Optimal Functions and Nanomechanics III

APP MTH 3022/7106

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Lecture 15

Last lecture

- Looked at formulations of the Lennard-Jones potential
- Applied this to the problem of calculating the interlayer spacing in graphene
- Reviewed surface integration basics
- Began calculating the interaction potential for a carbon nanotube and an interior point.

Reminder

To recap we have Thus the interaction energy between the point and the cylinder E_c is given by

$$E_c = \eta_c b \left(-AK_3 + BK_6\right),$$

where η_c is the atomic surface density of the cylinder and

$$K_n = \int_{-\infty}^{\infty} \int_{-\pi}^{\pi} \frac{d\theta\, dz}{[(b-\delta)^2 + z^2 + 4b\delta \sin^2(\theta/2)]^n}.$$

And we determined this was

$$K_n = \frac{\pi^2 (2n-2)!}{2^{2n-3}[(n-1)!]^2 (b-\delta)^{2n-1}} F\left(n - \frac{1}{2}, \frac{1}{2}; 1; -\frac{4b\delta}{(b-\delta)^2}\right).$$

At this point we can simplify the expression a little more by making use of a quadratic transformation

$$F(a,b;2b;z) = \left[\frac{1+(1-z)^{1/2}}{2}\right]^{-2a} \times F\left(a, a-b+\frac{1}{2}; b+\frac{1}{2}; \left[\frac{1-(1-z)^{1/2}}{1+(1-z)^{1/2}}\right]^2\right). \quad (1)$$

Although the right hand side of this expression looks horrendous we note that for $z = -4b\delta/(b-\delta)^2$ then the term $(1-z)^{1/2} = (b+\delta)/(b-\delta)$ which simplifies things immensely. So that

$$F\left(n-\frac{1}{2}, \frac{1}{2}; 1; -\frac{4b\delta}{(b-\delta)^2}\right) = \left(\frac{b-\delta}{b}\right)^{2n-1} F\left(n-\frac{1}{2}, n-\frac{1}{2}; 1; \frac{\delta^2}{b^2}\right).$$

So the integral K_n is given by

$$K_n = \frac{\pi^2(2n-2)!}{2^{2n-3}[(n-1)!]^2 b^{2n-1}} F\left(n-\frac{1}{2}, n-\frac{1}{2}; 1; \frac{\delta^2}{b^2}\right),$$

and therefore the total energy for the interaction of the point with a cylinder E_c is given by

$$E_c = \frac{3\pi^2\eta_c}{4b^4}\left[-AF\left(\frac{5}{2}, \frac{5}{2}; 1; \frac{\delta^2}{b^2}\right) + \frac{21B}{32b^6} F\left(\frac{11}{2}, \frac{11}{2}; 1; \frac{\delta^2}{b^2}\right)\right].$$

This is a succinct result but remember at this stage we have only calculated the interaction of a cylinder with a point and now we must handle the second cylinder.

Now we consider a cylinder inside of the first cylinder where the inner cylinder is parametrically given by $(\epsilon + b_1 \cos\theta_1, b_1 \sin\theta_1, z_1)$ where $-\pi < \theta_1 \leqslant \pi$ and $-\infty < z_1 < \infty$.

If we were to calculate the total interaction energy, because the two cylinder are infinite in extent we would not get a finite result. What we do instead is to consider a single ring around inner cylinder which gives the interaction energy *per unit length*. To perform this calculation z_1 is arbitrary and so we take $z_1 = 0$ for convenience and we note the line element is $\mathrm{d}\ell = b_1\,\mathrm{d}\theta_1$. So the energy for two cylinders E_{cc}, radius b_1, b_2 is given by

$$\begin{aligned} E_{cc} &= \eta_c \int_{-\pi}^{\pi} E_c b_1\,\mathrm{d}\theta_1 \\ &= \frac{3\pi^2\eta_c^2 b_1}{4b_2^4}\left(-AL_5 + \frac{21B}{32b_2^6}L_{11}\right), \end{aligned}$$

where L_n is given by

$$L_n = \int_{-\pi}^{\pi} F\left(\frac{n}{2}, \frac{n}{2}; 1; \frac{\delta^2}{b_2^2}\right) \mathrm{d}\theta_1,$$

