MECHANICS OF A SUSPENDED MEMBRANE: CASE OF GRAPHENE

A project report submitted by
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CERTIFICATE

This is to certify that the matter embodied in the report entitled "**MECHANICS OF A SUSPENDED MEMBRANE: CASE OF GRAPHENE"** has been carried out by **Mr. Abhijeet Kumar** at Department of Physics and Department of Electrical Engineering, Indian Institute of Technology - Madras, Chennai, under our guidance and supervision during the period **19/05/2016-10/07/2016**.

Dr. MANU JAISWAL

DECLARATION

I hereby declare that the matter embodied in the project report entitled "**MECHANICS OF A SUSPENDED MEMBRANE: CASE OF GRAPHENE**" is the result of investigations carried out by me under the guidance of **Dr. Manu Jaiswal**, Department of Physics, Indian Institute of Technology Madras during the period **19/05/2016-10/07/2016**.

Abhijeet Kumar

ACKNOWLEDGEMENT

On the very outset of this report I would like to express my sincere and heartfelt obligation towards all the persons who have helped me to complete this project.

I am ineffably indebted to ***Dr. Manu Jaiswal****, Department of Physics,* ***IIT Madras*** *and would like to express my deepest gratitude to him for his invaluable guidance and encouragement for helping me to complete this work.*

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Finally and most importantly, my heartiest thanks to my parents and my family who have been my motivation throughout my career.

CONTENTS

Abstract

Because of its remarkable fundamental properties, graphene has attracted intense interest in recent years. Being a single atom thick, yet having huge mechanical and elastic strength allows it to obtain certain configuration on top of a corrugated surface under finite strain or load.

The aim of this project is to understand and model the morphology of graphene layer on top of a nano sphere by obeying the continuum theory of elasticity. First we model the height profile of a free standing 1-D membrane under finite load and then extend this model into 3-D as in case of graphene on top of a nano sphere. The load is variable and can also be induced by electric field.

1. INTRODUCTION

1.1 What is Graphene?

Graphene is an allotrope of carbon consisting of a single 2-Dimensional layer of carbon atoms arranged in perfectly hexagonal lattice.

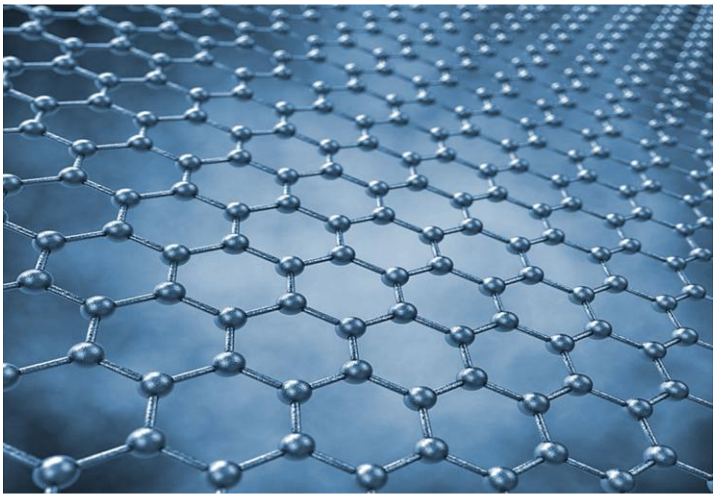


Figure 1: A structural model of Graphene sheet

Many of its remarkable properties make Graphene an extraordinary material such as its atomic thickness, extremely light weight still very strong, huge flexibility and elasticity, very high electron mobility etc. zero band gap of Graphene is its most significant property and is the reason behind its unusual electronic behaviour.

Being a perfectly 2-dimensional material, Graphene doesn't exist in Free State. Electronic and mechanical properties of Graphene are highly influenced by the strain induced on it and the substrate underlying it.

1.2 Vision and Applications:

The influence of strain on the electronic and mechanical properties of Graphene is one of its most interesting features. Zero band gap actually limits the use of Graphene in electronic industry, but by applying strain the band gap and hence the electronic properties of Graphene can be controlled.

Lots of effort has been made in this context to create the best opportunities to make more application of Graphene in electronic and several other fields. The outcome has been limited though as controlling the strain being applied to Graphene is still difficult. Still because of its uniqueness and partial success over controlling its properties has made Graphene a promising candidate for the next generation electronic material.

1.3 Motivation:

It is known that by inducing strain, we can tune the electronic behaviour of Graphene in desired manner. This can lead to variation in the elastic and mechanical properties of Graphene as well. In this project we study the morphology of the Graphene membrane on top of a nano sphere and variation in its elastic (such as strain) and mechanical properties (such as energy, wrinkling etc). Analysing the electronic properties such as electron mobility is also a part of future plan.

2. ELASTIC THEORY OF MEMBRANE

2.1 Continuum theory of elasticity

The elasticity and mechanics of a membrane can be explained very well by the continuum theory of elasticity [18, 19]. In our project we obey the continuum theory of elasticity to study the elastic and mechanical properties of the Graphene membrane.

In continuum theory of elasticity, the two fundamental quantities to describe the elasticity phenomena are strain (deformation in a material with respect to its equilibrium position) and stress (internal forces against the deformation).

2.1.1 Strain:

Strain is a dimensionless quantity defined as the change in length of a body with respect to its original length under deformation, when the deformation is within a continuum limit.

Displacement for an object in 3-Dimension is expressed as

$$\boldsymbol{u_{ij}} = \begin{bmatrix} \frac{\partial u_x}{\partial x} & \frac{\partial u_x}{\partial y} & \frac{\partial u_x}{\partial z} \\ \frac{\partial u_y}{\partial x} & \frac{\partial u_y}{\partial y} & \frac{\partial u_y}{\partial z} \\ \frac{\partial u_z}{\partial x} & \frac{\partial u_z}{\partial y} & \frac{\partial u_z}{\partial z} \end{bmatrix}$$

For a small displacement in 2-dimension, the product of two infinitesimally small displacement $(\frac{\partial u_x}{\partial x}, \frac{\partial u_y}{\partial x})$ etc can be ignored and we get the strain tensor as

$$u_{ij} = \frac{1}{2}\left[\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right]$$

2.1.2 Stress:

The internal forces of the body oppose its deformation till the deformation is within elastic limit that tends the body to return back to its equilibrium position. The stress tensor constitutes the internal forces and is given by

$$\sigma = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}$$

Under static equilibrium, $\sigma_{xy} = \sigma_{yx}, \sigma_{xz} = \sigma_{zx}, \sigma_{yz} = \sigma_{zy}$.

There are a couple of sets of parameters that can successfully describe the elastic properties of a material. These are λ, μ and E, σ.

2.2 Elasticity in membrane:

Membranes are an example of very thin and soft material. Morphology of membranes on a substrate is mainly governed by various elastic energies, which consist of fundamental elastic parameters. Elastic energies corresponding to a membrane are discussed briefly as follows:

2.2.1 Bending Energy:

This is the energy of the membrane generated due to its bending. Bending energy is significant at atomic length scale though. The magnitude of bending energy [20] is given by

$$E_b = \frac{1}{2}\int k\left\{\partial_x{}^2 h(x)\right\}^2 dA$$

Where k is the bending rigidity;

dA is the area over which the integration occurs;

h(x) is the height profile of the suspended membrane.

2.2.2 Stretching Energy:

This is the energy stored in a membrane due to the stretching of the membrane. For a membrane stretched unidirectional along x-axis, the stretching energy [20] is given by

$$E_s = \frac{1}{2}\int T(x)\{\partial_x h(x)\}^2 dA$$

Where T(x) is the tension along the x-direction

2.2.3 Adhesion Energy:

When the membrane is attached to the substrate, the interaction energy between them is known as Adhesion Energy. It is given by

$$E_{ad} = \int \gamma dA$$

Where γ is the coupling constant strength for a membrane [21].

2.2.4 Elastic Free Energy:

Elastic Free Energy is the total potential energy associated with the membrane [18] and is given by

$$\mathcal{F} = k \int dxdy \left[\left\{ \partial_x{}^2 \mathrm{h(x,y)} + \partial_y{}^2 \mathrm{h(x,y)} \right\}^2 + 2(1-\vartheta) \left\{ \left(\frac{\partial^2 h(x,y)}{\partial_x \partial_y} \right)^2 - \partial_x{}^2 \mathrm{h(x,y)}\, \partial_y{}^2 \mathrm{h(x,y)} \right\} \right]$$

Where ϑ is the Poisson ratio of the material

Under a finite load, the elastic free energy for the membrane gets modified to

$$\mathcal{F} = \int dxdy \left[\frac{1}{2} k \left(\nabla^2 \mathrm{h(x,y)} \right)^2 + \frac{1}{2} \left(\lambda {u_{ii}}^2 + 2\mu {u_{ij}}^2 \right) - Ph(x,y) \right]$$

Where, λ and μ are the Lame's parameter;

P is the load;

u_{ii} is the trace of the strain tensor and u_{ij} is the sum of square of all the strain tensor elements

2.3 Euler-Lagrange's equations:

Maximizing or minimizing a function of elastic free energy (J) gives a set of three Euler-Lagrange equations. Solution to these equations with appropriate boundary conditions gives the height profile of the membrane.

$$J = \int_{x_1}^{x_2} \mathcal{F}\{y, y', x\} dx$$

J when extremized gives a set of Euler-Lagrange's equations [22]:

$$\lambda\partial_x u_{kk} + 2\mu \left(\partial_x u_{xx} + \partial_y u_{yx}\right) = 0$$

$$\lambda\partial_y u_{kk} + 2\mu \left(\partial_x u_{xy} + \partial_y u_{yy}\right) = 0$$

$$k\nabla^4 h - \lambda\left(\partial_x u_{kk}\partial_x h + \partial_y u_{kk}\partial_y h\right) - 2\mu\left(\partial_i u_{ij}\partial_j h\right) = P$$

2.4 Significance of elastic energies:

- Bending Energy is significant at atomic length scale only. [Appendix A]
- Experiments suggest that attachment and detachment of a membrane from the substrate are highly dependent on the domination of a particular elastic energy [21, 23].

