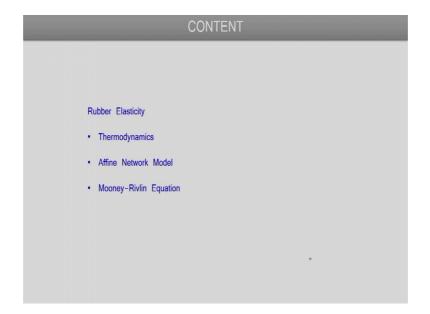**Introduction to Polymer Physics**
Dr. Amit Kumar
Department of Chemical Engineering
Indian Institute of Technology Guwahati

Lecture – 21
Rubber Elasticity

Hello everyone in the last couple of lectures we have been talking about the viscoelastic behavior of polymeric materials. In today's lecture we will discuss another very interesting property of certain polymeric materials which is referred to as Rubber Elasticity.

(Refer Slide Time: 00:44)

So, we will begin today with an introduction to the type of polymeric materials that exhibit this behavior and such polymers as refer to as elastomer. So, we will talk about a little bit about the elastomers and their common properties and then we will move on to a thermodynamic description of the rubber elasticity behavior. We will also discuss a model of this rubber elasticity which is based on a molecular kind of approach and that model is commonly referred to as affine network model. And, towards the end we will also look at a more phenomenological kind of approach to rubber elasticity which is given by the Mooney Rivlin equation. So, to begin with today let us start by discussing, what is an elastomer?

So, elastomers are basically polymeric materials which show certain interesting mechanical properties, so they exhibit very high reversible deformations. So, if we stretch an elastomeric material it can be stretched to several times its original length and when the applied force is removed the elastomeric material will attain it is original dimensions. So, it is a reversible kind of deformation that these materials show.

So, that is one interesting properties and also the material typically exhibit low Young's modulus. So, when we are discussing mechanical properties of polymeric materials, we discuss the typical range of Young's Moduli exhibited by different types of polymers. So, elastomeric materials typically show low Young's modulus, but since they are highly stretchable they show a high elongation at break.
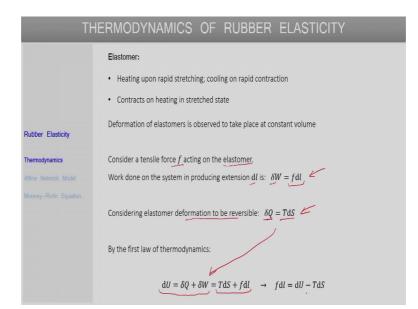
So, what are the at least at the molecular level what are the features that define an elastomeric polymeric material. So, one thing that a polymer one condition is that the polymers should be cross linked, so we should have a network polymer and typically the cross link density should be light. The other property of the polymer is that it should be above it is glass transition temperature, so it should be in it is rubbery state.

So, elastomeric properties will be exhibited by a rubbery polymers and another important point is that the polymers should be very should have a very low degree of crystallinity. So, if a polymer is highly crystalline then it will typically not show elastomeric kind of behavior. So, these points are listed here where the, it is mentioned that the polymers

should be cross linked it should be above the glass transition temperature and should have low degree of crystallinity and typical elastomeric polymers exhibit all these or satisfy all these conditions.

The mechanical behavior of elastomeric materials where which is a characterized by large reversible deformations, as well as a non-linear elastic kind of a behavior that is referred to as rubber elasticity and that is the focus of our discussion today. So, some of the important rubbery or elastomeric materials that are commonly used are poly butadiene, natural rubber, neoprene, butyl rubber and many other.

So, many rubbery kind of materials are elastomers where at the molecular level their network polymers and they exist above their glass transition temperature. So, as discussed rubber elasticity is just this non-linear elastic behavior of elastomers, where they very high reverse where elongations are exhibited.

(Refer Slide Time: 04:37)

THERMODYNAMICS OF RUBBER ELASTICITY

Rubber Elasticity

Thermodynamics

Affine Network Model

Mooney–Rivlin Equation

Elastomer:

- Heating upon rapid stretching; cooling on rapid contraction
- Contracts on heating in stretched state

Deformation of elastomers is observed to take place at constant volume

Consider a tensile force f acting on the elastomer.

