

# Study of Some Properties of Graphene by Spring-Mass Model

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## Abstract

In this project, some properties of graphene have been studied by considering its spring-mass model, taking the carbon atoms to be point masses and the  $sp^2$  bonds between them as massless springs. In this regard, some description has also been given of two-dimensional lattices and tiling by regular polygons.

## 1 Introduction

Graphene is a newly discovered two-dimensional allotrope of carbon. It is a one atom thick layer of carbon atoms connected by  $sp^2$  bonds in a honeycomb (hexagonal) arrangement. It can be considered to be a single layer of graphite. It is the basic unit of crystalline allotropes of carbon such as fullerene, graphite and carbon nanotubes.

Graphene has some interesting properties. It is of very low density, but very high mechanical strength. A sheet of graphene is hundred times stronger than a hypothetical iron sheet of the same thickness. This is due to the very strong  $sp^2$  bonds between the carbon atoms. It is also a good conductor of heat and electricity, and its properties are highly anisotropic. The energy-momentum relation shows that electrons in graphene have effective mass zero like photons.

While most of these properties can be studied by experiment and using quantum mechanics, some mechanical properties of graphene can be studied

by considering a spring-mass model of graphene. This has been attempted in this project.

## 2 Regular Tessellation

Tiling or tessellation involves covering a two-dimensional surface by repeating polygons (tiles) of a given shape. Here, we will consider tiling by regular polygons only.

At first, let us consider tiling by one kind of regular polygon. The sum of the internal angles of an  $n$ -sided polygon ( $n$ -gon) is  $(n - 2)\pi$ . Hence, each internal angle of a regular  $n$ -gon will be  $(1 - 2/n)\pi$ . An integral number of these polygons should meet at each vertex to form a total angle of  $2\pi$ . Therefore,

$$\nu = \frac{2\pi}{(1 - \frac{2}{n})\pi} = \frac{2n}{n - 2} \in \mathbb{N} \quad (n \in \mathbb{N}, n \geq 3),$$

where  $\nu$  is the number of polygons meeting at a vertex. For  $2n/(n - 2)$  to be an integer, the denominator must become 1 after cancellation of common factors. If  $n$  and  $(n - 2)$  have a common factor, their difference  $n - (n - 2) = 2$  must also be a multiple of that common factor. This implies that  $n$  and  $(n - 2)$  are mutually prime (if  $n$  is odd), or have common factor 2 (if  $n$  is even). Thus, only three polygons can be used for regular tessellation:

$$\begin{aligned} n - 2 = 1 &\implies n = 3 \text{ (Triangle)}, & \nu = 6; \\ n - 2 = 2 &\implies n = 4 \text{ (Square)}, & \nu = 4; \\ n - 2 = 4 &\implies n = 6 \text{ (Hexagon)}, & \nu = 3. \end{aligned}$$

For regular  $n$ -gons of side-length  $l$ , the perimeter is

$$P = nl,$$

and the area is

$$A = n \times \frac{1}{2} \times l \times \frac{l}{2} \tan \left( \left( \frac{1}{2} - \frac{1}{n} \right) \pi \right) = \frac{nl^2}{4} \tan \left( \left( \frac{1}{2} - \frac{1}{n} \right) \pi \right).$$

Their ratio is

$$\alpha = \frac{A}{P} = \frac{l}{4} \tan \left( \left( \frac{1}{2} - \frac{1}{n} \right) \pi \right).$$

Now,  $\alpha$  exists and  $\frac{d\alpha}{dn} = l \sec^2((1/2 - 1/n)\pi)/8 > 0 \forall n > 1$ . Therefore,  $\alpha$  increases for greater number of sides. Thus between triangle, square and hexagon, hexagon has the maximum area for a given perimeter.

For a two-dimensional lattice with  $N$  atoms and bond length  $l$ , a triangular lattice has about  $3N$  bonds and covers an area of about  $\sqrt{3}Nl^2/2$ . A square lattice will have  $2N$  bonds and will cover an area of  $Nl^2$ , while a hexagonal lattice will have  $3N/2$  bonds and will cover an area of  $3\sqrt{3}Nl^2/4$ . (Here, it is assumed that for polygons having  $n$  sides with  $\nu$  polygons meeting at a vertex, the number of bonds will be  $\nu n/2$ , and the area covered will be  $\nu/N \times$  area of each polygon. the actual number or area is less than this, but the discrepancy is small for a large number of atoms.) For a given number of atoms, the honeycomb arrangement as seen in graphene covers the largest area (and hence lowest surface mass density) and has the smallest number of bonds.