Now we make use of the series expansion of the hypergeometric series and in doing so we note that the argument $0 \leqslant \delta^2/b_2^2 < 1$ and thus the expansion is absolutely convergent hence L_n can be expressed as

$$L_n = \int_{-\pi}^{\pi} \sum_{k=0}^{\infty} \frac{(n/2)_k (n/2)_k}{(1)_k k!} \frac{\delta^{2k}}{b_2^{2k}} \mathrm{d}\theta_1$$

$$L_n = \sum_{k=0}^{\infty} \left(\frac{(n/2)_k}{k! b_2^k}\right)^2 \int_{-\pi}^{\pi} \delta^{2k} \mathrm{d}\theta_1,$$

where

$$\begin{aligned} \delta^2 &= (\epsilon + b_1 \cos\theta_1)^2 + b_1^2 \sin^2\theta_1 \\ &= (b_1 + \epsilon)^2 - 4\epsilon b_1 \sin^2(\theta_1/2). \end{aligned}$$

Now considering the final integral

$$\begin{aligned}\int_{-\pi}^{\pi} \delta^{2k} \mathrm{d}\theta_1 &= \int_{-\pi}^{\pi} \left[(b_1+\epsilon)^2 - 4\epsilon b_1 \sin^2(\theta_1/2)\right]^k \mathrm{d}\theta_1 \\ &= 2\int_{0}^{\pi} \left[(b_1+\epsilon)^2 - 4\epsilon b_1 \sin^2(\theta_1/2)\right]^k \mathrm{d}\theta_1 \\ &= 2\int_{0}^{1} t^{-1/2}(1-t)^{-1/2} \left[(b_1+\epsilon)^2 - 4\epsilon b_1 t\right]^k \mathrm{d}t \\ &= 2(b_1+\epsilon)^{2k} \int_{0}^{1} t^{-1/2}(1-t)^{-1/2} \left(1 - \frac{4\epsilon b_1}{(b_1+\epsilon)^2} t\right)^k \mathrm{d}t,\end{aligned}$$

which is again a hypergeometric function with $a = -k$, $b = 1/2$, $c = 1$ and $z = 4\epsilon b_1/(b_1+\epsilon)^2$. Hence

$$\int_{-\pi}^{\pi} \delta^{2k} \mathrm{d}\theta_1 = 2\pi(b_1+\epsilon)^{2k} F\left(-k, \frac{1}{2}; 1; \frac{4\epsilon b_1}{(b_1+\epsilon)^2}\right).$$

We can again apply the quadratic transformation (1) from a few slides ago which simplifies the expression to

$$\int_{-\pi}^{\pi} \delta^{2k} \mathrm{d}\theta_1 = 2\pi b_1^{2k} F\left(-k, -k; 1; \frac{\epsilon^2}{b_1^2}\right),$$

