Spray Theory and Applications

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Lecture – 08
Discussion on Interfacial tension

Yes, we will continue our discussion on sprays. Towards the end of the last class we completed our discussion on probability density function, probability size probability density function, and velocity probability density function. And we also looked at multivariate probability density functions, where more than one independent variable is used to describe the distribution.

What we want to do today is switch hats from all that mathematics and become engineers for a moment. So, we want to see what is a spray, and where is it used, and what are the different designs out there. And we will start to look at the merits and demerits of a few different commonly used designs for spray nozzles.

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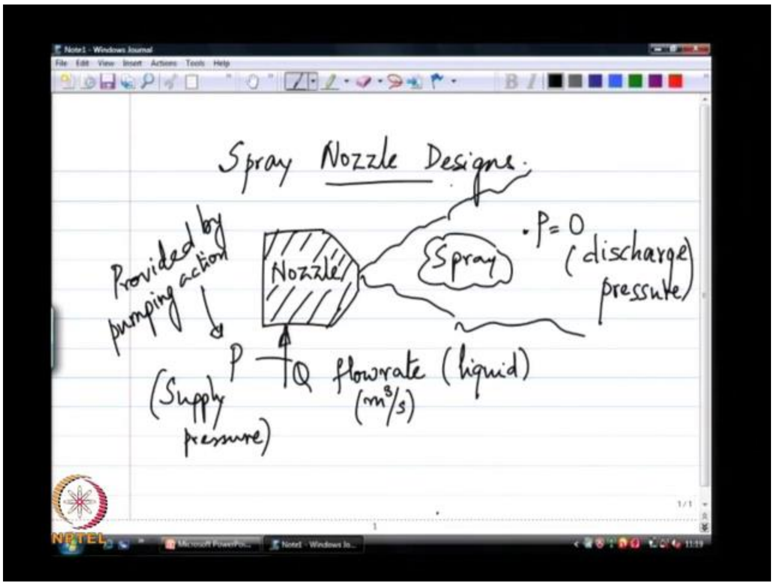

So, today's lecture is going to begin our discussion of Spray Nozzle as a mechanical entity, as a mechanical device with some emphasis on existing designs. Before we go much further let us just draw a brief schematic and we want to understand what it is that we are talking about that we call as spray nozzle. Again, we have used this perfume example many times; we will sort of use it again.

Essentially, in the context that I have a certain flow rate of the liquid; let us just take a very simple example where liquid is going in to my nozzle and I have a spray coming out on the other side. So this is my. If Q is a volume flow rate, so I will call this it is in units of meter cube per second and if this is coming in at some pressure delta P, so I will call this P is the supplied pressure; and I will assume for a moment that the pressure into which the spray is discharging is 0. This is a simplest example. In the case of a perfume spray this pressure P provided by some pumping action usually. In the case of a perfume spray, it is of course me depressing the plunger with my finger; that is a pumping action and in the process I increase the pressure of the liquid and that causes it to flow through my spray nozzle and eventually I get a spray.

So, in pure thermodynamic terms; if I look at this as a thermodynamic device, I have fluid going in at a certain pressure P at a certain volume flow rate Q, and I have the same volume flow rate coming out of the nozzle but in the atomized form. I have put in some amount of work in the process of driving this plunger and that work put in has to do something back for me; simple first law of thermodynamics. If I assume for a moment that the temperature of the perfume and the temperature of the fluid going in; the temperature of the perfume spray and the temperature of the fluid going in are the same there is no increase in the internal energy of the liquid itself which is basically a function of the temperature.

If I assume for a moment that everything is in an isothermal situation where there is no heat transfer then there is no Q either. So, all of the work that I have done is supposedly going into increase the surface area. I have just said something I want to see if I am right or wrong. The most ideal situation whatever plunger work I have done in pushing the plunger down should entirely go into creating it is a liquid surface area in this spray.

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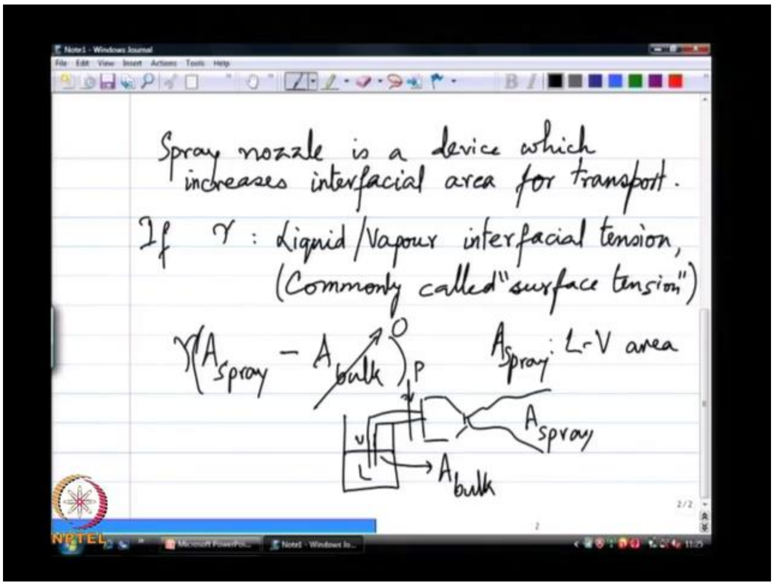

Spray nozzle is a device which increases interfacial area for transport.