Work done on the system in producing extension dl is: $\delta W = f dl$

Considering elastomer deformation to be reversible: $\delta Q = T dS$

By the first law of thermodynamics:

$$dU = \delta Q + \delta W = T dS + f dl \quad \rightarrow \quad f dl = dU - T dS$$

So, next let us focus on the thermodynamics of this rubber elasticity phenomenon, if we talk about rubber elasticity as exhibited by elastomeric materials, then there are few very interesting kind of properties that these materials show. So, let us say if we have an elastomeric material like a rubber band and if it is stretched very quickly then it heats up and if the elastomeric material is kept in a stretched state and then it is allowed to contract rapidly then it cools. So, this is an interesting kind of property and there is something that can be easily observed. So, if one has a rubber band and if it is stretched

very quickly and placed on one's lips, then one can feel that rubber band heating up actually.

So, the that is the interesting kind of property, another very interesting property that this elastomeric materials exhibit is that when they are in a stretched straight, then if their temperature is increased then they tend to contract. And, this is a contrary to the behavior shown by many other common materials like metals and other materials where heating leads to an expansion. So, as stretched elastomer actually contracts when the temperature is raised, so that is another interesting kind of property. So, we will the briefly discuss the thermodynamics of rubber elasticity and try to see that some of these observations can be explained from that thermodynamic perspective.

So, one thing before we begin to notice that these elastomeric materials their deformation can be considered to take place at a constant volume and so what that means is that one can assume the elastomeric materials to be essentially incompressible, that is when it is deformed it is dimensions might change. But they change in such a way that the overall volume of the material remains unchanged.

So, this is an assumption that will be employed in the thermionic description as well as affine network model that we will discuss today. And, this assumption is a justified one because several observations actually confirmed this kind of assumption. Where the deformation actually happens had an almost constant volume for elastomeric materials, so we will make that assumption and start our development from there.

So, let us say that we have an elastomeric material and a force is applied to elongate it by a certain amount, if we consider tensile force f that is acting on the elastomer then the correspondingly the work done by this force in extending the elastomeric material by a small amount of length dl. So, that work done is given by this delta W or del W and that we can simply write it as the force times the elongation produced. So, we are talking about a tensile kind of force acting and a corresponding elongation produced along the direction of the force. So, the work done will simply be the force times the corresponding elongation that is f times dl.
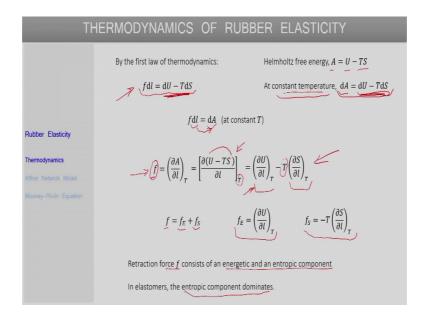
Typically when we talk about the work done on a system then we also consider what is called the pressure volume work. So, if you are familiar with the thermodynamics of gases then this pressure volume work is actually quite important, but as we discussed we

will consider the elastomeric materials to be incompressible and when deformed. So, if the volume is not changing that pressure volume work can be neglected. So, the work that no quantity of work involved in the deformation of elastomeric material that will that will only include this f times dl kind of term and this p dv term will not appear because volume is not changing.

Now, if we consider the elastomeric materials elongation or deformation to be reversible, then in that case the corresponding heat associated that also we can obtain from the second law of thermodynamics and that will just be the temperature times the change in entropy. So, we can for a reversible deformation we can say that the associated heat is equal to the temperature times the entropy change.

Now, we have these 2 terms and we can combine these and place them in the first law of thermodynamics for a closed system and then try to come up with an expression for this force or the force time's dl term ok. So, the first law of thermodynamics as we know states that the change in internal energy system is given by the heat added or removed from the system and the work done on the system or by the system. So, the form that we have written here where dU is equal to this del Q plus del W. So, in this format assumed is that the heat supplied to the system is taken as positive and work done on the system is taken as positive. Now, using the expression for the work done from here and the heat from here and substituting these two back here.

We get the expression that is dU will be equal to just T times entropy change plus f times dl and if you just rearrange the term then we can write this f times dl. The force times the a small amount of deformation or elongation to be equal to the internal energy change minus temperature times the entropy change. So, that is one expression which we have obtained by applying this first and second law of thermodynamics and assuming the deformation to be reversible as well as incompressible.

So, that is this expression that we just obtained, now if we talk about any cha process that is happening at a constant volume then the relevant free energy of interest is actually the Helmholtz free energy. So, Helmholtz free energy which we denote by A that is defined as internal energy U minus temperature times the entropy. So, if we now consider this change in a Helmholtz free energy dA at constant temperature then that we can simply write as dU minus TdS and since we are we are considering the change at a constant temperature. So, the minus S dt term which should also appear that will be 0, so at constant temperature we have this expression and we see that this the right hand side here exactly matches the right hand side on the this expression.