Also, for triangular lattice, each atom must have 6 bonds, which is not possible for carbon. Atoms having vacant  $d$ -orbital (such as sulphur) can exhibit hexavalency by  $sp^3d^2$  hybridization, but only when bonding with highly electronegative elements like fluorine, and the structure is not planar. For square lattice, each atom is tetravalent, which is possible for carbon, but the structure is tetrahedral ( $sp^3$  hybridization) and not square planar. Some coordination complexes may have square planar structures, but such structures will be highly unstable even if they exist. Hexagonal structure as found in graphene is achieved by  $sp^2$  hybridization of the carbon atoms.

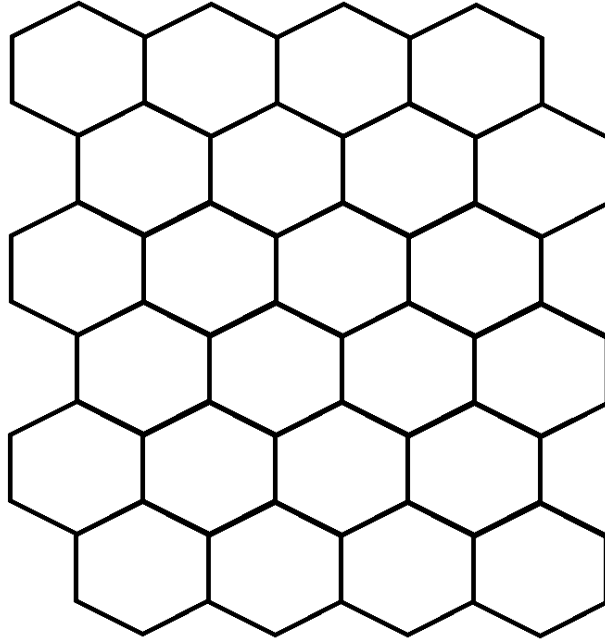


Figure 1: Honeycomb structure of Graphene sheet

We can also consider tilings where two different regular polygons (say

having  $m$  and  $n$  sides,  $m, n \in \mathbb{N}$ ;  $m, n \geq 3$ ;  $m \neq n$ ) have been used. In this case, there will be vertices shared by both kinds of polygons.

Let  $\mu$   $m$ -gons and  $\nu$   $n$ -gons meet at a vertex ( $\mu, \nu \in \mathbb{N}$ ). Then we can say that

$$\begin{aligned} \mu \left(1 - \frac{2}{m}\right) \pi + \nu \left(1 - \frac{2}{n}\right) \pi &= 2\pi \\ \implies \mu \left(1 - \frac{2}{m}\right) + \nu \left(1 - \frac{2}{n}\right) &= 2. \end{aligned}$$

Also, the total number of polygons has to be greater than 2, because the internal angle of any regular polygon is less than  $\pi$ , and hence two polygons will form an angle less than  $2\pi$ . It also has to be less than 6, because a point is completely surrounded by 6 triangles, and triangle has the smallest internal angle among all polygons. Therefore,  $3 \leq \mu + \nu \leq 5$ . If we assume without loss of generality that  $\mu \leq \nu$ , then we find five possible cases:

$$(\mu, \nu) \in \{(1, 2), (1, 3), (2, 2), (1, 4), (2, 3)\}$$

Let  $\mu = 1, \nu = 2$ . This implies  $1 - 2/m + 2 - 4/n = 2 \implies 2/m + 4/n = 1$ . This can hold only if there exist natural numbers  $k$  and  $l$  such that  $m = kt, n = lt$  ( $t \in \mathbb{N}$ ),  $k \neq l$ ,  $k|2$ ,  $l|4$ ,  $\gcd(k, l) = 1$ . Then the possible values that  $(k, l)$  can take are  $(1, 2), (1, 4), (2, 1)$ .

$$\begin{aligned} k = 1, l = 2 &\implies n = 2m \implies m = 4, n = 8; \\ k = 2, l = 1 &\implies m = 2n \implies m = 10, n = 5; \\ k = 1, l = 4 &\implies n = 4m \implies m = 3, n = 12. \end{aligned}$$

Similarly, if we consider all the cases, we will find six possible scenarios:

$$\begin{aligned} m = 4 \text{ (square)}, n = 8 \text{ (octagon)}, \quad \mu = 1, \nu = 2; & \quad (1) \\ m = 10 \text{ (decagon)}, n = 5 \text{ (pentagon)}, \quad \mu = 1, \nu = 2; & \quad (2) \\ m = 3 \text{ (triangle)}, n = 12 \text{ (do-decagon)}, \quad \mu = 1, \nu = 2; & \quad (3) \\ m = 3 \text{ (triangle)}, n = 6 \text{ (hexagon)}, \quad \mu = 2, \nu = 2; & \quad (4) \\ m = 6 \text{ (hexagon)}, n = 3 \text{ (triangle)}, \quad \mu = 1, \nu = 4; & \quad (5) \\ m = 4 \text{ (square)}, n = 3 \text{ (triangle)}, \quad \mu = 2, \nu = 3. & \quad (6) \end{aligned}$$