If γ : Liquid/Vapour interfacial tension, (Commonly called "surface tension")

$$\gamma(A_{spray} - \cancel{A_{bulk}}^{\,0})_P$$

A_{spray} : L-V area

So like we discussed, we looked at this argument earlier on. If gamma is the liquid vapour interfacial tension and it is very often called surface tension. Gamma time's area of the liquid vapour, so this is spray is the liquid vapour area in the spray form and a bulk is the same liquid vapour area. Let us say when the perfume was in the can so that typically this is much smaller than the A spray itself. So, you could even ignore it just for the sake of argument.

This is how much I have increased the surface energy of this spray. So, this increase in the surface energy of the spray; surface energy of this fluid essentially which is now in the spray form, it is the same liquid if I imagine for a moment there is no evaporation it is the same exact mass of liquid now in the same liquid phase which is now dispersed in the form of drops versus where it was all sitting in one bulk form. In the bulk form it had a certain interfacial area with it is own vapour. So, potentially imagine I have a can, so this is a bulk, this is vapour write above it, and this is liquid, I put a little straw in there draw liquid out I create this spray. So, there is some work done here and I get the spray. And on this side I have this A spray.

So, if the temperature of the liquid in the bulk container and in the spray form is the same there is really no heat transfer is no increasing in the internal energy, the only form of energy that as changed is this interfacial energy in the form of surface tension energy.

Now, before we go much further I want to take a small detour and talk about what surface tension is. We want to really understand; because that is the only purpose we have a spray nozzle. We want to understand what surface tension is, for just a moment to get a complete picture of why we need to push a plunger down against resistance, so pushing anything against something resisting amounts to work input; thermodynamic work input.

So, thermodynamic work input has a cost associated with it and that cost as to give a something in return, and more over that cost must be required to be incurred in order for this to happen. Therefore, let us look at what surface tension is in a very, very phenomenal logical sort of a view.

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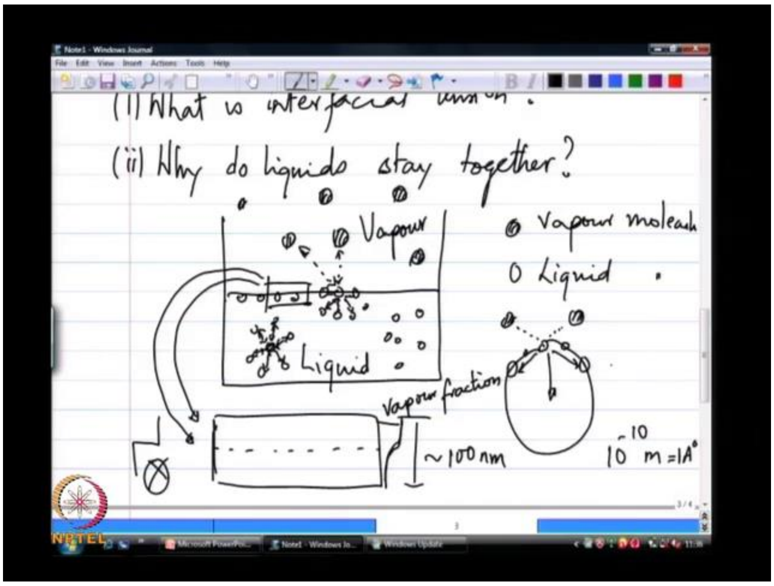

(I) What is interfacial tension?

(ii) Why do liquids stay together?

So, imagine for a moment. I will ask the question, what is interfacial tension? Commonly known as surface tension, I will take a container of liquid; a corollary to this is why do liquid stick together or stay together. So, what is so fundamentally different between a liquid and a gas? It is the same water, you know water vapour form it will go to fill the entire room, but in the liquid form it stays together in the form of a beaker.

And mind you that is not due to gravity, even if you will you seen these cool microgravity videos from the phase station where they can squeeze a drop of water out of a bottle and the drop of water would be oscillating and coming in it is goblet. So, the drop of water remains as one big closed entity even in microgravity. They are fact that liquid stays together it is not due to gravity, so very simple thought experiment and actual experiment to draw the conclusion from.

So this is liquid form here now, vapour. We all now know that this is matter is composed of molecules. This is a vapour molecule, and you open circle is a liquid molecule just for the sake of our own schematic. Now, we all know that liquids or molecules have weak forces you know that are exerted between each other. So, in the case of water for example these so called weak forces are actually quite strong, they called hydrogen bonding forces. So if I just simply take a molecule of water that is inside the liquid. Now like as I said this is a very, very simplistic picture, but I want you to sort of understand how this works only with standard disclaimer. So, it is only to understand the concept of surface tension. These molecules are not stationary, by any stretch of imagination they are all in some configuration of random motion.