hence

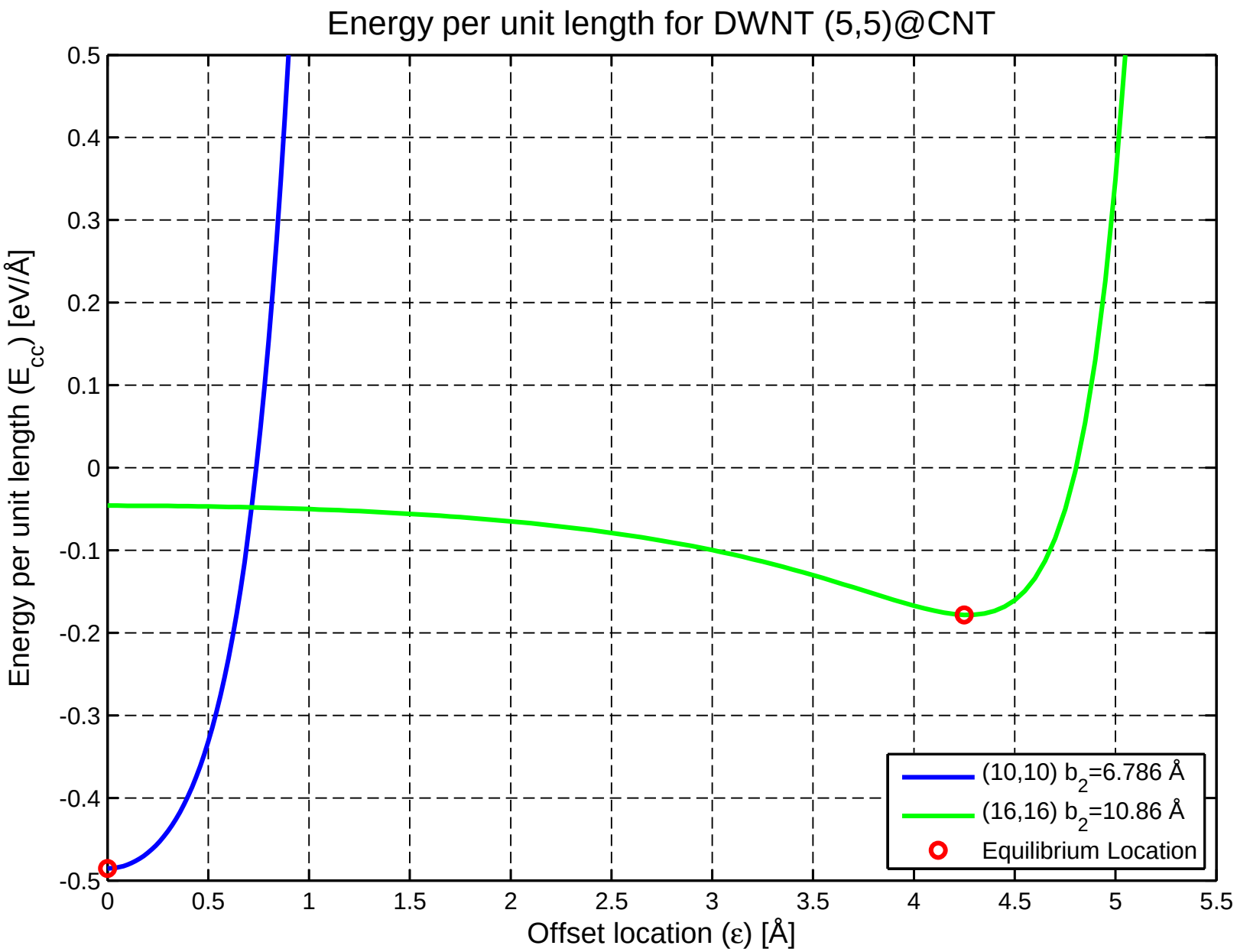
$$L_n = 2\pi \sum_{k=0}^{\infty} \left(\frac{(n/2)_k}{k!}\right)^2 \left(\frac{b_1}{b_2}\right)^{2k} F\left(-k, -k; 1; \frac{\epsilon^2}{b_1^2}\right),$$

and finally we just comment that this last hypergeometric function may be represented as a terminating series since a is a negative integer. Hence we may write

$$F\left(-k, -k; 1; \frac{\epsilon^2}{b_1^2}\right) = \sum_{j=0}^{k} \left(\frac{(-k)_j}{j!}\right)^2 \left(\frac{\epsilon}{b_1}\right)^{2j}.$$

Again we can now calculate the strength of the interaction per unit length between two carbon nanotubes, but the offset distance ϵ means we can also find the equilibrium location for the inner nanotube.

