Physics of Functional Materials and Devices

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Lecture - 34, Week 9

Introduction to the basic properties of liquids and melts

Welcome back to the course on Physics of Functional Materials and Devices. Today we would be the first lecture of week 9. Till now we have been mostly focusing on solid materials and how the properties of these materials can be tuned by either changing their composition or by changing the thermodynamic parameters. Let us move a step forward and see if you have melts and liquid phase of certain materials, what happens to their properties? Will the properties remain same or they will change if I have a liquid or a melt state? So, first you must understand the concepts of liquids and melts. After that we will try to understand the models which can explain the properties of these liquids and melts. To start one of the models which we will discuss in detail in today's lecture would be the Lindmann's melting rule and how it is utilized to explain the properties of melts or liquids. If you look into the liquids, melts or solids.

The basic characteristics which will differentiate them would be the shape and the forces which are acting between their atoms that result in the stabilization of various forms. For example, if you look into gases what do you have? Gases have weak atomic forces, but solids have strong ones. Molten substances are the ones which have forces which are in the intermediate range. If you take gas as an example, what do we believe that in such kind of systems? you have the condition where the atoms can move appreciable distances without any hindrances in their path.

In addition, the gas takes the shape of the container in which it is filled and has no fixed volume. What do we know about solids? Solids have atoms which are fixed or their extent of vibration around their mean position is quite small in comparison to that which you have in gases. Now, solids can be of different shapes and forms and you can make them to transform from one form to the other by changing their fabrication protocols. If you talk about liquids, they are more towards solids with atomic forces similar to that which you add to solids. Liquids will have definite volume, but will adopt the shape of the container

in which they are filled, but understanding their behavior is much more complex than understanding the behavior of solids.

Why? Because the atomic motion is not as predictable as that in solids. Hence, the transport properties and the theories which you develop to explain the behavior in solids cannot be extended straight away to liquids. So, you are unable to explain directly the properties of viscosity, thermal or electrical conduction or even diffusion. So, let us today start and see how the properties change in liquids and melts and can we use these modulated properties in some applications. The whole idea if you look into the published literature then Eyring introduced the vacancy model for liquids around 1930s.

Which offered a partial, but just quantitative explanation of certain properties which were being seen in liquids not qualitative it is quantitative. Now, what was hypothesized? They believed that a liquid maintains a structure similar to the related solid, but with the very clear difference. The liquids have significantly more vacancies than the solids. This is what was hypothesized and the vacancy concentration between the molten substances and the solids was basically thought to be the reason behind most of the properties which were showing dissimilar characteristics. So, if this model was supposed to be true, then the X-ray plots of melts should have shown the presence of long-range ordering.

In the liquid states also just like what you see in solids because vacancies do not impact the diffraction pattern to appreciable amount if you have long range ordering. That is where a serious objection to this model was brought in because no such effect was found in the X-ray diffraction plots. You were not seeing diffraction patterns which are associated with long range ordering; hence something was different. So, Bernal suggested around 1950s 1960s that you have to take into consideration a hard sphere model to explain the properties of liquids. Basically, what you have to do? Here the structure of the liquids are to be considered as a random distribution of closed packed spheres.

These atoms were to be believed that they were situated at the corners of 5 different types of rigid polyhedral. Now, you had a polyhedral and the atoms were sitting at the corners. This model then took into consideration the fact that instead of long-range ordering you will have a short-range order, but they added an assumption. The assumption was that this short-range order would be static. So, it would remain like that.

So, what was the factor? With its fixed proportions of crystalline bodies describing a structure that does not vary with temperature that is what was coming in because you were believing that the short-range order was static. So, it should not change as a function of temperature. This is again the point where contradiction to the experimental results which were being seen from X-ray refractions of melt. of metals was observed. And, hence this model also became slightly away from the reality and it was important that you introduce new concepts or you had to add certain more parameters and features into either the Eyring

model or the Bernal model before it could explain the observed phenomena in melts or liquids.

And, it was in the later half of the 20th century that more precise model started coming into the literature. Now, what was the need? To explain these observations there was a need to have mathematical formulations that could describe the structure and from there you could correlate with the observed properties. And the first concept which was introduced was the pair distribution function. This pair distribution function deals with the relationship between a pair of atoms. an arbitrary atom which is considered to be a reference atom and an another atom which is somewhere at a distance from the reference atom.

ω_r is the average probability of finding another atom in a unit volume at a distance r from the reference atom. ω_0 is the probability of finding another atom in any randomly selected unit volume. So, why randomly selected? Because you are believing that the whole melt or liquid was in a homogeneous state. So, wherever I look into the environment they same. So, you could choose any unit volume and then from there you should be able to derive the factors which are controlling the properties of these melts or liquids.

