Simulation and Visualization of Nanodiamond and Nanographite

Joan Adler, Jeremie Zaffran, Amihai Silverman, Anastassia Sorkin, Or Cohen, Rafi Kalish

Physics Department, Technion, Haifa, 32000 Israel

Abstract

Carbon allotropes exhibit an enormous range of properties due to their varied hybridizations. Different hybridizations are correlated with different geometrical structures. We address the visualization of both the geometry and the electronic density for different cases including diamonds with defects and mixed diamond/graphite/amorphous samples, in order to explore this connection more deeply.

Keywords: diamond, amorphous carbon, visualization, electronic density

1. Introduction

We have modelled transformations between diamond (sp^3) and graphite (sp^2) allotropes of carbon in a long term Technion project of computational/experimental comparison. In our earliest calculations we modelled the degradation of diamond to graphite under irradiation and viewed the creation of split interstitial defects [1] and the graphitization of local regions in diamond[2]. Such graphitization leads to a breakdown of the diamond's insulating properties. Therefore it needs to be avoided in technological applications of diamonds and hence requires understanding. In more recent studies we studied damage along an ion track in diamond [3] and modelled the formation of nanodiamond and nanographite[4, 5]. Together with an excellent success rate of growth and identification of nanodiamonds came the rather surprising result of nanographite formation [5] in the case of slow cooling. This turned out to be an independent prediction of an experimental result found shortly thereafter[6].

Throughout most of these calculations we based decisions about local carbon hybridization on geometric information such as number of neighbours, bond lengths and angles. We used our AViz software to draw differently coordinated atoms and different bond lengths in color to aid our deductions[7, 8]. Cross comparison with experimental results has led to a high level of confidence in our deductions[9, 10, 11]. However a direct comparison of geometrical structure with the nature of the local electronic density would give even better support. In the case of models of diamond with impurities and defects, evaluating the local electronic density can lead to better understanding. In the present article we describe our approach to visualization of atomic and molecular electronic densities, for which we have introduced a semi-transparent dot approach to enable 3D viewing. We also discuss first steps towards direct visualization of electronic densities in carbon allotropes, and confirm that our previous conclusions based solely on geometry are valid.

2. Our approach

The nature of the simulation sample preparation used in several projects within our group [3, 4, 5, 10] has been extensively discussed elsewhere. We use a multiscale approach of molecular dynamics with the simple Stillinger-Weber potential for the largest samples, extensive time development with the better Brenner potential for intermediate sizes and tight-binding molecular dynamics (most recently with the Plato code [12]) to deduce local electronic configurations[11]. Samples of mixed diamond/graphite/amorphous carbon are prepared from intially translationally invariant diamond which is frozen in regions destined to model diamond and melted and rapidly solidified in regions destined for an amorphous structure.

Once the samples are created we view the atoms and "bonds" of the structure with AViz. An example is given in Figure 1 of the abovementioned nanographite found in the presence of 15 additional H atoms under pressure and slow cooling [5, 13]. Both hydrostatic and uniaxial pressure were applied and we observed that the graphite formed while the sample was still at high temperatures. This project used tightbinding molecular dynamics based on the OXON[14] code.

In a related Computational Physics group project motivated by educational use we have invoked an "off-label" AViz implementation to illustrate the electronic probability density from the H atom analytic solution in a smoke rendering form [15] using dots to enable semi-transparency. Com-

