Physics of Functional Materials and Devices

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Lecture- 35

Heat capacity and diffusion of liquids and melts

Welcome back once again to the course on Physics of Functional Materials and Devices. In the first lecture of this week, I had introduced to you the concepts of liquids and melts and you could clearly see that as we move from solids to liquids and melts, we were transforming our discussions from long range ordering to short range ordering. And the moment you start talking about short range ordering, it is clear that the properties of these liquids and melts may actually change. So, let us start today the discussion on the properties of liquids and melts. For example, What did we discuss in solids? We had talked about thermal expansion, we had talked about diffusion, we had talked about phase transitions, we had talked about the theories of diffusion. Let us see what happens to those phenomena when we move from solids to liquids and melts.

So, we will discuss the volume and density of liquids and melt. Is there any thermal expansion in these liquids and melts and if it is so, then how do you model it? Is it just linear or it is volume? Is it just that you have to consider the expansion till first order or you will have expansion terms which also has higher order terms? So, these concepts would also be discussed today and subsequently we will move to heat capacities, transport properties and diffusion in liquids. Now, let us see what happens in the case when you are talking about the terms volume and densities. Now the packing of the atoms and the inter atomic distances influencing their packing will impact the properties of the liquids.

This is what we have been studying from our school days. The volume of a given amount of a solid is closely related to its density. If it is porous then the volume can be large, if it is very dense then you can have the whole material actually compacting in a very small volume. If you have very high specific surface area then you can cover lot of surface by small amount of materials and if you have low specific surface area then even larger amount of material will not be able to cover the similar surface which you were able to cover with material which had much higher specific surface area. So, you can talk in terms of surface area, you can talk in terms of volume, you can talk in terms of area.

Mass is one thing which is independent of temperature, but there is a direct coupling between the relative density and volume changes in a homogeneous melt and how do you correlate them? Very simple what we have been doing earlier also holds good here.

$\rho = m/V$,where ρ is the density, V is the volume, m is the mass and $d\rho/\rho = dV/V$ if you take unit mass. So, this is what you can easily write. As we saw in the previous lecture, one of the models which is used to explain the behavior of liquids or metal wells is the hard sphere model. This model was able to explain the behavior of liquids and their properties such as viscosity and diffusion in them.

Now, Alder and Wainwright studied the motion of various kind of particles as a function of packing fraction p. This packing fraction is defined as the ratio of the total particle volume to the total volume of the crystal. So, that is why ΣI this = what? You have an NA $*(4/3 \pi r^3)/ V_m$. So, you take the Avogadro's number, you have the volume of the sphere and then you take the total volume of the crystal.

So, p is the packing fraction, V_i is the volume of atom i, r is the radius of the atom V_{total} is the total volume of the crystal and V_m is the volume of 1 kilomole of the crystal. So, you can have different forms of packing conditions. Volume will change when you go from solids to liquids. Even if you go from metals and semiconductors you will find that on fusion you will have two classes which will get formed. For example, class 1 here the elements increase their volume on melting and class 2 the elements decrease their volume on melting.

So, class I is typically let us say FCC or HCP type structures which increase their average volume by nearly 4.6% in comparison to BCC structures which show slightly less increase, but still there is an increase of around 2.7%. But if you compare elements when they are taken from solid to a molten state for example, gallium, silicon, germanium, bismuth, they show volume decrease and this is because of the sp^3 hybridization leading to strong symmetrical covalent bond in the tetrahedral space. Now when you go from solids to melts that means, you have increased the temperature and then you are modifying the overall positions at which the atoms are stable.

And therefore, the orbitals become more spherical and the structures become more compact when these bonds are going to break during fusion. So, they are going to break. Now you have two concepts, you have volume change because of fusion, you can also have volume change when you have heat of mixing change when metal melts are being mixed together. For example, let us take the density of a pure ideal melt. This can be derived if the molar volumes are known.

It has been seen that the real molar volumes of many binaries are a function of composition of their alloys. So, V_m alloy = $x_1 M_1/\rho_1 + x_2 M_2/\rho_2$. So, you can change the composition of the melts and then when you bring them together they can have different volume expansion or decrement. What happens to the thermal properties of liquids? Now, the volume thermal expansion as we know at a given pressure is defined as $\beta = 1 / V$, where V is the volume. $\partial V / \partial T$ at a given pressure.