On the next slide we plot the energy per unit length E_{cc} for a $(5,5)$ inner nanotube ($b_1 = 3.393$ Å) interacting with a $(10,10)$ and a $(16,16)$ outer carbon nanotube. We see that the nanotube prefers to lie on the axis of the $(10,10)$ nanotube but prefers to adopt a location approximately 4.271 Å off-axis of the $(16,16)$ tube.


Energy per unit length for DWNT (5,5)@CNT
Energy per unit length (E_{cc}) [eV/Å]
Offset location (ε) [Å]
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
(10,10) b_2=6.786 Å
(16,16) b_2=10.86 Å
Equilibrium Location

Nanotube@Nanotube Oscillator

In this device a double-walled nanotube starts with its inner nanotube extruded by some distance d out of the fixed, open ended, outer carbon nanotube. In this case the excess van der Waals force sucks the inner nanotube back into the nanotube. As in the fullerene@nanotube oscillator there is a reversal of direction at the opposite end of the outer nanotube which returns the oscillating inner nanotube to its starting location and the process then repeats.

We want to know for a particular double-walled nanotube

- Will the inner nanotube be sucked in to the outer nanotube? (acceptance condition)
- How much energy will be picked up by the oscillating nanotube? (suction energy)
- What will be the oscillatory frequency?

Model simplification

It turns out that the DWNT oscillator can be solved exactly without the following simplification, however the integrals are quite messy and they do not add much except some minor "edge effects" in most cases. Therefore for the purposes of the remainder of this section we will assume that the two nanotubes only interact along the section of the inner nanotube that is nested. That is the part of the inner nanotube that it actually inside the other tube.

The section of inner nanotube which is outside (or extruded) from the outer nanotube is assumed to not contribute to the interaction.

Furthermore, we will assume that the section of the tube which is inside the nanotube interacts as if it was inside an infinite carbon nanotube.

Acceptance Condition

In the case of the extruded inner nanotube the question is simply is the nanotube energetically favoured to be inside the outer carbon nanotube.

This question has already been addressed when we looked at the interaction energy per unit length of offset nanotubes E_{cc}. To simplify the analysis of the oscillator we will further assume that the two nanotubes are coaxial. So with reference to the expression for the interaction energy per unit length we have $\epsilon = 0$. Another way of thinking about this is we can use the expression for the interaction for a cylinder and a point E_c and multiply it by the circumference of the inner nanotube and the surface density of atoms for the inner nanotube.

Both methods result in the same expression for the interaction energy per unit length for coaxial nanotubes $E^{\star}_{cc}$, given by

$$E^{\star}_{cc} = \frac{3\pi^3 b_1 \eta_c^2}{2b_2^4}\left[-AF\left(\frac{5}{2},\frac{5}{2};1;\frac{b_1^2}{b_2^2}\right)+\frac{21B}{32b_2^6}F\left(\frac{11}{2},\frac{11}{2};1;\frac{b_1^2}{b_2^2}\right)\right],$$

where b_1, b_2 are the radii of the two nanotubes and η_c is the atomic surface density for the nanotubes.

So for any two nanotubes with radii b_1 and b_2 we can calculate the interaction energy per unit length $E^{\star}_{cc}$. If $E^{\star}_{cc} > 0$ then the inner tube is too large to be accepted by the outer tube and the inner tube will not be sucked back into the outer nanotube. In fact it will be pushed out by van der Waals interactions alone.

Suction Energy

Given the model simplifications outlined a few slides ago the question of suction energy is simply the difference in energy between the extruded nanotube and the fully encapsulated nanotube. We already have the interaction energy per unit length, given by $E^{\star}_{cc}$ and since the extrusion length d forms a part of our initial conditions, then the suction energy W is given by

$$W = -E^{\star}_{cc} d.$$

Or another way of thinking about this is that the energy gained by the inner tube being sucked back into the nanotube is equivalent to the work done in extruding the inner nanotube in the first place. This is simply a statement of conservation of energy.