Attachment of the membrane with the substrate occurs in a region where the bending rigidity dominates, and the region where the membrane detaches from the surface, strain energy dominates. In this region, the bending energy can be neglected easily.

2.5 Affect of strain on membrane: Wrinkles

Wrinkles are a complex phenomenon found at every length scale [20]. Wrinkles are generated mainly due to the imbalance due to the in-plane stresses. Wrinkling in a membrane can occur with or without a substrate underlying it. It can be generated either by compressing the substrate or stretching the membrane by applying strain. If the strain is applied in longitudinal direction, wrinkles get generated in the transverse direction due to the Poisson effect. This happens because the clamped ends prevent the film from contracting laterally, which leads to the imbalance in the stress in transverse direction.

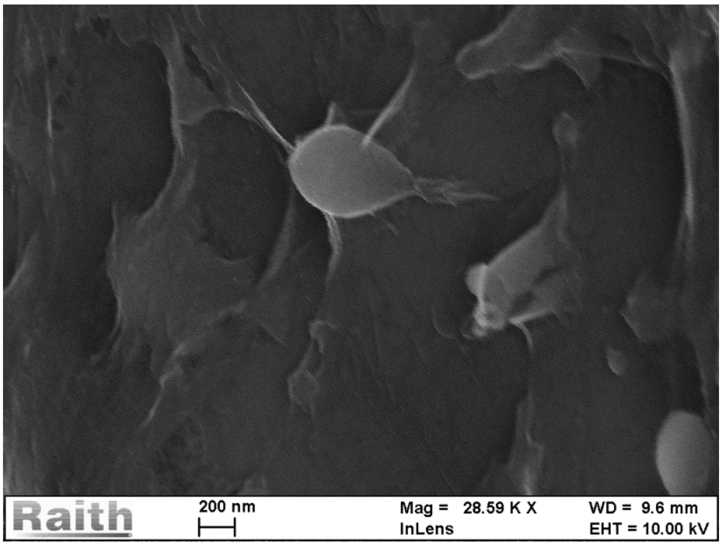


Figure 2: wrinkles formation in Graphene membrane on top of a nano sphere (SEM images)

Graphene is one atom thick and it experiences wrinkles easily due to its low bending rigidity. Wrinkles in Graphene can significantly disrupt and slow down the electronic movement.

3. MEMBRANE ELASTICITY: ANALYTICAL AND EXPERIMENTAL APPROACH

In the previous section, we obtained the Euler-Lagrange's equations that explain the morphology of a membrane under strain/load. Now we try to solve this equation analytically to obtain a solution for some specific cases.

3.1 Example: Clamped Graphene membrane under finite load

Consider a suspended Graphene membrane under finite load 'p' clamped at both ends. Consider the membrane to be wide so as to not to worry about the transverse direction. Now the situation becomes effectively 1-Dimensional [21].

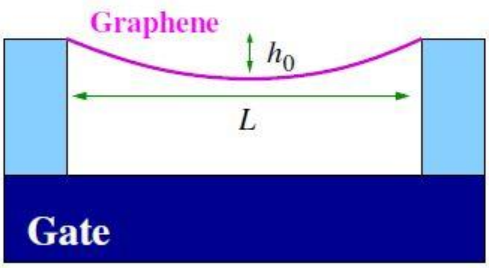


Figure 3: Suspended Graphene membrane with clamped edges. The load is due to back gate induced electric field.

Let the membrane be clamped between two ends X =0 and X =1m. Consider the variation of height in X-direction. The Euler-Lagrange's equations can be modified into

$$u = constant;$$

$$\partial_x^2\left[k{\partial_x}^2 - (\lambda + 2\mu)u\right]h(x) = P$$

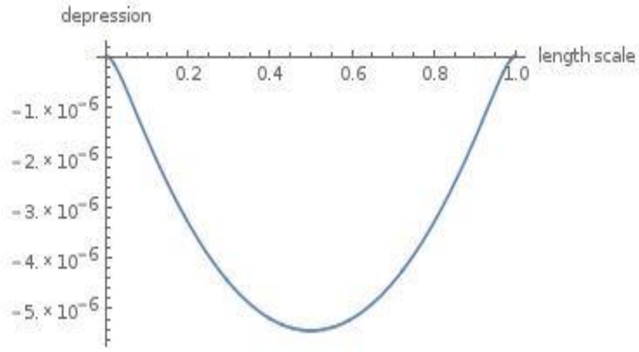
3.2 Analytical Solution:

The simplified Euler-Lagrange's equation is a 4th order differential equation that cannot be solved analytically. We use Mathematica software to solve this equation under certain boundary conditions.

For this particular case, the boundary conditions are

$$h(0) = h(1) = 0 \; and$$
$$h'(0) = h'(1) = 0$$

Elastic parameters for Graphene are k= 1eV; 3λ≈μ≈900eV, P= 0.1ev/m³.



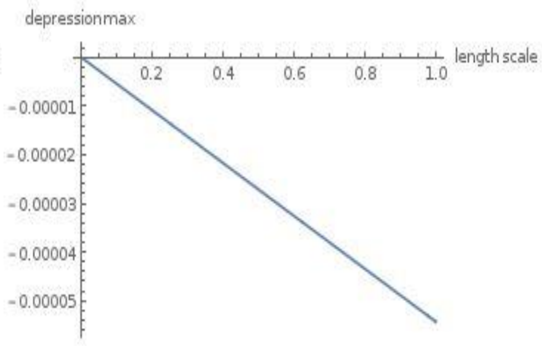


Figure 4a: Height profile of Graphene membrane *Figure 4b: Max. Depression vs. Load*

3.3 Calculation of strain:

The strain in the membrane can be calculated easily with the help of the formula by solving the following equation:

$$u = \frac{L' - L - \Delta L}{L + \Delta L} \approx \frac{L' - L}{L} - \frac{\Delta L}{L}$$

Where

$$L' = 2\int_0^{\frac{L}{2}} dx\, \sqrt{1 + 2|\nabla h|^2} \approx L + \int_0^{\frac{L}{2}} dx[\partial_x h(x)]^2$$

L' is the strained length while L is the original length of the membrane.

(Calculations done in **Appendix C**)

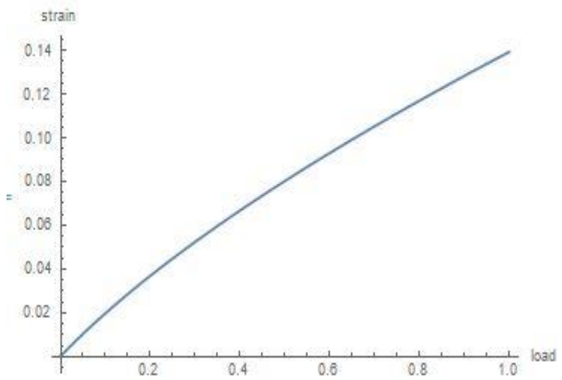


Figure 4c: strain vs. load plot

3.4 An attempt to validate membrane theory for 3-Dimensional objects

The Euler-Lagrange's equation solved to obtain the height profile and the strain were for a 2-dimensional co-ordinate system further approximated into 1-Dimension. Next objective is to understand, how closely this theory matches with the deformation of some macroscopic elastic materials in 3-Dimensional system.

We collected 4 samples:

1. Rubber (7cm x 1cm)
2. Polyethylene (7cm x 1cm)
3. Cloth-cotton (7cm x 1cm) and
4. PDMS (6cm x 1cm)

Figure 5: Rubber Cloth Polyethylene PDMS

Though the thicknesses of these samples are not negligible with respect to the other two dimensions, we try to obtain analytical solution of their deformation using the 1-Dimensional Euler-Lagrange's equation.

The deformation was also observed experimentally under similar conditions.

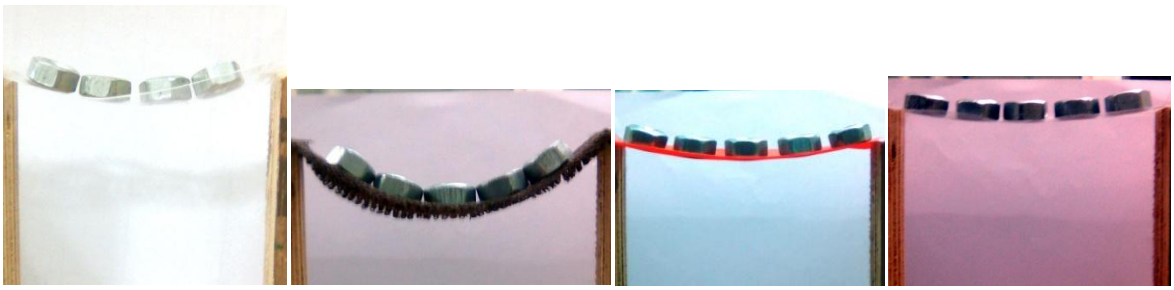


Figure 6: PDMS, Cloth, Rubber, and Polyethylene under uniform load (from left to right)

The result obtained in both cases are summarised in the following table: (detail calculation in Appendix B)

Table I: Maximum depression for different samples:

Material	Max. depression Theory	Max. depression Experiment	Order of error
Rubber	0.0008152	0.005005	~61
Polyethylene	0.0001623	0.004374	~27
Cotton	5.173E-6	0.017208	~3300
PDMS	0.00851	0.0078416	~0.921

We observe that the theoretical result vary in quite large proportion with respect to the experimental result. Keeping the difference in the fundamental scenario for both the case (such as considerable thickness of sample, 3-dimensional system, absence of perfectly ideal sample), we expected the error to be within a factor of 10, unlike we have observed. (In case of cotton cloth, the error was too high due to highly non idea sample)

Still it gives us some understanding about the connection between these two different scenarios. We can propose a better and closer to perfection model in future that could explain the elastic properties of microscopic as well as macroscopic materials.