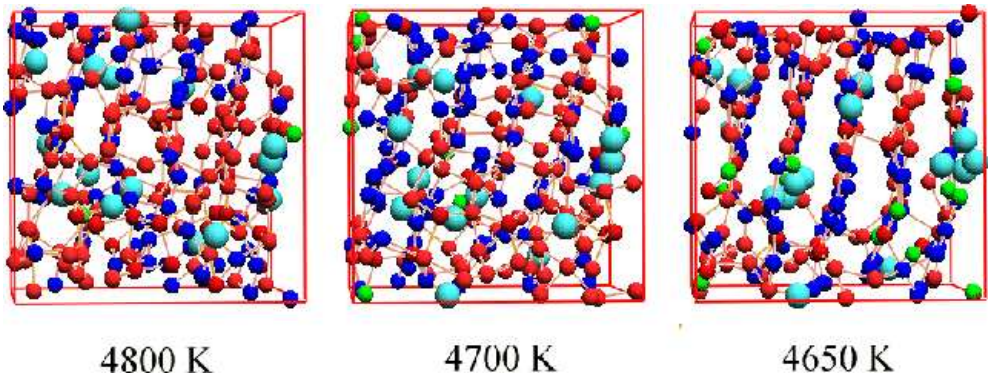

Figure 1: Snapshots of AViz visualization of hydrogenated liquid carbon at 3.9g/cc pressure with 15 H atoms during cooling. Red atoms represent 4-fold coordinated C atoms, blue represents 3-fold and green represents 2-fold coordinated C atoms. The large light-blue balls represent H atoms.

bined with color and rotation it gives excellent insight into the nature of the different electronic states[16].

Quite recently we began a new track of AViz applications to illustrate the electronic density resulting from simulations in the same way. The first studies [17] concentrated on simple molecules, but this idea is ripe for extension to our diamond/amorphous/graphite structures to confirm that the coordination/bond angle criteria we have used to determine the hybridization determinations are justified. In the next section we describe the techniques developed for simple molecules, and then discuss progress toward their extension to periodically bounded larger samples.

We note that there are many more recent, quite standard implementations of similar approaches to surface electronic density emulating STM images, but most do not use color as well as concentration to indicate the density of their "smoke". Nor do they make 3D images which can be rotated and sliced as ours can to peer inside the sample. In less transparent visualization some unique nanostructures may be overlooked.

3. Electronic density in atoms and molecules

In order to draw the electronic density we (obviously) first need to calculate it. For H this was almost trivial since it is part of the well-known analytic solution. Details of this calculation and the transformation to AViz input are on [16]. In brief, one calculates the electronic density on a grid,

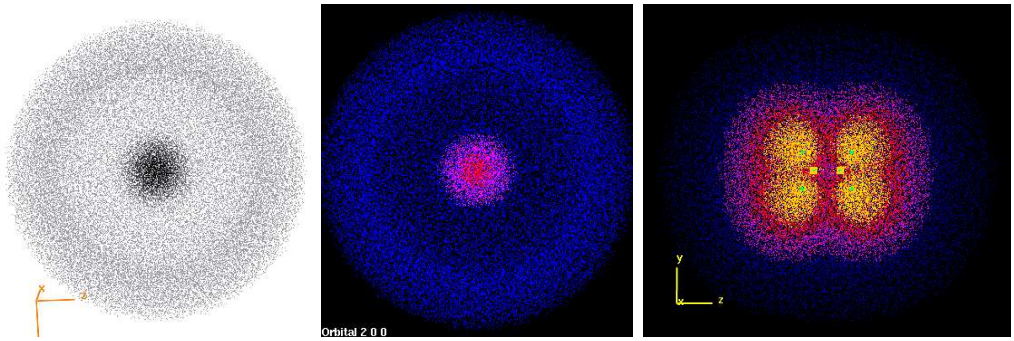

Figure 2: AViz dot visualizations of electronic density of the 2s state of an H atom in greyscale, and in color, and an ethylene molecule in color. The atoms in the ethylene are indicated by small squares, and the color scale of the desity ranges from orange (most dense) through red and pink to blue (least dense) in all cases.

and defines a box around each grid point. Dots are then drawn at randomly chosen points within the box at a density equal to the local electronic density. The "off-label" AViz use means that each of these points is given x, y and z coordinates and is drawn using the dot feature of AViz. The .xyz format is common to many molecular visualization packages, but its normally used to indicate atoms, not density points. For the hydrogen 2s case the datafiles contain some 50,000 points, rather larger than those typically used in atomic visualization, although since they are not solid spheres, the renering time is reasonable. In Figure 2 we show the AViz visualization of the electronic density of the 2s state of the H atom in both greyscale and color. Animated gifs of these samples in rotation are found at [16].

For molecules there is, of course, no analytic solution. To calculate the electronic density of the molecules we used GAMESS [18, 17] but the rest of the procedure is similar. In Figure 2 we show the colored electronic density of ethylene. Note that because the density is not shown with solid curves we can peer nicely into the sample. In Figure 3 we show a methane molecule both with all orbitals and stripped of the lower densities. We may also explore specific orbitals as shown in Figure 4, where the F2 orbitals is shown.

