xensor.nl.

Next I will describe a little bit about how the technique works and what it actually measures, which will explain how “AC” and “calorimetry” fit into the name. Calorimetry is the act of measuring the amount of heat transferred into a system when a change occurs. Often calorimetry measures a property called heat capacity, which is the amount of heat needed to raise the temperature of a system by one degree in temperature. Here, an AC voltage is applied to create a temperature change, hence “AC” nanocalorimetry. Heat capacity can also be thought of as measuring the number of molecular motions in a system (how freely a molecule can move around). For example, molecules in liquids are able to move in many more ways than molecules in a solid. In my experiments, I am interested in the heat capacities of glasses and liquids, which are not the same. Glasses have a lower heat capacity because they have fewer molecular motions allowed whereas liquids have a higher heat capacity because they have more molecular motions (think about how a liquid can flow freely vs. a glass which is solid-like by observation). As shown in Figure 7, we can use the heat capacity to learn about the kinetic stability of a glass, since we can track the transformation of glass into liquid upon heating.

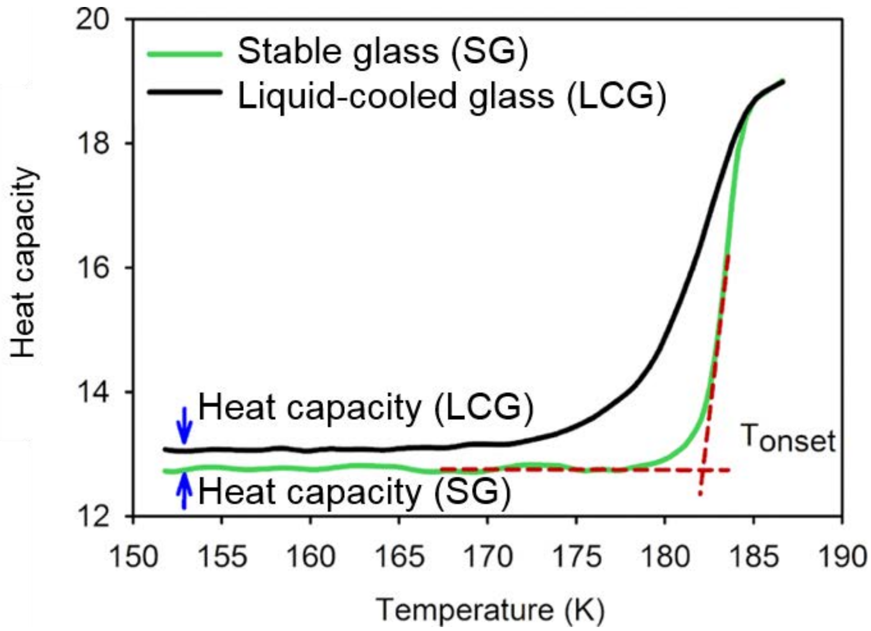


Figure 7. Sample data from an AC nanocalorimetry measurement. Heat capacity is plotted as a function of temperature for two glasses, a stable glass (green curve) and a liquid-cooled glass (black curve). Both glasses have lower heat capacities than the liquid (high temperature end) but the stable glass has a lower heat capacity than the liquid-cooled glass. The stable glass also has an increased onset temperature relative to the liquid-cooled glass, which indicates kinetic stability. Modified and reproduced with permission from Ref. [3].

Figure 7 shows sample data from an AC nanocalorimetry measurement. Heat capacity is plotted as a function of temperature for two glasses, a stable glass, shown in green, and a liquid-cooled glass, shown in black. The rise in heat capacity at high temperatures indicates the transformation from glass to liquid; the transformation is complete when the heat capacity begins to level off, here at just above 185 K. Both glasses have lower heat capacity than the liquid and the stable glass has a lower heat capacity than the liquid-cooled glass. This is related to the well-packed nature of the stable glass; remember the Tetris picture (Figure 4). The molecules in the stable glass are well-packed so their motion is limited, leading to a lower heat capacity (since heat capacity measures the number of ways a molecule can move around). By comparison the liquid-cooled glass is poorly packed, so the molecules have more freedom to move around which results in a higher heat capacity than the stable glass. Just as in Figure 5, you can see the kinetic stability of the stable glass as indicated by the increased onset temperature relative to the liquid-cooled glass. The data in Figure 5 was collected from a technique done outside the vacuum chamber whereas the data in Figure 7 was collected *in situ*. Nevertheless, you can get comparable information from both methods, illustrating that data collected from a glass made with a low glass transition temperature molecule can be just as informative.

1.6 Conclusions

As I have illustrated in the preceding paragraphs, glasses are a ubiquitous material that have been prevalent in our world for a long time. They have some unique properties, namely that they are constantly evolving over long time periods in the process known as aging. My research has focused on studying stable glasses, which are prepared by physical vapor deposition. Stable glasses are well-packed and can be heated to higher temperatures than ordinary liquid-cooled glasses, which makes them a promising material for potential applications in organic electronics and pharmaceuticals. In all of my work I studied simple, small organic molecules which served as model systems for answering fundamental questions about stable glasses. Since the molecules are small, they have glass transition temperatures below room temperature and thus they must be studied *in situ*. I illustrated that an *in situ* AC nanocalorimetry measurement provides the same information as an *ex situ* measurement, validating the utility of *in situ* measurements.

There is still a lot to be understood about the field of stable glasses, since they are a relatively new discovery that happened in 2007. While the research in the Ediger group is at the forefront of this progress, there are a lot of other research groups around the world whose research is equally important. For instance, there are so many other ways that stable glasses can be studied beyond what we do at UW-Madison. Computer simulations, single molecule measurements, and more complex *in situ* experiments and experiments at national government laboratories are all essential to piecing together the puzzle of stable glasses. The field is a great example of how truly important collaboration and communication are to progressing research and understanding.

1.7 References

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