Size dependent phase stability of carbon nanoparticles:
Nanodiamond versus fullerenes

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Over the past 15 years, a number of studies have reported findings comparing the relative stability of diamond and graphite, at the nanoscale. In light of more recent experimental and theoretical results concerning the transformation of nanodiamonds into carbon-onions, it is considered important to extend this body of work to included fullerenes. Presented here is a study of the phase stability of carbon nanoparticles, with particular attention given to the relative stability of nanodiamonds and fullerenes. The structural energies have been calculated using density functional theory within the generalized gradient approximation using the Vienna ab initio simulation package, and used to determine the standard heat of formation for respective carbon phases as a function of the number of carbon atoms. Our results show that in contrast to previously reported studies, nanodiamond is not necessarily the stable phase a the nanoscale, but instead occupies a “window” of stability between ~1.9 and ~5.2 nm. © 2003 American Institute of Physics.

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I. INTRODUCTION

For decades, it was known that graphite was the stable form or carbon at atmospheric pressures and that diamond, while harder, denser, and more durable, was merely metastable. With the discovery of buckminsterfullerene in 1980 the door was opened for a new era in carbon science, and scientists were introduced to a new carbon allotrope. Buckminsterfullerene and the extensive family of fullerenes (while not a true graphitic phase), share many structural characteristics with graphite such as sp² hybridization and six membered rings. The question of the mechanism of formation of fullerenes is currently hotly debated by fullerene research groups. It is agreed however, that the relative phase stability of graphite and fullerenes can be attributed to size dependence, and although the graphene-like structure of fullerenes is strained due to the curvature of the surface (and graphite is not), it is this strain that causes fullerenes to be more stable than other forms of sp² carbon at the nanoscale. ¹

Recent interest in nanocrystalline diamond has prompted a number of researchers to re-examine the phase stability of diamond in the new nanosize regime. The transformation of nanodiamond to carbon-onions has been observed experimentally²–⁴ with a transformation temperature that is dependent on the size of the particle, and has been modeled theoretically⁵–⁹ at various levels of sophistication. Similarly, the reverse transformation of carbon-onions to nanocrystalline diamond has also been observed experimentally,⁵–¹⁴ and modeled¹⁵ by means of atomic-scale computer simulations.

The experimental discovery that nanodiamonds transform to carbon-onions, and vice versa, appear to be contradictory to theoretical work compiled regarding carbon phase stability.⁶⁻²² Badzian et al. suggested that small hydrogennated nanodiamonds may be more stable than graphite, and Hwang et al. outlined a chemical potential model¹⁹ and a charged cluster model²⁰ to describe the relative stability of small diamond and graphite clusters in their study of low pressure diamond synthesis. Winter et al.⁵ also outlined a method for investigating carbon particle phase stability based on the heat of formation of graphene sheets and hydrogenated nanodiamonds. Most recently, Jiang et al.²² have calculated the size dependence of the diamond-graphite transition, using the Clausius–Clapeyron equation.

All of the above-mentioned methods predict nanodiamond to be the stable phase of carbon in the range less than about 6 nm. The present study represents an extension of this body of work, offering complementary findings regarding the phase stability of dehydrogenated nanodiamond particles. By treating only dehydrogenated nanodiamonds a direct comparison with fullerenes has been made possible.

Formation energy. The method of estimating the phase stability of nanoparticles used here is to determine the heat of formation, as a function of particle size. This technique was outlined by Winter and Ree,⁵ and is described in the following.²³ The atomic heat of formation of graphite (ΔH²⁰⁰(G)) and diamond (ΔH²⁰⁰(D)) clusters is expressed in terms of the C–C bond energy E_C, the C–H bond energy E_CH, and dangling bond energy E_DB, such that:

ΔH²⁰⁰(G) = \frac{1}{2}(3N_C-N_H)E_CC + N_HE_CH + N_CE_CC ΔH²⁰⁰(G)
+ N_HΔH²⁰⁰(CH)
+ \frac{1}{2} N_CE_CC \epsilon_{vdw},

ΔH²⁰⁰(D) = \frac{1}{2}(4N_C-N_DB)E_D + N_DBE_DB + N_CE_CC ΔH²⁰⁰(D)
+ N_DBΔH²⁰⁰(DB).

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where \( N_C \) is the number of carbon atoms, \( N_{DB} \) is the number of dangling bonds on the surface of the particle, \( N_H \) is the number of terminating hydrogen atoms, \( \Delta H^o_f(C) \) is the standard heat of formation of carbon at 298.15 K, \( \Delta H^o_f(H) \) is the standard heat of formation of hydrogen, and \( E_{vdw}^{cc} \) is the van der Waals attraction between graphite sheets. A dehydrogenated surface has been used for nanocrystalline diamond and fullerene. In the case of fullerenes we know that the strain energy associated with curvature of the spherical sheets, the bending term provides the strain energy associated with curvature of the spherical structure.

\[
E = E_{bend} + E_{stretch} = E_{strain} + E_{cohesive}.
\]  

