

Physics of Functional Materials and Devices

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Lecture - 36

Viscosity, electric and thermal conduction of liquids and melts

In this third lecture of the week let us continue our discussion on liquids and melts. In today's lecture I will start discussing on two other phenomena's which we had studied in solids, but how do these phenomena's get modified when we talk in terms of liquids or melts. that is what we are going to talk about and these phenomenas are viscosity and diffusion. So, in today's lecture what are we going to talk about? We will talk about viscosity, then we will talk about diffusion and then you will see how these two processes impact the thermal conduction and electrical conduction in melts and alloys. The term viscosity has been introduced to you from lower level school classes, maybe from class 11th, 12th onwards at least. What is viscosity? We had started learning about this term as a measure of a fluids resistance to flow.

So, something which opposes the flow. And if you are talking in terms of liquids, we talk in terms of viscous fluids or non-viscous fluids. Therefore, if there is a resistance in the flow of the fluid, it can be in the liquid phase or gaseous phase. What will happen? Viscosity would also try to prevent the change in the shape or movement of the neighboring portions relative to one another and they it will oppose the total flow.

You can have viscosities which can be measured quantitatively or it can be qualitatively. So, you can actually try to measure this specific value for viscosity coefficients or you can talk in terms of whether the liquid is less viscous or more viscous. For example, if you take water and honey as two common example. Water we say is a fluid having lower viscosity whereas, honey has higher viscosity. If you look into the concept of tangential stress, what are you doing? You have a body and you are applying a tangential stress to it.

So, if you have force per unit area which is proportional to the velocity v and is inversely proportional to the distance between the two plates. Let us say you consider two plates and

then you consider the distance between the two. Then you know that $F/A = -\eta * dv/dy$ and tangential stress is defined as τ which is force by area. Therefore, you can write $\tau = -\eta (dv/dy)$, where τ is the frictional force, η is the dynamical viscosity coefficient of the liquid, v is the velocity and dv/dy is the velocity gradient. Now, you can also write $\tau = -\eta$ gradient of v .

Therefore, what you see that your tangential stress is proportional to velocity gradient. If you have liquids then generally we consider two types of liquids. What are those? One is Newtonian type liquids and the other we call it as non-Newtonian type liquids. What are Newtonian liquids? These are the ones which obey the Newton's viscosity law. Here the fluid are those that have viscosity, but the viscosity is not affected by the shear rate.

If all other features are equal, then flow speeds or shear rates do not change the viscosity, this is what we mean. Mostly you will find that liquids which you deal with are Newtonian fluids, but there are many liquids that do not belong to this group. For example, you have water, air, alcohol, glycerol and thin motor oil. How do we actually calculate the stationary fluid flow under the influence of pressure in Newtonian liquids? Why? Because where is the liquid flowing? Liquid is flowing through some pipe or where it is being asked to move from one region to the other. To start let us say we are talking about a cylindrical tube.

What is the pressure difference that is from 0.1 to 0.2 is basically $p_2 - p_1$. Now, you have the total radius as r the inner radius as dr and then you have the thickness of the small element which is there as dr . length which you consider is l .

So, the net force is what $(p_2 - p_1) \pi r^2$. Frictional forces are caused by viscosity of the liquid which are acting along the cylindrical surface of the volume element. Therefore, the frictional forces would be $-\eta dv/dy * 2 \pi r L$. This we had seen in the previous slide and now we are talking about in terms of the volume element. These retarding friction forces equal to the pressure force and the net force would be then 0.

If this is the condition then you separate the variables and integrate. What you will get that as a function of r you will get $v = \Delta p / 4 \eta L (R^2 - r^2)$ This is a equation which is giving a parabolic function. Therefore, the velocity profile which you see in a tube is of parabolic shape. Now, if I have to consider the total flux that is you are considering the total amount of fluid which is flowing through the tube. Then you will have dv/dt you are considering $flux = \pi R^4 \Delta p / 8 \eta L$.

This is called the Hagen Poiseuille's Now, you know how to treat Newtonian liquids. What about non-Newtonian liquids? These are the liquids that do not follow the Newton's law of viscosity, which means they have variable viscosity that depends on the stress. In this kind of fluids what will happen? Viscosity can change when under the force you are monitoring

the given liquid or the alloy. Examples you can have catch ups which become runnier when you shake it. custard, toothpastes, paints, blood and others.

Let us see what is the relationship between the shear stress and velocity gradient in non-Newtonian liquids. The τ is given by constant $\times dv/dy$ that is the velocity gradient. Newton's law is a special case of Oswald's law that is given for non-Newtonian liquids. When n is replaced by 1, then Oswald's law becomes equals to Newton's law. But if you consider the fluids that obey the Oswald's law then those are generalized Newtonian fluids.