Now, a molecule that is deep inside the liquid is subject to these equal and opposite forces from several molecules that are surrounding the one liquid molecule. Like I said this is not a static picture it is a very dynamic picture, but you can imagine it as a snap shot of that dynamics. Now where the same molecule was on the surface there is only in some very crude way half the number of those molecules pulling it in to the liquid, and you have these gaseous phase molecules, a vapour phase molecules right above on the other side of the interface. And these forces are much weaker.

So, inter molecular force between a liquid and a vapour is much weaker than liquid, liquid inter molecular force. And the reason for this is because; one the vapour phase molecules are much further apart, so the mean free path that is one physical quantity that actually separates liquid phase from a gaseous phase. The mean free path which is the distance a particular molecule as to travel before it encounter its nearest neighbor or before it encounters another molecular collusion; is that distance is what we called mean free path. That mean free path is much, much higher in the vapour phase in comparison to liquid phase.

In some sense these are liberated molecules, they have been liberated from the same liquid phase and they are now much freer to move a part and around. So, these liberated molecules exert far less force on the surface molecules compare to the once bellow there. As a consequence if I look at this knot on a flat meniscus like I have drawn, if I look at this on a circular drop. So, if I take a sphere and do this argument that I have two neighboring molecules there been pulled this way this is being pulled this way, this is a vapour phase molecule that are much farther away, these are very weak forces. The vector sum of all the forces essentially is a force that acts towards the radius of curvature.

Again like I said do not take this very far in your own mind either it is just to show the concept that, that there is like a stretching force at the interface or on every fluid entity on the surface that causes in to sort of exert a force towards its own radius of curvature. As a consequence you can see how the whole blob of liquid stays together. So, the net result of all this is, that if I take a certain volume of liquid; let us say I take a cube of liquid and I leave it in thin air in a microgravity condition these kinds of forces essentially drive that cube of liquid towards a configuration where the surface area is the minimal.

So, if you take this argument further and further the point where any dynamics of this blob of liquid in microgravity will stop is where it has minimized it is own surface area. And the minimal surface area for a given volume happens to be a sphere. Therefore, drops are mostly spherical unless acted upon by other forces. So that is the sort of a 5 minute summary of a surface tension and it is origins with all standard disclaimers. Now I want to also mention the disclaimers that go into this.

Now first of all; if I look at this region, if I look at this sort of an interfacial region and I zoom out, and let us say this is on the order of a 100 nanometers now. Mind you a water molecule is only a few angstroms, so 10 power minus 10 meters is 1 angstrom. Water molecule is only like a few angstroms and in diameter, if you want to think of it as itself as a spherical entity which itself as an approximation. But if I now take a cell that is the 100 nanometers in thickness, so it is like much bigger than any one molecule; at least two orders of magnitude bigger than any one water molecule.

Now on this length scale I have to have in zoomed into this length scale I want to see; what does the water look like? Water is liquid and vapours and they coexist that is essentially what we learn in thermodynamic, that the gaseous phase right above the liquid would be fully saturated with water vapour to the point where the partial pressure of the vapour right adjacent to this meniscus is equal to the saturation vapour pressure at that temperature.

So I just want to mention this to show you that really speaking if I now still come draw a line and I will draw this as a dotted line, just too sort of recreate what we observed in the macro scale. If this was water in a beaker, as far as my I could tell it was a sharp meniscus in the beaker. That meniscus on this zoomed in scale is no longer sharp, first point. This meniscus is so dynamic that you have this so called vapour phase molecules going back into the liquid phase, the liquid phase molecules coming back out as vapour phase; that you cannot really identify a set of molecules as being permanently in the vapour phase and I said that is permanently in the liquid phase. So, that is the first point to make.

So, if I now draw like a vapour fraction there is a thickness to this. If this is vapour fraction which is the fraction of the water molecules that are in the vapour phase versus the fraction of the water molecules that are in the liquid phase, this is not a sharp transition like our eye would like us to believe on the macro scale observation. On the micro scale this is a very diffuse interface, the thickness is on the order of tens of nanometers.

So, all this very simplistic argument where I use the word molecule in a very loose way has to be taken with this reality in our own mind. Now the second point is that because of; but the fact that there is a an imbalance in the molecular forces between a pair of molecules in the liquid and a pair wise and the same pair wise force between a liquid and a vapour molecule or for that matter even a vapour, vapour molecule is real. So, that difference in the intermolecular forces is essentially the origin of this interfacial tension.