For our periodically bounded samples, we have chosen to use VASP[20, 21] to calculate the elecronic densities. In preparation for the larger samples, we returned to some of the simple molecules with the VASP code. For the moment we are using slice visualization with VESTA [19], although we plan to move to VASP/AViz in the future in order to better observe internal

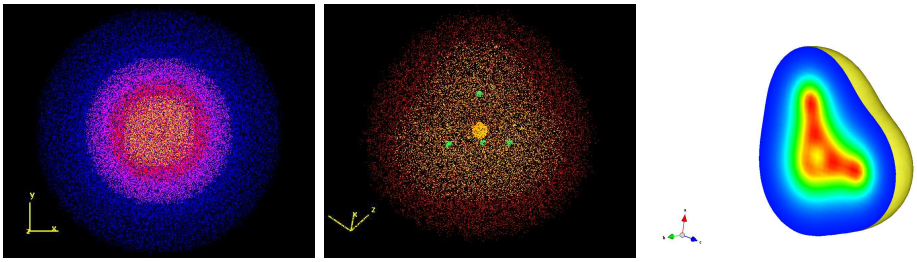

Figure 3: Electronic density of a methane molecule calculated/visualized with GAMESS/AViz, the same image stripped of the lowest densities and a methane molecule cut in the middle calculated/visualized with VASP/VESTA. Atoms are indicated by small squares(AViz) and electronic density ranges from orange (most dense) through red and pink to blue (least dense) in AViz and red to blue via green in VESTA.

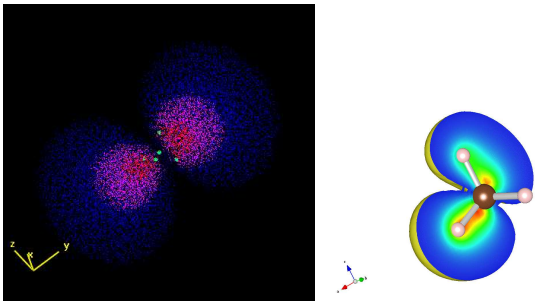

Figure 4: Electronic density of the F2 orbital of a methane molecule with GAMESS/AViz, and the F2 orbital of a methane molecule cut in the middle drawn with VASP/VESTA. Atoms indicated by small squares(AViz) and balls (Vesta) and electronic density ranges from orange (most dense) through red and pink to blue (least dense) in AViz and red to blue via green in VESTA.

structure. The move from the solid to the dot visualization for many atom samples is currently limited by the very large datafiles that are needed.

In Figure 3 we compare images of the electronic densities of CH_4 in the GAMESS/AViz version with a cut through the center of the VASP/VESTA version. Despite the VESTA solid visualization rather than the 3D dot-smoke type, one can confirm that the main features agree. Note that VESTA images also include green in the color range, the AViz ones use only a red-blue scale for better depth perception. In Figure 4 we also make a comparison between the F2 orbitals only. Again a very similar structure is seen.

The VASP/VESTA visualization of benzene is shown in Figure 5. We show the full sample with a plane indicating where the image is cut to show

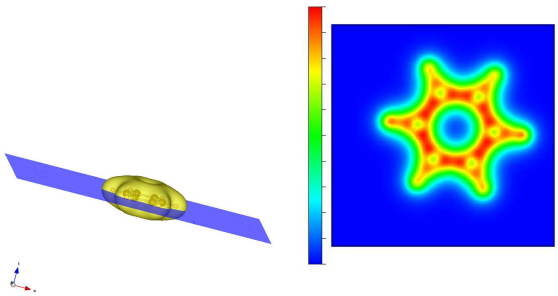

Figure 5: Electron density of benzene from VASP/VESTA. The benzene consists of a six-C ring with an H attached outside each C atom. The density ranges from blue (least dense) to red (most dense).

the electron density. This style of presentation is shown for a simple molecule to clarify the presentation of our new results below.

4. Electronic density in solids

After validating that we are correctly implementing the VASP/VESTA approach (see the comparisons in Figures 3 and 4; and note that the Figure 5 benzene results reproduce other independent calculations) we began calculating the electronic density of a series of systems selected from our previous calculations. In all cases the atomic coordinates are known. We considered diamond, graphite, graphene and nanotubes. All these visualizations can be viewed on [22],and gave correct results for their structure. We observe a consistent image signature of, for example, an sp^2 bond as seen in between the carbon atoms in the ring of benzene in Figure 5.

