CHGN 125

MOLECULAR ENGINEERING AND MATERIALS CHEMISTRY: A DESIGN BASED APPROACH TO INTRODUCTORY CHEMISTRY

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I. MOLECULAR ENGINEERING: AN OVERVIEW

1-1 SCIENCE AND ENGINEERING

It is not uncommon for universities to separate science from engineering—they offer students a college of engineering and a college of arts and sciences. The practice of dividing science and engineering has contributed to the misconception that engineering exists separately from science. This may have been true several hundred years ago, but in the modern world, it just isn't so. Let's see why.

Imagine that you have been given the task of constructing a bridge over Clear Creek. The act of building this bridge is an example of engineering. But the first thing you should note is that the task, as stated, is meaningless. What distinguishes engineering from random construction is that engineering begins with a well-formed set of objectives. The bridge will fulfill some purpose. It might be a pedestrian bridge, or a temporary way to move large trucks across the creek during highway construction. The form of the finished bridge will depend on its eventual function. Therefore, an engineering project will begin with a set of performance goals. Our bridge must be capable of transporting pedestrians and bicyclists across Clear Creek; should have a substantial lifetime; require minimal maintenance; and should harmonize with the surrounding environment.

After identifying these performance objectives, the engineer's next step is to specify the bridge properties, which differ from performance goals in that they are quantifiable. For example, one of our performance goals is to accommodate pedestrian and bicycle traffic; now we must determine how many bicycles and pedestrians will cross the bridge. We may find that at noon on most Saturdays in the summer the bridge may need to support a peak load of 40 pedestrians and 10 cyclists at one time, a load of about 5,000 kg. Hence, our bridge must support about 5,000 kg; and when fully loaded we may specify that it should deflect no more than 1 cm. Alternatively we might decide that instead of designing for this peak load, we will design for the average load and construct a gate that limits the number of people on the bridge at any one time. Obviously, we can imagine bridges having vastly different properties that satisfy the same performance goals.

Once the bridge properties have been determined, it is time to move to the phase that most people think of as engineering—the design of the structure. Just as there are many property sets that will satisfy the performance goals, there are many structures that will accommodate the desired set of properties. For instance, to minimize bridge deflection to 1 cm we could use a center support, or we could build it of more rigid materials supported only at its two ends. (Of course, any single decision will have an impact on other performance goals, like the bridge's cost and its harmony with the environment.)

After the bridge has been designed, it must be constructed. As in the other phases, there will be many possible construction strategies (also called process strategies). We might choose to build the bridge somewhere else and deliver it to the site; we may choose to build it where it will ultimately sit; or we may choose a combination of both.

Regardless of our decision, we see that engineering has four steps that can be summarized as follows: **Performance** goals require **properties** that are satisfied by a **structure** that can be **processed** (built). Or simply: Performance => Properties => Structure => Process.

But wait! This was supposed to be a discussion of science's role in engineering, and we have yet to use the word "science." This is because science is hiding in the background of every phase. How do we know how to design a bridge that will deflect only 1 cm under a specified load? For thousands of years the only way to find out was to build a bridge and measure its deflection, which led engineers to build bridges that looked similar to the ones that came before. New designs plucked from their imaginations had the unfortunate habit of falling down. Then in the seventeenth and eighteenth centuries scientists began to apply their talents to engineering.

Two such scientists were Leonard Euler and Daniel Bernoulli, who used science to predict the load-carrying and deflection characteristics of beams. (You will use their equations if you take strengths of materials). Suddenly, engineers were free to use their imaginations to build new things like the Eiffel Tower, the Ferris wheel, the Statue of Liberty and many of the great steel bridges and buildings constructed as part of the Second Industrial Revolution. Science allowed these engineers to predict the properties of their constructions before being built.

Euler and Bernoulli's major advance was the discovery of a structure-property relationship. They had developed equations that predicted how a beam of a given shape and material (structure) would deflect under a load (property). The Euler-Bernoulli beam equation is an example of one such structure-property relationship. Thousands (if not millions) of such relationships are known—and many more remain to be discovered.