4. MORPHOLOGY OF GRAPHENE ON TOP OF A NANO SPHERE

In the previous section we studied the height profile of some samples clamped between two ends rather than suspended over a patterned surface. Now we will study and analyze the case both experimentally and analytically where Graphene membrane is put on top of a nano sphere.

4.1 Experiment:

The Experiment consists of two main steps:

1. Transfer of Poly Styrene Nano Sphere (PSNS) on SiO_2 substrate and then transfer of Graphene on top of PSNS.
2. Analysis of the observed pattern using Scanning Electron Microscope (SEM).

Transfer of PSNS on top of SiO_2 and then transfer of Graphene on PSNS is a long process and require several experimental steps. These steps are discussed briefly as follows:

4.1.1 Cleaning the SiO_2 wafer:

- Solution of Acetone and IPI water (1:1) was taken in one cleaned beaker. After putting the wafer in the solution, the solution was sonicated for 5 minutes.
- Immediately after this, the wafer was transferred into a DI water solution and the solution was sonicated again for 5 minutes. The process was done immediately to avoid the residues on the surface of the wafer arising due to the evaporation of chemicals.
- After sonication, the DI water was removed and the wafer was given a gentle blow of N2 gas in order to dry it.

4.1.2 Transfer of PSNS on SiO_2 substrate:

PSNS used in the experiments were in a colloidal solution of DI water with ~ 1% concentration. This was further diluted to ~ $0.25\text{-}10^{-7}\%$

concentration. PSNS solution was transferred to SiO_2 substrate by using Drop casting technique.

Drop casting method: In drop casting method, a drop of PSNS solution is transferred on the substrate using a micropipette of adjustable volume. The substrate is now kept on a hot plate to dry out.

4.1.3 Wet transfer of Graphene

- A small piece of Copper strip with Graphene layer on its both sides is taken and fixed on a glass slide using a scotch tape.
- A small amount of coating material PMMA is added to the top layer of the substrate and the substrate is fixed in a spin coater. It is rotated now at very high speed spin coater for certain time under certain fixed conditions so as to spread out the PMMA layer uniformly over the substrate.
- The substrate is now put on a glass slide with its top surface with PMMA layer touching the glass slide. Now the top layer of Graphene is removed using a blunt knife.
- The Copper substrate (now with only one layer of Graphene) is exposed to an etchant solution in a Petri dish. The etchant etches away the copper in few hours so that we only have the Graphene layer left with PMMA layer on top of it.

Figure 7a: A strip of copper with Graphene layer on its both sides

Figure 7b: copper substrate Coated with PMMA layer

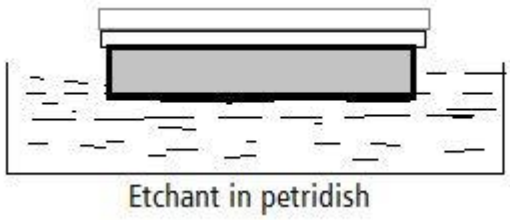


Figure 7c: Copper substrate with Graphene and PMMA layer put in a petridish with etchant in order to etch the Cu layer away

4.1.4: Scoop out method:

- The Graphene layer with PMMA layer on its top is scooped out from the DI water solution using the SiO_2 substrate (having PSNS on its top).
- The sample is given a gentle blow of N2 gas to remove the water droplets and is put on the hot plate to stabilize the Graphene layer with PMMA on its top on the substrate.
- The sample is put in Acetone solution for 20-30 minutes to remove the PMMA layer coating and thus we get a single Graphene layer on top of PSNS. A small amount of PMMA might still remain on the Graphene layer though.

4.2 Analysis using SEM:

Few images of the prepared sample were taken using a Scanning Electron Microscope. Optical Microscopic Images don't explain the phenomenon clearly as its resolution is not high enough to view the nano spheres individually.