You can clearly see the difference in the velocity profiles in Newtonian liquid and non-Newtonian liquids. So, as the flow continues in Newtonian liquids you do not see the change in profile whereas, in non-Newtonian liquids you can clearly see that the velocity gradient is changing the profile shape. Let us see how can we correlate viscosity in terms of the pair distribution function which we had introduced in the previous lecture. If you use the definition for pair distribution function which we introduced in the previous class you will find that η would turn out to be $2 \pi / 15 * (m / KB T)^{1/2} * (\omega_0)^2$ and then the integral 0 to ∞ $g(r) \partial \phi$ which is a function of $r / \partial r, r^4$ raise to integral over dr . Now, you have $g(r)$ as the pair distribution function.

So, you can actually calculate what is going to happen in these kind of liquids. Now, if there is something flowing from one end to the other, what are you talking about? You are talking about mass flow, mass flow means diffusion. If there is diffusion then you have a viscosity term which is opposing. This means that you can ask a logical question is there a relationship between the diffusion and the viscosity coefficients. We had seen from the Fick's law that the flux can be written as $-D * (d \ln c / dy)$, where c is the concentration.

You could also like that the flux from a volume element is equal to $c * 1 * V_\gamma$ that is equal to $c V_\gamma$ if you are taking the volume element as 1 meter². Using these two equations you can write $V_\gamma = -D / c * dc / dy = -D$ and d / dy of $\ln c$. If you see the solute atom and consider each of them as sphere with the radius r and this whole combination which is forming the fluid is actually being considered. So, but you have a viscous drag and therefore, you are going to consider a viscous solution.

The force acting on an atom now which will be required to maintain the motion because you are talking about flow that means, some force is being applied is given by Stokes law. and $= 6 \pi \eta r V_\gamma$. Now, let us consider for 1 kilo mole, what would be the force acting? It would be the Avogadro's number $NA * 6 \pi \eta r V_\gamma$. Now, let us take a step forward. If you have the term where you are going to now write the work done to move any atoms that is the Avogadro's numbers 1 mole, 1 kilo mole or 1 mole. Atoms at distance dy against the frictional force, this would be given by the free energy $-\Delta G$ or as the change as $d\mu$ where μ is the chemical potential.

This would turn out to be $d\mu$ is equal to $-F dy$. Hence, the relationship between D and η would become $D = \frac{KB T}{6 \pi \eta r}$ please remember KB is the Boltzmann constant and r is the radius of the atoms. This relation is called as Stokes Einstein relation. What can you see from here? You can clearly see if you change temperature, but you are not changing the value of η then diffusion should increase. If you increase η for a given temperature then diffusion will decrease.

And these concepts are extensively used in devices where you are talking about any liquid flow such as electrolytes in batteries or even you can have electrolytes in any other biosensors. So, there the role of diffusion as well as viscosity coefficients become critical and you also now know that there is a relationship between the two. You had seen that $KB T$ is in the numerator. Obviously, there would be temperature effect. What would be the temperature effect? You will find that viscosity coefficient is inversely proportional to the diffusion coefficient and the temperature dependence of the diffusion coefficient is inversely proportional to that of viscosity coefficient.

This is what you saw in the previous slide and you can also write the temperature dependence of η as $\eta = \eta_0 \frac{T}{T_0} e^{\frac{U_a}{KB T}}$ of the viscous fluid that is the activation energy. This is the activation energy of the fluid and upon $KB T$. What would be the empirical relation? You have the relation which is given between η and T . So, if you plot them as a function you will find that for different materials let us say zinc, lead, gallium, indium, bismuth, tin, cadmium, antimony you have different nature of the diffusion in them and clearly you will have the consequence that is the viscosity coefficient would be different in these parameters. Now, when we can go to dilute alloys, we had liquids melts and now when let us see can we talk about similar concepts in dilute alloys.

Now, in viscosity in fluids we had considered Newtonian or non-Newtonian type liquids. What about dilute alloys? Here the viscosity of the alloy melts decrease with increase in temperature and the viscosity of binary alloys vary with the composition of the alloy. This is what you will see in dilute alloys. For example, iron carbon melts you can clearly see that as a function of temperature at different temperatures you can get different order of viscosity coefficients in them. If you have these parameters, you can clearly see we had talked about in terms the activation energies.

Now, let us write them in terms of Gibbs molar free energy of activation. You will find that the expression for coefficient of viscosity using thermodynamical models would be $A e^{-\frac{\Delta G_{activation}}{RT}}$ and the $\Delta G_{activation}$ is a function of both composition as well as temperature. If you have these binary alloy melts, what is happening? It is the binding energy between the particles in the liquids or melts and their configuration that is depending on the motion of atoms, molecules or ions and along with that the interactions between the two. Hence, you can write the Gibbs molar free energy of activation for an

alloy as a summation of all the contributions coming from different fractions of components. So, you can write summation 1 and 2 if it is a binary alloy.