Hence, the pair distribution function g(r) is defined as the relative probability of finding another atom in a unit volume at a distance r from a reference atom.

$$\text{So, } g(r) = \omega_r/\omega_0.$$

Now, the probability of finding the second atom within the volume element dv equals what? It will be equal to ω_r times dV. Consider that the volume element is of spherical shell with the radius r and thickness dr. What will you obtain? You will see that the probability of finding the second atom at a distance r from where? From the reference atom independent of the direction. So, it is in any of the direction because you are considering a homogeneous condition would be what that is equal to dW

$$dW = \omega_r \, dV$$

that if you consider the spherical shell, you will have

$$dW = \omega_r 4\pi r^2 \, dr$$

$$\text{or } dW = g(r) \, \omega_0 \, dV.$$

What would it then look like? It would look like as $g(r)\omega_0$. Why? Because

$$\omega_r = g(r) \, \omega_0$$

and then you have,

$$dW = g(r) \, \omega_0 \, 4\pi r^2 dr.$$

This function g(r) ω_0 $4\pi r^2 dr$ is a radial distribution of function. The shape of g(r) will reveal the interaction between the atoms, if there were to be no interaction at all. the atoms were independent of each other. The probability would be same everywhere and g(r) would then turn out to be equal to 1, but that is not true. You have short range ordering, if you have short range ordering that means, there are going to be interactions.

So, the deviation of the g(r) value from the average value will indicate the interactions between the atoms. If you look into the figure, then you will find that the radial distribution function is showing short range order in the liquid because the curve approaches the value 1 after a few deviation cycles. So, as a function of r if you plot the radial distribution function the value of the short-range order and is reaching the value of 1 and you will find that this is what is happening in liquids. Now, the g(r) curve intersects the r axis, it is cutting the r axis. Where is it doing that? Is it at 0? No, it is intersecting the g(r) curve at a given r value, but it tends to be 0 for small values of r.

The intersection point corresponds to the diameter of the atom. Why? Because the second atom cannot come closer to the reference atom than the double radius of the atoms. So, that is a very interesting information which you can derive from the curve. in principle the pair distribution function is calculated with the aid of statistical mechanics. So, in practice what are you going to do? We know that it is impossible in most of the cases to calculate this pair distribution function because you will have to find out the total potential energy of the system, how it is getting distributed, what is the volume element you will take, how the short-range order is getting stabilized.

So, lot of information is required before the value of g(r) can be calculated. Therefore, the pair potential Φ_{ij} is defined as the potential energy between an atom and its surrounding neighbors. If you choose an atom as the reference atom, the pair potential is defined as $\Phi(r)$. Now, pair potentials can be derived using the principles of quantum mechanics. But again, this is very difficult for all atoms except maybe for hydrogen and helium so far, because you end up having multi body problems and because of that it is difficult to calculate the energy associated with multi body problems.

Therefore, what you find that to address this limitation various models of $\Phi(r)$ are actually utilized. Let us see few of these models which are used to define the nature of $\Phi(r)$. The first one is your hard sphere potential, the second one is your inverse power potential, the third one is the 612 Lennard Jones potential and then you have the ion-ion potential. So, then shapes of the $\Phi(r)$ the pair potential as a function of r are quite different and you use these models to find out the nature of interactions between the reference atom and any other neighbors or an atom which is randomly chosen from the point of reference atom. For example, in ion-ion potential what you consider that you have,

$$\Phi = \frac{A}{r^2} \cos(2K_F r)$$

what is this? Here A is a parameter.

So, you can choose one of the parameters which you believe is playing the dominant role in deciding the interactions. r is the distance between the atoms and K_F is the radius of the Fermi sphere. then you can model the whole process. We know that what are melting points of solid metals? that they are at a given pressure the melting points of an element is the temperature at which element can exist in stable form both as a solid and a liquid. So, you have coexistence of both solid and liquid phases at the melting point.

This is what Lindemann used and suggested that crystal melts when the thermal vibrational amplitude of the atoms exceeds a certain fraction of the inter atomic distance. When this fraction was chosen as 10 percent you will obtain a relation which is,

$$v = \sqrt{C(\frac{T_M}{M V_{\mathrm{m}}})^{2/3}}$$

where C is a constant T_M is the melting point of the solid v is the average vibrational frequency of the atoms, M is the molar weight and V_{m} is the molar volume of the solid. So, using these features which we have introduced today you will find that there are differences between solids, liquids and melts. To explain the features which you observe in liquids or metal melts, one has to introduce the concept of pair distribution function. Now, if you have the pair distribution function to evaluate the whole concept is not trivial.

Therefore, you use various forms of Φ(r) that is pair potential and it then is able to explain certain features which are observed in liquids and melts. Based on this basic information you will see that properties of liquids and melts can be explained and you can have models that would easily fit the experimental data and will add a physical significance to the observations. To develop better understanding about the concepts of liquids and melts you can follow these books which give you more information about the chapter on liquids and melts and in the next lecture I will talk to you about the properties of liquids and melts. Thank you very much.