Optimal Functions and Nanomechanics III
APP MTH 3022/7106

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Lecture 14

Last lecture

- Introduced Appell's hypergeometic function $F_1(a; b, b'; c; x, y)$
- and Elliptic integrals $F(\varphi, k)$ and $E(\varphi, k)$
- Compared the discrete and Continuum approach to modelling intra-molecular interactions
- Introduced van der Waals interactions and the modelling of these using the Lennard-Jones potential

Lennard-Jones potential

The Lennard-Jones potential describes the interaction between two non-bonded atoms and is given by

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

where A and B are referred to as the attractive and repulsive constants, respectively, and ρ is the distance between the atoms.

In many cases the values $m = 6$ and $n = 12$ are adopted, and this is commonly referred to as the 6-12 potential. For hydrogen bonding interactions a 10-12 potential is used and it should be noted that there are a number of other empirically motivated potentials in the literature, such as the Morse potential.
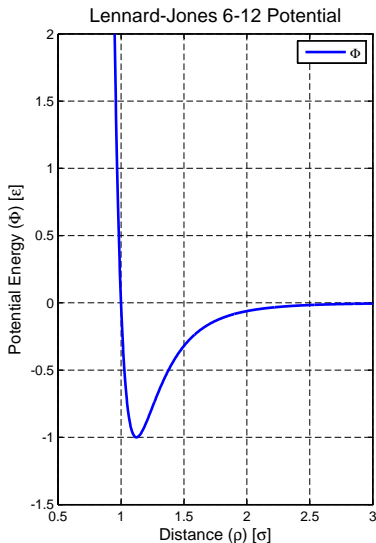
6-12 potential - Alternative formulation

Alternatively, the Lennard-Jones 6-12 potential can be written in the form

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

where σ is the van der Waals distance and ϵ denotes the energy well depth. This form of the potential is related to the that on the previous slide by the expressions

$$\sigma = \left(\frac{B}{A}\right)^{1/6}, \quad \epsilon = \frac{A^2}{4B}.$$

Lennard-Jones 6-12 Potential

Modelling considerations

The van der Waals force is a short-range force, and therefore on using the Lennard-Jones potential to represent the interaction between molecular structures it is only necessary to include the nearest neighbour interactions. For example, investigating the behaviour of a molecule near the open end of a carbon nanotube we can for this purpose consider the tube to be semi-infinite in length.

The Lennard-Jones potential is applied between non-bonded (i.e. atoms on separate molecules) and non-polar (i.e. non-electrostatic) atomic interactions and has been successfully applied to a number of carbon nanostructures. For example, two identical parallel carbon nanotubes, between two C_{60} fullerenes, and between a carbon nanotube and C_{60} (both inside and outside the tube).

Parameters for carbonaceous systems

Numerical values of the Lennard-Jones constants for carbon-carbon atoms and atoms in graphene-graphene, C_{60}-C_{60} and C_{60}-graphene are shown in the following table.

	A	B	ϵ	σ
	[eV·Å^6]	[eV·Å^{12}]	[eV]	[Å]
carbon-carbon	20.0	34 800	0.00286	3.47
carbon-graphene	17.4	29 000	0.00261	3.44
graphene-graphene	15.2	24 100	0.00240	3.41

These values have been determined empirically.

Example 2

Calculate the interaction energy E and the van der Waals force $\boldsymbol{F_{vdW}}$ for a single carbon atom a perpendicular distance z from an infinite graphene sheet.

Solution: With reference to a Cartesian system of coordinate and without loss of generality we can position the graphene on the xy-plane $(x, y, 0)$ and give the carbon atom a coordinate $(0, 0, z)$. The the distance between the atom and a typical point on the plane is given by

$$\rho = (x^2 + y^2 + z^2)^{1/2}.$$

So applying the continuum approach the interaction energy is given by

$$E = \eta \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} -\frac{A}{(x^2 + y^2 + z^2)^3} + \frac{B}{(x^2 + y^2 + z^2)^6} \, dx \, dy.$$

Example 2

We rewrite this as

$$E = \eta(-AI_3 + BI_6), \quad I_n = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{dx\, dy}{(x^2 + y^2 + z^2)^n}.$$

As η, A and B are given we just need to evaluate the integral I_n for $n \in \{3, 6\}$.

