Visualization Techniques for Modelling Carbon Allotropes

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Abstract

Carbon takes many different forms, each with its own electronic structure and has a fantastic range of properties. As well as graphite/diamond, a hexagonal diamond called londsdaleite, and amorphous carbons of sp2, sp3 and mixed natures there are all the fullerenes, graphene, nanotubes etc. Fortunately, their different electronic structures take distinct geometrical forms, so that deducing the geometry of a sample that has been simulated is a crucial step towards understanding its properties. Visualization is essential for understanding sample geometries. AViz [1] is an Atomistic Vizualization package developed at the Technion that can be freely downloaded and installed. Both still and animated AViz implementations for viewing data from our atomistic simulations of carbon allotropes enable understanding of the simulation results and when compared with laboratory experiments and theoretical models provide insight into nanodiamond growth, gas flow in nanotubes, nanotube vibrations and other topics of current research interest.

Key words: carbon, molecular dynamics, visualization

1 Introduction

Prior to 1967 the equilibrium carbon phase diagram was believed to include gas and liquid phases as well as two solid forms, diamond and graphite. In 1967 a second form of diamond, londsdaleite, or hexagonal diamond was observed in meteorites. Amorphous carbon of different types and mixtures of all of the above have been the focus of intensive interest for the last twenty years. The aim of developing synthetic diamonds has been realised far more sucessfully than the alchemists dream of transforming base metals to gold, and probably with more useful industrial applications. Computational alchemy (better known as atomistic simulations) is a useful tool that complements experiment for researching carbon allotropes. One example is the analysis of graphite to

diamond conversion and nanodiamond growth especially in the presence of hydrogen [2].

In 1985 the discovery of fullerenes ushered in a new era for the study of carbon allotropes. The isolation in 2004 of single graphene sheets intensified research in this area. In this paper, we concentrate on issues of visualizing these diverse allotropes from a purely geometrical viewpoint. Such visualization is needed so that when we undertake computational alchemy (a.k.a. make atomistic computer simulations) we can view the sample development and final states. (It goes without saying that such visualization is invaluable in the code debugging stage.) Since space is limited here, not all images can be shown, and since color is essential for some we have selected two cases that are relatively clear in black and white. At some appropriate places in the text we will refer the interested reader either to pages on our website [3] where these are shown in color, or to journal references with color images online.

2   Carbon Atoms and Phase Diagram

A carbon atom has 6 electrons, 6 protons and some neutrons, each of which has a wave nature. To visualize in this detail even if we had a nucleus with overlapping 10cm wave packets for 6 protons and neutrons, 6 appropriately scaled wavepackets for electrons, would lead to an atomic radius of 10km!

We could transform the nucleus to single point, and concentrate on the 3 dimensional visualization of the electrons BUT the electronic density of even the single electron of a single hydrogen atom is tricky. (It is generally done with techniques such as smoke rendering.) We have developed an "offlabel" adaption of our atomistic visualization package AViz which uses dots in different colors to help indicate density for such cases. However, it would be very hard to draw electronic densities in any way that the underlying lattice structure could be understood for tens of atoms in a solid sample. Thus one turns to a different approach in order to visualize the different carbon allotropes. We selected a ball and stick modelling in the spirit of common chemical visualization packages, but with significant extensions including viewing capability for more than a million atoms and others that will be described below.

The two main macroscopic equilibrium allotropes of solid carbon, diamond and graphite have deep differences. The former is a hard insulator, the latter a soft conductor. There are sp^2 hybridized orbitals for the 3 in-plane nearest neighbours in sheets of graphite, and the 4 nearest neighbours of the diamond lattice are sp^3 bonded.

If we visualize the lattice structure with "atoms" drawn as balls, we may use

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color to indicate the number of neighbours. Using "bonds" drawn as sticks between atomic centers to separate the atoms and assist in the realization of perspective we can obtain insight into structures of hundreds or thousands of atoms. In the simplest implementations we use different colors for the different hybridizations of the carbon atoms. In more complex implementations we may extend this by choosing different colors for 4 fold coordinated atoms that are neighbours of 3 fold coordinated ones, or even different colored bonds connecting atoms of different coordinations [1].

Both experiment and simulations cover many different mixtures of different allotropes. These include diamond - graphite conversions and intermediate amorphous phases at high temperatures and pressures and mixed diamond - graphite - amorphous phases from CVD growth at low pressures. Most of these are either nanoscale themselves or nanoscale in regions of interest. Identification of these structures provides a REAL VISUALIZATION challenge in simulations. Fullerenes, nanotubes etc are all nanoscale and while in isolation these are quite easy to identify graphically, once they are transforming or interacting their visualization also becomes a challenge.

3   Examples of Visualization Challenges and their Resolution.

Londsdaleite: in addition to its cubic(c-D) diamond form, sp^3 bonded carbon also has a hexagonal diamond form. Londsdalite,(h-D) was first identified in 1967 from the Canyon Diablo meteorite at Barringer Crater and is believed to form when meteoric graphite falls to Earth. The allotropes h-D and c-D have similar structures, but differ in the stacking order of the carbon layers apparent in the long range radial distribution function graphs [4], as shown in Figures 1 and 2 of [4]. Comparison with these reference structures enabled us to determine whether c-D or h-D was formed in our nnanodiamond growth process under pressure.