So, you have only two components. So, you can write $\sum_1^2 x_i \Delta G_i^{\text{activation}} + \text{the Gibbs free energy of the mix} + 3 R T x_1 x_2$. You can if you plot these parameters you will find that these models are quite nicely explaining the variation in the coefficients that are observed in typical binary alloys. So, the model which you just proposed is able to fit the data. So, if the solid symbols are the experimental data, the lines are the simulated data using the model and both of them superimpose nearly within the error bars and therefore, your model is correct and you can extend this model to explain the behavior of viscosity coefficient or diffusion in binary alloys. There are various methods by which you can measure the error.

The first one is the commonly used capillary tube method. What will happen? You have a liquid sample in the middle, you mark two places in the capillary tube and then you monitor the time it takes for a known amount of melt to pass through a heat resisting glass or a glass tube and move to the next level. Obviously, the viscosity coefficient can then be calculated from the measurements of the collected melts that will get accumulated in the capillary tube after a given time. If you know the radius of capillary tube and the length you can calculate the viscosity coefficients. The other one is oscillating vessel method.

Here the vessel containing a viscous fluid is hung through a fiber with a mirror. So, you have a mirror which is attached to a vessel containing the viscous fluid. Now, the vessel is set to circularly oscillatory motion around a vertical axis. So, it is now made to oscillate around a vertical axis. The motion is gradually damped due to the viscosity of the melt.

What you have to do? The time period and the damping of the decreasing oscillations are measured and the viscosity coefficient is calculated from the time taken for the system to damp completely from there you can find out the viscosity coefficient. Similarly, you have the oscillating cylinder method in this what you do you have a suspension wire just like in the previous case then you have a mirror then you take the outer cylinder where you have placed the liquid in a way that the cylinder is set into the liquid melt sample which is contained in a outer cylinder. So, there is an inner cylinder and a outer cylinder. So, you place a inner cylinder inside the viscous fluid which is contained by an outer Now, the system under an harmonic linear motion by external driving force is monitored. So, you apply a external driving force and you believe it is a harmonic linear motion.

Now, what you do? It is more like forced oscillation case. The amplitude of the motion is now measured. when the cylinder is surrounded by air or vacuum or viscous metal melt. What you will monitor or observe is the amplitude is reduced in the case that is when the inner cylinder is now being monitored and its motion is being felt. by the mirror and you

can reflect that image on a scale and then find out the amplitude of the motion of the inner cylinder.

and from reducing amplitude which you can clearly see from the ocean of the reflected ray on a scale, you can find out the viscosity coefficient of the melts. once you have these parameters you can use them to calculate the thermal conductivity of pure melts. So, if you have the thermal conductivities of pure melts as a function of temperature you can clearly see they vary significantly. It is not always that you will have a decrease case where it would be decreasing trend or increasing trend. So, you can move from one metal melt to other and you may see different magnitude.

So, there is no linear relationship, it depends upon the element which has been used to fabricate the metal melts. Similar is the case for thermal conductivities in alloys, you can clearly see as a function of the solute changes, you will find that the thermal conductivities of alloys can also change. If you have understood what we had discussed in the previous slides, you should be easily able to explain the reasons why thermal conductivities of alloy melts also change as a function of temperature. Finally, you have the electrical conductivity in melts. Electrical conductivity $\sigma = 1/\rho$ Now, resistivities of most metals increase on melting.

If that is the case you will find that the resistivity of the liquid and if you take the initial as the electrical conductivity of the material at the melting temperature as ρ_L . Then the temperature dependence is given as $\rho = \rho_L + \alpha (T - T_m)$ So, this is clear that electrical conductivity of metal melts also change as a function of temperature. Finally, you will find that you can relate the just like Weidman's law you can have relationship between the thermal and electrical conductivities and this is $\lambda/\sigma = \pi^2 (KB)^2 / 3 e^2 * T$. And, if this is a constant you have $\lambda/\sigma = \text{constant} * T$, where the value of constant turns out to be $2045 * 10^{-8} \text{ W}\Omega\text{per/K}^2$ So, now you understand that the properties of liquids and melts are quite different from their solid counterparts. If you heat a material and take it from solid state to liquid state and then to the gaseous state.

You will see significant changes in their response characteristics and if the response characteristics change you can use those variations to apply in various applications and make devices using the solid phase of a material or liquid phase of a material or melt or gaseous phase of an element or melts. I hope now you understand the difference between Newtonian and non-Newtonian fluids, how the properties can change and there is a relationship between viscosity, diffusion, conductivities as well as thermal and electrical conductivities in liquids and melts. Please go through these books for attaining more knowledge about this topic and from next lecture we will move to an interesting part of this course that is applications of the materials which we have discussed this till now in various devices. Thank you very much.