In this case the integral is most easily handled by changing to polar coordinates, that is we make the substitution $x = r\cos\theta$, $y = r\sin\theta$, which means $x^2 + y^2 = r^2$ and $dx\, dy = r\, dr\, d\theta$. This gives

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

$$= 2\pi \left[-\frac{1}{2(n-1)(r^2 + z^2)^{n-1}} \right]_0^{\infty} = \frac{\pi}{(n-1)z^{2n-2}}.$$
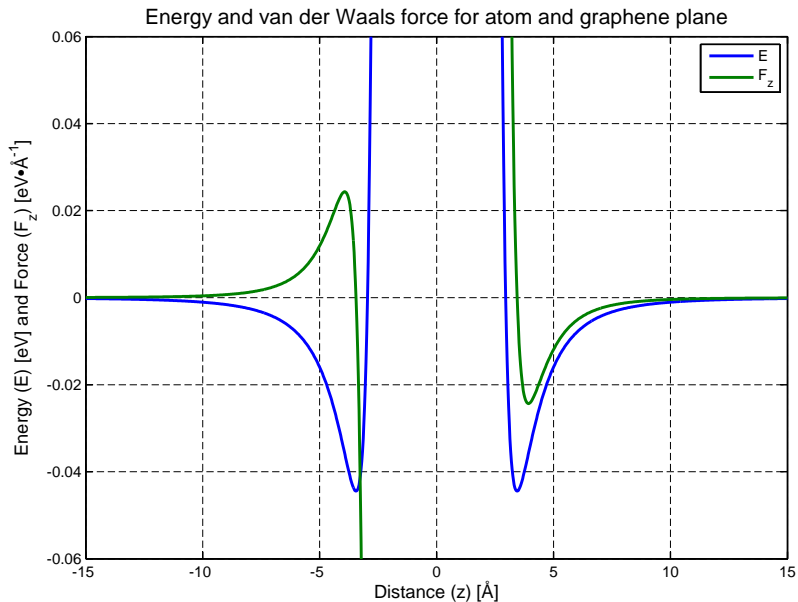
Example 2

Substituting back in the expression for E we obtain

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

To calculate the force acting on the atom we use $\boldsymbol{F_{vdW}} = -\nabla E$, and since E is independent of x and y, we only need to consider a force acting in the z-direction F_z.

$$F_z = -\frac{\partial E}{\partial z} = \pi\eta \left(-\frac{4A}{2z^5} + \frac{10B}{5z^{11}} \right) = 2\pi\eta \left(-\frac{A}{z^5} + \frac{B}{z^{11}} \right).$$

If we use $A = 17.4$ eV·Å^6, $B = 29\,000$ eV·Å^{12} and $\eta = 0.3812$ atoms·Å^{-2}, we can graph the interaction energy and van der Waals force for an atom some distance z from a flat plane of graphene.

Energy and van der Waals force for atom and graphene plane

Example 3

What is the interaction energy for two parallel infinite planes of graphene at some separation distance z?

Solution: This problem can be conceptualised as the previous problem applied to every atom in the second plane of graphene interacting with the first plane. If the planes are truly infinite the interaction energy would also be an infinite sum of a non-vanishing term and therefore infinite.

Example 3

However we can calculate an interaction energy per unit area. The number of atoms per unit area is given by η and each atom would interact individually with the other plane (as per the last example). Therefore the interaction energy per unit area (E_{pua}) is given by

$$E_{pua} = \pi\eta^2 \left(-\frac{A}{2z^4} + \frac{B}{5z^{10}} \right),$$

although here we would use $A = 15.2$, $B = 24\,100$ (the values for graphene-graphene).

Interaction Energy per unit area for two graphene planes
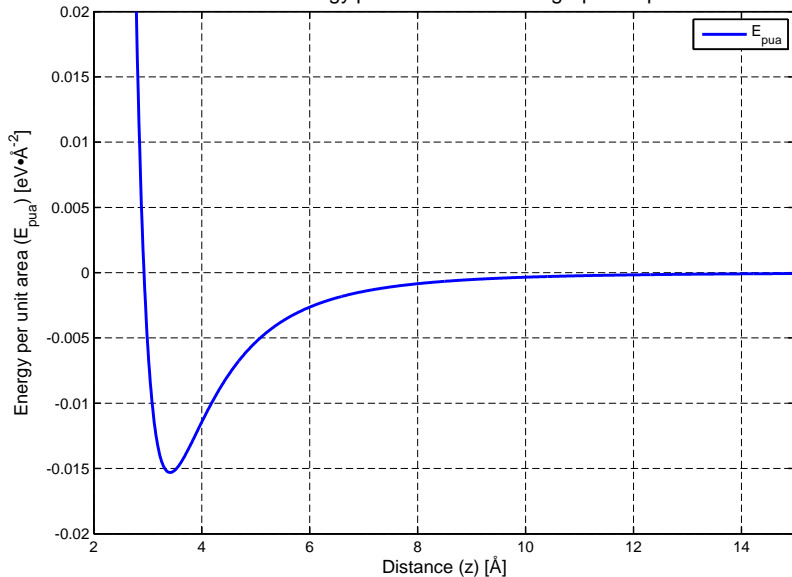
Equilibrium spacing

All other things being equal two molecules will tend to be found at the distance which minimises their interaction energy. This is equivalent to the location where the van der Waals force is equal to zero since this is the derivative of the energy and the derivative at an extremum is zero.