So, I have a certain intermolecular force while the molecules are in the liquid phase the same pair of molecule after they are liberated; now the I use the word liberated because it actually is in some sense liberation process it requires some sort of a heat transfer, some sort of a way by which I add some kinetic energy for you to break loose of this meniscus this interface. And that liberation process causes the vapours to become much more free to move around. As a result the intermolecular forces in the vapour form are much less than the intermolecular forces of the same chemical constituent water while the material is in the liquid phase.

So, this is the origin of interfacial tension. So, whatever we said you know like I have one way of liberating this molecule which is heating. Essentially, if I want to increase this surface area it has to be against the wishes of the liquid itself. The liquid left to itself like I took the example of a little if I took a cube of water and released all walls of the cube it would essentially slowly evolve towards the sphere that is the minimal surface area.

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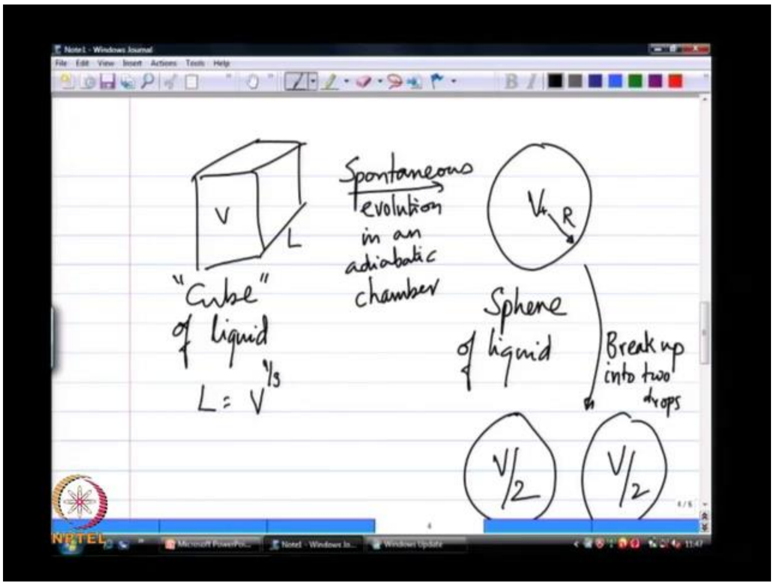

If I want to take this sphere, I will take a very simple example; I take a cube of certain volume V, the stable configuration of this is a sphere of the same volume V. Now, if I want to break this up into two drops, so let us just take a simple break up process. I want to break this sub somehow into two drops each of volume V over 2. This is the simplest atomization problem. What is the energy required? Let us just look at that.

Now let us look at the before and after. This process is spontaneous. This process is spontaneous meaning that I do not have to input any external work to make it go from a cube to a sphere, whereas to make it go from a sphere of volume V to 2 spheres of volume V over to each I have to input some sort of a work. I mean it sort of intuitive I want to put some numbers around this in just a moment. I want to also show you that this is spontaneous. I do not want you to believe me, although it is you can.

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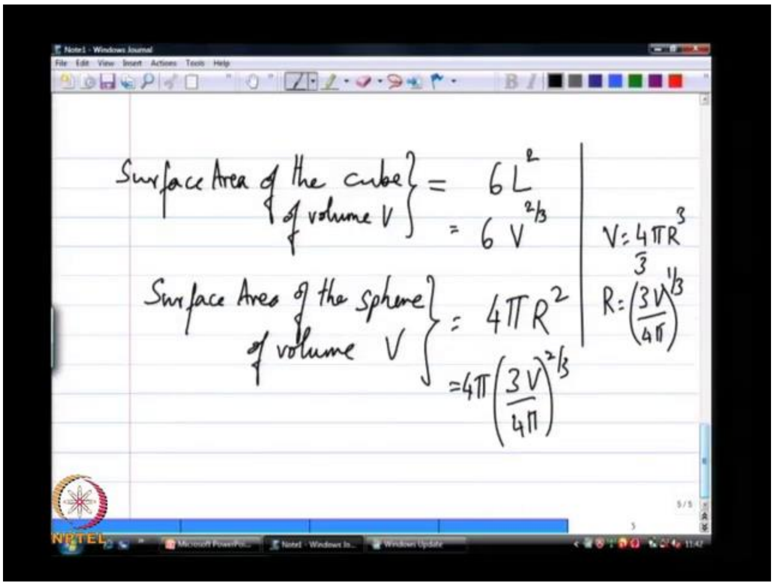

$$\left.\begin{array}{r}\text{Surface Area of the cube}\\ \text{of volume } V\end{array}\right\} = 6L^2 = 6V^{2/3}$$

$$\left.\begin{array}{r}\text{Surface Area of the sphere}\\ \text{of volume } V\end{array}\right\} = 4\pi R^2 = 4\pi\left(\frac{3V}{4\pi}\right)^{2/3}$$

$V = \frac{4}{3}\pi R^3$

$R = \left(\frac{3V}{4\pi}\right)^{1/3}$

I am sure imagine from your own intuitions, but let us say if I take this surface area of the cube if the volume is V each side is V power one-third. The surface area of this cube would be 6 times L squared which is 6 times V power two-third.