So, from by comparing these 2 what we can say is that this term fdl force times the deform deformation that is equal to the change in Helmholtz free energy at constant temperature ok. So, another way to write this is that we can say that the force is simply the change in Helmholtz free energy with changing elongation or changing deformation at a constant temperature. So, we can take this dl here and we get f equal to dA dl at constant temperature. So, we can express that as a partial derivative in this form where we can say that this force is equal to the rate of change of a Helmholtz free energy with change in elongation at a constant temperature.

This expression basically relates the force to elongation as well as the thermal in quantity which is a Helmholtz free energy and Helmholtz free energy as we have just discussed is

defined as U minus TS. So, we can substitute that in place Helmholtz free energy here and then separate this term into 2 separate derivatives, one will be del U del l at constant T and the second will be minus T times del S dell at constant T and we are taking this temperature T outside because the partial derivative is at constant temperature.

So, we see what we see is that the force that we have here that is a that can be expressed as this combination of 2 terms the first term is an energetic term, it depends on the internal energy of the system and how it changes with elongation. The second term is entropic in origin and which captures how the entropy of the system changes with elongation. So, we can write this f as f E plus f S and energetic and an entropic contribution, where this energetic part is simply del U del at constant T and the entropic contribution is minus T times del S del l at constant T.
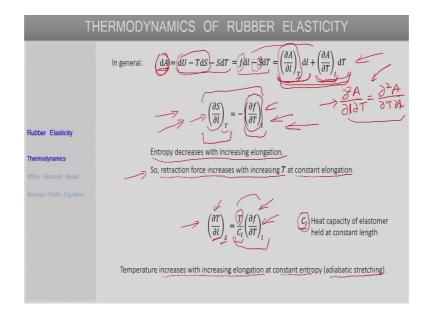
So, now the interesting properties that are observed a for in elastomeric materials, the important characteristic that these materials have which leads to such interesting properties is that for the deformation of elastomeric materials is the entropy change that is a dominant term. So, if we consider this expression here then the second term which contains the contribution of due to entropy change, that dominates over the term due to the energy or internal energy change and this is the reason why the some of the interesting properties of elastomers are observed.

So, this force f so this is the force half that we are talking about this is a tensile force and this also the retraction force that the elastomer will develop. So, if we are pulling the elastomer down let us say elongating it, then the elastomeric material will develop a retraction force which will try to pull it back to it is original dimension. So, this force can also be thought of as a retraction force, as we discuss it consists of 2 components energetic and entropic and for elastomers the entropic component is the dominant one and that is why it exhibits several interesting properties.

On the other hand if we consider common materials other materials like metals, so there if deformation takes place the atomic positions change from their equilibrium positions. So, that leads to a increase in internal energy and the corresponding response is primarily due to the change in internal energy. So, the entropy change there that contribution is not that strong, but for elastomeric material is the entropy change here produced due to deformation that contributes primarily to the retraction force generated.

This entropy change takes place because when the elongation force acts and the materials deform the chains get stretched. So, in the stretch state the chains actually lose entropy and that entropic driving force tries to bring the elastomeric material back to its original dimensions, so that the entropy can be increased again. So, that is an important factor that determines several of the important properties of other interesting properties of elastomers.

(Refer Slide Time: 15:39)

So, now if we again go back to the expression for change in Helmholtz free energy dA, so this in the previous slide we had written this change at a condition of constant temperature. If we just write this change dA in a general form without imposing any constant temperature condition, then we can write this dA is dU minus TdS minus S dT. So, we will have 3 terms here and we already know that dU minus TdS this term is just the force f times dl that we have already established, so that we can substitute here. So, we get dA in general this change in Helmholtz free energy is just f dl minus S dT.

Now the dA which is the total differential of the Helmholtz free energy that one can always write in this form provided that we are saying, that the Helmholtz free energy is a function of the elastomeric length l and temperature T. So, if that is considered then we can always write this d the total differential in this form and this is standard kind of mathematical relation. So, what we are saying is that the total change in Helmholtz free energy, that is due to the change in Helmholtz free energy because of changing length.