Now, β is nearly constant within the temperature range from melting point to boiling point. Therefore, V_m which is a function of temperature can be written as the volume V_m^M which is the molar volume at melting point + $[1+\beta(T - T_M)]$, where T_M is the melting point, T is the temperature , β is the volume thermal expansion coefficient at constant pressure and $V_m(T)$ is the molar volume at the given temperature of T where you are taking the reading. In melts and liquids what is happening? you will find that atoms are able to move relatively more freely compared to that in solids. Therefore, the inter atomic distances are not going to be constant, but if you look over a period of time you will find that the average inter atomic distance will increase as a function of increasing temperature. So, you can calculate the thermal expansion coefficient.

What did we calculate earlier? We had seen that the density of a liquid or melt = ρ that is equal to M/V_m. Now, combining the information of V_m that was obtained during the thermal expansion calculation. We can write $\rho = 1/ V_m^M * [1+\beta(T - TM)]$, where M is the molar weight of the liquid given that if β is quite small you can actually write the expansion as $\rho = \rho_m - \Lambda(T - TM)$, where ρ_m is equal to M/V_m^M is the density at the melting point and $\Lambda = -M\beta/V_m^M$ is a proportionality factor. So, if you increase the temperature then what is going to happen? The thermal increase in the volume corresponds to a decrease of density of the melt or liquid. This is what we can derive from the above equation.

If β was not to be small, you had significant expansion or contraction. Then, a expansion series will develop and β and Λ are no longer proportional and then only one of them can be regarded as a constant, other will become dependent on the parameter which was believed to be independent parameter. So, there are various factors which comes into picture, if you want to calculate density of melts, you want to calculate the thermal expansion, each of them have significant impact on the other. Let us see what happens to heat capacity. We know that specific heat is the quantity of heat that must be added to a substance of a given mass in order to raise its temperature by 1^0.

So, Q= C mΔt, where Q is the quantity of the heat absorbed by a body m is the mass of the body, Δt is the rise in temperature and C is the specific heat capacity of the substance and which is dependent on the material. You can write as a function of constant volume or constant pressure and you can use the internal energy U or enthalpy H while writing the values of C_v and C_p. Can the theory of specific heat or heat capacity which was discussed in solids be extended to what is there in liquids and melt? You will find that the starting points can be similar, but there are significant What are there? The motion of the atoms in liquid states is quite complex than what you were believing in solids. As a result, it is not possible to describe the motion of atom very easily as a function of time. Now, if you cannot do that, what will happen? it would be difficult to determine the frequency of vibrations because we are not knowing the way the atoms are going to move or vibrate.

Hence, the number of energy levels in the liquid would be much larger than in solids because you have to consider all possible states. Let us write the molar internal energy. So, the total internal energy for 1 kilo mole of monoatomic liquid is U= 3/2 RT +φ bar. In using the pair distribution functions you can extend and you can write the value of U. If you know the Grison rule which is connecting the volume expansion in solids due to the rise in temperature with the atomic heat of the solid and its compressibility at absolute 0, you will be able to find out what is the heat capacity at constant volume.

Similarly, you will be able to derive and write the value for heat capacity at constant pressure. And then you can take C_p - C_v the difference in these heat capacities at constant volume and constant pressure which will turn out to be β^2VA θ_D/k(T-θ_D) where θ_D is the Debye temperature, VA ,θ_D is the molar volume in kilo moles of the liquid at the Debye temperature, β is the coefficient of volume expansion, k is the isothermal compressibility of the liquid. So, you can also find out the difference C_p - C_v. If you plot these values at constant pressures, then if you compare the molar heat capacity at constant pressure of solids and liquids, you will find that you can clearly see that the nature of liquids are quite different from that of solids. Now, the experimental evidence it clearly indicates that the heat capacities decrease slightly with the increase in temperature.

In addition, the heat capacities of liquids vary with temperature this you can see from this curve. Now, the heat capacities of metal melts are of the same magnitude as those of corresponding solids. but you will find that the heat capacities at constant pressure of the corresponding metal melts seems to be constant over a considerable temperature range. So, you see they are not changing they are nearly constant and in addition to that the temperature dependence is small and an average value is used within the given temperature intervals. So, for metals with low melting points you can write the C_p values as $C_p = (a + bT + c/T^2 + dT^2)$, where a, b, c, d are the parameters which are used for fitting the data.