4.2.1 Scanning Electron Microscope Images

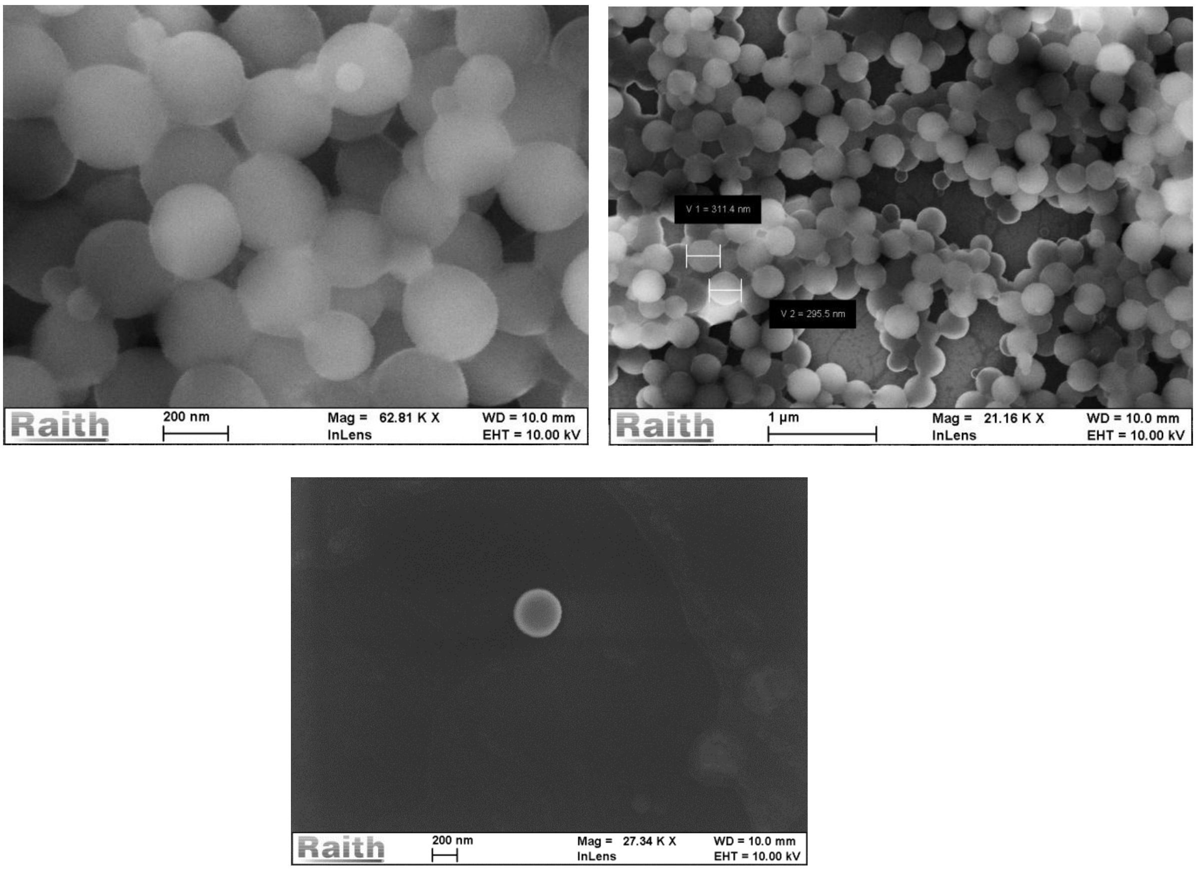


Figure 8: PSNS as seen under SEM

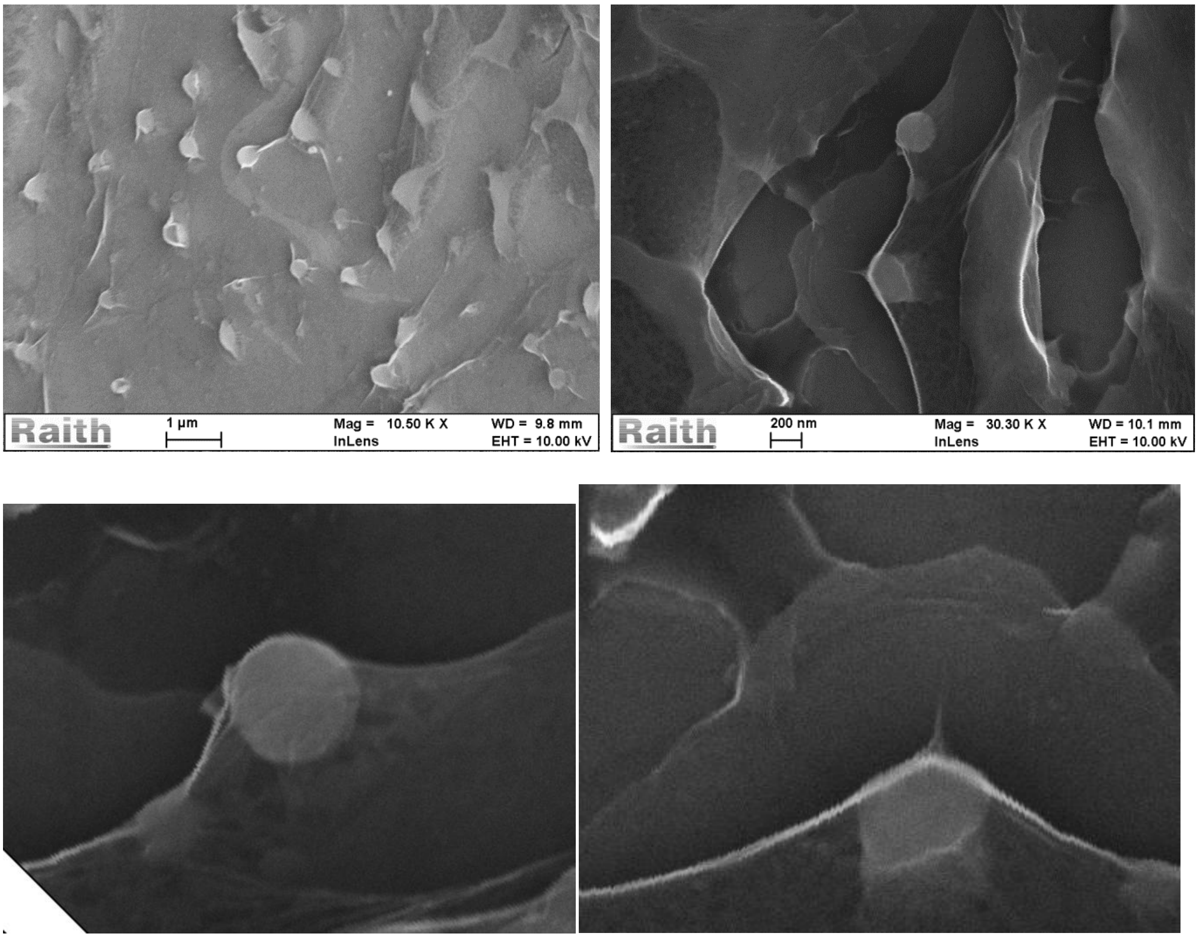


Figure 9: SEM images of Graphene membrane on top of PSNS

Software named 'Enguage Digitizer' was used to analyze the image of Graphene on a single Nano sphere. This gives us the data points of the curvature of Graphene on the nano sphere. By defining the Axes points and origin of the co-ordinate, data points were plotted in 'origin' software. The resulting plot is shown below:

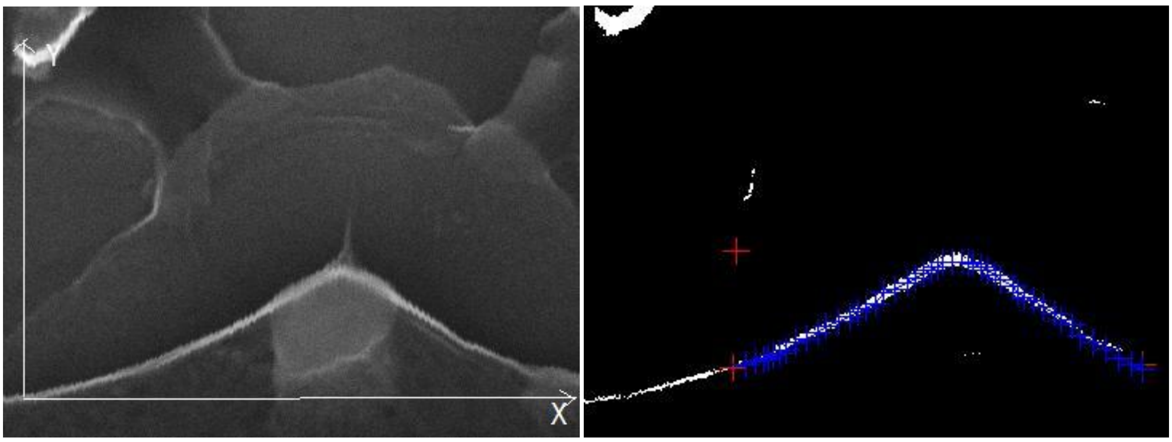


Figure 10: Data points taken using Digitizer software

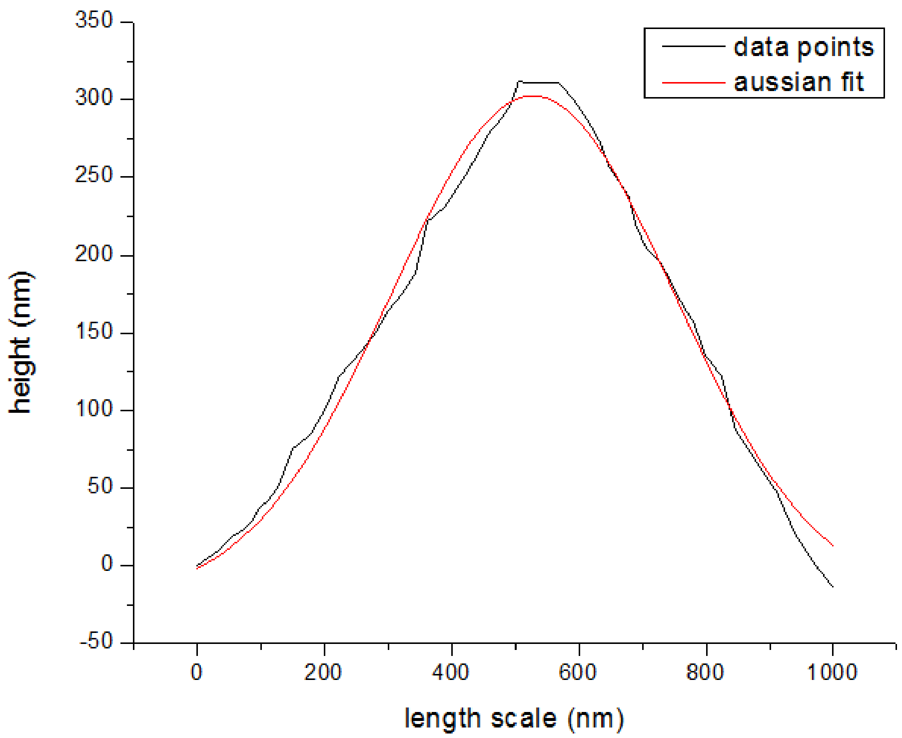


Figure 11: fitted height profile plot in origin

Thus we obtain the experimental view and the curvature of the Graphene membrane suspended on a nano sphere. Our next objective is to solve this problem analytically.

[This section of the report is completely motivated by the thesis work of my senior and co-guide Vani Yadav.
The samples were prepared by Vani Yadav during her previous work and the SEM images were taken by Shaina P. R.]

5. ANALYTICAL SOLUTION TO GRAPHENE PROBLEM

In this section, we will try to solve the Graphene problem using mathematical approach in order to obtain its morphology on top of a nano sphere.

5.1 Geometry and mechanics of membrane:

Graphene layer suspended on a nano sphere has a three dimensional geometry as can be seen in the figure 11. Let's assume the centre of the nano sphere to be at (0, y, 0) with the substrate in XZ-plane. So, the height profile (h(x, y)) of the Graphene layer varies in the Y-direction.

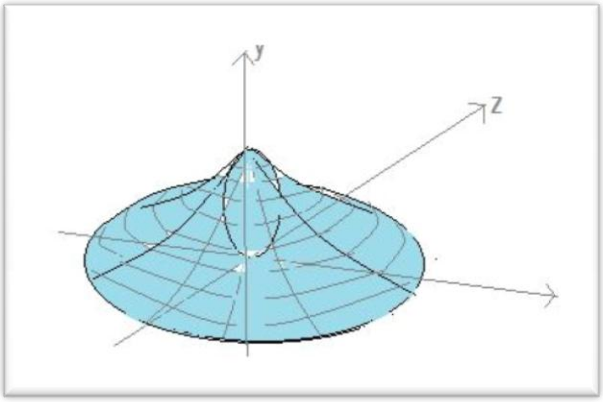


Figure 12: 3-D geometry of Graphene membrane

Mechanics of a membrane is already discussed earlier in section 2. We follow the same mechanics here.

Recall that the free energy of an isotropic membrane under some load is given by

$$\mathcal{F} = \int dxdy \left[\frac{1}{2}\, k\, (\nabla^2 \mathrm{h(x,y)})^2 + \frac{1}{2}\left(\lambda {u_{ii}}^2 + 2\mu {u_{ij}}^2\right) - Ph(x,y)\right]$$

Extremizing a function of this free energy using the variational principle, we had obtained a set of three Euler-Lagrange's equations:

$$\lambda \partial_x u_{kk} + 2\mu\left(\partial_x u_{xx} + \partial_y u_{yx}\right) = 0$$

$$\lambda \partial_y u_{kk} + 2\mu \left(\partial_x u_{xy} + \partial_y u_{yy}\right) = 0$$

$$k\nabla^4 h - \lambda\left(\partial_x u_{kk}\partial_x h + \partial_y u_{kk}\partial_y h\right) - 2\mu\left(\partial_i u_{ij}\partial_j h\right) = P$$

These equations are complicated and non homogeneous higher order partial differential equations that cannot be solved analytically even after simplification. This complication forces us to make some approximations to simplify these equations into 2-Dimensions.

5.2 Simplification in 2-dimensions:

We view the figure of Graphene on top of a nano sphere in 2-dimesion (A cross section in X-Y plane). This view is similar to the case of taking a tilted image of the suspended Graphene membrane using SEM.

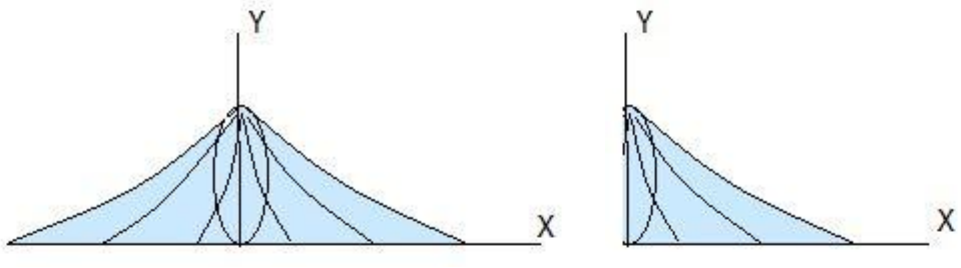


Figure 13: 2-D cross section of Graphene membrane on top of a nano sphere

Now it is possible to solve this simplified problem analytically in X-Y plane with the height profile in Y-direction varying as a function of X.