Let me be clear this is not surface, but the surface area is 4 pi R squared. Where, R happens to be the radius of this, but what I know is that V itself is 4 over three pi R cubed. So, R is 3V over 4 pi raise to the power one-third. So, this is 4 pi times 3V over 4 pi raise to the power two-thirds.

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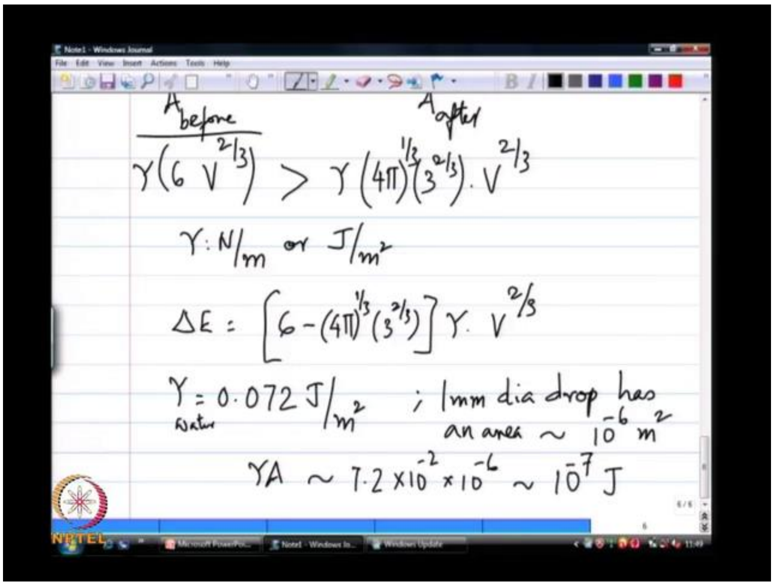

$$\underbrace{\gamma(6V^{2/3})}_{A_{before}} > \underbrace{\gamma(4\pi)^{1/3}(3^{2/3}) \cdot V^{2/3}}_{A_{after}}$$

$\gamma : N/m$ or J/m^2

$$\Delta E = \left[6 - (4\pi)^{1/3}(3^{2/3})\right]\gamma \cdot V^{2/3}$$

$\gamma_{water} = 0.072\ J/m^2$; 1mm dia drop has an area $\sim 10^{-6}\ m^2$

$$\gamma A \sim 7.2 \times 10^{-2} \times 10^{-6} \sim 10^{-7}\ J$$

Which if I simplify, this becomes 4 pi raise to the power one-third times 3 raise to the power two-thirds times V raise to the power two-thirds. That is the surface area of this sphere of the same volume V. If I compare the two surface areas I have 6 times V power two-thirds, so this is in some sense A before, A after is 4 pi times one-third times 3 raise to the power two-thirds times V raise to the power two-thirds.

You can with some simple numerical manipulations see that 6 is greater than this number in front of V power two-thirds. So, the process is heading in the direction of decreasing interfacial energy. So, all other forms of energy remain in the same, temperature, chemical energy say I do not know you know if there is some spontaneous reaction also happening, all other forms of energy remaining the same interfacial energy alone is decreasing which is sufficient to make it a spontaneous process.

Now, here is a question I do not want to dwell too much on it, but I think you should think about it yourself. The cube of liquid has 6 times V power two-thirds energy, no wait I did not say this correctly; there is also gamma, but that gamma is the same gamma is the interfacial tension. So, gamma as units of Newton per meter or Joules per meter squared. So, it is in units of energy per meter squared. So that when multiplied by area gives me energy. You had gamma times 6 times V power two-thirds Joules of energy, the same cube of liquid after it becomes a sphere as gamma times this much the 4 power one-third, times 3 power two-thirds times V power two-thirds amount of energy. If I do this I can see quickly that there is a decrease in the energy. So, if all other forms of energy remain the same where has this energy gone?

So, delta E is 6 minus 4 pi power one-third; this much energy which used to be in interfacial energy somehow not to be accounted for. And really it is speaking what has happened is this as become dissipated. So, if I really look at this process as an adiabatic process where, adiabatic constant volumes so it is like a very trivial case, but essentially I have not allowing any work to be input, I am not allowing any heat transfer across my system boundary. If I take this and in this spontaneous evolution process that much energy is still inside the adiabatic chamber in the form of heat, because that energy has been dissipated that dissipated energy is essentially goes to heat the drop slightly too that this much magnitude.

Just to give you some numbers here, I want to make your gamma has units for water 10 power minus 7 Joules that is like an approximately in order of magnitude. That is the kind of interfacial energy we are talking about for the case of a 1 mm diameter drop. If 1 mm is the diameter of the drop that is 10 power minus 3 meters, the interfacial area is on the order of 10 power minus 6 meters; the 10 power minus 6 meters multiplied by this gamma for water which is 0.072 happens to be like I am approximating 7 to be like a 10 for example in this simple calculation.