In the case of the previous example of two graphene planes the van der Waals pressure P_{vdW} (force per unit area) is

$$P_{vdW} = -\frac{\partial E_{pua}}{\partial z} = 2\pi\eta^2 \left(-\frac{A}{z^5} + \frac{B}{z^{11}} \right),$$

Solving $P_{vdW} = 0$ we find the equilibrium spacing z_0 is given by

$$z_0 = \left(\frac{B}{A} \right)^{1/6} = \sigma.$$

Equilibrium spacing

With reference to the table given earlier this means $z_0 = 3.41$ Å. However earlier we said that the interlayer spacing in graphite is approximately 3.35 Å. Is there a reason for this discrepancy?

The answer is yes. In graphite each plane not only interacts with its nearest neighbour but with all planes in the graphite. To model this we may assume there is an infinite number of planes all separated by the same distance z. Then the total interaction energy per unit area for each plane is given by

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

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

Equilibrium spacing in graphite

Now for $m > 1$, $\sum_{n=1}^{\infty} n^{-m} = \zeta(m)$, the Riemann zeta function. Thus

$$E_{pua} = 2\pi\eta^2 \left(-\frac{A\zeta(4)}{2z^4} + \frac{B\zeta(10)}{5z^{10}} \right).$$

Minimising the van der Waals energy per unit area we obtain

$$z_0 = \left(\frac{B\zeta(10)}{A\zeta(4)} \right)^{1/6} = \sigma \left(\frac{\zeta(10)}{\zeta(4)} \right)^{1/6},$$

and it is known that $\zeta(4) = \pi^4/90$ and $\zeta(10) = \pi^{10}/93555$. Therefore in bulk graphite the interlayer spacing is $z_0 = 3.37$ Å, which is closer to the experimentally obtained value of 3.35 Å.

Recap on scalar surface integration

When performing the integration of a scalar quantity, like $\Phi(\rho)$, over a surface $\mathcal{S}$ we do this in three steps.

1. Select an appropriate parameterisation of $\mathcal{S}$ in terms of two variable, say u, and v.

2. Calculate the area element dA from the parameterisation

3. Evaluate the double integral

$$\int_{v_0}^{v_1} \int_{u_o}^{u_1} \Phi(\rho(u,v)) \, dA.$$

Selecting a parameterisation

The surface integrals we will be dealing with in this course will be two-dimensional surfaces embedded in three-dimensional space. This means there will be a two variable parametersation which can be expressed as a vector of dimension three which can be considered a position vector $\boldsymbol{r}$ for a point on the surface. Some common examples are

The $x - y$ plane : $\boldsymbol{r} = (u, v, 0)\,, \quad -\infty < u, v < \infty$

Sphere of radius a : $\boldsymbol{r} = (a \cos u \sin v, a \sin u \sin v, a \cos v)\,,$
    $-\pi < u \leqslant \pi, \quad 0 \leqslant v \leqslant \pi$

Cylinder of radius b : $\boldsymbol{r} = (b \cos u, b \sin u, v)\,,$
    $-\pi < u \leqslant \pi, \quad -\infty < v < \infty$

Calculating the area element dA

The first thing to consider is the tangent vectors in the direction of the two parametric variables u and v. These are given by the partial derivatives of position vector $\boldsymbol{r}$ taken with respect to those variables. So the tangent in the u direction is $\partial \boldsymbol{r}/\partial u$ and similarly the tangent in the v direction is $\partial \boldsymbol{r}/\partial v$.

With these tangents known it is now a matter of determining the area of the parallelogram whose two sides are these tangent vectors. Recalling that the area of this parallelogram is given by the magnitude of the cross product of the two vectors forming the sides.

Putting this together we have the following formula

$$dA = \left| \frac{\partial \boldsymbol{r}}{du} \times \frac{\partial \boldsymbol{r}}{dv} \right| du\, dv.$$

Example 4

Determine the area element dA for the cylindrical surface given by $\boldsymbol{r} = (b \cos u, b \sin u, v)$.