Making the assumption that, for the general case, the strain in an elastic sphere can be modeled by considering the bending and stretching of a suitable elastic sheet, the bending energy (\( E_{strain} \)) per unit area (\( A \)) is given in terms of the sheet thickness (\( h \)), by

\[
\frac{E_{strain}}{A} = \frac{\kappa}{2} \int_{-h/2}^{+h/2} \frac{z^2}{R^2} \, dz = \frac{\kappa h^3}{24R^2},
\]

where \( \kappa \) is the bending modulus of the sheet, and \( R \) is the radius of curvature. The strain energy per carbon atom is therefore:

\[
\frac{E_{strain}}{N_C} = \frac{A \kappa h^3}{N_C 24 R^2}.
\]

For a fullerene, if we assume a spherical model, then \( R \) is also equal to the mean radius, \( A = 4\pi R^2 \), and \( N_C = 4 \pi R^2 \rho \). We have also assumed here that the number density \( \rho \) is a constant. This results in an expression for the strain energy per carbon atom, which is linearly dependent on the inverse square of the curvature of the structure:

\[
\frac{E_{strain}}{N_C} = \frac{A \kappa h^3}{N_C 24 R^2}.
\]

Note that the coefficient is scaling invariant, and that the strain energy \( E_{strain} \) is a constant. This is a suitable definition for use here as \( E_{strain} \) may be obtained by fitting the calculated energy to the inverse of the square of the fullerene curvature. Therefore, including this term in Eq. (1), the heat of formation for a fullerene is now given by

\[
\frac{\Delta H^o_f(F)}{N_C} = \frac{3}{2} E_{CC}^D + \Delta H^o_f(C) + \frac{E_{strain}^F}{R^2}.
\]

II. DISCUSSION

The nanodiamond and fullerene structures were relaxed using the Vienna Ab initio Simulation Package (VASP).26,27 We used ultrasoft, gradient corrected Vanderbilt type pseudopotentials28 as supplied by Kresse and Hafner,29 and the valence orbitals are expanded on a plane-wave basis up to a kinetic energy cutoff of 290.00 eV. The crystal relaxations were performed in the framework of DFT within the generalized-gradient approximation, with the exchange-correlation functional of Perdew and Wang (PW91).30 Using this method, the calculated lattice parameter for bulk diamond of 3.561 Å, the \( sp^3 \) bond length of 1.541 Å, the band gap \( E_g \) of 5.46 eV are all in excellent agreement with the experimental values of 3.566 Å,31 1.544 Å,31 and 5.48 eV respectively. Hence the same critical parameters were used in the study of the diamond nanocrystals.

In order to fully relax the structures, both the ions and supercell volume were relaxed. Each ionic step consisted of a minimum of three electronic steps (and a maximum of sixty electronic steps), followed by calculation of the Hellmann–Feynman forces. Thus, both the symmetry and the lattice parameter of the nanocrystals were free to alter, resulting in expansions or contractions of the entire structures. The relax-
ations were performed for a minimum of 20 ionic steps. A detailed description of this technique may be found in Ref. 33, and results for bulk diamond in Ref. 34.

A. Diamond, nanodiamond, and graphite

As a first step in this study, the heat of formation for graphite was considered, to offer a benchmark. The van der Waals attraction $E_{\text{vdw}}$ has been calculated by Guo, using a graphene force field, to be 0.056 eV. Thus, using the experimental values for $D_0(H)$ = 2.259 eV, $E_{\text{vdw}}^2 = 3.507$ eV, and $E_{\text{vdw}}^2 = 4.917$ eV, the atomic heat of formation for graphite $D_0^G(N_C)$ was determined as a function of $N_H/N_C$ as given in Eq. (11). As the experimental values were used for graphite it is reasonable to assume that these results will be accurate,

$$\frac{D_0^G(N_C)}{N_C} = 14.836 \text{ eV} + \frac{N_H}{N_C} \times 3.308 \text{ eV}. \quad (11)$$

Next, the heat of formation of cleaved bulk diamond and relaxed nanodiamond were determined separately. Recognizing that $D_0^G(DB)$ is the dissociation energy of the C–C bond, Eq. (4) becomes

$$\frac{D_0^G(DB)}{N_C} = 2E_{\text{CC}}^D + \frac{N_{DB}}{N_C} \left( E_{\text{DB}}^D + \frac{1}{2}E_{\text{CC}}^D \right) + D_0^G(C). \quad (12)$$

Previously, the cohesive energy of bulk diamond and nanocrystalline diamond has been calculated and found to be 7.39 and 7.71 eV, respectively. This equates to $E_{\text{CC}} = 3.695$ eV for bulk diamond and $E_{\text{CC}}^D = 3.855$ eV for nanodiamond. From the same linear fit to the spin polarization corrected energy per ion versus number of dangling bonds per ion used previously to determine the cohesive energy, the slopes give $E_{\text{DB}}^D = 1.433$ eV for bulk diamond and $E_{\text{DB}}^D = 1.619$ eV for nanodiamond. So, using the value of $D_0^G(C) = 7.432$ eV, with the values of $E_{\text{DB}}^D$ and $E_{\text{CC}}^D$ given for the above-mentioned bulk diamond and nanodiamond, the atomic heat of formation for diamond and nanodiamond $D_0^G(DB)/N_C$ was determined as a function of $N_{DB}/N_C$ as given in Eq. (13) for nanodiamond.

