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How Shape of Simulated Graphene Sheets Affects Debye Scattering Patterns

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HOW SHAPE OF SIMULATED GRAPHENE SHEETS AFFECTS DEBYE SCATTERING
PATTERNS

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HONORS PROJECT

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INTRODUCTION

Objective

The objective of this project was to report and explain the results of performing Debye scattering calculations on simulated two-dimensional carbon crystals (i.e. single atom-thick sheets of carbon atoms) called graphene. Debye scattering of simulated systems is a way to analyze materials without physically handling them because Debye scattering patterns accurately predict electron diffraction patterns of those materials [1]. Electron diffraction is a way to measure the differences in atomic structure from one material to another and can be used to identify a particular structure [2-4]. By observing and analyzing the way that the Debye scattering pattern changes as the shape of a simulated graphene sheet changes, a better understanding can be gained about how electron diffraction patterns will change with differences in the atomic structures of carbonic materials.

Pre-solar dust grains

This project was developed from the necessity of finding a way to identify a unique atomic structure found in the cores of pre-solar carbon dust grains found in primitive meteorites. Formed in the atmospheres of red asymptotic giant branch (AGB) stars, these carbon dust grains exhibit a unique core-rim structure (Fig. 1) [4].
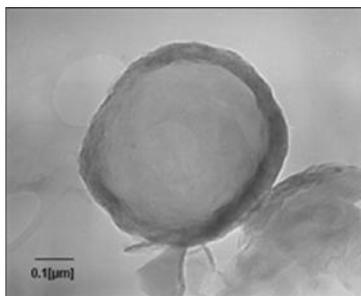

Figure 1: A TEM image of a graphite grain with a core-rim structure. Electron diffraction data from the cores of this and similar grains suggests a crystalline structure consisting of unlayered graphene. (Image reproduced with permission from Mandell [1])

Electron diffraction powder patterns of the rim reveal the structure of ordinary graphite – layers of graphene sheets held together through van der Waals bonding at about 3.4 Å. However, the core – which comprises the majority of the grain and has a density less than that of the graphitic rim – has an unusual electron diffraction pattern unlike that of any other known form of carbon [5-10] (Fig. 2) [8-9].
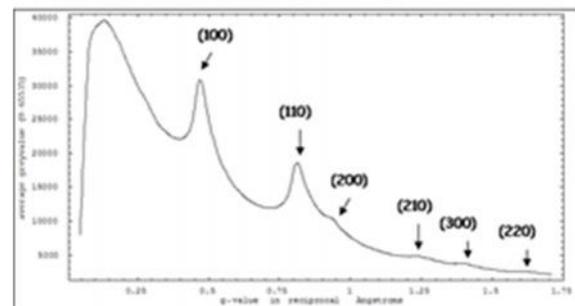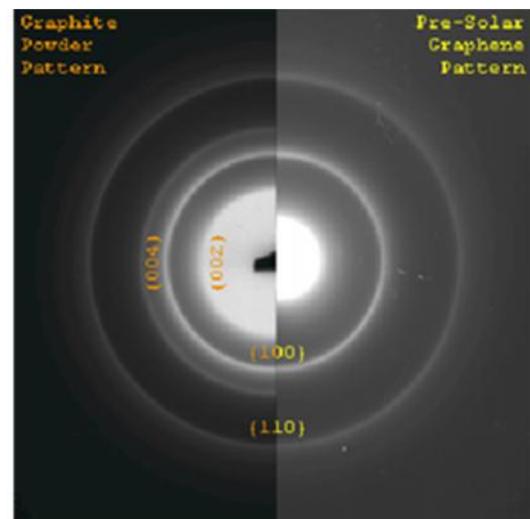

Figure 2: Shown at the top, electron diffraction pattern of common graphitic powder on the left half of the picture and the pre-solar dust grains of interest on the right half of the picture [8]. The rings correspond to the in-plane (hk0) graphite periodicities shown in the graph at the bottom [9]. Observe the absence of any inner ring, (and the absence of a peak that should appear at the red dotted line at around 3.4 angstroms) corresponding to graphitic layering.