For a test system for the solid samples, we selected one of the early systems modelled[1] in our experiment/computation comparison project where sp^2, sp^3 and intermediately hybridised atoms are present. We chose a case with mostly sp^3 and only a few sp^2 hybridized atoms, making visualization relatively simple. The calculation was made for periodically bounded sample of some 512 carbon atoms initially in a diamond structure, and in order to gain clarity we visualise only 126 atoms from the center. This was a very simple molecular dynamics calculation, using the Tersoff potential at zero temperature, however it illustrates the formation process of a split interstitial defect for what we think was the first time. In animated versions one

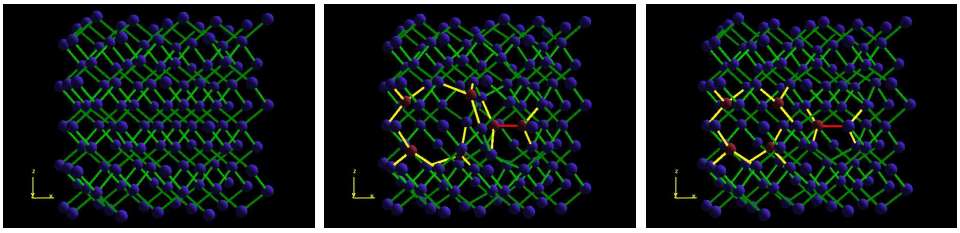

Figure 6: AViz visualization of atomic configurations of initial diamond sample, 49th out of 250 frames, and final state. Blue atoms are 4-fold coordinated, red 3-fold coordinated, bonds between two 3-fold coordinated atoms are drawn in red and bonds between a 3-fold and a 4-fold atom in yellow.

observes the vibrations of the phonon excitations in the sample. An AViz animation of some 250 png files can be viewed at the AViz website [23]. One atom (initially near the left of the image) is displaced with a kinetic energy of some 60eV. In Figure 6 we show the initial state, which is a perfect diamond lattice, before the atom is displaced, the 49th frame where the atom is displaced but not yet settled and the final configuration, a Frenkel pair of a split-interstitial and a vacancy. Atoms with a perfect 4-fold (sp^3) coordination are in blue, and those with a 3-fold (sp^2)coordination in red. Bonds between diamond atoms are in green, bonds between one 3-fold and one 4-fold in yellow and two 3-fold atoms in red. Our criterion for sp^2/sp^3 differentiation in [1] was simply to count neighbours within 1.65 $\mathring{A}$. In this case there was a gap in bond lengths between 1.65 and 2.1 $\mathring{A}$, but in futher studies with amorphous phases [3, 4, 5] the distribution is less clearly divided. This is a large part of our motivation to directly observe the electronic density.

We selected the 49th frame to make a full study of the electronic density with VASP/VESTA. In Figures 7 and 8 we show the system with a ball and stick representation and a plane of the electronic density that goes through the central bond of the split interstitial. This electron density is then shown in perspective and finally the full view from above is shown for clarity. We observe that the shorter bond of the split interstitial has a charge distribution reminiscent of that of graphite between two adjacent carbon atoms. A graphite sample also sliced through the middle of the atoms is shown for comparison.

We now plan to continue these explorations for samples with interfaces between amorphous sp^2 atoms and original undamaged diamond to obtain guidelines for how to etch out the sp^2 material and leave a flat sp^3 surface.

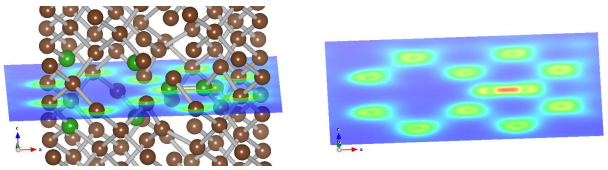

Figure 7: 2 views of the 49th frame sample showing its electronic density from VASP/VESTA. The green atoms are the 3-fold coordinated ones and in the electronic density slice red indicates the highest density, blue the lowest.