Of these, scenario (2) is discarded, because even though two pentagons and a decagon can meet at a vertex to completely surround the point, a periodic arrangement is not possible. This is because each pentagon has to be surrounded by pentagons and decagons alternately, which is not possible as it

has an odd number of sides. Thus we finally get five ways two tile a plane with two kinds of regular polygons. Tessellations using triangles and hexagons can be done in two ways ((4) and (5)). It is worth noting that octagons or dodecagons can also be used (along with squares and triangles respectively), though each of this can not be used alone for regular tessellation.

Situations with three or more polygons can be similarly found, though the mathematics gets more complicated for more polygons.

### 3 Stretching of Graphene Sheet

We consider a spring-mass model of the graphene sheet, with each carbon atom as a point mass and each  $sp^2$  bond as a massless spring. Thus, each point mass is attached with its three nearest neighbours by identical springs. The spring-mass network is in the  $xy$  plane, and a force is applied along the  $z$ -axis on a point far away from the edges (this point is taken as the origin). The edges are fixed. We assume the applied force to be much greater than the weight of the point masses, i.e. we can neglect the sagging of the graphene sheet due to its own weight for the time being.

First, we consider a point mass displaced by  $z$  from the equilibrium position, while its neighbour, connected by a spring of natural length  $l$  and force constant  $k$ , is displaced by  $z_0$  (Figure 2). The  $z$ -component of the resulting spring force will be

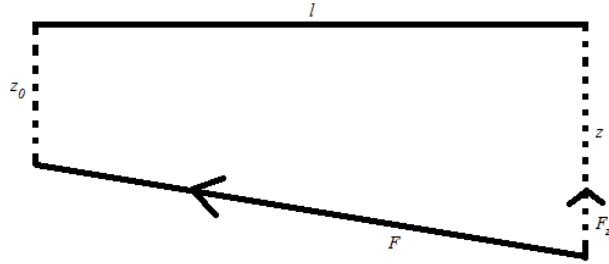


Figure 2: Two point masses connected by spring

$$F_z = k(\sqrt{l^2 + (z - z_0)^2} - l) \times \frac{(z - z_0)}{\sqrt{l^2 + (z - z_0)^2}}$$

$$= k(z - z_0) \left( 1 - \frac{l}{\sqrt{l^2 + (z - z_0)^2}} \right).$$

We will have a similar expression for each nearest neighbour. We assume that the  $x$  and  $y$ -components of the forces due to the nearest neighbours will cancel, so that we can focus our attention on the  $z$ -component only.

Let us consider one spring-mass chain extending from the point of application of the force to the edge (Fig. 3). Let the displacement of the particle at  $i$ th position from the point of application of the force be  $z_i$ . Then  $z_i < z_{i-1}$ ,  $\forall i$ .

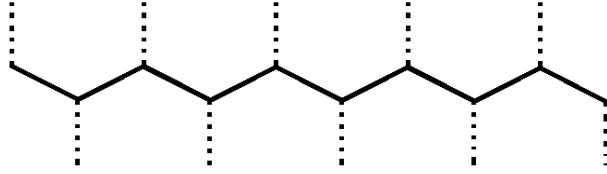


Figure 3: A spring-mass chain in Graphene sheet

Now, each particle experiences opposite forces due to its two nearest neighbours that are on opposite sides in the chain (one neighbour, situated perpendicular to the chain, is assumed to have almost same displacement as the particle we are considering, so it has no contribution to the force). For equilibrium, they must be equal in magnitude. Therefore, we have

$$k(z_i - z_{i+1}) \left( 1 - \frac{l}{\sqrt{l^2 + (z_i - z_{i+1})^2}} \right) = k(z_{i-1} - z_i) \left( 1 - \frac{l}{\sqrt{l^2 + (z_{i-1} - z_i)^2}} \right).$$

The function

$$f(x) = kx \left( 1 - \frac{l}{\sqrt{l^2 + x^2}} \right), \quad x \in \mathbb{R}, \quad k, l > 0$$

is increasing and hence injective. Therefore  $z_{i-1} - z_i = z_i - z_{i+1} = c$  (say)  $\forall i$ , which implies

$$z_i = ci$$

( $c$  is a constant), i.e.  $z_i$  is linearly related to  $i$ . From the figure, it is obvious that  $r_i$ , the distance of the  $i$ th particle from the point of application of the force, is also linearly related to  $i$ . Thus we can say that  $z_i$  is linearly related to  $r_i$ , i.e.  $z \propto r$ .