As well as the change in Helmholtz free energy because of changing temperature and these 2 combined to produce the overall change, so that is what this total differential represents. And, from this expression what we can say is that the f here and this we have already talked about previously also f is just the changes in Helmholtz free energy at co with respect to length at constant temperature and similarly the S here by comparison or this minus of S will simply be equal to this term here del A del T at constant l.

So, both the Helmholtz free both the retraction force and the entropy can be related to change in Helmholtz free energy. Now for any differential the like dA if it is an exact differential, then we can apply a condition whereby the second derivative of this Helmholtz free energy. Let us say with respect to temperature and length is independent of the order in which the individual derivatives are taken.

So, if we can what we are trying to highlight here is that this del square A del l del T will be equal to del square A del T del l. So, the order in which the derivative is taken with respect to temperature and l that is immaterial and both these cases result in the same expression. That is the property of any exact differential and all the thermodynamic state variables are exact differentials, so they will sat Helmholtz free energy will also satisfy this condition and if you apply this condition then it can be shown that rate of change of entropy with respect to the deformation del S the del l at constant T that is just minus del f del T at constant l.

So, this is a kind of a Maxwell relation for elastomeric materials and this as we discussed can be obtained by applying this condition for exact differential in the expression that we have. So, now that we have this relation between the entropy change with length and the retraction force length with temperature, this relation actually can help us in explaining one of the interesting properties exhibited elastomers.

So, we discussed earlier that if an elastomeric elastomer is in the stretched state and if it is heated if the temperature is increased then it contracts. So, this kind of a thermodynamic relation actually explains that behavior, so what we obtain from the relation here is that the retraction force increases with increasing temperature at constant elongation and how we come to that conclusion is that when as elastomer is elongated so that chains get stretched.

So, in that case entropy always decreases entropy of the system will decreases, so since the entropy decreases with increasing elongation. So, this is the left hand side is a negative term because with increasing ls is decreasing. So, this derivative be a will have a negative value and since that is equal to minus of this term. So, this the partial derivative del f del T at constant del that can be positive for elastomers.

So, what that implies is that as a temperature is raised the retraction forces also increased if the elastomer is maintained at a constant elongation. So, that is what we have mentioned here and another way to look at it is that as we have a elongated elastomer or stretched elastomer and if we heat it then the retraction force tends to increase. So, if the elongation is not maintained constant then the elastomeric material will tend to contract, because a retraction force that is pulling it back will tend to increase. So, this thermodynamic expression explains that behavior of elastomeric materials.

Another interesting property of elastomeric materials that we discussed was that if it is stretched rapidly it heats up. So, this another thermodynamic expression that can be developed which explains that behavior. So, we without going to details we will just say that it can shown that the change in temperature of an elastomeric material with changing length at constant entropy that can be shown to be equal to this term ok. Where the Cl is just a heat capacity of an elastomer at constant length, so for gases we talk about heat capacity at a constant volume or at constant pressure. So, here for an elastomeric material and equivalent quantities it is heat capacity at constant length and that is what the Cl represents.

So, on the right hand side here the temperature this is this T which is always the absolute temperature in let us say the Kelvin scale or any absolute scale so it is always positive. The Cl heat capacity is also positive and we just discussed that this del f del T at constant l, this derivative we discussed from this relation and that this derivative is also positive. So, the right hand side of this expression is positive and what that means is that at constant entropy if the length is increased for an elastomer, the temperature will also increase this del T del l will be positive.

So, temperature increases with increasing elongation at constant entropy and this kind of constant entropy elongation can be thought of as equivalent to an adiabatic kind of elongation where there is no heat flow involved ok. So, adiabatic stretching corresponds

to this kind of a condition and what this says is that as the elongation is increased the temperature increases, so that is a thermodynamic description of rubber elasticity. Now let us discuss a little bit about model of rubber elasticity that takes into account the molecular approach to this phenomenon.

(Refer Slide Time: 23:15)

The model that we will discuss is a simple kind of model and is refer to as affine network model, then of course other models which are more sophisticated. But since this is an introduction to rubber elasticity, we will restrict ourselves to this simple model which gives reasonable predictions at least at low elongations. So, this affine network model was originally proposed by Kuhn and the key assumption of this model is that the deformation of the entire network is affine deformation.

So, what that means is that when the deformation takes place the material undergoes the same relative deformation throughout. So, if the overall specimen of our elastomer is deformed by a certain ratio it is dimensions are changed by a certain ratio, then even at the molecular scale the corresponding chains, their dimensions also scaled by that same ratio so that is what this affine deformation implies in this case.

