ELASTIC ENERGY IN FOLDED GRAPHENE SHEETS

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Introduction

In graphite moderated nuclear reactors graphite must withstand the bombardment of high energy neutrons of up to 2MeV. This energy is dissipated in the material largely by means of collisions with carbon nuclei in the graphite lattice. The weakly interacting neutrons travel a relatively long distance into the material before colliding with a nucleus. This primary knock-on atom interacts strongly with surrounding material and causes a cascade of damage along its path. The resultant damage changes the properties of the graphite, such as its dimensions, and thermal and electrical conductivity, amongst others[1]. The standard (atomic displacement) model for radiation damage in graphite cannot on its own quantitatively account for dimensional changes with irradiation that takes place at reactor temperatures[2]. The aggregation of interstitials into prismatic dislocation loops appear to account for between a half and a tenth of the c axis dimensional change. A proposed model[3] for radiation damage suggests buckling and folding of sheets of graphite layers, which may be able to account for a number of observed properties. X-ray diffraction simulations on unit cells containing folded layers show characteristics displayed by experimental samples, with evidence of the presence of line defects. Continuum elastic calculations on folded graphene layers using appropriate intrinsic properties of graphene[3] show correlation with DFT calculations of nanotube formation energies[4].

X-ray Diffraction Simulations

Simulated X-ray diffraction images were produced using CrystalMaker software with unit cells composed of about 1700 atoms containing a folded layer.

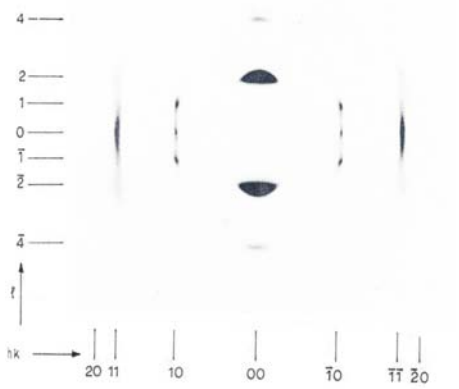

Fig. 1 Image from literature showing superposition of two precession diffraction runs about high symmetry axes [5].

Oscillation and precession images about axes of high symmetry, namely $11\bar{2}0$ and $10\bar{1}0$ were recorded as well as altering the wavelength in accordance with the experimental conditions. The experimental images exhibit, in particular, streaks between $10l$ diffraction spots indicative of the presence of line defects. These streaks are evident in our simulation as shown in Fig 2.

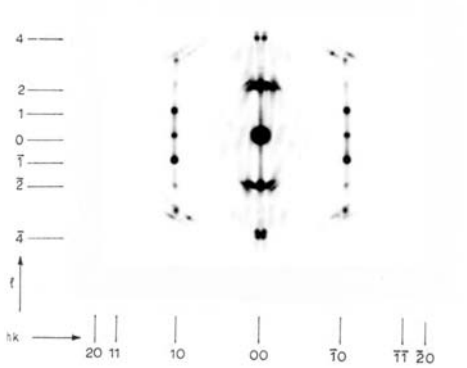

Fig. 2 Simulated precession diffractograms from a ruck and tuck defect.

Elastic Energy stored in folded graphene

The equation for free energy due to bending of thin plates has been used to calculate the elastic energy stored in sheets of graphene folded into nanotubes of various radii. Landau and Lifshitz provide the small displacement approximation equation for deformation of a membrane[6]. In our work we need to account for large displacements, so we opt to sum bending moments as in equation (1), dividing the length, l, of the membrane into n sections:

$$E_b = \frac{\kappa}{2} \sum_{i=1}^{n} C_i(t)^2 \cdot \frac{l}{n} \cdot \Delta z \qquad (1)$$

where κ, equal to 1.41eV, is the flexural rigidity, C is the curvature and Δz is the length of tube. The results are compared directly to Density Functional calculations (using LDA) of nanotube energy formation as a guide to the effectiveness of the method. This benchmarking provides a way to gauge the credibility for its use in further calculations such as that of the folded layer, the "ruck and tuck" defect. Taking the energy as a sum of bending moments is an approximation which ignores stretching or compression of the membrane, which should be the case for membranes which slide freely over each other (i.e. C_{44}=0). Applied to a simple, parametric representation of the folded layer we obtain a line energy of approximately 5 eV/Å, broadly equivalent to two small nanotubes of radius 2 Å.

Graph comparing formation energies of various radii nanotubes from calculations using DFT and classical elasticity

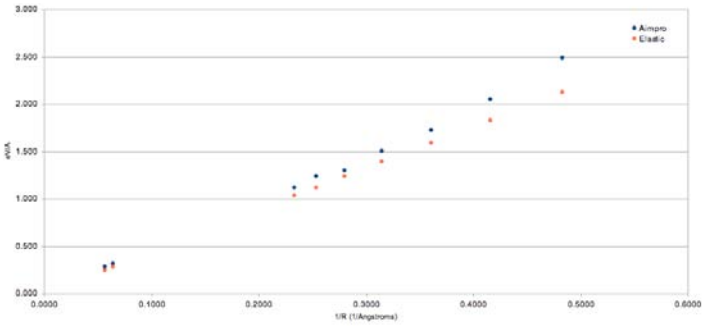

Fig. 3 Graph showing free energy due to bending alongside nanotube formation according to DFT using LDA. Plot is energy vs 1/radius

Remarks and Discussion

The simulated X-ray diffraction images show promising characteristics when compared to experimental diffractograms obtained from neutron irradiated graphite. The streaks between 10*l* spots, indicative of line defects, are reproduced by the linear folded defects, known as the ruck and tuck defect. The correspondence between the mushroom shapes of the 002 diffraction spots and their simulation in the ruck and tuck is not exact, but it is expected that averaging over different sizes and orientations should improve this.

The elastic energy calculations for nanotubes approach the DFT energies for tubes of radius higher than 2.5 Å. The discrepancy increases for very small tubes of 2 Å or smaller probably due to electronic contributions to the energy. These results bring confidence to the use of this method for folded graphite sheets as the extremes of curvature of the ruck and tuck defect is comparable to that of small nanotubes of 2.5 Å.

Further experimenting with continuum methods will allow us to move away from computationally expensive atomistic quantum calculations and access larger length scales likely to be appropriate to radiation damage problems.

References

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