A Joule itself is a very, very, very, very, very, very small unit of energy; you know it is like hardly any energy. So, we are talking 10 power minus 7 Joules that is like a very tiny number, very tiny amount of energy. Just to give you an idea if you burn a 40 volt light bulb for one second you consumed 40 Joules of electricity. You have not gotten 40 Joules of light energy, you have got most of it as heat, but the consumption is 40 Joules for 1 second. So, it is a very, very, very small unit of energy, kilo Joule is more realistic in many different real engineering situations.

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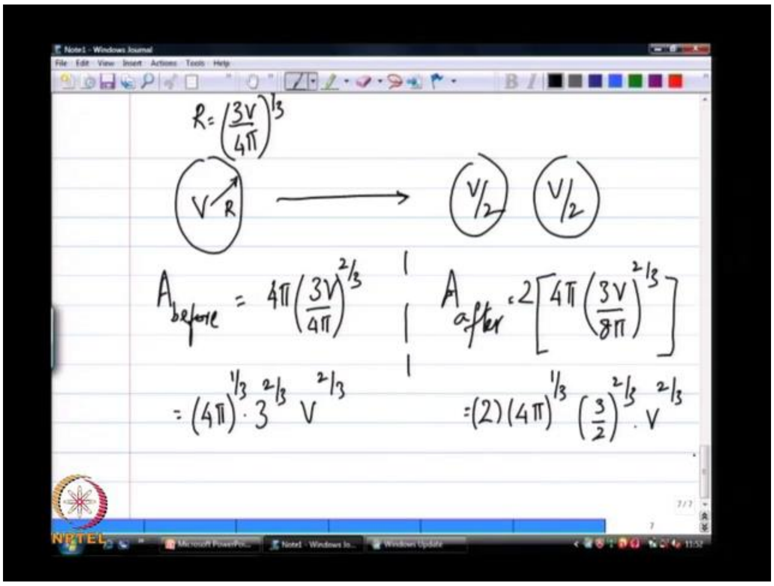

$$R = \left(\frac{3V}{4\pi}\right)^{1/3}$$

$$A_{before} = 4\pi\left(\frac{3V}{4\pi}\right)^{2/3}$$

$$= (4\pi)^{1/3} \cdot 3^{2/3}\, V^{2/3}$$

$$A_{after} = 2\left[4\pi\left(\frac{3V}{8\pi}\right)^{2/3}\right]$$

$$= (2)(4\pi)^{1/3}\left(\frac{3}{2}\right)^{2/3} \cdot V^{2/3}$$

So, if I want to go from 1 drop of liquid of volume V to 2 of the same volume, what is the energetic cost involved? The surface area here is now, this is the before situation is 4 pi times 3V over 4 pi raise to the power two-thirds. In this particular instance I have 2 drops each one having 4 pi R squared, but that R is different; the R in this case 3V over 4 pi raise to the power one-third. R in this case would be based on the volume being V over 2 not V, so that is the only difference. So if I replace this V with V over 2, I get 3V over 8 pi raise to the power two-thirds.

So, this is the before picture and this is the after picture. Let me simplify this slightly what do I get, I get this 4 pi raise to the power one-third 3 raise to the power two-thirds V power two-thirds. On this side, I have 2 times 4 pi, I will take a 4 pi out of this and lead the 2 in there. I have the same 4 pi raise to the power one-third, but I have 3 over 2 raise to the power two-thirds times V raise to the power two-thirds.

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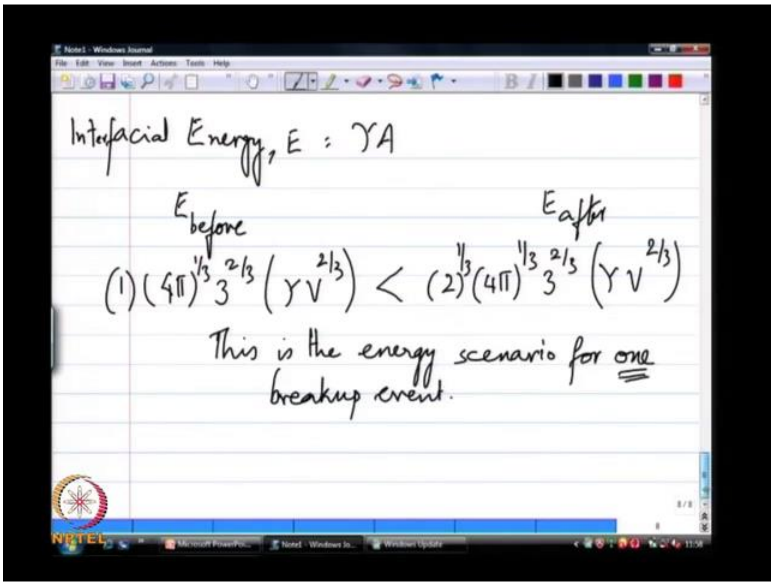

Interfacial Energy, $E = \gamma A$

$$\overset{E_{before}}{(1)(4\pi)^{1/3}3^{2/3}(\gamma V^{2/3})} < \overset{E_{after}}{(2)^{1/3}(4\pi)^{1/3}3^{2/3}(\gamma V^{2/3})}$$

This is the energy scenario for one breakup event.