Let us just establish some of the nomenclature that we will you we will be using in discussing this model. So, let us say that initially we have a very elastomeric material or elastomeric sample having length L x naught L y naught in L z naught in the xyz direction. So, that is the original dimension and after deformation the let the lengths the

new lengths be L x L y and L z in the 3 dimensions. So, now the deformed lengths can be related to the original lengths through certain factors and these factors are referred to as a deformation factors or extension ratios and they are represented by the symbol lambda. So, L x the deformed length in the x direction will simply be lambda x times L x naught which is an additional length in the x direction, similarly L y will be lambda y times L y naught and L z will be lambda z times L x naught.

So, this is how the extension ratios or the deformation factors are defined and if you look closely then these factors are actually related to the strain. So, we have discussed earlier that the strain is the ratio of the elongation produced in the material or the deformation produced by the original dimension and whereas here if we look at these expressions the deformation factors lambda they are simply the ratio of the deformed length to the original dimension.

So, one can relate the strain to these factors through a simple kind of an expression. So, the strain let us say the strain in the x direction will correspond to lambda x minus 1, same in the strain in the y direction will be e lambda y minus 1 and the strain in the z direction will be lambda z minus 1. So, these factors and strains are related through this very simple kind of expression.

So, now if you consider at the level of the polymer chains or the polymer network, then let us say that the end to end distance of a network strand there let that vector the end to end vector be represented by R R naught. So, this vector r naught and we are talking about the networks stand in the initial original or and deformed stat and let Rx naught Ry naught Rz naught be the components of this vector in the 3 directions. So, now when we talk about network strand what we mean is in the network polymer that we have, the network strand is the portion of a chain that is between 2 cross linked points. So, as we discussed earlier a network polymeric is a polymer which consists of several cross linked points.

So, it is the chains are cross linked with each other and a network strand corresponds to portions of a chain which exists between 2 such cross linked points. So, this end to end vector R naught they corresponds to that of network strands in this model and again when the material is deformed. Then in that case the end to end vectors will also change their magnitude and the affine deformation assumption that we are making that leads to

the fact, that the in the deformed state the end to end vector will have components which will be related to the undeformed end to end vector components through again the same factors lambda x lambda y lambda z.

So, the factors that relate the undeformed and deformed dimensions of the overall material, those same factors also relate the undeformed and the deformed end to end vector dimensions of the network strands and that is the affine deform Affine deformation assumption coming in. So, now with this kind of expressions and definitions let us proceed.

(Refer Slide Time: 28:16)

So, in the very first week we talked about isolated ideal polymer chains and we discussed the fact that the end the end to end vectors their distribution can be represented as a Gaussian distribution, provided that the dimension of the end to end vector is very much smaller than the fully or elongated length of the chain. So, the end to end vector dimension is much smaller than n times l then this Gaussian kind of distribution can be assumed to be valid for the end to end vector distribution.

So, if that assumption is valid so if the elongation is not too high then in that case it can be shown we will not go through the derivation here. But it can be shown that the entropy change associated with a deformation will simply begin by the expression, that we have here that is delta S will be equal to minus n times k B by 2 lambda x square plus lambda y square plus lambda z square minus 3 and these 3 as the other deformation

factors or the extension ratios defined in the previous slide k B is the Boltzmann constant and n is the number of network strands that are present in our network polymer sample or the elastomer ok.

So, n is the number of network strands and as we discussed these network strands are nothing but the chains that are between 2 cross linked points in the network. Now this delta s expression once we have that we can also obtain an expression for the Helmholtz free energy so or the change in Helmholtz free energy, so change in Helmholtz free energy at constant temperature delta e we can always write it as delta U minus T delta S. Because we defined a as U minus T S so delta S it will be delta U minus T delta S at constant temperature.
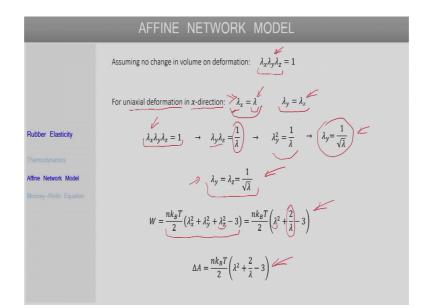
Now, for elastomeric deformation or the deformation of elastomers, we have discussed that the contribution of the energy change or the energetic part that is very weak and entropic contribution is the dominant one. So, in the this when discussing the change in the Helmholtz free energy we will again neglect the change in internal energy and primarily attribute the change in Helmholtz free energy to the change in entropy of the system. So, so neglecting the delta U term we can just write delta S minus T delta S and the delta S we have already stated here, so the Helmholtz free energy change that can be given by this expression for an isothermal deformation at constant temperature.