Oscillatory Dynamics

We now have to consider nanotubes which are finite in length. So assuming with have a fixed outer tube of length $2L_2$ and an oscillating inner nanotube of length $2L_1$, where we assume $L_2 \geqslant L_1$.

Now we arrange out coordinate system so that the tubes axes are collinear with the z axis and the centre of the outer tube is located at the origin. This means the ends of the fixed outer nanotube are at the position $z = \pm L_2$.

Finally, we denote the centre of the oscillating inner nanotube is at the location $z = Z$. This places the ends of the inner nanotube at $z = Z \pm L_1$.

Location of the Inner Nanotube

There are, at most, five states that the inner nanotube can adopt.

1. $Z < -L_1 - L_2$, inner tube is fully extruded in the negative z-direction.
2. $-L_1 - L_2 < Z < L_1 - L_2$, inner tube is partly extruded in the negative z-direction.
3. $L_1 - L_2 < Z < -L_1 + L_2$, inner tube is entirely contained in the outer nanotube.
4. $-L_1 + L_2 < Z < L_1 + L_2$, inner tube is partly extruded in the positive z-direction.
5. $Z > L_1 + L_2$, inner tube is fully extruded in the positive z-direction.

An understanding of the four cutoff points, $Z = \pm L_1 \pm L_2$, is critical.

Interaction Energy

So taking the fully extruded state as the zero energy level, then as the tube moves from the full extruded state (1) to the fully enclosed state (3) the total potential energy E_{cc} increases by the interaction energy per unit length $E^{\star}_{cc}$ times the length of the interaction $L_1 + L_2 + Z$, that is

$$E_{cc} = (L_1 + L_2 + Z)E^{\star}_{cc}, \quad \text{for state (2),}$$

Up to a maximum when $Z = L_1 - L_2$ of $E_{cc} = 2L_1E^{\star}_{cc}$. Likewise as the tube moves from the fully enclosed state (3) to the fully extruded to the right state (5) then the potential energy is given by

$$E_{cc} = (L_1 + L_2 - Z)E^{\star}_{cc}, \quad \text{for state (4).}$$

For states (1) and (5), $E_{cc} = 0$ and for state (3), $E_{cc} = 2L_1E^{\star}_{cc}$.

This can be expressed in a single equation using the Heaviside unit step function $H(x)$ which is defined as

