Variational Calculus and its applications in Control Theory and Nanomechanics
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Lecture 63 Introduction to Nanomechanics Part 3

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So, my Lennard Jones also known as the LJ potential is defined as the interaction energy or the potential function is

$$\phi(\rho) = -A(\rho)\rho^{-m} + B(\rho)\rho^{-n}$$

where, my A represents the attractive component because of the minus sign and B represents the repulsive component because of the plus side. So, then and my ρ is the distance between two atoms or the atoms under consideration or the structures under consideration and then typically these coefficients m, n these are natural numbers. So, sometimes these are also called as the Lennard Jones mn-potential which tells us what is the strength of the attractive as well as the strength of the repulsive components of the potential. So, for example if my $m = 6$ and $n = 12$, which is the most common occurrence of Lennard Jones potential in almost all the physical models that are used, also known as the 6-12 LJ-potential. So let me term it as example A. Another potential that is frequently used is the 5-10 potential and 10-12 LJ-potential, frequently used to model the hydrogen bonding. So, if I were to plot the L-J potential, see above. If we were to plot the following function,

$$\phi(\rho) = 4\epsilon\left[-\left(\frac{\sigma}{\rho}\right)^6 + \left(\frac{\sigma}{\rho}\right)^{12} \right]$$

where ϵ and σ are real constants. Then if I were to plot this L-J potential, I see that this looks like the plot given above. So, in this part of the potential we have the repulsion and other part of the potential represents the attraction potential. We will see that, for this potential, we definitely have the minima and the minima and the minima here is given by the ϵ where ϵ is also known as the potential depth, also known as the energy well-depth. So, suppose I model my carbon nanotube with L-J potential, then my well-depth will denote this parameter ϵ as shown in this example. So, ϵ is the well-depth and σ is the distance from 0 to this minimum of the L-J potential. So σ is Vander Waals distance and it turns

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out to be $\left(\frac{B}{A}\right)^{1/6}$. Well, all we have to do is just take the derivative of ρ and set it equal to 0 and that will give me my ρ^* or critical value which is σ. So this is a typical example of the L-J potential that we will be using ,so we can see that Vander Waals interactions are usually short range interaction. Why? Because, notice that as ρ goes to infinity the interaction nearly goes to 0. So, in fact, I would say that the Lennard Jones potential represents a short range repulsion but medium range attraction, which means that if I have that ρ goes to 0, then I can see that we are in the repulsive range. If ρ goes to infinity then it is very weakly attractive and in the intermediate range, we have some reasonable attraction via this potential. So, what I said is the following.

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So, Vander Waals interaction energy in general is short range only nearest neighbor interaction and ideally modeled by L-J potential. We have seen that all these properties of Vander Waals interaction are quite appropriately captured by L-J potentials and these Vander Waals interaction energies are typically applied to non-bonded/non-polar structures. So these are very different than ionic interactions or covalent interactions. So then let me start our basic modeling effort by looking at the interaction of a point with a plane. For example, a carbon atom with a graphene sheet. So I am going to step by step build up the model where eventually we are going to look at the oscillatory mechanics of 2 carbon nano rods. So, let me look at the first of the example to discuss. So find the interaction energy (E) and the Vander Waals force (F_{vdw}) for a single carbon atom, a distance z from an infinite graphene sheet. So, we have a graphene sheet where the sheet contains these tessellated hexagonal rings, and so on so forth and then, we have a carbon atom which is sitting on top, well it is on top of this sheet and we want to model the interaction of this carbon atom with the sheet.

So assume to model this interaction, let me place this carbon atom at a convenient location to the sheet. So, we are going to assume that the carbon atom coordinate is $0, 0, Z$ where, Z is the distance of the carbon atom from the sheet and the sheet is on the $x - y$ plane. So these are my assumptions. The position of the sheet is given by the $x - y$ plane is $x, y, 0$, which means ρ which is the distance between the carbon atom, ρ which is the distance between the carbon atom and the graphene sheet is given by $[\sqrt{x^2 + y^2 + z^2}]^{1/2}$. Then let me model the interaction or the Vander Waals interaction of this atom with the sheet using our Lennard Jones potential or the 6-12 potential.