Now, this Helmholtz free energy is also equivalent to the work associated with this deformation. So, the work or the isothermal reversible work of deformation W that we can write simply as this delta A and that will be given by the same expression that that we have here. So, it is dependent on the temperature the number of a network strands present as well as the extents the issues in all 3 directions. These are some of the important expressions for this model and then next we will try to simplify these expressions for a specific kind of deformation.

So, right now we have taken or developed this model assuming different levels of deformations in the different directions. Now, if we focus specifically on what is called a uniaxial deformation, where the primary deformation will be in one direction and some associated deformation in other directions will be there and if we assume incompressible deformation then we can further simplify these expressions. So, that is what we will do

next now if we assume incompressible deformation where no volume changes takes place.

(Refer Slide Time: 32:08)

Then what we can say is that the product of the 3 extension ratios that will be equal to 1 and something that one can easily verify. So, if the initial volume is v naught that will be equal to L x naught plus times Ly naught times L z naught and the deform volume v will be L x times L y times L z and if we equate v naught to v that is the volume is if the volume is not changing then it can be shown that the product of these 3 factors is just one.

So, that comes due to the incompressible deformation assumption, next we will consider the case of uniaxial deformation only in a certain direction that is the x direction in our case and we will say that this lambda x the extension ratio in the x direction. We will just represent that as simply lambda and the primary deformation is taking place in this x direction and in the y and z directions some corresponding deformation will take place, so that the volume remains unchanged and the deformations in y and z directions will be equal, so that the lambda y will be equal to lambda z.

Now, since we have this condition because volume is not changing and lambda x we have represented as simply lambda. So, we can say that the product lambda y times lambda z is just 1 over lambda and since lambda y and lambda z themselves are equal.
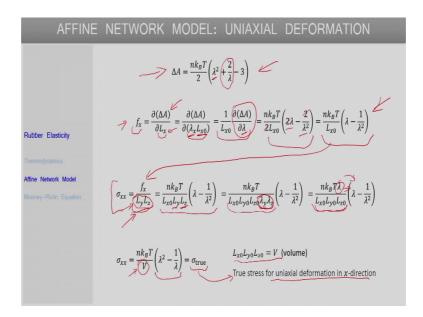
So, what we can see next is that lambda y square is just equal to 1 over lambda and finally lambda y is 1 over square root of lambda.

So, if we have a deformation lambda taking place in the x direction correspondingly in the y and z direction 1 over a square root of lambda deformation will also take place. So, now as if lambda y and lambda z are equal then we can simply say that lambda y and lambda z are just both equal to 1 over square root of lambda and once we have these this expression as well as this expression the. We can go back to the expression for the work of deformation or the change in Helmholtz free energy due to the deformation and substitute these values for the 3 lambdas and try to simplify those expressions.

So, if we go back to the expression for the work, then we had this expression previously and for lambda x square will simply substitute that by lambda square, lambda y square will be just 1 over lambda lambda y square is 1 over lambda same lambda z square will also be 1 over lambda, so they can be added to get this 2 over lambda term. So, this is the expression that we get for uniaxial deformation where no volume change taking place, similarly since I have no strain energy is just equal to this work of deformation or the helmholtz free energy change that is equal to the work of deformation, so for that also the same expression will apply.

So, now that we have these 2 expressions what we can do is try and develop an expression that relates the stress to the deformation. So, a stress strain or stress deformation kind of expression that captures the mechanical behavior like mechanical properties of these elastomers that is what we will attempt to develop next.

So, this is the expression that we just derived and we have discussed earlier, that the retraction forces this f is just simply equal to the partial derivative of the Helmholtz free energy with respect to the deformation. So, if you are talking about f x the force in the x direction, then that we can say as the partial derivative this delta A associated with deformation with respect to the dimension in the x direction which is L x or the change in dimension in the x direction which is Lx.

So, again this L x which is a deform dimension at any point of time during the deformation process that we can write as lambda x times L x naught, where L x naught is the undeformed dimension in the x direction and this L x naught is a constant so that we can take outside. So, we just get this expression and here since we are talking to a uniaxial deformation instead of lambda x we are simply using lambda here. Now, if we consider this partial derivative that can be obtained by taking the derivative of this expression with respect to lambda and if we do that what we get is this expression here.