Diamond transformation to graphite: an abinitio calculation [5] showed the stages of transformation of diamond to graphite by surface graphitization. Groups using classical potentials failed to reproduce this. We [6] succeeded using Tersoff potentials presumably because we were very careful with equilibration in a simulated annealing type of relaxation. To show the lattice coordination and hence indicate the nature of the bonds we used yellow for 3 fold coordinated atoms and blue for 4-fold, (the colors being selected for their transformation to light and dark grey in black and white representation) and images of ours compared to [5] are shown in Figures 1-3 of [6].

Color-coding both atoms and bonds: the split interstitial defect is known to be the most stable defect in diamond. Prior to our study, [7] the path to its

formation was unclear. We displaced carbon atoms with an energy of 64EV to mimic the endstage of the damage cascade after ion-implantation. To locate the split interstitial within the 5,000 atom diamond sample we changed the bond color of the specific bondlength characteristic of the defect. The defect jumped out at us as is shown in the images of [7].

Fullerene visualization/use of slicing: AViz has several options which alone or in combination can enhance threedimensional viewing. A series of images at different depths of zoom, combined with slicing at a specific fixed depth show the internal structure of fullerenes like C480 and C240 nicely. A few stages in the zoom animation are shown in Figure 1, and the full color animation is shown at [8]. A slice, (used with the indicate only option) provides a background plane against which nanotube detail can be seen. This is especially useful to determine whether small changes have occurred in the structure.

Diffusion in nanotubes: for a study of diffusion of hydrocarbons in nanotubes we developed several visualization/animation tricks. One useful one is to start an animation of a diffusion process by firstly rotating the nanotube with all nearest neighbour bonds drawn in to give spatial perspective and depth. However the bonds block the diffusing atoms from view, so once the geometry is established in the viewer's perception, the bonds are erased to enable a clear view of diffusion in the nanotube interior. Color selections (blue-grey for nanotubes) and bright pink for diffusing atoms were designed to make diffusing molecules show clearly thru the nanotube walls. A manuscript [9] with results from this project is in preparation.

Tracks of hydrogen diffusion in diamond: when only a few atoms are diffusing and we wish to observe their path, we can use the tracks option to record the diffusion route. This was used in [10] to determine which interstitial sites hydrogen atoms preferred in a diamond crystal. For ease of viewing, in such a cumulative image, the diamond crystal atoms should be drawn in their equilibrium position.

Drawing only bonds of specific length: the stretch and compression of nanotubes under bending may be too slight to view clearly in a simple animation. However using the AViz option to only draw bonds of a specified length enables us to see which parts stretch, which compress, and where atoms move out of their equilibrium positions. We will show an example of this below.
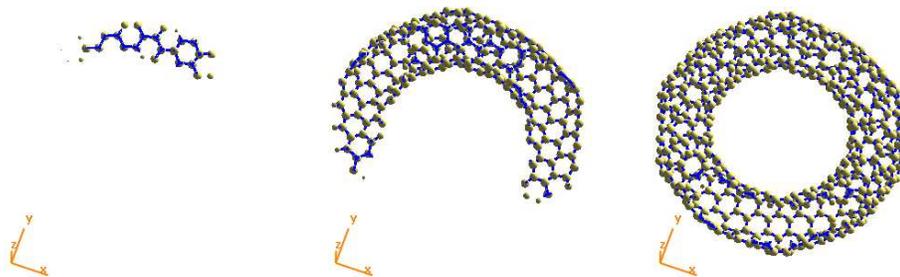
Fig. 1. 3 of 45 stages in a fullerene zoom animation, showing how the hollow tube is structured.

4 Pedagogy and Validation

In an earlier section we mentioned the obvious that visualization is invaluable in code debugging. It is also essential to code validation because when errors related to precision or boundary conditions occur - atoms tend to move in unexpected ways that cannot always be picked up as quickly from studying energy averages or velocities. It is so much easier to see if a sample is melting by viewing movement directly (especially if you color-code original positions in layers with a color gradation and look for color mixing) than by calculating mean squared displacements and averaging. The eye averages behaviour of many atoms better than do calculations.

One of the special aspects of visualizing atomistic simulations of this type is that for well-chosen problems and sample geometries with correct boundary conditions we really can obtain simulations/animations that really mimic reality. This is especially useful when we can validate the code by providing an animation that gives results that look like the experimental system we are modeling, or like an analog experiment. The canonical example of this is the nanotube discussed in the previous section - a nanotube, whose vibrational behaviour is somewhat like that of a stretched string and rather more like that of a spring that has a finite crosssection. Under strong tension, if the spring is clamped at one end, but free at the other, the behaviour will become quite chaotic. If the atomic movements are not very large, then it is hard to view or calculate deformations above the thermal noise. If only bonds of selected lengths are drawn one can see immediately which regions stretch and which compress. In Figure 2 an AViz example is given, where only bonds somewhat longer than the equilibrium value are drawn. You can see the tension moving in a pulse to the right. If you take any spring from the demonstration lab or toyshop, hold it at one end and pull on the other, you will observe similar behaviour.

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Fig. 2. A nanotube showing three stages in the early movement of a pulse of lengthened bonds as it is pulled to the right. At a later time this nanotube become quite chaotic.

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