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Using Lennard Jones 6-12 potential, I see that my interaction energy is E which is

$$E = \eta \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[\frac{-A}{(x^2 + y^2 + z^2)^3} + \frac{B}{(x^2 + y^2 + z^2)^6} \right] dxdy$$

First component in the square bracket is ρ^6 and second component is ρ^{12}, thus 6-12 potential. So, this is my interaction energy. Note that the constant η is the average number of atoms per unit area of the graphene sheet. So, we are calculating the average interaction energy. Now, all I have to do is to evaluate this double integral. I can write down this double integral as

$$= \eta[-AI_3 + BI_6], \text{where A and B are constants, where, } I_n = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{dxdy}{(x^2 + y^2 + z^2)^n}.$$

So all I do is I evaluate for a general n plug n = 3 and 6. Notice that the factor $(x^2 + y^2 + z^2)$ tells us that we should use the cylindrical polar coordinates. Z is fixed, so the only variables in our integration are r, θ. So, we are going to use cylindrical polar coordinates with Z fixed. So changing to polar coordinates because Z is fixed, I see that my intergral turns out to be

$$I_n = \int_0^{2\pi} \int_0^{\infty} \frac{r \, dr}{(r^2 + z^2)^n} \qquad\qquad = \frac{\pi}{(n-1)z^{2n-2}}$$

and then, from here I can plug all these values and I see that my interaction energy is

$$E = \eta\pi \left[\frac{-A}{2z^4} + \frac{B}{5z^{10}} \right]$$

So from here I can calculate my Vander Waals force. I had need to differentiate with respect to Z or the axial coordinate.

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So my Vander Waals force is

$$F_{vdw} = \frac{\partial E}{\partial z}$$
$$= \pi\eta\left[\frac{-4A}{2z^5} + \frac{10B}{5z^{11}}\right]$$
$$= 2\pi\eta\left[\frac{-A}{z^5} + \frac{B}{z^{11}}\right]$$

So, typically the values of these constants for a graphene sheet are follows. I see that my A is given to be 17.4 electron volt Angstrom 6 and the constant B is the quantity 29000 electron volt Angstrom 12 and my constant η comes out to be 0.3812 atom per Angstrom square. Let me just quickly plot my interaction energy and my force. So, my x coordinate is the axial component Z is in Angstrom. So, the interaction energy is an even function of Z. So, these are my curves for E and if I were to plot the force, I see that the force follows the curves. So, the force is also the maximum at the same point where the energy attains the minimum. So F_Z and the force in the other half is as follows. So what I am trying to show is my force curve is anti-symmetric because of the odd terms and my energy curve is symmetric because of the even terms and hence, we can see that the minimum or the maximum force is given by the minimum of the energy curve and vice versa. So then I would like to go one step further and calculate the interaction energy of two parallel graphene sheets. So, the next problem that I want to highlight, find the interaction energy of two parallel infinite plates of grapheme, at a distance Z. So, the graphene sheets are separated by a distance Z.

Now, so we have two infinite sheets of graphene, so these are all Z tending to minus infinity, tending to infinity. And I want to find the intersection of these two infinite sheets. Now, notice that when we found out the intersection of a point with a sheet, we got a finite answer, so that the natural way to model this setup is we sum up the point sheet interaction. Now on two infinite sheets there are infinitely many points, which mean that we are doing an infinite sum of a finite quantity or an infinite sum of the point sheet interaction and we expect the answer to be infinite. So instead of finding the answer, that is the interaction energy of two infinite sheets, I am going to find out the answer as the interaction energy of two infinite sheets per unit area of the two sheets. So I am going to find out the interaction energy per unit area to get a finite answer. So as I just said the following, the interaction energy is an infinite sum of a non-vanishing term and it is infinite sum of a non-vanishing term and it is infinite. So, we instead calculate the interaction energy per unit area.
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Calculate I.E. per unit area.

atoms per unit area: 'η' and each atom interacts individually with the other plane. ✓

I.E per unit area : $E_{pua} = \eta E$ → found in Eg 3

$= \pi \eta^2 \left[\dfrac{-A}{2z^4} + \dfrac{B}{5z^{10}} \right]$

Take: $A = 15.2$, $B = 24100$ (Typically values of graphene sheet interaction) η: same as in Eg 3

Equilibrium Spacing btwn two sheets

$P_{vdw} = -\dfrac{\partial E_{upa}}{\partial z} = 0$

Experimentally 'z_0' reported $\boxed{z_0 = 3.35 \,\text{Å}}$ $z_0 = \left(\dfrac{B}{A}\right)^{1/6} = \boxed{3.41 \,\text{Å}}$

Using L-J 6-12 potential!

I.E : $E = \eta \displaystyle\int_{-\infty}^{\infty} \int_{0}^{\infty} \left[\dfrac{-A}{(x^2+y^2+z^2)^3} + \dfrac{B}{(x^2+y^2+z^2)^6} \right] dx\, dy$

Assume A, B : constants.

ρ^6. ρ^{12}

Avg. # atoms / area of graphene sheet.

$= \eta \left[-A\, I_3 + B\, I_6 \right]$ where $I_n = \displaystyle\iint_{-\infty}^{\infty} \dfrac{dx\, dy}{(x^2+y^2+z^2)^n}$

Changing to Polar - coord!