This problem is similar to the problem of finding the morphology of a 1-Dimensional membrane clamped at two ends. The governing equations in both the cases are the same.

$$u = constant;$$

$$\partial_x^2\left[k{\partial_x}^2 - (\lambda + 2\mu)u\right]h(x) = P$$

In case of Graphene layer on top of PSNS, the PMMA residues act as load (along negative Y-direction). The two ends in this case are first, the point where the membrane leaves the nano sphere and second, where it touches the substrate.

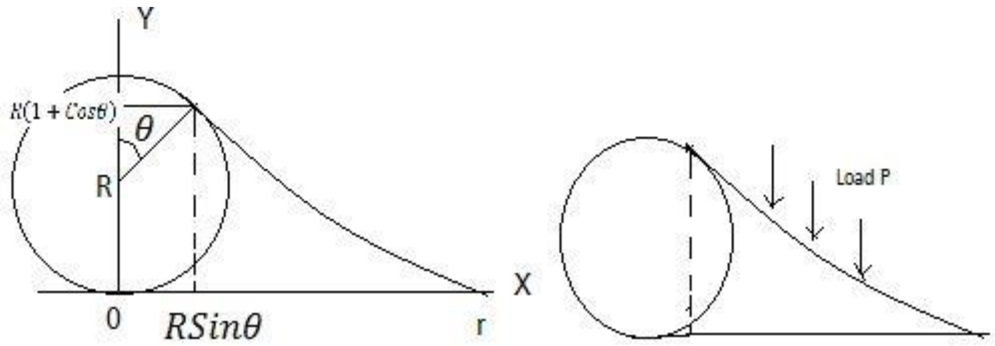


Figure 14: Simplest view of the membrane on top of the nano sphere

Thus we have two regions on the nano sphere, one, the region over which the membrane is attached to the nano sphere and the other is between the points where the membrane detaches from the nano sphere and touches the substrate.

5.3 Analytical solution:

For the nano sphere of radius 'R', the detachment point for the membrane is RSinθ. Let the membrane touches the substrate at X= 'r'.

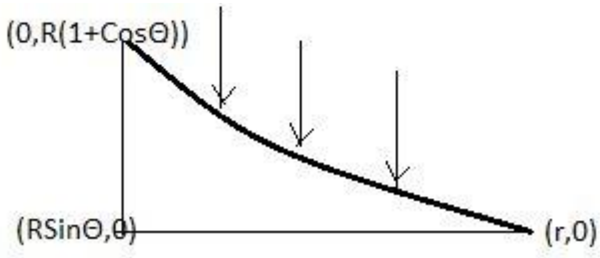


Figure 15: Graphene membrane problem in its simplest from

Boundary conditions for the 1-Dimensional problem are

$$h(RSin\theta) = R(1 + Cos\theta);$$
$$h(r) = 0;$$
$$h'(RSin\theta) = -Tan\theta \ and$$
$$h'(r) = 0$$

The 1-Dimensional Euler-Lagrange's equation is solved using these boundary conditions with the help of 'Mathematica' software. We analyze the solution under different conditions such as different values of load and angle of detachment, their energies and their inter dependence.

5.3.1 Variation of Height profile of Graphene membrane against different parameters:

- **Height profile against varying load for fixed angle of detachment:**

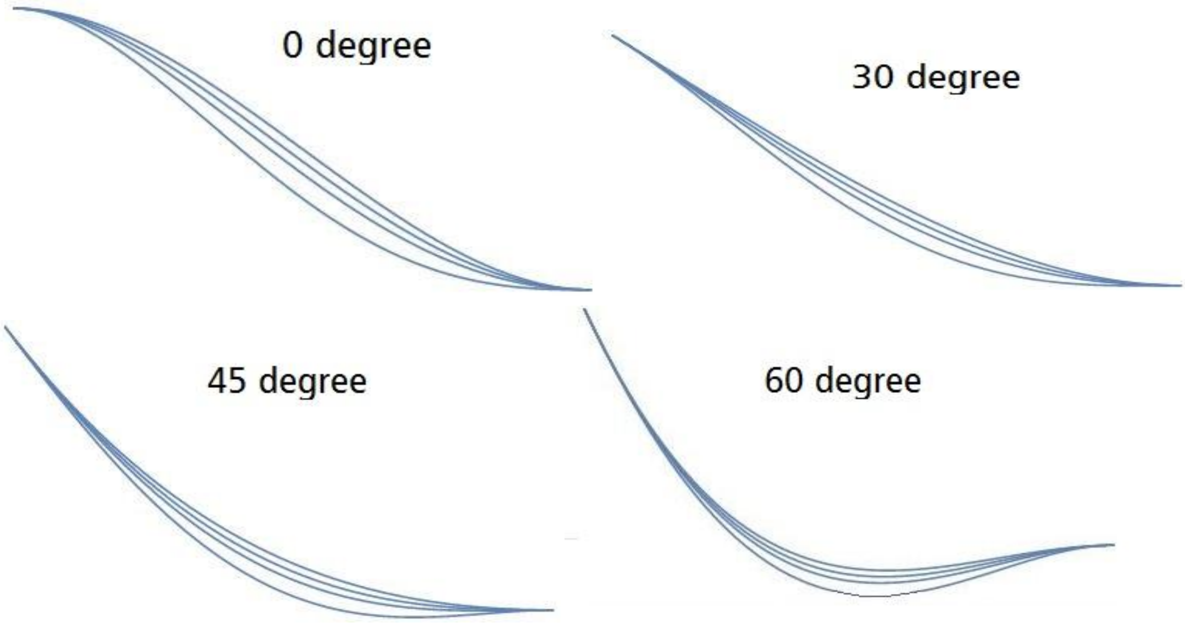


Figure 16: height profile under different values of load (0N/m, 1N/m, 10N/m and 20N/m). Increasing load in downward direction.

We observe that as the load increases, the depression in the membrane increases and it sags more.

- **Height profile against Angle of detachment under fixed load:**

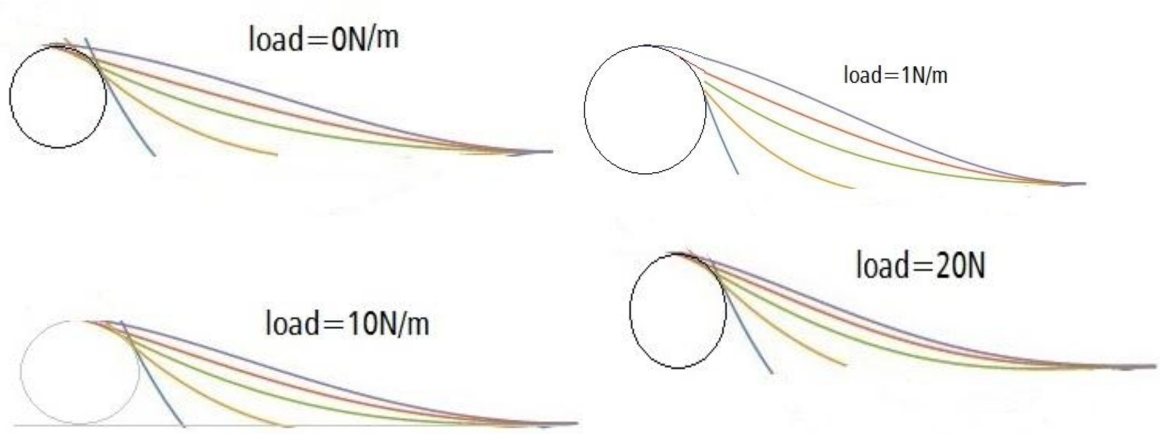


Figure 17: height profile against varying angle of detachment (0^0, 30^0, 45^0 and 60^0). Angle increasing in downward direction.

The observation is again as expected. The depression in the membrane increases as the angle of detachment increases. In some cases, the membrane touches the substrate before its ideal end point. This occurs either due to excess load or higher angle of detachment that creates more depression in the membrane.

5.3.2 Elastic energies of the membrane:

We calculated different energies of the membrane (Bending, Stretching and Adhesion) under a set of fixed parameters. The nature of Adhesion energy is opposite to the other two energies. Therefore, the total elastic energy of the membrane can be written as

$$Total\ Energy(E) = Bending\ Energy\ (E_b) + \ Stretching\ Energy(E_s) - Adhesion\ Energy\ (E_{ad})$$

As known, the bending energy is significant at atomic length scale only. We observe the same in our experiment. The magnitude of bending energy is negligible compared to the other two energies.

Individual energy plots against the angle of detachment (under different values of load) are shown below:

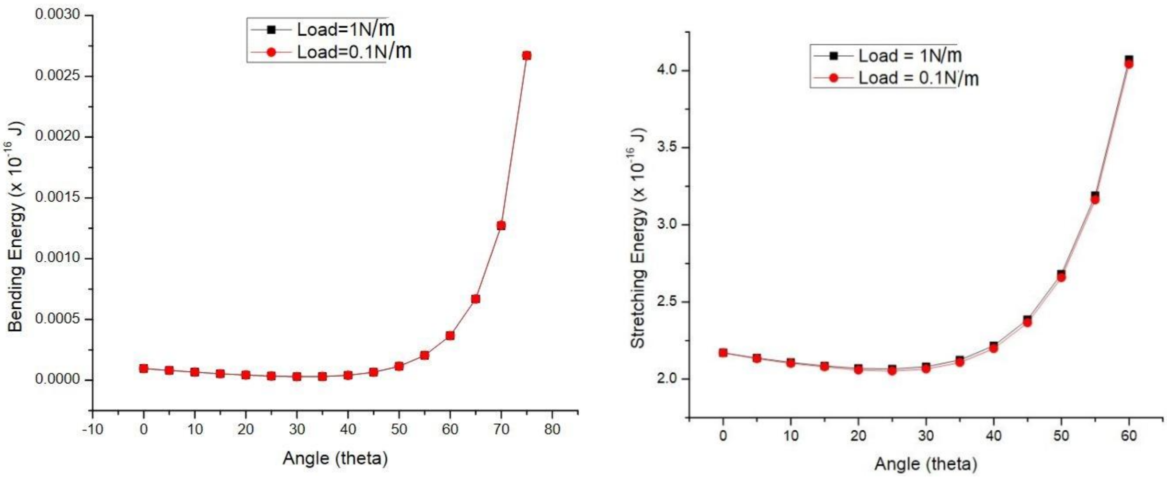


Figure 18: Bending Energy and Stretching Energy as a function of Angle under fixed load

Both bending and Stretching Energy first decrease with increasing angle of detachment, attain minimum value at an angle of 30^0, and then increase rapidly.