Now comes the next phenomena which we had discussed for solids, can those be understood in liquids. We had seen that when there is diffusion what is happening it involves mass transport, if it is viscosity it involves momentum transport, if it is thermal conduction it has the movement of heat energy or energy, if it is electrical conduction then it is the transport of charge So, what happens to the transport properties in liquids? We know for example, in Fick's first law $J = - D\,dc/dl$ when you are talking about the diffusion in certain system in the system which we are considering now are liquids. J is the flux or net amount of diffusing atom passing through a cross sectional per unit area per unit time. D is the diffusivity, c is the concentration of diffusing atoms and l is the coordinate in the diffusing direction. Now, what will happen to diffusion when you are talking in terms of liquids? It is slightly more complicated than solids and it is not easy to always straight forward explain the phenomena of diffusion in liquids for two reasons.

Why? Because the relative motion of the atom is easy in liquid and there is no unique activation energy to the atom and hence you do not know what is the energy barrier which has to be overcome before the system can move from one side to the other. But a simple model for diffusion in liquids is still based on the concept of activation energy and it is written as that D which is the diffusion coefficient is going to be dependent on a factor D_0 which is independent of temperature. And it will vary exponentially to a factor which is minus U_a^{diff} activation barrier / kBT. So, U_a difference activation is the average activation energy of diffusion per atom. kB is the Boltzmann constant and therefore, kBT is the energy or thermal energy you are talking about.

To explain it further in disordered media you have to then consider the fluctuation theory. This is for pure melts and it is able to explain the phenomena of diffusion in pure melts to reasonable extent and it is believed that you can write the value of D in pure melts as $(3Zcoord\ NA\ kB^2\ T^2) / (96h\ (-\Delta H_{vap})\alpha^2)$, where Zcoord is the coordination number of atoms. Now, if you are unable to predict the distance up to which the atoms are going to move, what is the average distance they will move, what are the atoms which will arrange around them, then it is difficult to always predict the quadration number of the atoms. And therefore, this number itself is going to vary and that is why you can now understand why there are complications while you model the phenomena of diffusion in liquids and $-H_{vap}$ is the molar heat of vaporization of the melt and α is a materials constant. Now, there is another model which is based on significant structure theory or Eyring's theory and it is slightly different than what we had been discussing till now.

Here it is believed that the value of D is given by $BT + D_0 \exp^{(-\Delta H_a{}^{diff} act/kBT)}$. The more complicated model which tries to explain all the phenomena is the random barrier theory and it believes that it will consider the impacts of disorder in the liquids by substituting it with a effective medium. So, you will consider a effective medium which is behaving like the liquid and then you will end up getting the value of T. You can also write the theory of dense gases which will then give you the value of diffusion coefficient and this is the equation which was explained by Enskog. Now when you see so many models you get confused.

The whole idea which one should understand is this. You have a phenomena like diffusion or a phenomena which is more on transport in liquids or melts. You need so many models to explain the observed data and none of them is able to explain the observation throughout in all the temperature range. This means that the phenomena itself is quite complicated and you need different postulates to actually explain the observed theta. For that different roots are used and you come up with some kind of a mathematical formulation based on certain assumptions or postulates and till those postulates are proven wrong you continue to believe that that those are the beliefs which cannot be questioned.

So, you move from one model to the other to the other and you try to fit the experimental data. So, if you look into the values of diffusion coefficients which are there and if you have some gases dissolved at low concentrations in metal melts, you will find that the value of D can be slightly different, if you have let us say in iron you have hydrogen as diffusing element or you have nitrogen as diffusing element or you have oxygen as diffusing element, then you will find that the values are slightly different. Obviously, the lighter is the interstitial atom, the easier is the manner in which they can move in the solvent and larger would be their diffusion coefficient in the melts. So, you have seen today that there are various transport properties in liquids and melts. There are factors which seemingly were independent for example, density and thermal expansion, but each of them impact the other quite significantly and using both of them the values of parameters like expansion coefficient or densities can be estimated.

You have a simple phenomena of diffusion which is not as simple as it seemed in solids. Here in liquids and melts the phenomena of diffusion is much more complicated. You need lot of models to explain the observed data and none of the models is able to completely explain the observed experimental data. We have also introduced the concepts of theory of dense gas, the hard sphere model and I hope you would be now understanding that. modeling of solids is much easier than modeling and simulations in liquids and melts.

To develop further understanding you can once again refer to these books which have dedicated chapters on melts and liquids and in the next lecture I will continue with some more applications and properties of liquids and melts. I thank you for attending lecture number 2 of week 9. Thank you very much.