Electron diffraction

Electron diffraction can be used as a way to identify different materials because each type of material has a unique atomic structure and therefore has a unique electron diffraction pattern [11]. The data from the carbon dust grains shows that within the cores, there are very thin (atomically thick) structures, but no van der Waals spacing. This indicates graphene sheets without the usual graphitic layering. Unfortunately, the electron diffraction measurements taken of the cores included a sample size of hundreds of millions of atoms (thousands of individual graphene sheets) which makes it difficult to know the exact size, shape and orientation of each of the sheets. Fortunately, a formula was developed over a hundred years ago by Peter Debye [1], known as the Debye scattering formula,

$$I(q) = \sum_{i=1}^{N} \sum_{j=1}^{N} f_i(q) f_j(q) \frac{\sin(qr_{ij})}{qr_{ij}},$$

that mathematically models electron diffraction patterns for a simulated system of particles and therefore can be used to look at a smaller sample size of atoms in order to determine smaller variations of structure. The results from these calculations can then be compared to the electron diffraction pattern from the stardust.

Debye scattering

The results of Debye scattering calculations on a two-dimensional sheet can be interpreted in two ways, either there are infinitely many identical sheets that have each been observed from a different orientation or there is one sheet that has been observed from every possible orientation. However, this involves many, many individual calculations as each particle in the

system must be compared to every other particle in the system and is therefore impractical without the use of a computer. For the purposes of this project, the computational software, Mathematica, was used to create a system of particles, to calculate the Debye scattering, and to plot the resulting pattern (Fig. 3).
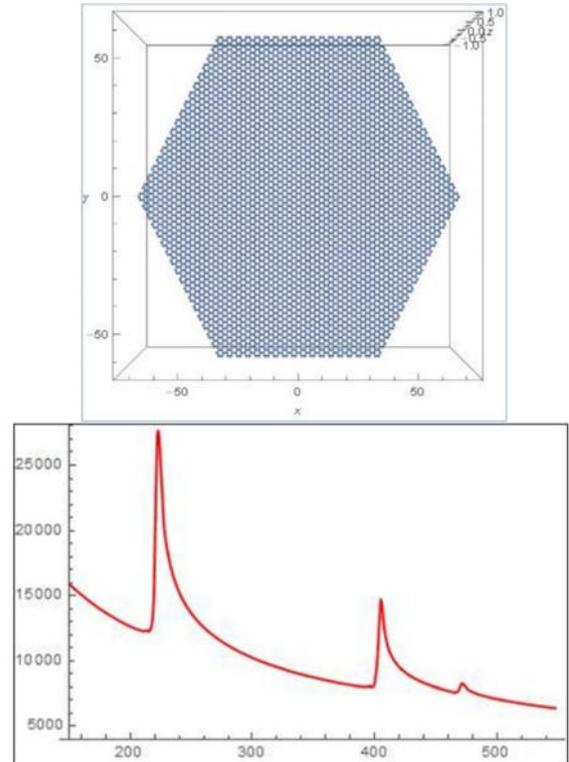

Figure 3: A hexagonal sheet of 5114 atoms (top) along with its corresponding Debye scattering pattern (bottom).

Debye scattering compared to electron diffraction

Once a Debye scattering pattern of a simulated system has been calculated, it can be mathematically compared to an electron diffraction pattern of a real material, and a difference of patterns can be determined. Previous research showed that when compared to the stardust's electron diffraction pattern, an isotropically-grown

hexagonally-shaped graphene sheet of particles with carbon spacing of 1.42 Å had a relatively low root mean square (RMS) difference (an RMS difference of of 0 would mean there is no difference between the two patterns) of 382. The Debye scattering pattern of a simulated triangular-shaped graphene sheet had an even lower RMS difference of 332 when compared to the stardust, and it could be seen that the leading edge of each peak – the first peak in particular – was changing with the change in sheet shape [6].

RESEARCH

Gathering and plotting data

For this project, Mathematica was used to create a set of 18 isosceles triangular-shaped graphene sheets ranging from 36 atoms to 2114 atoms in size. Each sheet was cut at a different apex angle – half of the vertex angle – in 5° increments, varying from 0° to 85° (the 0° sheet actually being a single line of hexagonally-bonded particles).
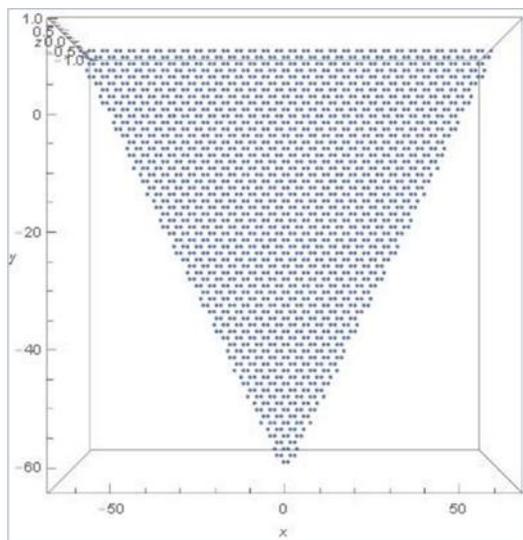
Figure 4: An isosceles triangular-shaped graphene sheet of 2068 atoms cut at a 40° apex angle.