In addition to structure-property relationships, there are also process-structure relationships. For instance, the glass in your car's windshield and in your home's windows appear to be the same, but appearances are deceptive. When struck, window glass breaks into sharp shards, while a windshield does not. The two forms of glass have different properties because they were processed differently, and in this case, reflect a process-structure relationship.

These structure-property and process-structure relationships join engineering with the applied sciences. The engineer uses these relationships to build things. The scientist discovers new relationships, making it possible to build new things. (This distinction between science and engineering is still artificial; engineers are not precluded from discovering new process-structure-property relationships, and scientists are not precluded from their systematic application.)

Much of your time at Mines will be spent learning and applying process-structure-property relationships, and Chemistry is no exception. It is a structure-properties course, where you will learn how structure can give rise to properties. What distinguishes this course is the kind of structure-property relationships we will be investigating. Before expanding on this point, however, it is important to more thoroughly describe the terms we will be using: process, structure and properties. For reasons that will become obvious, we will begin with structure.

1.2 EVERYWHERE YOU LOOK: STRUCTURE

Let's begin our investigation of structure with one familiar to almost everyone—the Golden Gate Bridge. If we were to ask a metallurgist and a civil engineer to comment on its structure, it is likely the two descriptions would be radically different. To understand why, imagine what you would see as you approached the bridge from some distance away.

From a kilometer or so, the bridge appears as a monolithic construction that serves to move cars and trucks from San Francisco to Marin County. But as you move closer, several structural subsystems are readily apparent. At 100 meters, you can clearly see the arrangement of beams and girders that constitute the roadway.

From ten meters, you discover the details of the bridge's main art deco supports, allowing us to deduce the processes that were used to assemble these substructures.

At one meter, the structure of the main and supporting cables begins to reveal itself. The main cables appear as giant pipes from which the bridge hangs. But if you could turn back the clock to the time of its construction, you would see that the main cables were built from thousands of high-strength wires, each on the order of 10^{-2} m in diameter and individually pulled across the Golden Gate and then bound together to form the large cable.

Move even closer and observe a fragment of the bridge under an optical microscope. You will see a mosaic structure composed of individual pieces with characteristic sizes on the order of 10 to hundreds of microns (10^{-6} m). The actual shapes, sizes and distributions of the mosaic pieces, called grains, will differ depending on the part of bridge from which the sample is taken. The pieces making up the high-strength wires are uniform and elongated, while those from the girders are comparatively irregular. Some of the steel's properties result from the arrangement and sizes of these grains. If you increase the power of your microscope, the structure of the grain is revealed as a regular array of spherical atoms. Every so often, though, these arrays are punctuated by defects where a small number of atoms have been displaced slightly form their regular positions—much like a few members of a marching band being out of line. These defects are a few nanometers (10^{-9} m) apart. Yet change the number and spacing between these defects just a bit, and a material may be transformed from soft and ductile to strong but brittle. Zooming in on the regularly arranged atoms, you

Fig 1-1

see that they are not solid and spherical at all but only appear that way due to very rapid electron motion, producing a topography of picometer (10^{-12} m) sized peaks, valleys and ridges of electron charge. It is the electrostatic repulsion and attraction between these topographical features that both holds the atoms of the steel together and simultaneously gives steel its resistance to compression.

You could now dive deep into the electron cloud to find a massive nucleus at its center. The nucleus, in turn, is built from a finer set of structural features, *et cetera, et cetera*. In fact, it appears that empty space has a structure that could be as small as the Planck length, 10^{-35} m. (Check out http://www.wordwizz.com/pwrsof10.htm for more information.) From an engineering perspective, however, our interest extends to those structures that can be manipulated—processed—and the smallest structures we can manipulate are the peaks, valleys, and ridges of electron charge, while the largest are more than kilometer in size. [1]

Between these two extremes lies the engineering structural hierarchy. When a civil engineer is asked to describe the structure of the Golden Gate Bridge, she is most likely to comment on its structure as seen from great distance. On the other hand, a metallurgical engineer might describe the microstructure (the composition and arrangement of metallic grains) of the various steels used in the bridge. What is important is that we engineers characterize structure in terms that are related to things that we know how to manipulate. Our perception of structure is inseparable from the processes we use to manipulate the components of this structure.