So, the interfacial energy is gamma times the area, gamma is surface tension we looked it a number for water. By the way water happens to be among the more commonly observed liquid water happens have one of the highest surface tension, highest interfacial tension liquid vapour interfacial tension. The reason for that is this very strong hydrogen bonding in between water molecule. So, water in many respect is a very unique liquid and it is a burdens on land is also not fortuitous, thing is some sort of a reason why water is also commonly found and for very high interfacial tension. There is some implications to at that people are now discovering for like even the evolution of life itself, at least water base life.

This some interesting aspects to water having such a high interfacial tension, so if this is the interfacial energy I will move this around the little bit to this side to make myself room for another symbol. So, the E before is this 4 pi raise to the power one-third 3 raise to the power two-thirds times gamma times V raise to the power two-thirds. E after is 2 times 4 pi raise to the power one-third 3 raise to the power two-thirds, except I want to absorb this 2 raise to the power two-thirds in the denominator as 2 raise to the power one-third appear times this same gamma V raise to the power two-thirds.

The only difference between these two is I have a factor 1 here and I have a factor 2 raise to the power one-third here; 2 raise to the power one-third is greater than 1. So, clearly we are going against the gradient of decreasing energy or we are increasing the interfacial energy. The amount of increase is this 2 raise to the power one-third minus 1 times the rest of the factor that is how much is the actual magnitude of energy that we have raised.

Now, if V is small let us say 1 mm versus 100 micrometers which is 0.1 mm, as V decreases the actual magnitude of energy require to break it up decreases for any one break up event to happen. But if I start off with the certain volume of liquid in the bulk container. So, I want to take let us say one plunger depth, one plunger push produces let us say 0.5 milliliters of perfume dispersed into a spray. So, I start off with the volume 0.5 milliliters, I imagine 1 drop that is 0.5 milliliters for me to disperse this into as many drops as required each of the size; let us say 50 micrometers, that is the calculation we did on the very first day. The one drop which is 0.5 milliliters in volume, just to compare drops to drops. Although, the perfume in the container is not in the form of a drop, but just to be fair in our comparison; one drop of volume 0.5 milliliters compare to as many drops as needed each of diameter 50 micrometers, but all the drops put together containing the same volume of perfume or liquid.

The interfacial area of this dispersion of drops would be much, much greater than the surface area of these 0.5 milliliters. And that is what we call we calculated as this little 10 centimeter by 10 centimeter square, that is how much interface we would create between the liquid and the vapour, that is how much interfacial energy I have to add. Gamma times that interfacial area is the amount of interfacial energy that I have to add.

So, let us go back to just looking at that for a moment with the numbers that we now know. So, we did this calculation before.

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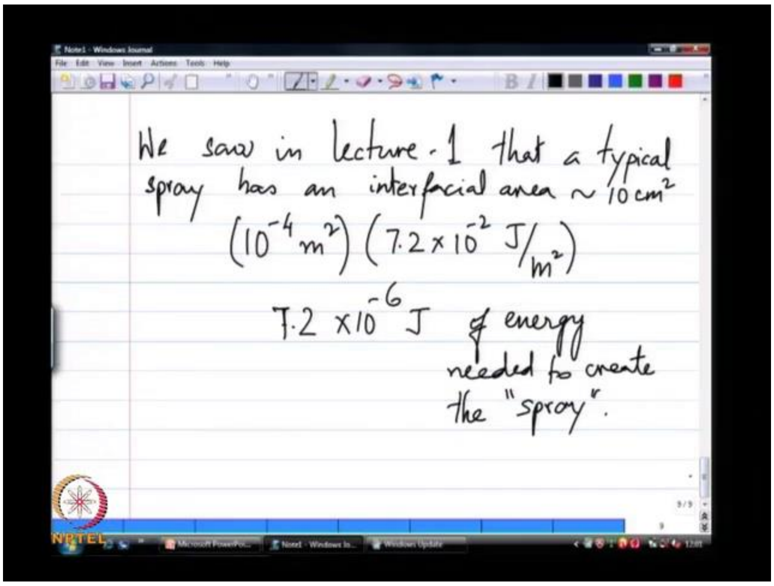

We saw in lecture-1 that a typical spray has an interfacial area $\sim 10\,cm^2$

$$(10^{-4}\,m^2)\,(7.2 \times 10^{-2}\,J/m^2)$$

$7.2 \times 10^{-6}\,J$ of energy needed to create the "spray".