For the other chain (Fig. 4), the situation is slightly more complicated, as each atom has two neighbours on one side and one on the other. However, if take any two adjacent particles (say the  $i$ th and  $(i + 1)$ th particles) to constitute a system and find the forces on it, we will find that  $z_{i+2} - z_{i+1} =$

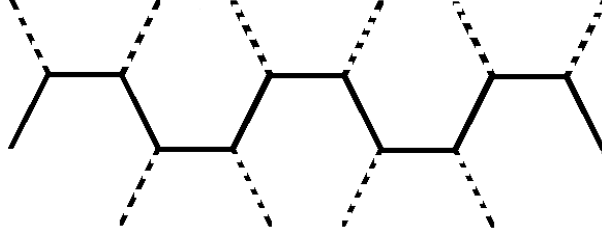


Figure 4: Another kind of spring-mass chain in Graphene sheet

$z_i - z_{i-1} \forall i$ . This implies  $z_{2j+1} - z_{2j} = \text{constant} = c_1$  (say)  $\forall j$ , and  $z_{2j} - z_{2j-1} = \text{constant} = c_2$  (say)  $\forall j$ . Therefore,

$$z_i = c_1 \left\lceil \frac{i}{2} \right\rceil + c_2 \left\lfloor \frac{i}{2} \right\rfloor \approx \frac{c_1 + c_2}{2} i = ci, \text{ i.e. } z_i \propto i$$

( $c_1$  and  $c_2$  are constants,  $c = \frac{c_1 + c_2}{2}$ ). Similarly,

$$r_i \approx \frac{3}{4} li, \text{ i.e. } r_i \propto i$$

( $l$  = length of spring = bond length). Therefore,  $z \propto r$  in this case as well. In general, we can say that  $z \propto r$  in all directions, i.e. the nature of the relation between  $z$  and  $r$  is independent of the third cylindrical coordinate  $\phi$ .

Hence, for a circular graphene sheet of radius  $R$  with the force applied at its centre, it will form a cone ( $z = Kr$ ,  $K$  is a constant,  $r < R$ ). For a square sheet with edge-length  $a$ , the displacement will be  $z = K \max\{x, y\}$ ,  $K$  is a constant,  $|x|, |y| < \frac{a}{2}$ . For a rectangular sheet with dimensions  $a, b$ ,  $z = K' \max\{x/a, y/b\}$ ,  $K'$  is a constant,  $|x| < a/2$ ,  $|y| < b/2$ . If the applied force is not concentrated on a point (e.g. a heavy solid body is placed on the graphene sheet), the portion of the sheet in contact with the solid body will tend to conform with the shape of the body, but the rest of the sheet will form a conical surface as shown above.

Let the force applied at the centre of a circular graphene sheet be  $F$ . The central point mass is displaced by  $z_0$ , and each of its three nearest neighbours by  $z_1$ . Therefore,  $F = 3k(z_0 - z_1)(1 - l(l^2 + (z_0 - z_1)^2)^{-1/2})$ . From this, if  $F$  is known, we can find  $z_0 - z_1$ . Since  $z \propto r$ , from the radius of the graphene sheet, we can determine its depression. Also, the maximum force that can be applied on the sheet without rupturing it can be found from the breaking load of the springs (i.e. the force at which the carbon-carbon bonds will break). It is very high due to the strong  $sp^2$  bonds, and graphene is a very strong material in spite of having a low surface mass density.

If we consider the weight of the particles, then the upward force due to one spring has to balance the downward force due to the other spring, as well as the weight of the point mass, i.e.  $k(z_i - z_{i+1})(1 - l(l^2 + (z_i - z_{i+1})^2)^{-1/2}) = k(z_{i-1} - z_i)(1 - l(l^2 + (z_{i-1} - z_i)^2)^{-1/2}) + mg$ . Hence the gradient of the deformed sheet changes from the edge to the point of application of the force. While it is difficult to analytically find the shape of the graphene sheet in this case, it can be estimated numerically.

## 4 Further work that can be done

The solutions regarding stretching of graphene sheet that were found here can be checked with experimental data. Numerical solutions to problems involving the sagging of the sheet due to its own weight can be attempted. Also, from the forces on the carbon atoms, the vibrational modes of a graphene sheet may be found. It is difficult to find, because the system of differential equations is not homogeneous and may be hard to solve even by numerical methods. However, if it is solved, it may also give insight on thermal conduction through graphene. While the bonds were represented by springs in this model, the resistance to change in bond angle (i.e. bending) was neglected. In a more detailed model, they should also be considered, maybe by a separate set of springs joining alternate atoms.

## 5 Acknowledgements

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