How are we to define structure so as to please the civil engineer, the metallurgical engineer and all the other engineering practitioners? We could define structure as the arrangement of the parts from which something is constructed. This definition however, leaves us with the same problem we had before—various disciplines will think of "parts" in different contexts. So, let's simply define structure as the arrangement of matter. The civil engineer will see the matter composing girders and beams that support the bridge as being purposefully arranged to give desirable properties; and the metallurgical engineer

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[1] *Over the last 50 years or so we have discovered that human kind has inadvertently manipulatecd structure on a planetary scale. The possibility that we can move from accidental to purposeful manipulation has led some to speculate about the feasibility of a new engineering discipline called geoengineering.*

will think of the matter from which the grains are composed as being purposefully arranged to give desirable properties. Consensus!

1-3 PROCESS

With our definition of engineering structure as the arrangement of matter, a process must involve the rearrangement of matter, or alternatively a change of structure. A random pile of beams and girders may be rearranged into a bridge. The pile began with one arrangement—one structure—and ended with a new arrangement—a new structure. Without exception, such structural change involves energy. A process can either store or release energy through the rearrangement of matter, but both require a change of structure. For example, bolting two bridge components together is a process. A tiny amount of energy is stored as elastic energy as the atoms in and around the bolt are shifted ever so slightly from their unbolted positions. More dramatically, when metals are forged, a comparatively large amount of energy is used to change the structure of the grains making up the metal. Generally speaking, there are three ways to store (or realize) energy in (from) a structure: chemically, thermally, and mechanically. We will discuss each of these in more detail in the next chapter.

1-4 PROPERTIES

A substance's properties result from the manner through which it stores and exchanges energy. As illustrations: a substance's heat capacity (a property) is defined to be the amount of thermal energy that must be stored to increase its temperature by some fixed amount; a material's hardness is related to the amount of mechanical energy that can be stored in the defects mentioned in the last section; and a substance's stiffness is determined by the amount of energy that can be stored and recovered from the interactions between the peaks, valleys and ridges of the electron charge. Note that all of these properties have something in common—they can be measured. Unlike performance, properties are inextricably linked to measurement and the device used to make these measurements.

Properties can be further characterized as intrinsic or extrinsic. Intrinsic properties are characteristic of a particular substance or molecule and cannot be changed. Extrinsic properties can be altered by adding more of something. The strength of the Golden Gate Bridge's roadbed could be increased by supporting it with more girders. Or, its strength could be increased by using the same number of girders but ones that are wider. The strengths of the bridge and of the girders are extrinsic properties. Perhaps surprisingly, the strength of the steel making up the girders is also an extrinsic property. Forge or hammer a girder and it will become stronger. In this case, the increased strength is the result of adding more defects to the steel's grains. Strength is a property that depends on the process history of the material.

On the other hand, intrinsic properties do not depend on processing history. The melting point of the steel is independent of the size of the girders or of their processing history. Another intrinsic property is a substance's stiffness, a quantity called its modulus. As a final and important example, the amount of energy needed to make a defect is an intrinsic property. While more energy can be stored by increasing the number of defects and thereby alter an extrinsic property, the energy to make a defect is fixed for a given substance and hence this energy is an intrinsic property. In fact, as with this example, all extrinsic properties are ultimately determined by a material's intrinsic properties.