By varying only one variable (the degree of the vertex angle), any changes in the Debye pattern can be attributed to dependence on that parameter and the change in coherence width for each graphene lattice spacing caused by the change in shape.

Analysis of data

In order to compare the Debye scattering patterns to the stardust, it was first necessary to transform the data using several operations. First, the patterns were normalized and then adjusted for the number of atoms. Next, the background noise from the Debye patterns – an effect of the calculations – was subtracted, to then be replaced by the background from the stardust's diffraction pattern. Finally, the Debye patterns were scaled for intensity to account for differences in thicknesses of structures between the two-dimensional simulated graphene sheet and the three-dimensional stardust cores. Mathematica was then able to perform a spline fitting (or "least squares") routine to fit the data for a direct one-to-one comparison between the Debye scattering patterns and the stardust's electron diffraction pattern.
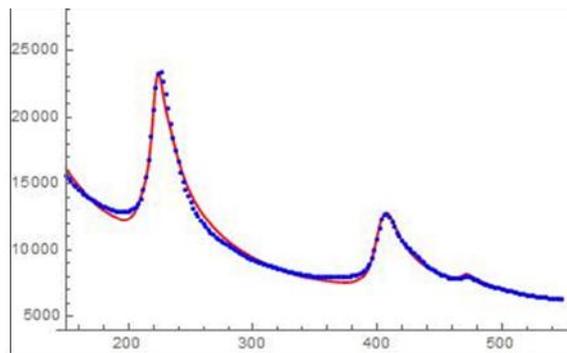
Figure 5: Debye scattering pattern for a 65° apex angled triangle (red) fitted to the electron diffraction pattern of the stardust (blue).

After adjusting all of the patterns in this fashion, it can be seen that the RMS

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difference changes dramatically with only a small change in the vertex angle of the triangular sheet. The closest fit to the stardust was with the 65° degree apex-angled triangle with an RMS of 318 – a lot lower than in the previous study, but still not close enough for conclusive determinations of the structure of the stardust. In order to understand these results better, the triangles need to be recut in larger dimensions (all starting with about a thousand atoms) and the process repeated. This will also allow for a better understanding of how changing sheet shape affects the peak shapes in diffraction.

Presentation of results

This research was presented as a poster for the Fall OSAPS Regional Materials Science conference held here at BGSU this past October. Also in October, this research was presented in an invited student talk at this year's Women's in Physical Sciences, "WoPhyS" Materials Science Conference held at the University of Nebraska at Lincoln. In addition, there are plans to include these results in a paper for peer-reviewed publication after more research is conducted over the next several months.

FUTURE PLANS

2017 spring semester

There is a lot more left to be explored with regards to this research and therefore several tasks will be pursued next semester. The first task is to recut the triangles with about a thousand particles each (ensuring that each triangle has the same number of atoms) and then calculate their Debye patterns. These patterns may then be compared to each other

so that we can work to build a predictive model for peak shape based on known coherence width of lattice spacings in the graphene sheet. Secondly, we would like to observe how the Debye pattern changes if the formula is calculated using a cluster of the simulated graphene triangles (at least one of each apex angle) randomly oriented together. The third task will be to attempt to use the data points of an electron diffraction pattern of a physical object to reverse the Debye scattering calculations in Mathematica and therefore determine the locations of particles in a system. Fourth, we plan to add defects to the hexagonal in-plane bonding of the graphene sheets (creating pentagonal bonding) allowing the two dimensional sheet to curve in a third dimension, and finally, continue to calculate the Debye scattering patterns of simulated three-dimensional objects created using models for core-rim grain formation for comparison with the stardust.

Exploration of possible formation models

The nano-structures found in the cores of the stardust grains do not match any known structures of carbon, but there is reason to hypothesize that the cores of these grains are the result of the rapid freezing (quenching) of a liquid carbon droplet. Since the liquid phase of carbon is not yet controllable or even sustainable in laboratory conditions due in part to its high melting point, atomic simulation software is currently the only viable method for examining the behavior of carbon under the desired conditions. Molecular dynamic programs like LAMMPS can be used to simulate the condensing of carbon into frozen liquid droplet-like objects that the Debye scattering formula can be applied to.

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