So, if we differentiate this with respect to lambda we will get 2 lambda and differentiating this as a term with respect to lambda gives us minus 2 over lambda square so those are the 2 terms here. And, finally upon simplification by cancelling the factors 2 here we get this expression for f x the force in the x direction. Now, is now if we have this f x we can also develop an expression for the corresponding stress sigma xx. So, this corresponding this normal tensile stress associated with this force f x, that we can write

as f x divided by the corresponding cross section area on which this f x is acting. So, f x is a force directed along the x direction, so it will act on a surface that is again perpendicular to the x axis and that lies in the yz plane.

So, for so on that face of elastomeric sample the corresponding cross sectional area will be simply L y times L z that is what we have used here. And, if we substitute the expression for f x from here if this is the expression is substituted here then we get this expression. And, now L y and L z if you see here these 2 are the deformed dimensions, so the cross section area that we are considering here that is a cross section area at any point of time during the deformation process. So, it is the deformed cross sectional area. Now, this L y and L z also we can write in terms of the corresponding undeformed dimensions and the extension ratio. So, L y is just lambda y times L y naught and L z is lambda z times L z naught.

So, if you do that we will get this expression, now lambda y we have already discussed for the uniaxial deformation lambda y is just 1 over square root of lambda and then same applies for lambda z as well. So, the product lambda y lambda z that will just be 1 over lambda, so if we make that substitution this lambda comes up over here in place of the lambda y lambda z here and we have this product here. So, this lambda we can of course take inside here and this product this is just the volume of our elastomeric material which is not changing during deformation that is the assumption.

So, L x times L y times L x naught times L y naught times L z naught that is just a volume. So, if we represent the volume of a elastomeric material by V that is what we can get in the denominator here. And, taking this lambda in here we get lambda square minus 1 over lambda in here and this is kind of stress this is referred to as a true stress because, it is defined based on the deformed cross section ok. So, in this definition we have considered the cross sectional area in the deformed state. So, such stress is referred to as true stress and we already discussed that this product is just the volume of the sample. And, this sigma true is the true stress for uniaxial deformation in the x direction in our case.

So, that is a true stress expression that we already developed, but apart from this kind of a definition of the stress there is another definition that is very common that is called the engineering stress or the nominal stress. And, the difference in the definition is that the engineering stress is defined based on the undeformed cross sectional area. So, if we talk about this engineering stress it is based on undeformed cross sectional area. And, the expression for the sigma engineering this engineering stress is just a corresponding force divided by the cross section in the undeformed stage.

So, that is why we have used L y naught and L z naught and again this f x if we substitute this f x the expression for f x from the previous slide, then we get this expression and this product is simply the volume as we have already discussed. So, and we get this volume here. So, the expression for engineering stress is this here.

The factor that appears in both the these definitions for engineering stress as well as for the true stress, this factor n times k B times T divided by the volume that is referred to as the shear modulus of the elastomer and represented by G. So this n k B T by V that is the shear modulus of the elastomer G. And, this n by V this number of strands per unit volume or the volume or the number density of the network strands present in the polymer sample that we can represent as this nu. So, this nu is just this n by V factor here and one can relate this expression or this n by V factor to the density of the elastomeric material and this M s which is what is called the number average molar mass of the

network strand and the they can be related in this fashion ok. So, all the symbols that we have used here they are again defined here, where we as we discussed these are shear modulus needs the number of network strands per unit volume, rho is the density of the overall network polymer and this M s is the number as in molar mass of a network strand.

So, network strand is the portion of a chain that that is between 2 cross linked points. So, the numbers as more than mass of such network strands, that is what this ms represents and the shear modulus can be written in terms of this M s and rho like this or in terms of the number of network stands in volume like this, both are equivalent. So, finally the expression that we have derived for this model is that the engineering stress is given by G times lambda minus 1 over lambda square, where G is the shear modulus. The true stress is G times lambda square minus 1 over lambda. And, if we compare these 2 the engineering and the true stress then they can they can be simply related by this deformation factor the extension ratio lambda. So, the engineering stress is just a true stress divided by lambda, when we are considering this a uniaxial deformation ok.

