Colloids and Surfaces
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Lecture-14
Problem On Scaling of Vanderwaal Interactions

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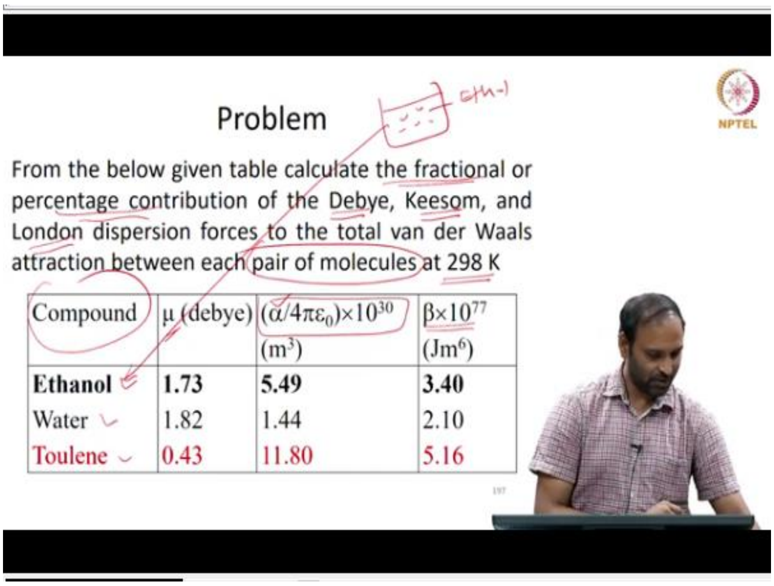

Problem

From the below given table calculate the fractional or percentage contribution of the Debye, Keesom, and London dispersion forces to the total van der Waals attraction between each pair of molecules at 298 K

Compound	μ (debye)	$(\alpha/4\pi\varepsilon_0)\times10^{30}$ (m^3)	$\beta\times10^{77}$ (Jm^6)
Ethanol	**1.73**	**5.49**	**3.40**
Water	1.82	1.44	2.10
Toulene	0.43	11.80	5.16

So, there is a table that is given to you okay, you are supposed to calculate the fractional or percentage contribution of Debye, Keesom and London dispersion forces to the van der Waals attraction for each pair of molecules at 298 Kelvin okay. So, what you have been given different compounds ethanol, water, Toluene 3 cases okay.

And you have been given what is the dipole moment right and the term that involves polarizability is given and beta is also given okay. So, that means if I take a container which has ethanol okay, the large number of atoms and molecules of ethanol right okay. So, if I take a case like that okay what is the contribution of these 3 interactions to the total van der Waals interaction right that is the question.

So, how do we go about doing that?. So, with whatever we have discussed so far do you think we can attempt this problem yes, no, yes right okay.

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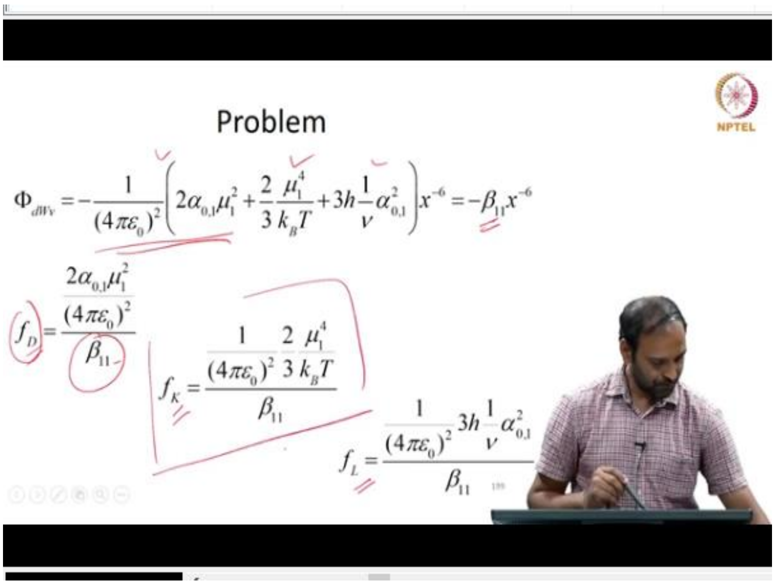