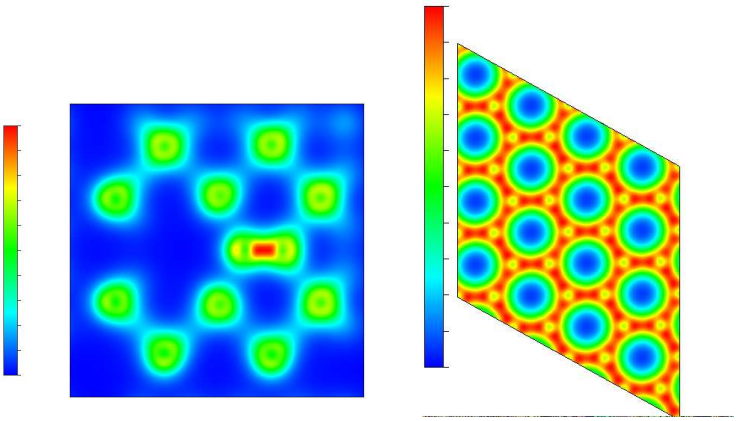

Figure 8: A view of the 49th frame sample showing its electronic density from VASP/VESTA from above compared with a sp^2 bond in graphite.

Acknowledgements: JZ thanks the Physics Department at the Technion for hospitality. Some of these calculations were performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Institut für Materialphysik of the Universität Wien [20, 21]. A Sorkin is now at the Department of Electrical Engineering at NTU in Singapore and O. Cohen is at the Department of Physics of Complex Systems at the Weizmann Institute of Science.

References

[1] D. Saada, J. Adler and R. Kalish, (1998), International Journal of Modern Physics, C, **9**, 61-9.

[2] D. Saada, J. Adler and R. Kalish, (1999), Phys. Rev. B, **59**, 6650-60.

[3] A. Sorkin, J. Adler and R. Kalish, (2004), Phys. Rev B. **70**, 064110.

[4] A. Sorkin, J. Adler and R. Kalish, (2006), Phys. Rev. B **74**, 064115.

[5] A. Sorkin, R. Kalish and J. Adler, (2008), Phys. Rev. B., **78**, 155435.

[6] E. H. T. Teo, W. K. P. Yung, D. H. C. Chua, B. K. Tay, (2007), Advanced Materials **19**, 2941-2945.

[7] J. Adler, Computing in Science and Engineering (2003), **5**, 61-65.

[8] J. Adler, Y. Gershon, T. Mutat, A. Sorkin, E. Warszarski, R. Kalish and Y. Yaish, "Recent Developments in Computer Simulation Studies in Condensed Matter Physics, XVIII", (2006), edited by D. Landau, S. P. Lewis and B. Schuttler, 56-60.

[9] S. Prawer, I. Rosenblum, J. O. Orwa and J. Adler, (2004), Chemical Physics Letters, **390**, 458-61.

[10] Sh. Michelson, R. Akhvlediani, A. Hoffman, A. Silverman and J. Adler, (2008), Phy. Stat. Sol. (a) **205**, 2099-107.

[11] E. Warszawski, J. Adler, A. Hoffman and A. Silverman, (2010), Physics Procedia **3**, 1381-1385.

[12] S. Kenny, A. Horsfield, H. Fujitani, (2000), Phys. Rev. B **62** 4899.

[13] Ph. D thesis of A. Sorkin, Technion, (2006).

[14] A. P. Horsfeld, (1997), Phys. Rev. **56**, 6594-6602.

[15] S. Johnson, W. Potter, K. Malkin, Proceedings of the International Conference on Simulation in Engineering Education, (1994), **26**, p. 199-202.

[16] http://phjoan23.technion.ac.il/∼phr76ja/joeyfox/Hydrogen.html

[17] http://phelafel.technion.ac.il/∼orcohen/DFTVisualize.html

[18] http://classic.chem.msu.su/gran/gamess/index.html

[19] http://www.geocities.jp/kmo_mma/crystal/en/vesta.html

[20] G. Kresse and J. Furthmüller, (1996), Phys. Rev. B **54**, 11 169.

[21] G. Kresse and D. Joubert, (1999), Phys. Rev. B. **59**, 1758.

[22] http://phycomp.technion.ac.il/∼jeremie

[23] http://phycomp.technion.ac.il/∼aviz