Solution: First we determine the tangent vectors

$$\boldsymbol{r}_u = (-b \sin u, b \cos u, 0),$$
$$\boldsymbol{r}_v = (0, 0, 1).$$

Then working out the cross product

$$\boldsymbol{r}_u \times \boldsymbol{r}_v = \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ -b \sin u & b \cos u & 0 \\ 0 & 0 & 1 \end{vmatrix} = (b \cos u, b \sin u, 0),$$

and so (assuming $b > 0$) the area element dA is given by

$$dA = |\boldsymbol{r}_u \times \boldsymbol{r}_v| \, du \, dv = b \, du \, dv.$$

Example 4

Determine the surface area for the spherical surface given by
$\boldsymbol{r} = (a \cos u \sin v, a \sin u \sin v, a \cos v)$.

Solution: Differentiating to find the tangent vectors

$$\boldsymbol{r}_u = (-a \sin u \sin v, a \cos u \sin v, 0),$$
$$\boldsymbol{r}_v = (a \cos u \cos v, a \sin u \cos v, -a \sin v).$$

Then working out the cross product

$$\boldsymbol{r}_u \times \boldsymbol{r}_v = \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ -a \sin u \sin v & a \cos u \sin v & 0 \\ a \cos u \cos v & a \sin u \cos v & -a \sin v \end{vmatrix}$$
$$= (-a^2 \cos u \sin^2 v, -a^2 \sin u \sin^2 v, -a^2 \sin v \cos v),$$

Example 4

and so, noting that $\sin v \geqslant 0$ for $v \in [0, \pi]$, the area element dA is given by

$$dA = |\boldsymbol{r}_u \times \boldsymbol{r}_v| \, du \, dv = a^2 \sin v \, du \, dv.$$

To find the surface area we simply integrate unity over the surface. In this case

$$\text{Area} = \int_0^\pi \int_{-\pi}^\pi a^2 \sin v \, du \, dv.$$

Taking out the constant a^2 and performing the trivial u integral we obtain

$$\text{Area} = 2\pi a^2 \int_0^\pi \sin v \, dv = 2\pi a^2 \left[-\cos v \right]_0^\pi = 4\pi a^2.$$

N.B. in this case the variable part of the area element (namely $\sin v$) is positive throughout the range of v for this surface and so absolute values are not necessary.

Double-walled Carbon Nanotubes (DWCNT)

A double-walled carbon nanotube is simply one carbon nanotube contained within another.

The "@" notation is used to denote the encapsulation from smallest to largest. For example a (5,5)@(10,10) denotes a (5,5) carbon nanotube encapsulated within a (10,10) carbon nanotube.
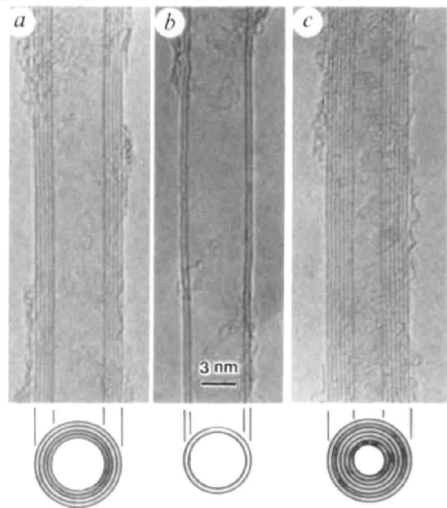
Double-walled Carbon Nanotubes (DWCNT)

Double-walled carbon nanotubes have very similar morphology and properties as compared to single-walled carbon nanotubes, while improving significantly their resistance to chemicals. This is especially important when *functionalisation* is required to add new properties to the carbon nanotubes.

Functionalisation refers to the grafting, by covalent bonds, of chemical functions to the nanotube surface.
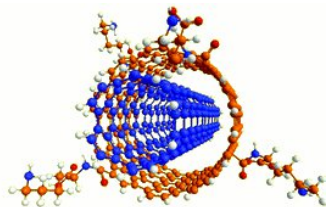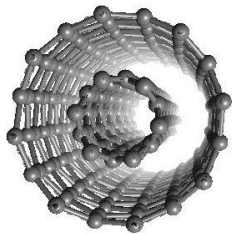
Modelling a double-walled carbon nanotube