Problem

$$\Phi_{dWv} = -\frac{1}{(4\pi\varepsilon_0)^2}\left(2\alpha_{0,1}\mu_1^2 + \frac{2}{3}\frac{\mu_1^4}{k_BT} + 3h\frac{1}{\nu}\alpha_{0,1}^2\right)x^{-6} = -\beta_{11}x^{-6}$$

$$f_D = \frac{\frac{2\alpha_{0,1}\mu_1^2}{(4\pi\varepsilon_0)^2}}{\beta_{11}}$$

$$f_K = \frac{\frac{1}{(4\pi\varepsilon_0)^2}\frac{2}{3}\frac{\mu_1^4}{k_BT}}{\beta_{11}}$$

$$f_L = \frac{\frac{1}{(4\pi\varepsilon_0)^2}3h\frac{1}{\nu}\alpha_{0,1}^2}{\beta_{11}}$$

Let us look at this. So, this is if you have 2 identical molecules right 1 and 1 that will be the total van der Waals force of interaction right. So, each of the terms okay as well as the overall interactions have the same x power - 6 dependence right. If that is the case what I can do is I can take each pre-factor right divided by this term beta that will give you the fractional contribution of okay Debye, Keesom and London dispersion forces right. So, if you go back and look at okay then you can calculate each of them right.

So, that is a same term right. So, every pre-factor that you have here 1, 2 and 3 that divided by beta will give you the fractional contribution okay. Let us try and calculate one by one.

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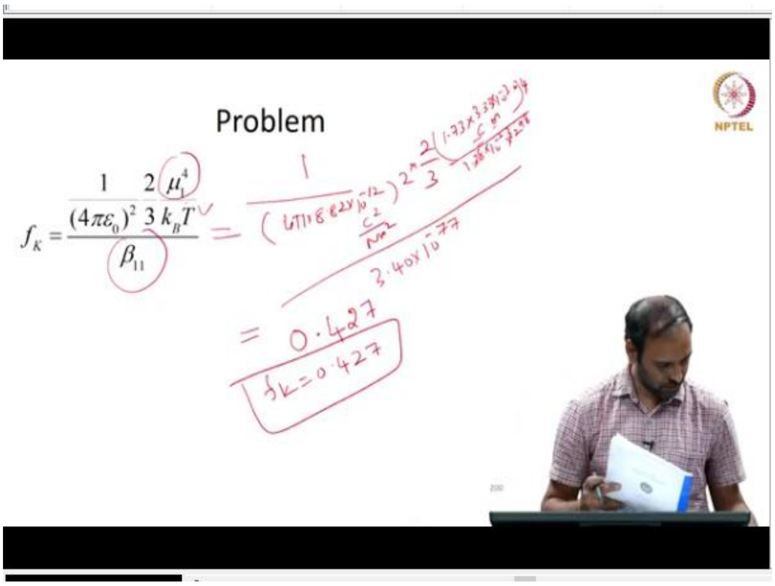

Problem

$$f_K = \frac{\frac{1}{(4\pi\varepsilon_0)^2}\frac{2}{3}\frac{\mu_1^4}{k_BT}}{\beta_{11}} = \frac{\frac{1}{(4\pi\, 8.82\times10^{-12}\,\frac{C^2}{Nm^2})^2}\times\frac{2}{3}\frac{(1.73\times3.33\times10^{-30})^4}{1.38\times10^{-23}\times298}}{3.40\times10^{-77}}$$

$= 0.427$

$$\boxed{f_K = 0.427}$$

So, if you go back to the problem so I have been given mu right, the dipole moment okay, that is given to me okay, temperature is given, beta is given okay. I can calculate this right 1 divided by 4 pi epsilon 0 is 8.82 into 10 power - 12 right - 12, it is a coulomb square per newton meter square okay.

That is the unit SI units okay, that is whole square okay multiplied by 2 by 3 into yeah 1 by 4 pi epsilon 0 is directly 9 into 10 power - 12, you can also use that yeah, you can do that as well yeah, yeah 2 by 3 times mu 1 okay mu 1 is given to 1.73 right is 1.73 Debye, okay I need to convert Debye into Si units for that you are going to use a conversion factor which is 3.33 into 10 power - 30 okay.

That the unit will be coulomb meter right it is a dipole moment, charge times the distance right. So, that is coulomb meter okay, that is to the power 4 right, because you know you have mu 1 to the power of 4 there okay divided by kB is 1.38 into 10 power - 23 times 298, that is the temperature that is given whole divided by beta 11, that has also been given to you it is 3.4 into 10 power - 77 okay. You just work it out quickly and then let me know what the number that you get.