So, just to complete this thought here, this is for single breakup event 10 centimeter squared. 10 centimeter squared is 10 power minus 4 meters squared, this times the 7.2 into 10 power minus 2 Joules per meter squared. So, that is about 7.2 into 10 power minus 6 Joules of energy.

So, the amount of interfacial, all the way I said the objective of a spray is to take a liquid break it up where I have increase the interfacial area, therefore the interfacial energy. But the actual amount of interfacial energy increase is on the order of 10 power minus 6 Joules. Clearly one plunger push by any sort of an estimate is much, much, much more than 10 power minus 6 Joules 1 micro Joule. The amount of energy that we input in 1 perfume spray plunger push is much more than 10 power minus 6 Joules.

So, something is not adding up like if you are only off by a factor of 10 it is something is not adding up here. So, where is all that energy that we are going, energy that we are inputting into this perfume spray going? One; so, we started to say work is required to increase interfacial area that was the whole, why we said we need sprays.

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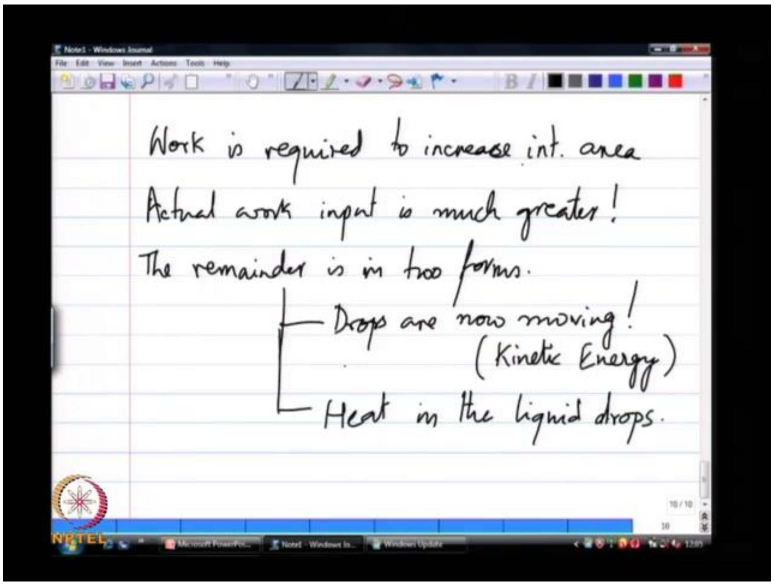

Work is required to increase int. area

Actual work input is much greater!

The remainder is in two forms.

- Drops are now moving! (Kinetic Energy)
- Heat in the liquid drops.

But the actual work input is much greater, we just saw that. The reminder of this energy is in two forms. One, drops are now moving.

So, there is a kinetic energy associated with that drop motion that did not exist before. When the perfume was sitting in the bottom of the can, the bulk fluid velocity of that perfume was nearly 0. But after the plunger as done it is thing the perfume drops are now moving, so there is half m V squared for each and every drop. So, if I have a million drops each drop of some mass, some micro grams of mass it is velocity let us say some tens of meters per second or 1 meter per second; 1 meter per second is like a very reasonable number for a small scale spray.

So, we are looking at energy contained in every drop and there are a million of these drops. We saw that as an order of magnitude. So, if the first and foremost sort of hidden reservoir of all the plunger work is in the form of droplet motion. Droplet motion contains much more energy than the interfacial energy itself. So I had water, let us say in the form of 1 stationary 0.5 milliliter blob, for me to break this up ideally if I create stationary 50 micrometer drops the only amount of energy needed would be 10 power minus 6 Joules. If I say that is my only objective I should only do that unfortunately a spray nozzle cannot just do this, even though that is our stated purpose. It also has to move the drops, we will see in the moment while. It also has to create this additional kinetic energy and that happens to engulf, that happens to be the reservoir of the bulk of the plunger work and only a tiny minuscule fraction actually goes to increase the interfacial area; so most of the energy that we put is in the form of droplet motion which is now half m V squared kinetic energy.

The other source is a slight increase in the temperature or I would not say temperature it is basically heat in the drops. This is because, if I assume that these drops are viscous the break up process involves some amount of dissipation, at any sort of a dissipation involves converting a higher source of energy; surface energy, mechanical energy, these are all higher sources of energy it involves taking the higher sources of energy and creating not source higher quality energy and creating lower quality energy, these are all very, very vague terms you know I should not be describing them since you are talking thermodynamics.

But essentially what we are saying is that some forms of energy are more useful to us then other forms of energy. Heat happens to be one of the lowest forms of energy, least useful forms of energy. A moving shaft or rotating shaft or a moving mass is the highest form of energy, because if we can do something with it like grain flower you know do a lot of the more useful aspects of what a man or women needs in their daily lives.

So, essentially while we set out to increase interfacial area we are actually increasing the droplet kinetic energy, and as a wind fall we are increasing the interfacial area. So, this is what a spray nozzle does. We will see some designs of spray nozzles in the next lecture that try to do this.