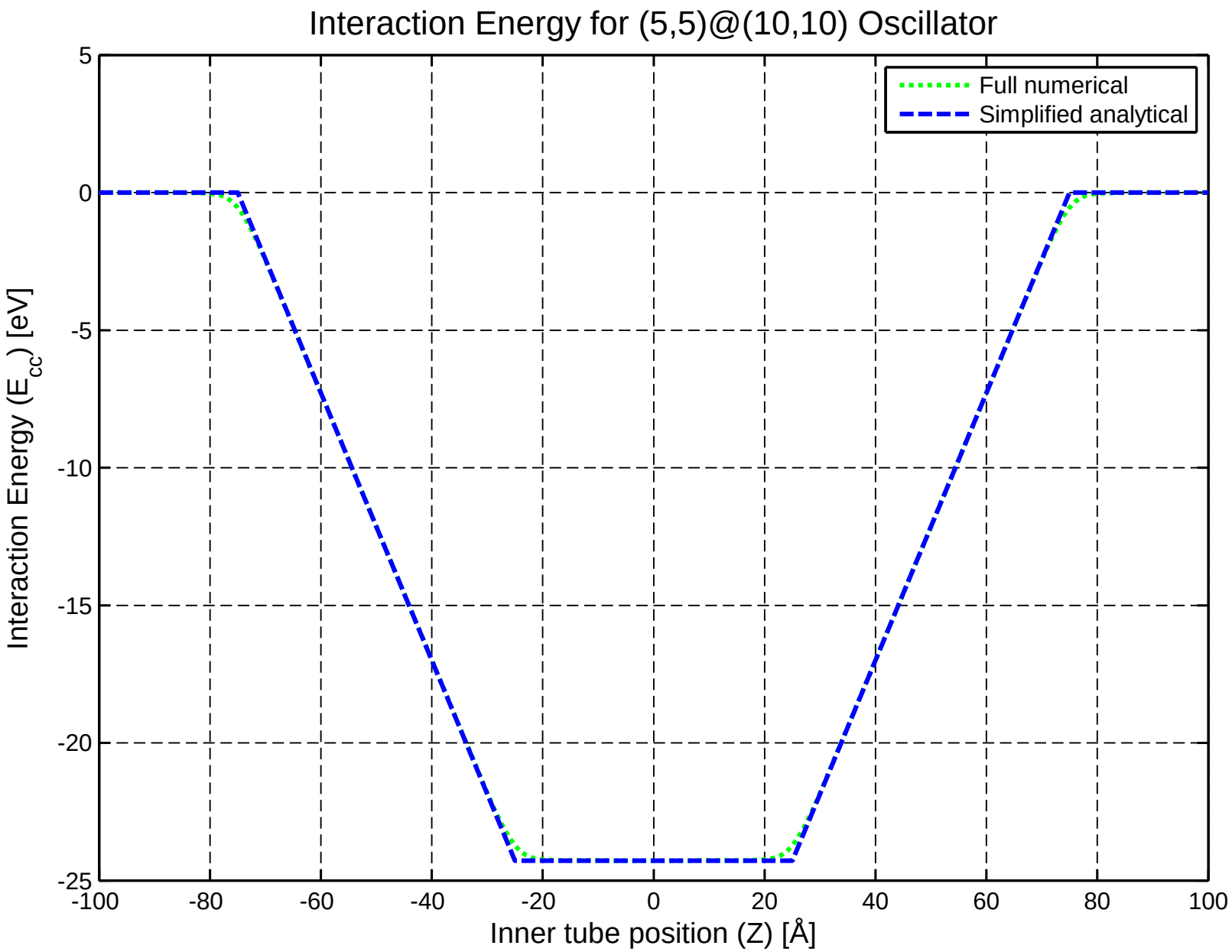
$$H(x) = \begin{cases} 0, & x < 0, \\ 1, & x > 0, \end{cases}$$

and using which E_{cc} is given by

$$E_{cc} = E_{cc}^{\star} \left[(Z + L_+)H(Z + L_+) - (Z + L_-)H(Z + L_-) \right.$$
$$\left. -(Z - L_-)H(Z - L_-) + (Z - L_+)H(Z - L_+) \right],$$

where $L_+ = L_2 + L_1$ and $L_- = L_2 - L_1$.

For $b_1 = 3.393$ Å, $b_2 = 6.786$ Å, $L_1 = 25$ Å, and $L_2 = 50$ Å, we obtain the following energy profile.


Interaction Energy for (5,5)@(10,10) Oscillator
Full numerical
Simplified analytical
Interaction Energy (E_{cc}) [eV]
Inner tube position (Z) [Å]
5
0
-5
-10
-15
-20
-25
-100
-80
-60
-40
-20
0
20
40
60
80
100