$$\frac{D_0^G(DB)}{N_C} = 15.142 \text{ eV} + \frac{N_{DB}}{N_C} \times 3.547 \text{ eV}. \quad (13)$$

The atomic heats of formation for cleaved diamond (bulk diamond fragments), nanocrystalline diamond (relaxed nanodiamond crystals), and graphite were then plotted as a function of the number of carbon atoms. An empirical best fit was applied to the data sets, and the point of intersection determined, giving an estimate of the number of atoms at which a transition in phase stability occurs. In each case the equation of best fit was used, to which no physical meaning was assigned.

The results show that “cleaved” bulk diamond fragments are more stable than graphite for clusters less than 2345 atoms (approximately 2.4 nm in diameter), but are unstable compared to relaxed nanodiamonds of the same size. This is not surprising as it has been shown by many researchers that the structure of nanosized bulk diamond fragments alters upon relaxation. It was also found that relaxed nanodiamonds are more stable than graphite for crystals consisting of less than 24 398 atoms. This equates a crystal diameter of approximately 5.2 nm, beyond which graphite is the stable form of carbon, and diamond is metastable. This is lower than the PM3 results of Winter et al., but is in agreement the model of Jiang et al. at 298.15 K.

B. Nanodiamonds and fullerenes

In order to determine the atomic heat of formation for fullerenes, it is first necessary to obtain the cohesive energy and the strain energy, both of which may be found by fitting Eq. (14) to the energy per ion versus $1/R^2$:

$$\frac{E}{N_C} = \frac{k h^3}{\rho 24} \frac{1}{R^2} + \frac{E_{\text{cohesive}}}{N_C}, \quad (14)$$

where $E$ is the total fullerene energy calculated explicitly with DFT, and $E_{\text{cohesive}} = (3/2)E_{\text{CC}}^F$. Here a problem arises in the estimation of the radius of curvature $R$ for many of the fullerenes, as an atom may oppose the center of a ring on the other side of the fullerene. Therefore it is better to obtain $R$ from the spherical approximation $N_C = 4 \pi R^2 \rho$, where $\rho$ was calculated easily from the $C_{60}$ fullerene and found to be 0.37 $N_C/A^2$. A number of the estimated radii were checked against the “measured” values of $R$ (where possible), and found to be an excellent approximation.

Hence, the strain energy and cohesive energy obtained from the slope and intercept of the energy per ion versus $1/N_C$ were 5.19 and 7.81 eV, respectively (see Fig. 1). The calculated strain energy is slightly lower than the value of 6.56 eV of Hua et al. using a quantum mechanical force field method (MSXX FF), but the cohesive energy is in excellent agreement with the cohesive energy of graphite at 298.15 K of 7.8 eV.

Using these results the atomic heat of formation was determined from Eq. (10), and plotted as a function of the number of carbon atoms. The C–C bond energy was extracted directly from the cohesive energy, as $E_{\text{cohesive}} = (3/2)E_{\text{CC}}^F$. Once again, a best fit was applied and the intersection with the nanodiamond results found. This intersection occurred at 1127 atoms, which is approximately equiva-
lent to nanodiamond crystals of 1.9 nm in diameter. It is also interesting to note that the intersection point for graphite and fullerenes was 11 218 atoms. The relative ranges of stability of each carbon allotrope is given in Table I. In Table I the far right column refers to cubic nanodiamond particle sizes only, and that fullerenes or graphite particles with an equivalent number of atoms may vary in diameter.

III. CONCLUSIONS

It has been shown here, using a heat of formation model previously used successfully by Winter et al.,\textsuperscript{5} that nanocrystalline diamond is not necessarily the stable form of carbon at the nanoscale. Instead, fullerenes are the most stable form of carbon for small clusters, resulting in a “window” of stability for nanodiamond, in the range of approximately 1.9–5.2 nm in (cubic) diameter, beyond which graphite is most stable. In all but this range from ~1127 atoms to ~24398 atoms, diamond is metastable.

These results are considered to be very useful in explaining the transition of nanocrystalline diamond to carbon-onions, during \textit{ab initio} relaxations. The upper limit of fullerene stability falls above the upper limit of the capability of current computers, using \textit{ab initio} methods, thus in the size range of all recent \textit{ab initio}\textsuperscript{5} or semiempirical\textsuperscript{5–8} studies, fullerenes are the most stable phase of carbon.

Our results are further supported by a number of other experimental and theoretical investigations. Recently nanocrystalline diamond has been obtained directly from carbon nanotubes at high pressure,\textsuperscript{37} and the theoretical relaxation of carbon multiwalled nanotubes has been performed using the empirical many-body potential energy functional and (canonical) molecular dynamics at 1 K\textsuperscript{38,39} by Erkoç et al., showing the beginning of their transformation into what is best described as ta–C nanorods, in line with experimental observations.\textsuperscript{40}

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