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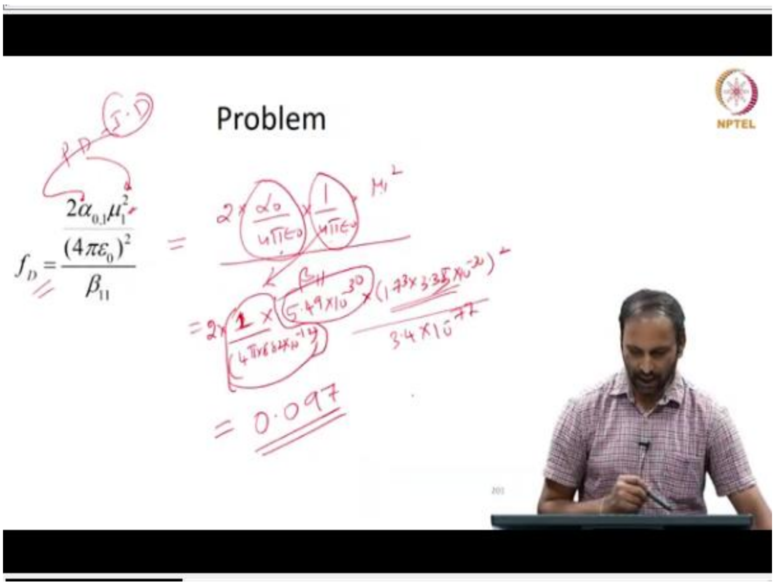

Problem

$$f_D = \frac{\frac{2\alpha_{0,1}\mu_1^2}{(4\pi\varepsilon_0)^2}}{\beta_{11}}$$

Okay, so is the number that you get, the number that I have is 0.427 what I have okay. There is a lot of exponents with very large numbers right. So, - 77 you have 10 power - 30 times 4 will be - 120 right yeah, yeah 0.41, that is fine yeah 0.41 is okay I mean you know 0.41 yeah okay anyway. So, that is the order that you should get okay. So, similarly I can go back and look at f D.

That is the Debye interaction which is the interaction between a permanent dipole and a induced dipole right. Therefore you have a term that corresponds to the permanent dipole right**.** That is the dipole moment and the induced dipole then there is a term that with alpha which is polarizability okay. Therefore so this is the fractional contribution to the Debye interaction.

So, this quantity has been given to you alpha 0 divided by 4 pi epsilon is given in the table multiplied by 1 over 4 pi epsilon 0 okay mu 1 square divided by beta 1 1 right. So, 2 is here 1 over 4 pi epsilon 0 is this, alpha 0 divided by 4 pi epsilon 0 is given 5.49 into 10 power - 30, that is been given to you and there is again mu 1 square 1.73 3.35 10 power - sorry this is 3.33 10 power - 30 whole square now okay divided by beta which is 3.4 10 power - 77 okay.

If you work this out the number that you should get is 0.097 okay. So, let us go back 0.097 that is 0.0 not that okay, this is 0.097 right and this came out to be 0.427 right. Now we want to calculate f L right, we have done that, we have done this we want to calculate what is the contribution of the London dispersion forces?. So, how do we do that?. So, you know this value okay, what is that yeah right you can do that right f L + f D + f K should be equal to 1 right.

The fractional contribution has to be 1, therefore 1 - of 0.097 right 0.427 should give you what is f L right, you could have calculated but of course you can get planks constant but you do not know what is nu right, but other parameters are given okay. But if you knew nu I could have calculated but we do not know that. So, therefore f L what is the f L that you get? Right 0.476. Let us look at if our calculations are right.

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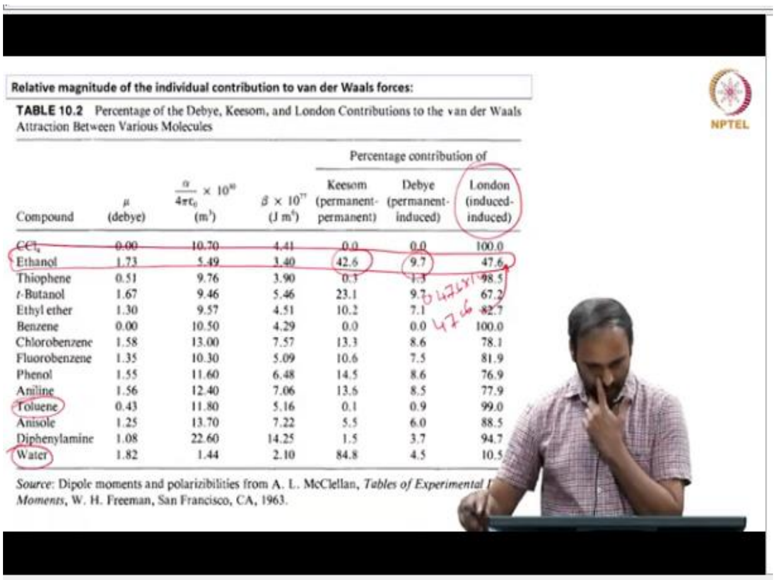

Relative magnitude of the individual contribution to van der Waals forces:

TABLE 10.2 Percentage of the Debye, Keesom, and London Contributions to the van der Waals Attraction Between Various Molecules

Compound	μ (debye)	$\frac{\alpha}{4\pi\epsilon_0} \times 10^{30}$ (m^3)	$\beta \times 10^{77}$ ($J\ m^6$)	Percentage contribution of Keesom (permanent-permanent)	Debye (permanent-induced)	London (induced-induced)
CCl_4	0.00	10.70	4.41	0.0	0.0	100.0
Ethanol	1.73	5.49	3.40	42.6	9.7	47.6
Thiophene	0.51	9.76	3.90	0.3	1.3	98.5
t-Butanol	1.67	9.46	5.46	23.1	9.7	67.2
Ethyl ether	1.30	9.57	4.51	10.2	7.1	82.7
Benzene	0.00	10.50	4.29	0.0	0.0	100.0
Chlorobenzene	1.58	13.00	7.57	13.3	8.6	78.1
Fluorobenzene	1.35	10.30	5.09	10.6	7.5	81.9
Phenol	1.55	11.60	6.48	14.5	8.6	76.9
Aniline	1.56	12.40	7.06	13.6	8.5	77.9
Toluene	0.43	11.80	5.16	0.1	0.9	99.0
Anisole	1.25	13.70	7.22	5.5	6.0	88.5
Diphenylamine	1.08	22.60	14.25	1.5	3.7	94.7
Water	1.82	1.44	2.10	84.8	4.5	10.5

0.476×100

47.6

Source: Dipole moments and polarizibilities from A. L. McClellan, *Tables of Experimental* *Moments*, W. H. Freeman, San Francisco, CA, 1963.

Okay that was ethanol right. So, we just calculate this to be 0.476, that is a percentage contribution multiplied by 100 should give you 47.6 exactly the same number right, you are again 9.7 and 42.6 right. So, similarly you can do a repeat the same calculation for the other molecules that have been asked. So, one is water, other one is toluene right okay. So, you can try and do a similar exercise.

So, this basically gives you a feel for calculating numbers and you know and then you know see if you have done the right thing right. So, because we are talking about fractions, so you know everything has to be less than 1 right and all of them should sum up to 1, the total fraction contribution should show you know sum up to 1 okay. So, if you know that you should be able to get this out okay. Yeah. So, maybe we will stop here.

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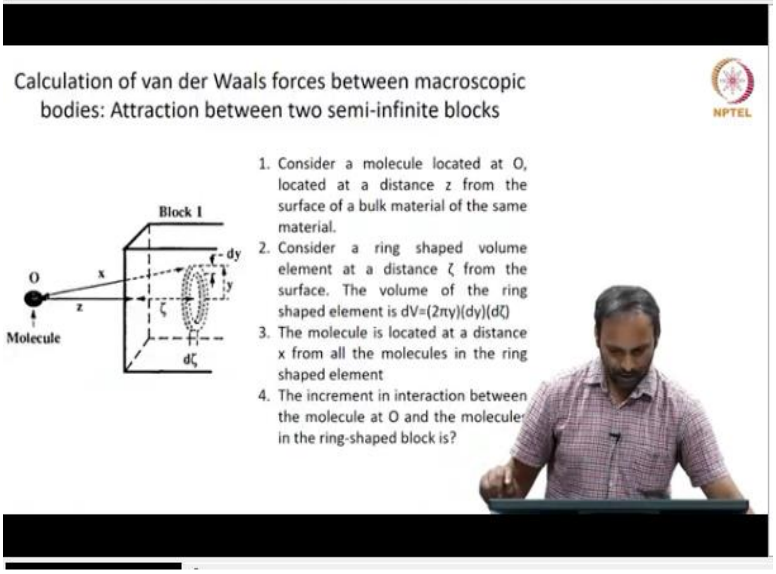

Calculation of van der Waals forces between macroscopic bodies: Attraction between two semi-infinite blocks

1. Consider a molecule located at O, located at a distance z from the surface of a bulk material of the same material.
2. Consider a ring shaped volume element at a distance ζ from the surface. The volume of the ring shaped element is dV=(2πy)(dy)(dζ)
3. The molecule is located at a distance x from all the molecules in the ring shaped element
4. The increment in interaction between the molecule at O and the molecules in the ring-shaped block is?

So, what we are going to do in the next class is to look at if you have 2 blocks okay, we will do a simple exercise where I have 2 semi infinite blocks, we will try and calculate the van der Waals force of interaction between them. Exactly similar way that we did for you know when we did the scaling arguments okay. We will try and work out an expression you know that we could use for calculating van der Waals force of interaction between 2 blocks. So, that is what we will try and do in the next class.