We can also observe that the magnitude of Bending Energy is about 10^4 times smaller than the magnitude of stretching energy.

Adhesion Energy Plot:

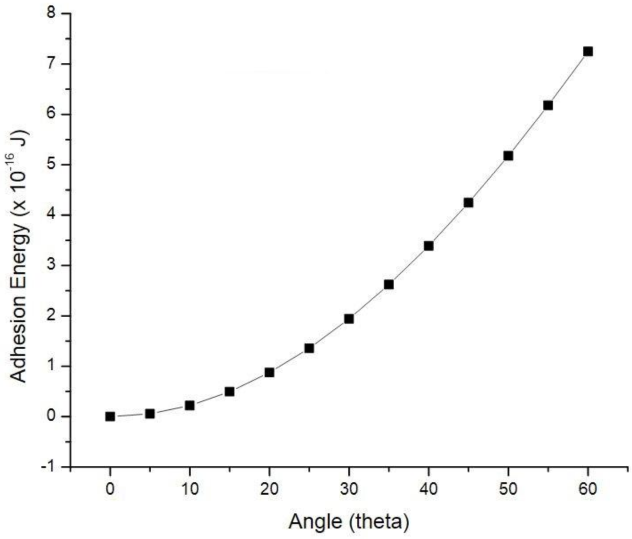


Figure 19: Adhesion energy against angle of detachment

Adhesion Energy increases with the increasing angle of detachment.

Combining all these energies together gives us the following plot:

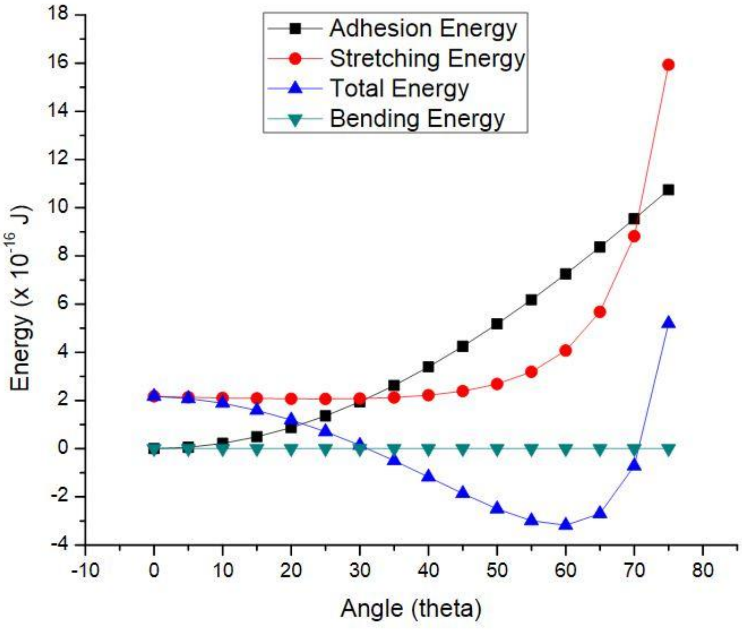


Figure 20: Total energy as a function of angle under fixed load (1N/m)

We observe that the total energy of the membrane becomes Minimum at an angle of detachment of 60^0 from the nano sphere. Though both bending energy and stretching energy reach their minimum at an angle of 30^0, the magnitude of adhesion energy in a region between 30^0 and 70^0 dominates them and the total energy becomes negative.

5.3.3 Individual Energy plots against load for fixed angle:

Bending Energy:

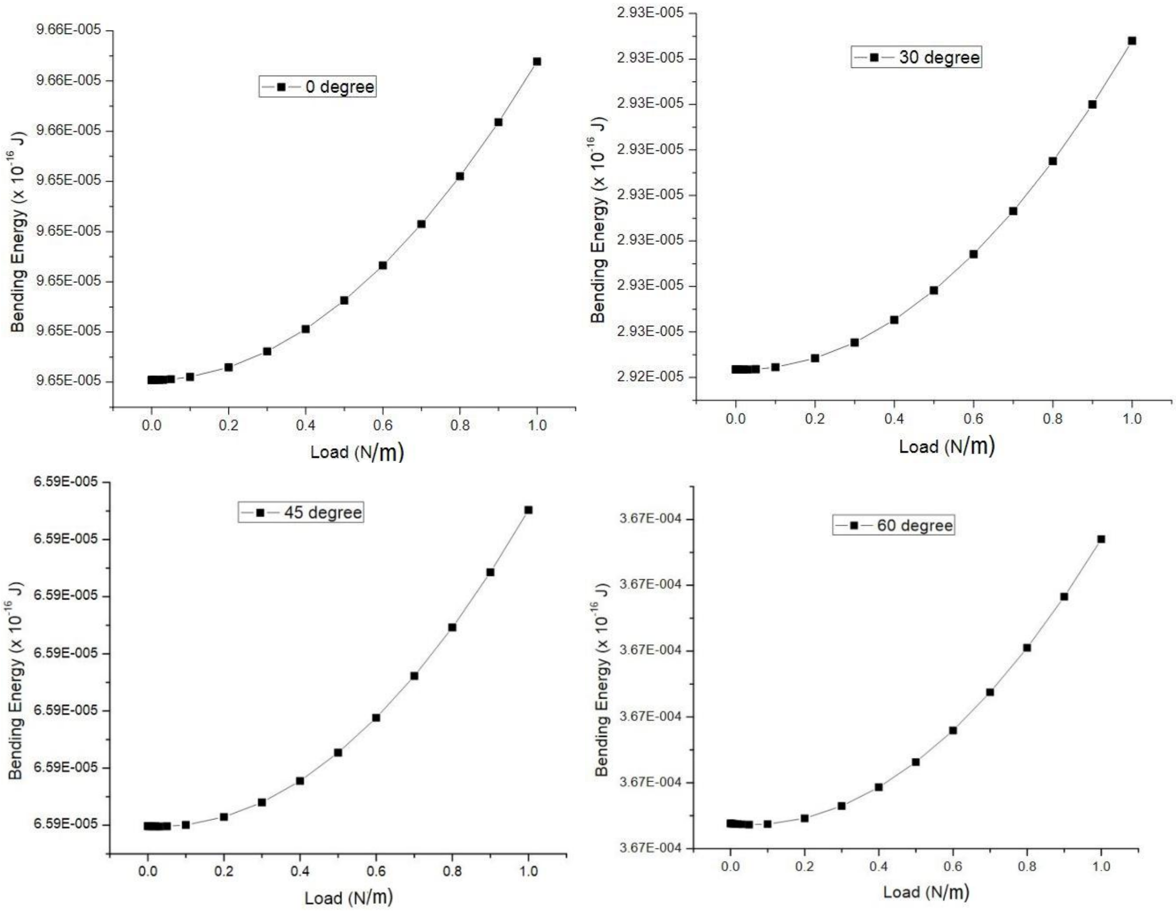


Figure 21: Bending Energy against load for different angle of detachment

Stretching Energy:

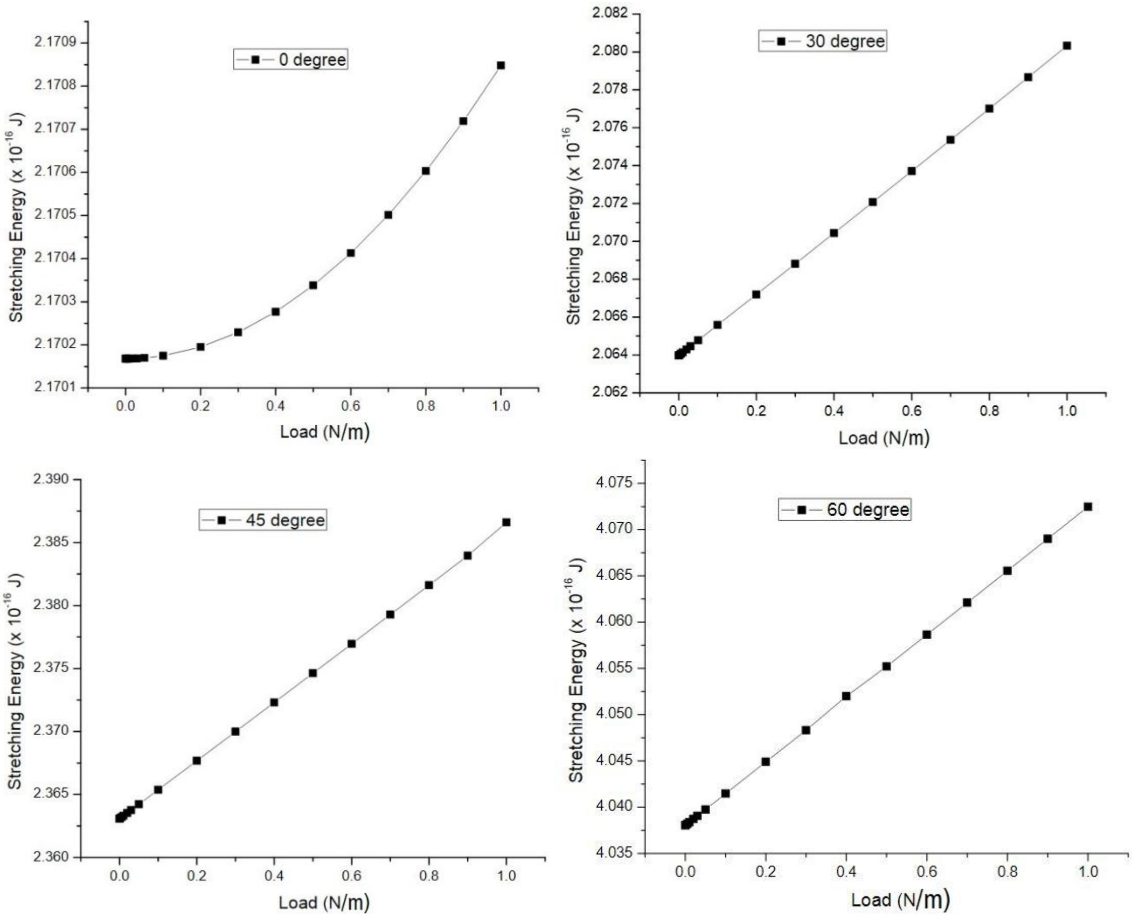


Figure 22: Stretching Energy against load for different angle of detachment

Magnitude Analysis:

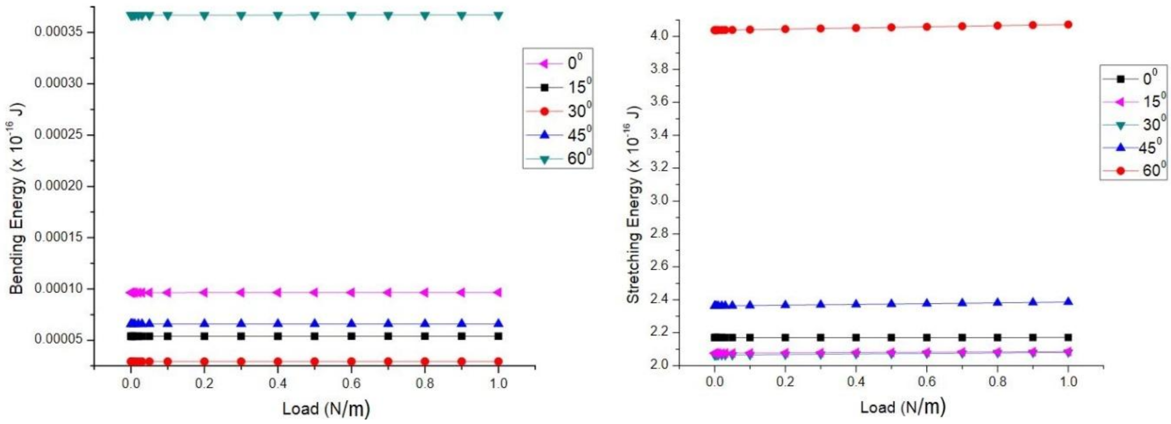


Figure 23: Magnitude of Bending Energy (left) and Stretching Energy(right) against loa

Variation of bending and stretching energy against load (for fixed angle) is similar to its variation against detachment angle (for fixed load). Both the energies reach minimum at angle 30^0 for all applied loads and become maximum at the angle of 60^0. However, these energies are dominated by the adhesion energy near this region so that the total energy becomes negative.

Though it is observed that as the angle of detachment increases beyond 60^0, bending and stretching energies increase more rapidly and dominate the adhesion energy again (detailed calculation in Appendix D).

6. CONCLUSION

Obeying the continuum elastic theory for a membrane and understanding the response of membrane under finite strain and load, we obtain the height profile of Graphene membrane under several conditions and approximations. An attempt was made to validate the 2-Dimensional membrane theory on 3-dimensional objects. Finally, the morphology of Graphene membrane on top of a nano sphere was obtained and studied analytically under some key assumptions.

Several parameters such as angle of detachment and load on the membrane play crucial role in defining the morphology of Graphene. The analytical solution, however considers the ideal situation whereas in real picture, several other phenomena such as wrinkles etc play important role. A small attempt is also made to study the significance of wrinkles and to find the morphology of the Graphene membrane under electric field.

Thus we get some understanding of the Graphene membrane on top of a nano sphere under finite load. Still miles are to be covered in order to get a sound understanding of it and to make it applicable in electronic devices.

7. FUTURE PLAN

Euler-Lagrange's equations in the case of 3-Dimensional system were solved by considering a 2 dimensional cross section of the entire system, under which the membrane is treated as a single 1-Dimensional strip. 3-Dimensional view is approximated to be similar to the 360^0 rotation of 1-Dimensional membrane. Though this gives us a good approximated model, the problem can also be solved in other ways such as transforming the Euler-Lagrange's equations in 3-Dimensional spherical co-ordinate system etc.

Next plan is to have a detailed understanding of the significance and role of wrinkling phenomenon in the morphology of Graphene membrane. Another objective is to study the same morphology under applied electric field and to observe the variation of electron mobility in each case (which is expected to increase). Once obtained, the result can be very useful and applicable in the field of making electronic devices more efficient.

All these efforts will certainly help us to have a sound understanding and control over Strain induced electronic properties of Graphene.

APPENDIX: A

Significance of bending energy:

An attempt was made to verify that the bending energy of a suspended membrane is significant at atomic length scale only.

In order to verify this, the height profile for the membrane was obtained at different length scale and under different conditions (presence and absence of bending rigidity). Absence of bending rigidity transforms the case into stretching of the membrane. Bending rigidity is related to the bending energy of the membrane.

After obtaining the height profile, maximum depression was calculated 1) presence and 2) absence of bending rigidity. It was observed that the maximum depression in both the cases were almost equal in magnitude for a length scale till the order of nano meter. But as it enters the atomic length scale, maximum depression in case of bending becomes significant.

Calculation:

Case of Graphene:

$$\partial_x^2\left[k{\partial_x}^2 - (\lambda + 2\mu)u\right]h(x) = p,$$

$$(k = 1eV, 3\lambda = \mu = \frac{900eV}{nm}, u = 5\%, p = \frac{0.1ev}{m^3})$$

Table II: Result

Length of the Membrane (m)	Maximum depression (m)	
	k ≠ 0	k = 0
10-3	1.19047573E-19	1.19047619E-19
10-4	1.1904715E-21	1.19047619E-21
10-5	1.190429E-23	1.190476E-23
10-6	1.190011E-25	1.190476E-25
10-7	1.185829E-27	1.190476E-27
10-8	1.1440047E-29	1.190476E-29
10-9	7.3126411E-32	1.190476E-31
10-10	2.537576E-35	1.190476E-33
10-11	2.6034832E-39	1.190476E-35

APPENDIX: B

Observation of height profile in macroscopic objects:

The experiment was performed on 4 samples (Rubber, Polyethylene, Cotton cloth and PDMS) by obeying the 2-Dimensional membrane theory as discussed in section 3.

Table III: Elastic properties of some materials:

Material	Young's modulus (GPa)		Lame's 1st parameter(GPa)		Poisson's ratio	Bending rigidity (J)	
	Min.	Max.	Min.	Max.		Min.	Max.
Rubber	0.01	0.1	0.164	1.64	0.499	0.11E-5	0.11E-4
Polyethylene	0.13	0.52	0.511	2.047	0.46	1.37E-5	5.48E-5
Cloth	3.3	---	2.851	---	0.35	3.125E-4	---
PDMS	0.000360	0.000870	0.000773	0.00186	0.43	2.93E-7	7.08E-7

Table IV: set of parameters:

External load applied: ~ 0.155N

Material	Thickness (mm)	Weight (N)	Area (m^2)	Strain	Total Load (N)	Load intensity (Nm^{-2})
Rubber	0.204	0.040	7x10-4	~ 5%	~ 0.16	~ 228
Polyethylene	0.069	0.010	7x10-4	~ 2% -5%	~ 0.155	~ 220
Cloth	~ 200	0.025	7x10-4	~ 5%-10%	~ 0.1575	~ 225
PDMS	~ 0.232	0.045	6x10-4	~ 5%	~ 0.16	~ 265

RESULT: MAXIMUM DEPRESSION (m)

Equation followed:

$$\partial_x^2\left[k{\partial_x}^2 - (\lambda + 2\mu)u\right]h(x) = p$$

Table V: Rubber

Young's modulus	Max. depression Theory (m)	Max. depression Exp. (m)	Order of error
0.01 GPa	**0.00008152**	**0.005005**	**~ 61**
0.1 GPa	8.152E-6		~ 613

Table VI: Polyethylene

Young's modulus	Strain	Max. depression Theory (m)	Max. depression Exp. (m)	Order of error
0.13 GPa	2%	**0.0001623**	**0.004374**	**~ 27**
	5%	0.00006502		~ 67
0.52 GPa	2%	0.00003928		~ 111
	5%	0.00001598		~ 273

Table VII: Cloth

Thickness	Strain	Max. depression Theory (m)	Max. depression Exp. (m)	Order of error
0.1mm	5%	**5.1730E-6**	**0.017268**	**~ 3300**
	10%	2.591E-6		~ 6600
0.2mm	5%	2.591E-6		~ 6600
	10%	1.297E-6		~ 13000

Table VIII: PDMS

Young's modulus(GPa)	Max. depression Theory (m)	Max. depression Exp. (m)	Order of error
0.000360	**0.00851**	**0.0078416**	**0.921**
0.000870	0.00353		2.221

TABLE IX: ELASTIC PROPERTIES OF SOME MATERIALS:

*(**E**: Young's modulus, **μ:** Shear Modulus, **λ:** Lame's first parameter, **σ:** Poisson's ratio, **B:** Bulk modulus, **K:** Bending rigidity)*

$$\lambda = \frac{E\sigma}{(1+\sigma)(1-2\sigma)};\ \mu = \frac{E}{2(1+\sigma)};K = \frac{Eh^3}{12(1-\sigma^2)};B = \frac{E}{3(1-2\sigma)}$$

Material	Thickness	Strain	E (GPa)	μ (GPa)	λ(GPa)	σ	B(GPa)	K	Method	Reference
Rubber band	0.5 mm	5%	0.01-0.1	0.0006 0.0033-0.033	0.164-1.64	0.499	0.166-1.66	0.11E-4 - 0.11E-5 J		[1],[2]
		5%	0.004	0.000013	0.0124	0.45-0.499	0.0133	5.20E-5 J	Frequency response function method	[16]
Low density Polyethylene	0.1mm	5%	0.13 – 0.52	0.117 0.0445-0.178	0.511-2.047	0.46	0.541-2.164	1.37e-5 – 5.48E-5 J	Stress-strain measurement	[3]
PDMS	0.1mm	5%	0.000360 – 0.000870	0.000203 0.000125-0.000304	0.000773 - 0.00186	0.43	0.000875-0.00207	2.93E-7 – 7.08E-7 J		[4], [17]
Cotton fabric	0.1mm	5%	3.3	1.222	2.851	0.35	3.66	3.125E-4 J	Stress-strain measurement	[5]
Graphite	0.1nm	5%	1020	440 425	283.33	0.2	566.66	1 .41E-19 J (~1eV)	DFT	[6],[7]
Mono layer Graphene	0.34 nm	~ 19%	2400	280 1000	666.66	0.2	444.44	1.2eV (8.18E-18 J i.e. 5.106eV)	Raman spectroscopy, Chemical vapour	[8],[15]
		~ 5%	1029	447.39	190.083	0.1732	490	3.510E-18J i.e. 2.19eV	DFT	[9],[10],[13], [14]
Bi layer Graphene	0.45 nm	~ 19%	2000	---	---	---	---	35.5eV	Raman Spectroscopy	[9],[11]
		~5 %	800	---	---	---	---		DFT	[12]

APPENDIX: C

Mathematica Calculations:

- **Height profile of graphene membrane:**

$$k = 1eV, (\lambda + 2\mu) = \frac{2100eV}{nm}, p = \frac{0.1eV}{m^3}, L = 0.0001m$$

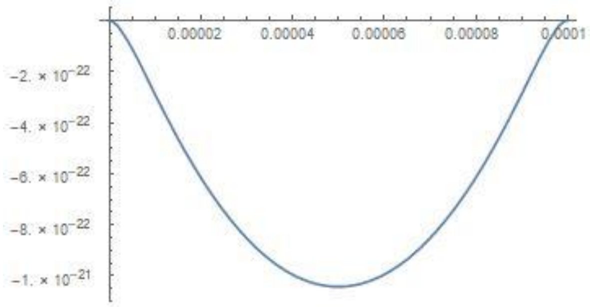
1. **Bending rigidity ≠ zero:**

In[18]:= solution = DSolve[{ h''''[x] - 2100000000000*0.05 h''[x] == -0.1, h[0]== 0, h[0.0001] == 0, h'[0] == 0, h'[0.0001] ==0}, h[x], x]

Out[18]= {{h[x]->\[ExponentialE]^(-324037.034920393 x) (-1.469555713924697*^-22+1.4695557139246999*^-22 \[ExponentialE]^(324037.034920393 x)-1.2429007094362668*^-36 \[ExponentialE]^(648074.069840786 x)-4.7619047619047606*^-17 \[ExponentialE]^(324037.034920393 x) x+4.761904761904763*^-13 \[ExponentialE]^(324037.034920393 x) x^2)}}

In[19]:= Plot[h[x]/.solution, {x, 0, 0.0001}]

Out[19]=



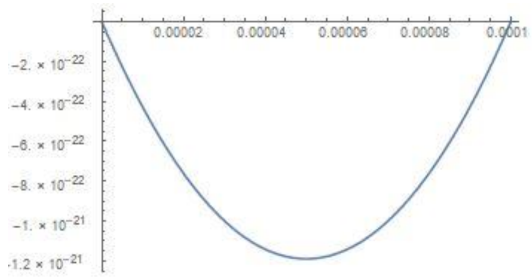
2. **Bending rigidity = 0:**

In[21]:= solution = DSolve[{ - 2100000000000*0.05 h''[x] == -0.1, h[0]== 0, h[0.0001] == 0}, h[x], x]

Out[21]= {{h[x]->-4.761904761904763*^-17 x+4.761904761904763*^-13 x^2}}

In[22]:= Plot[h[x]/.solution, {x, 0, 0.0001}]

Out[22]=



3. **Finding strain:**

In[2]:= solution = DSolve[{ - 2100000000000*u h''[x] == -0.1, h[0]== 0, h[0.0001] == 0}, h[x], x]

Out[2]= {{h[x]->(-2.380952380952381*^-18 x+2.380952380952381*^-14 x^2)/u}}

In[3]:= f[u] = Integrate[D[h[x]/.solution,x]^2, {x,0,0.0001/2}]

Out[3]= {9.448223733938019*^-41/u^2}

In[4]:= sol = Solve[u - f[u]*10000 + 100 ==0, u]

Out[4]= {{u->-100.},{u->-9.720197391996738*^-20},{u->9.720197391996738*^-20}}

In[5]:= strain = u/.sol[[3]]

Out[5]= 9.720197391996738*^-20

4. <u>Strain vs. load:</u>

In[24]:= solution = DSolve[{ - 2100000000000*u h''[x] == -p, h[0]== 0, h[0.0001] == 0}, h[x], x]

Out[24]= {{h[x]->(2.380952380952381*^-13 p (-0.00009999999999999999 x+x^2))/u}}

In[25]:= f[u] = Integrate[D[h[x]/.solution,x]^2, {x,0,0.0001/2}]

Out[25]= {(9.448223733938016*^-39 p^2)/u^2}

In[26]:= sol = Solve[u - f[u]*10000 + 100 ==0, u]

Out[26]= {{u->-33.333333333333336-(3.19669798277406*^14-5.536843322617611*^14 \[ImaginaryI])/((-7.056000000000002*^39+9. p^2+3.))^(1/3)-(8.689522102952159*^-13+1.5050693775805895*^-12 \[ImaginaryI]) ((-7.056000000000002*^39+9. p^2+3.))^(1/3)},{u->-33.333333333333336-(3.19669798277406*^14+5.536843322617611*^14 \[ImaginaryI])/((-7.056000000000002*^39+9. p^2+3.))^(1/3)-(8.689522102952159*^-13-1.5050693775805895*^-12 \[ImaginaryI]) ((-7.056000000000002*^39+9. p^2+3.))^(1/3)},{u->0.16666666666666666 (-200.+3.836037579328872*^15/((-7.056000000000002*^39+9. p^2+3.))^(1/3)+1.0427426523542592*^-11 ((-7.056000000000002*^39+9. p^2+3.))^(1/3))}}

In[29]:= u/.sol[[3]]

Out[29]= 0.16666666666666666 (-200.+3.836037579328872*^15/((-7.056000000000002*^39+9. p^2+3.))^(1/3)+1.0427426523542592*^-11 ((-7.056000000000002*^39+9. p^2+3.))^(1/3))

APPENDIX: D

Elastic energy calculation was performed mathematically using their respective formulae after calculating their height profile.

Bending, stretching and adhesion energy magnitudes are given by

$$E_b = \frac{1}{2}\int k\{\partial_x{}^2 h(x)\}^2 dA$$

$$E_s = \frac{1}{2}\int T(x)\{\partial_x h(x)\}^2 dA$$

$$E_{ad} = \int \gamma dA \qquad\qquad respectively.$$

Parameters taken for the Graphene membrane on top of a nano sphere are

$$k = 1eV, 3\lambda = \mu = \frac{900eV}{nm}, u = 5\%,$$

$$T(x) = 0.1 - 1\ mN;$$

$$\gamma \approx 1meV$$

$$Radius\ of\ the\ nano\ sphere \approx 120nm;$$

$$r \approx 600nm;$$

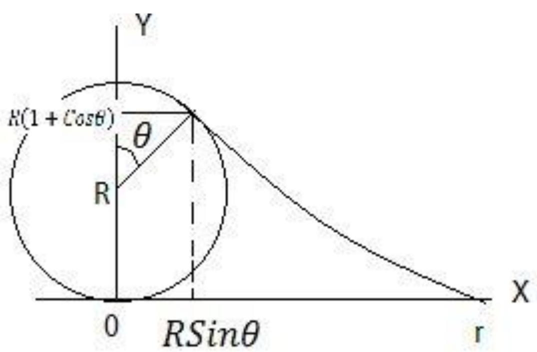


Figure: Graphene membrane on top of nano sphere in 2-D picture

The load in case of the Graphene problem is the PMMA residue left on the top of the membrane. Its value could not be calculated exactly. So its value was assumed to be within a range of 0.1 to 1 N/m.

Bending, stretching and adhesion energy were calculated for different load and angle of detachment.

However bending and stretching energies correspond to the single 1-Dimensional strip. We make an approximation here. Knowing that this strip will have same morphology under a fixed boundary condition, we assume to achieve a 3-Dimensional view by rotating this strip by 360^0. Thus we get the desired picture of the membrane on top of the nano sphere.

Rotating the strip by 360^0 includes an additional term in the bending and stretching energy formula that is

$$\int_{\emptyset=0^0}^{360^0} r d\emptyset$$

Whereas the adhesion energy is not affected since it is the interaction energy between the membrane and the nano sphere and in not associated with any particular dimension.

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