We engineers are very good, and getting better, at manipulating structure to give desired extrinsic properties. We are less accomplished at altering structure to provide the right set of intrinsic properties. As a result, we tend to improve existing molecules and materials, or simply stumble upon new ones, rather than to engineer new molecules. Was steel the best material to use in the construction of the Golden Gate Bridge? We don't know, there may very well be something much better. To design such a substance though will require that we know a lot more about the process-structure-property relationship controlling intrinsic properties.

Roughly 50 years ago Walter Kohn and Pierre Hohenberg proved that the structure giving rise to intrinsic properties is the charge density—i.e., those peaks, valleys, and ridges of electronic charge at the bottom of the engineer's structural hierarchy. About 25 years ago, the tools needed to "see" the structure of the charge density began to emerge. And over the last ten to fifteen years these tools have become common place. (Some of these tools are readily available to you here at Mines.)

Together these innovations have bestowed on you a unique opportunity to discover and apply the process-structure-property relationships responsible for intrinsic properties. You are the generation of scientists and engineers who will forge the disciplines that will allow us to design the substances we use, instead of using those we know. In the future when you are designing a prosthesis that requires an unheard-of set of properties—no problem, the structure-property relationships necessary to design the material will be well known. When a new drug is required to inhibit a newly discover biochemical reaction—no problem, the tools necessary to design the molecule will be available. And when you are called upon to build a new water purification system that will remove harmful organic contaminates from the drinking water of a third world nation—no problem, you will know how to do it. **Welcome to the future world made possible by molecular engineers.**

1-5 WHAT IS COMING UP IN THE WEEKS AHEAD?

Our task ahead is first to understand the science on which all process-structure-properties relationships are built. This task may sound a bit daunting—it took the scientists that came before us more than 5000 years to figure it out—but thanks to the great scientific discoveries of last two centuries, we now know that just two laws of nature control the way a process's energy is distributed in atomic systems. Thus, our exploration begins with the science of process structure relationship. You will discover through labs, reading and lecture exactly how nature allows energy to be stored in structures, which in turn, depends on the various structures that are available to atomic systems—i.e., just about every system of interest to engineers. For the next few weeks you will probe the science of energy storage in, and the structure of, atomic systems, with particular emphasis on engineering materials such as metals, semiconductors and glasses.

Once you have mastered the basics of energy storage and structure, we will turn to an investigation of material's properties. Why do some things bend and others break? Why does most stuff expand on being heated? The answer is these questions is tied up in energy storage. Some structures like that of copper, store energy differently than do other materials like window glass.

My favorite part of the class begins in about seven weeks when we bring it altogether to study the process-structure-property relationships that allow us to design all the amazing electronics that make your smart phone and laptop computer possible. What are the structure-property relationships that make solar cells and LED lights work? You will come to understand these.

Finally, we will look ahead and see that if we are to continue to advance technologically, we must discover, new process-structure-property relationships. In the last few weeks of class you will have an opportunity to try your hand at uncovering these relationships.

I am looking forward to an exciting and productive semester. I hope you are as well.

1-6 PROBLEMS FOR THE CURIOUS

1) What is the performance goal that requires windshield and window glass to have different properties?

2) From you reading of Bronowski's *Ascent of Man*, find an example where properties were considered a consequence of process rather than structure. How did this understanding influence the way technology was developed?

3) From Bronowski's perspective, what are some important performance criteria that have driven technological advance? Justify your answer.

4) Give an example from architecture of an important structure-property relationship. Did the discovery of this relationship necessitate the development of a process-structure relationship? (You will need to do research here. The answer is not in the *Ascent of Man*.) If so, describe this process-structure relationship in a little detail.

5) Do a little research on Jacob Bronowski and then comment on this description of him by a student from a previous class. "Jacob Bronowski was the Swiss Army knife of scientists."

6) All but one bridge over I-70 between Golden and Idaho Springs looks like the one on the left

The single exception is at exit 254, shown on the right. This structure is much more expensive than the others, so why was it built this way? What is the structure-property relationship that required the more expensive bridge?