We begin by considering the outer nanotube with a radius b which is given parametrically by $(b\cos\theta, b\sin\theta, z)$ interacting with an interior point P given by $(\delta, 0, 0)$. Thus δ is the off-axis distance of the point and since it is interior to the nanotube we require $\delta < b$. Furthermore we are assuming a nanotube of infinite extent, thus $-\pi < \theta \leqslant \pi$, and $-\infty < z < \infty$.
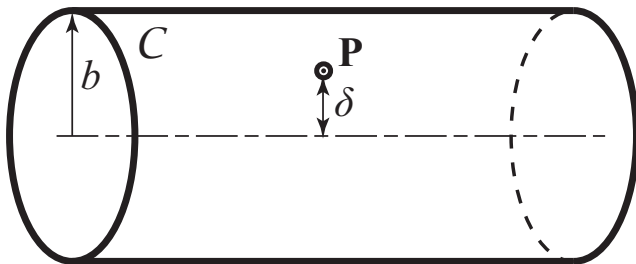
Interaction energy: point with cylinder

So the area element for the cylinder is $dA = b\,d\theta\,dz$, and the distance from the point to the surface of the cylinder ρ, is given by

$$\begin{aligned}
\rho^2 &= (b\cos\theta - \delta)^2 + b^2\sin^2\theta + z^2 \\
&= b^2 + \delta^2 + z^2 - 2b\delta\cos\theta \\
&= (b-\delta)^2 + z^2 + 4b\delta\sin^2(\theta/2).
\end{aligned}$$

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

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

Interaction energy: point with cylinder

We can separate the two integrations by substituting
$\lambda^2 = (b - \delta)^2 + 4b\delta \sin^2(\theta/2)$ and making the change of variable
$z = \lambda \tan \psi$ which gives

$$K_n = \int_{-\pi/2}^{\pi/2} \int_{-\pi}^{\pi} \frac{\lambda \sec^2 \psi \, \mathrm{d}\theta \, \mathrm{d}\psi}{(\lambda^2 + \lambda^2 \tan^2 \psi)^n}$$

$$= \int_{-\pi/2}^{\pi/2} \cos^{2n-2} \psi \, \mathrm{d}\psi \int_{-\pi}^{\pi} \frac{\mathrm{d}\theta}{\lambda^{2n-1}}$$

We showed earlier that the leftmost integral can be written as a
combination of factorial terms, specifically

$$\int_{-\pi/2}^{\pi/2} \cos^{2n-2} \psi \, \mathrm{d}\psi = \frac{\pi(2n-2)!}{2^{2n-2}[(n-1)!]^2}.$$

So all that remains is the θ integral

$$\int_{-\pi}^{\pi} \frac{\mathrm{d}\theta}{\lambda^{2n-1}} = \int_{-\pi}^{\pi} \frac{d\theta}{[(b-\delta)^2 + 4b\delta\sin^2(\theta/2)]^{n-1/2}}.$$

Next we note that the integrand is an even function of θ so the integral for the negative and positive parts of the range of integration are the same thus

$$\int_{-\pi}^{\pi} \frac{\mathrm{d}\theta}{\lambda^{2n-1}} = 2\int_{0}^{\pi} \frac{d\theta}{[(b-\delta)^2 + 4b\delta\sin^2(\theta/2)]^{n-1/2}}.$$

Now we make the substitution $t = \sin^2(\theta/2)$ from which we derive
$\mathrm{d}\theta = t^{-1/2}(1-t)^{-1/2}\mathrm{d}t$, which gives

$$\int_{-\pi}^{\pi} \frac{d\theta}{\lambda^{2n-1}} = 2 \int_0^1 \frac{\mathrm{d}t}{t^{1/2}(1-t)^{1/2}[(b-\delta)^2 + 4b\delta \sin^2(\theta/2)]^{n-1/2}}$$

And after some rearrangement we arrive at

$$\int_{-\pi}^{\pi} \frac{d\theta}{\lambda^{2n-1}} = \frac{2}{(b-\delta)^{2n-1}} \times$$
$$\int_0^1 t^{-1/2}(1-t)^{-1/2}\left(1 + \frac{4b\delta}{(b-\delta)^2}t\right)^{1/2-n} dt.$$

Now this final integral is the Euler integral form of the hypergeometric function, with $a = n - 1/2$, $b = 1/2$, $c = 1$ and $z = -4b\delta/(b - \delta)^2$. So we may write

$$\int_{-\pi}^{\pi} \frac{\mathrm{d}\theta}{\lambda^{2n-1}} = \frac{2}{(b - \delta)^{2n-1}} \frac{\Gamma(b)\Gamma(c - b)}{\Gamma(c)} F(a, b; c; z)$$
$$= \frac{2\pi F(n - 1/2, 1/2; 1; -4b\delta/(b - \delta)^2)}{(b - \delta)^{2n-1}},$$

and so putting this together with the previous integral result

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