So, this is a simple model for elastomeric deformation that is developed considering the molecular viewpoint, there are certain of course limitations with this model. So, one important limitation is that since, it assumes a Gaussian distribution of end to end distance. So, that is why when the extension or the elongation is high this, the model is not able to capture the actual behavior because, at high elongation so the chains become highly stretched. And, in that limit when the chains are highly stretched the Gaussian distribution approximation that does not work that fails at the molecular level. So, that is why this model also fails to capture the deformation behavior when the elongations are very high.

The other issue is that if the molar mass of or if the chains in the polymer are very long, then in that case apart from the chemical cross link side are present one can also have what is called physical entanglements between the chains. And, they these physical entanglements can act as physical cross links and that can also affect the stress strain behavior and the modulus of the material. So, these are things which are not captured by this material model, but since it is a simple model and it captures some of the features of rubber elasticity well. So, it is some it is something that we have discussed and another good thing about this model is that it based on molecular kind of interpretation.

The last thing that we will discuss on this topic is of what is called a phenomenological model, which is does not have any molecular interpretation behind it. But which is seen to actually capture the rubber elasticity behavior to a good degree of accuracy.

(Refer Slide Time: 44:34)

So, that model is typically called the Mooney-Rivlin equation and as this a phenomenological model and it does not rely on any molecular kind of a approach. So, it does not have any molecular insights built into it. And, one cannot draw any conclusions about the molecular nature all things happening at the molecular scale from this model. But it is a good model in the sense that it captures the rubber elasticity behavior quite well for a wide class of elastomers. In this model what is there is 3 strain invariants are considered. So, we will not go into the details of the derivation, we will just mention the key points. So, a strain invariant is a quantity which is independent of the coordinate system that we that we are choosing.

So, 3 different strain invariants are considered and these in strain invariance and nothing but combinations of the extension ratios that we have discussed previously. So, different combinations of the lambda x lambda y lambda z in constitute these different strain invariants. And, the free energy density of the elastomer is written as the difference between the strain invariants in the deformed state and the value of the strain invariants in the undeformed state. So, it is written as a function or a kind of a series power series of this difference.

So, we will again not going to the details of how further derivation is done, but we will again consider the simple case when we have just uniaxial deformation and the network polymer is incompressible. So, in that case as before lambda x we can represent simply by lambda and the lambda by lambda z both come out to be 1 over square root of lambda and it is identical to what we did for the affine network model ok.

So, under these assumptions we will get these relations between lambda and the Mooney-Rivlin equation without derivation we can state this equation in this form, where the true stress divided by lambda square minus 1 over lambda which is equal to the engineering stress divided by lambda minus 1 over lambda square. So, the these quantities are equal to 2 times C1 plus 2 times C2 over lambda where C1 and C 2 are constants of this model. And, if we compare this model the Mooney-Rivlin equation, with our affine network model. The previous model that we discussed then this equation reduces to affine network model in and in the case where the shear modulus of the elastomer is given by 2 times C1 and C2 is 0.

So, for these values of the Mooney-Rivlin constants the affine network model can be obtained from the Mooney-Rivlin equation. But even for many elastomers this C2 actually is not necessarily 0; it might it typically is seen to have some finite value and if for and in that case the elastomeric response is captured well by this equation.

So, if let us say one plots the quantity is sigma engineering versus lambda minus 1 over lambda square, if we plot this against 1 over lambda. So, what the affine model says is that since C2 is 0 and in this kind of a plot this 2 C2 will simply be the slope of the plot, so if these models were to apply then we should get horizontal lines in this plot. But for many materials the lines and not actually horizontal they have some slope and that leads to non-zero value of C2. So, but for this such non 0 C2 values this Mooney-Rivlin equation as is seen to fit experimental data for many elastomers quite well, so it is a good phenomenological kind of description of a rubber elasticity.

So, with this topic we will conclude our discussion of rubber elasticity and in this week we have discussed a few interesting properties of polymeric materials particularly viscoelasticity and rubber velocity. In viscoelasticity we talked primarily about linear viscoelasticity and some simple models that describe linear viscoelasticity behavior. We also talked about response to oscillatory stress and oscillatory deformation. And, today in

rubber elasticity we talked about the thermodynamics of rubber elasticity, as well as a simple molecular based model called the affine network model as well as a phenomenological model which is a Mooney-Rivlin equation to describe this phenomenon.

So, in the next week the lectures in next week we will focus on the dynamics of polymeric materials, in polymeric dynamics itself is a advanced topic. So, we will just touch upon the very basics introductory aspects of polymer dynamics. So, with that we will end this lecture here.

Thank you.