THE NATURE OF SOLIDS

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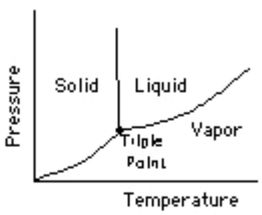
Before embarking on a study of solid state physics, perhaps we should ask what we even mean by the "solid state". Although the distinctions between the solid, liquid, and vapor states of matter have been a part of our common experience for a very long time, the very nature of solids has been dramatically revealed only over the last half-century in ways that were previously unimaginable and technologies have been developed that allow new structures and even new materials to be created.

At the very core of the question of the nature of solids is the atomic hypothesis. For well over two millenia, since the time of Democritus and Lucretius, the idea that everything is made of distinct atoms has been a part of natural philosophy, although neither understood nor accepted even by many natural philosophers and scientists over much of the intervening time. Even as recently as the beginning of the twentieth century - within the lifetime of some humans - the existence of atoms as individual constituents of matter could not be verified without some doubt, and it had been assumed that any direct observation would be impossible. Einstein's explanation, in 1905, of Brownian motion as indirect evidence of the effects of individual atoms and molecules was a significant contribution to the idea that all matter, even the air we breathe, is made of atoms and combinations of atoms. And the observation of the diffraction of x-rays by crystalline solids was even stronger evidence of the microscopic structure of materials. And now, only a lifetime later, distinct materials can be identified in terms of the arrangement of their constituent atoms. In our own conscious lifetimes (even those of the students reading this), it has become possible to observe individual atoms using scanning tunneling microscopy and even create and study new atomic structures by placing individual atoms. The atomic hypothesis has become the atomic fact - and we now know that all materials are constructed of individual atoms that are distinguishable and distinct. Furthermore, the study of atoms in the first half of the last century has led to an understanding of the very structure of the atoms themselves and to the remarkable conclusion that we now know the characteristics of every type of atom that is even possible in the entire universe with atomic number less than 110 and the organizing principles for any that are either discovered or manufactured that are heavier - even in the core of some distant supernova. Even if the "modern physics" concepts of quantum mechanics and relativity - which changed our worldview from the classical physics of the previous centuries - are replaced by a "new" physics, it will not change what we know about the possible atoms that can exist. All that can be changed are the underlying descriptions - the mathematical formalism that describes nature at the atomic level - but not the knowledge of the nature of the atoms themselves.

So the discussion of the nature of solids has to be the discussion of how the individual atoms coelesce into larger structures and take on the characteristics and properties of the many possible solids. The first question, I suppose, is "Why should atoms attract each other in order to form solids?" And the answer, of course, as it is for all "why" questions, is that it is energetically preferable for them to do so. That is not a very satisfying answer, in itself, and we should only be satisfied when we know why forming solids lowers the energy of the collection of constituent atoms. To deal with such questions will require dealing with the bonding mechanisms. And the bonding mechanisms between atoms is intimately related to the very structure of the atoms themselves. For that reason, we will begin our study with a review of atomic structure - how the quantum theory predicts how the electrons fill atomic orbitals (which leads to the structure of the periodic table) and then how that in turn predicts how atoms interact with each other in order to complete their atomic shells thus forming either molecules or the larger structures which we call solids. As we will see, there are a number of different possible bonding mechanisms, and which occur will determine the atomic arrangements and the physicsl properties of the resulting solids.

What IS the solid state of matter? Do all substances even exist as solids? It is useful to categorize or separate matter into several states or phases -

which, in general, behave quite differently from one another. The three obvious states of matter, which we all recognize in our normal experience are the solid, liquid, and vapor phases. We can use water as the common example - with the three states of water being ice, water, and steam. And our normal experience also indicates what determines the state - or phase - in which we can find that substance. Below the freezing point it is ice, above the boiling point it is steam - or vapor, and in between it is in the liquid form. And we also notice, from our own experience, that at the ice-point water and ice can exist in equilibrium just as water and steam can co-exist at boiling. But it is also true that changing the pressure can also change the temperatures at which those phase transitions occur. So the phases or states of matter for some chosen material depends both on temperature and on pressure. For that reason, absolute temperature and absolute pressure are referred to as state variables - that is, controlling them for some substance controls the state of the substance (liquid, solid, vapor).



A phase diagram is a useful way to display the states of matter for some substance. The curves which separate the phases represent the combinations of temperature and pressure for which the two phases which border that branch of the diagram are in equilibrium. There is also a triple point - a particular temperature and pressure at which all three of the phases are in equilibium. Materials for which the triple point pressure is less than atmospheric pressure will exhibit all three phases - solid, liquid, and vapor - at atmospheric pressure depending on the temperature (again, water being an obvious example). And that is the case for most, but certainly not all, materials. Carbon dioxide, for example, has a triple point pressure well above atmospheric pressure. As a consequence, CO2 exists in solid form (dry ice) at atomospheric pressure and as a gas, depending on the temperature, but does not have a separate liquid phase unless the pressure is raised above the triple point pressure. All of the elements will solidify at some temperature at atmospheric pressure except helium. Helium gas liquifies only when the temperature is lowered to 4.2 K - the lowest boiling point of any material - and will not solidify except at high pressures with the temperature maintained below one Kelvin.

How these 'factoids" are useful to us are to remind us of the nature of solids. If all materials are made of atoms, whether the material is a solid or a liquid or a vapor depends on whether the atoms form some relatively rigid bond with respect to their neighboring atoms or whether that bond is such that the atoms or molecules can move with respect to each other, yet form a surface (as in a condensed droplet), or whether they behave independently of each other and can only be contained with a closed volume. And the conditions that determine which of those states occur are temperature and pressure.

But even though atomic bonding and the structure of the resulting solids is important, we ultimately want to discuss the properties of the various types of solids that can form. Closely related to the atomic bonding are the mechanical properties of solids - how rigid or pliable the solid would be or how readily vibrations could be propagated through it. And closely related to how the atoms vibrate are the thermal properties of solids - thermal expansion, for example, or thermal conductivity and molar heat capacity. (And as we will see, the heat capacity of a solid will become an important measure of how the atoms vibrate.) But it is the electrical (or the electronic) properties of solids that will hold most of our interest. That is, depending on the bonding mechanisms that allow atoms to coelesce into solid form, there may be electrons that can migrate among the atoms or ions which then render the solid to be an electrical conductor. On the other hand, if the outer electrons of the atoms that form the solid are all participating in the bonding - in order to complete closed shells on the atoms - then the material would not be inherently conductive. These distinctions will need to be made carefully to fully understand the characteristics of metals, insulators, and semiconductors. In attempting to understand the behavior of the electrons in solids, we will find that our classical assumptions will be inadequate - that is, assuming that the electrons behave classically (like charged b-b's moving among the "bowling ball" atoms or ions) will yield behaviors that are not consistent with experiments. And resolving the inconsistencies will require applying quantum theory to the electrons and that in turn will give us a language to discuss the distinctions between metals, insulators, and semiconductors - and hence the language to deal with the properties of semiconductors and the devices that can be made from those materials. Finally, there are some "special states" that can be discussed - and a study of solid state physics would be remiss if those special states were not included. Magnetic materials and superconductors are intriguing and important types of solids that can only be understood following the discussion of normal solids.