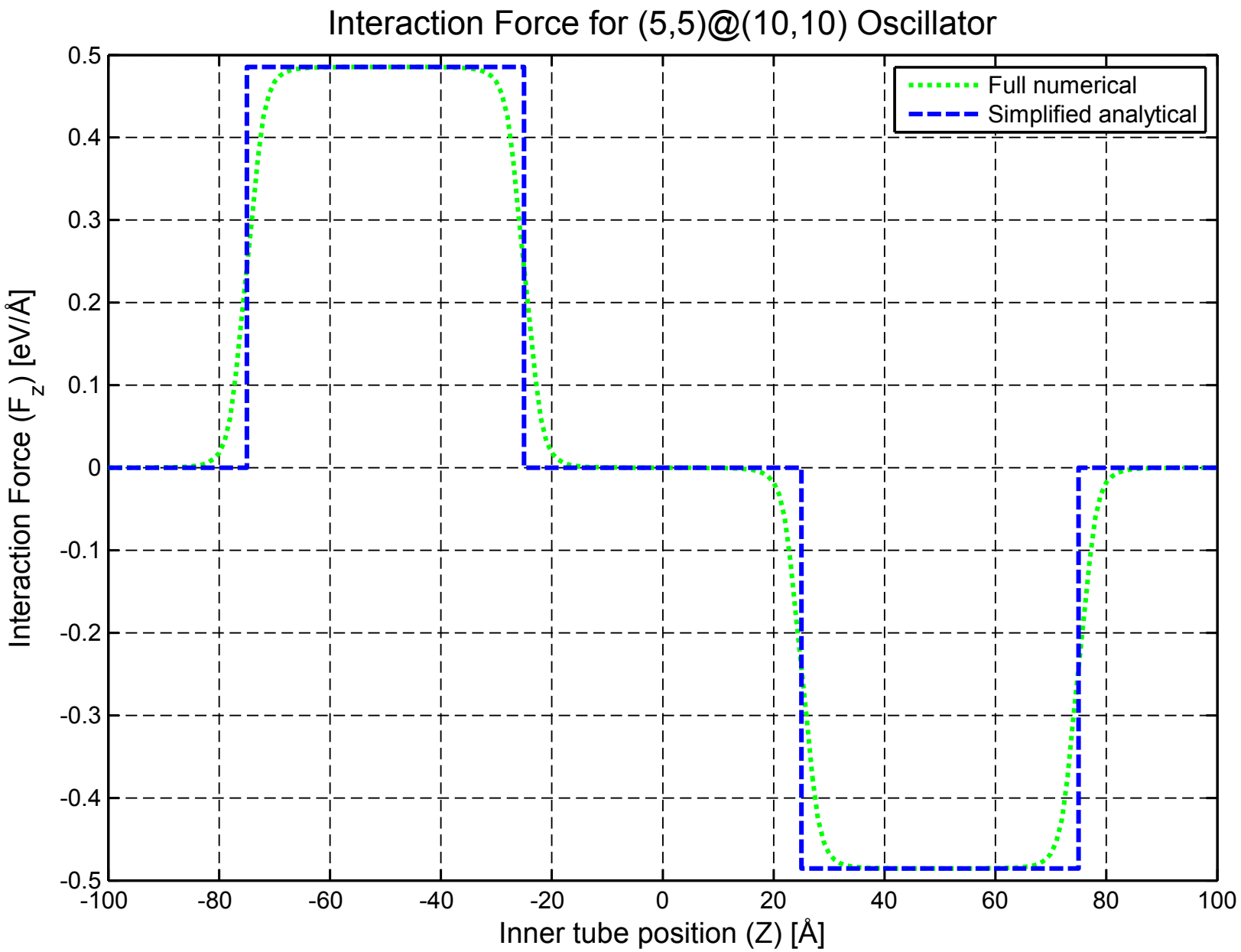
Interaction Force

As usual the force is the derivative of the energy so in an axially symmetric system $F_z = -\partial E_{cc}/\partial z$ and therefore the force is given by

$$F_z = -E^{\star}_{cc}\left[H(Z+L_+) - H(Z+L_-) \right. \\ \left. -H(Z-L_-) + H(Z-L_+)\right],$$

which equates to a force of magnitude $|E^{\star}_{cc}|$ acting to suck the inner nanotube back into the outer tube.

This is plotted for the same system as that of the previous slide.


Interaction Force for (5,5)@(10,10) Oscillator
Full numerical
Simplified analytical
Interaction Force (F_z) [eV/Å]
Inner tube position (Z) [Å]
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-100
-80
-60
-40
-20
0
20
40
60
80
100