$I_n = \displaystyle\int_{0}^{2\pi} d\theta \int_{0}^{\infty} \dfrac{r\, dr}{(r^2+z^2)^n}$

$E = \eta \pi \left[\dfrac{-A}{2z^4} + \dfrac{B}{5z^{10}} \right]$ $= \dfrac{\pi}{(n-1)\, z^{2n-2}}$

So, we calculate the interaction energy, interaction energy per unit area. So, let me just introduce the concept of η. So, I denote my number of atoms per unit area and each atom interacts individually with the other plane. Now which means that my interaction energy per unit area, let me denote it as $E_p ua$, per unit area. E of per unit area will be the answer that we found in example number 3. So the answer was:

$$E_{pua} = \eta E$$
$$= \pi \eta^2 \left[\dfrac{-A}{2z^4} + \dfrac{B}{5z^{10}} \right]$$

So we take, we take A to be 15.2, B to be 24100. These are typical values of graphene sheet interaction and what we find is the following. We find that η is the same as in example 3 that we have discussed few minutes back. Now, how can we find the equilibrium spacing between the two sheets, the static equilibrium? By minimizing the force, or finding the force or minimizing the energy. So, nature is going to provide us with the equilibrium when the energy of interaction is minimum.

So, it turns out that the equilibrium spacing between given by P_{vdw} is denoted as the the derivative of the energy, E_{pua} with respect to Z and set equal to 0. From here I get that my equilibrium spacing Z_0 turns out to be $(B/A)^{1/6}$, and that comes out to be 3.41 Angstrom. Now what is the issue here? The issue is that experimentally the values that are reported by these physical chemists, that is on the equilibrium spacing of these sheets is slightly lower. So experimentally, Z_0 is reported to be equal to 3.35 Angstrom. Although close but it is different than the values that we have found through our model. So, this question that is asked is where is the discrepancy in our model? And the discrepancy lies in the structure of graphene itself. We know that graphene has parallel sheets which are almost

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equidistant apart. So, which means that any point on one sheet of grapheme, not only interacts with its nearest graphene sheet but also interacts with all the other graphene sheets which are at distance Z, 2Z, 3Z, 4Z and so on so forth. So, we must include all those other graphene sheets which are at a larger and larger distance away from the sheet under consideration. So, this is the issue that I want to highlight.

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So, the reason for the discrepancy is that graphite atoms interact not only with its nearest neighbor but with all other planes. So which means that we have to incorporate the effect of all other graphite sheets that we have ignored which are lying parallel to each other. So the new model in our graphene structure is, we assume that there exists an infinite sheet such that the number of planes are all separated by the same distance. Let me call this distance as Z. So, one sheet is separated from the central sheet by Z, the other also by Z and so on so forth. So, if we were to find the total distance they become Z, 2Z, 3Z and so on so forth. So, which means that my total interaction energy will be the sum of each of these plates. So, that becomes:

$$E = 2\pi\eta^2 \sum_{n=1}^{\infty} \left[\frac{-A}{2(nz)^4} + \frac{B}{5(nz)^{10}} \right]$$

Notice that we are summing up the same quantity that we had introduced in our previous expression. I have replaced by Z, 2Z, 3Z and so forth, so on so forth. So inside the sum I have the same expression at different distances and outside I have also introduced a factor of 2 because each sheet interacts with the sheet above and below. So, the 2 is to take into account the sheet interaction above it and below

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it. Otherwise, we have to sum n from minus infinity to plus infinity. So, then this particular summation becomes:

$$= 2\pi\eta^2 \left[\frac{-A}{2(z)^4} \sum_{n=1}^{\infty} \frac{1}{n^4} + \frac{B}{5(z)^{10}} \sum_{n=1}^{\infty} \frac{1}{n^{10}} \right]$$

Notice that this particular summation is a famous Riemann Zeta function evaluated for n equal to, for 4 and the second summation is the the Zeta function evaluated at 10, where

$$\sum \frac{1}{n^m} = \zeta(m), \text{i.e. Riemann zeta function}$$

Also, $\quad \zeta(4) = \frac{\pi^4}{90}; \quad \zeta(10) = \frac{\pi^{10}}{93555}$

So again, I have picked up the handbook of mathematical functions and found out these values. Now finally, when we differentiate this interaction energy with respect to Z and set it equal to 0, I see that my Z_0 this time is going to be

$$Z_0 = \left[\frac{B}{A} \frac{\zeta(10)}{\zeta(4)} \right]^{1/6}$$

And this gives me after plugging in all the values for B, A as described previously, this gives me Z_0 to be 3.37 Angstrom. Notice how close is this value to our, to the experimentally reported value. So it turns out that the model had to incorporate certain additional term to realistically simulate the experiments. So I am going to continue my discussion on the modeling of the oscillatory motion of carbon nano rods in my next lecture by slowly building up this example. And towards the end of the next lecture, I am going to look at the variational form or the Hamilton's formulation of the oscillatory motion of carbon nano rods. So thank you very much for listening. Thanks a lot.

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