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Theoretical study of the nucleation/growth process of carbon clusters under pressure

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We used molecular dynamics and the empirical potential for carbon LCBOPII to simulate the nucleation/growth process of carbon clusters both in vacuum and under pressure. In vacuum, our results show that the growth process is homogeneous and yields mainly sp^2 structures such as fullerenes. We used an argon gas and Lennard–Jones potentials to mimic the high pressures and temperatures reached during the detonation of carbon-rich explosives. We found that these extreme thermodynamic conditions do not affect substantially the topologies of the clusters formed in the process. However, our estimation of the growth rates under pressure are in much better agreement with the values estimated experimentally than our vacuum simulations. The formation of sp^3 carbon was negligible both in vacuum and under pressure which suggests that larger simulation times and cluster sizes are needed to allow the nucleation of nanodiamonds. © 2008 American Institute of Physics. [DOI: 10.1063/1.2943679]

I. INTRODUCTION

Understanding the formation of carbon clusters under extreme conditions of temperature and pressure is of interest in several fields, from astrophysics to material science. Experimentally most information about these processes is obtained from the detonation of oxygen deficient explosives (TNT, TATB, nitromethane, etc.) which produces non-negligible quantities of carbon materials such as carbon blacks containing up to a few 10% of monocrystalline nanodiamonds.^{1–4} A recent study by Pantea *et al.*⁵ suggests that determining the characteristic composition and structures of these carbonaceous residues may provide information that may be used to identify the detonated explosive.

Experimental studies of the structure of detonation nanodiamonds showed that their size distribution is narrow and peaked around 3–5 nm ($\sim 5 \times 10^4$ atoms) with a unit cell very close to cubic bulk diamond (3.565 Å).^{1,2,6,7} The impact of their formation on the mechanical behavior of the detonation products is not well understood, although the energy released by their nucleation/growth may yield up to 10% of the total detonation heat,⁸ thus extending the thickness of the reaction zone ($\sim 10^{-3}$ m, ~ 100 ns) located between the front of the shock wave and the Chapman–Jouguet (CJ) point (the region where all chemical reactions are complete and the detonation gas starts expanding). During the detonation, the thermodynamic conditions (density, temperature, and pressure) at the CJ point reach ranges of 1.5–2.5 g/cm³, 2000–3500 K and 15–30 GPa, respectively. The phase diagram presented in Fig. 1 indicates that diamond is the most stable phase for bulk carbon under these conditions. Nevertheless in the particular case of small carbon clusters, the

coexistence lines are presumably located at lower temperatures and higher pressures.⁹ Then under the thermodynamic conditions corresponding to the detonation products, the formation of carbon clusters can begin either in the graphite or liquid phase, and one or several phase transitions could occur as the cluster size increases, including a final transition toward diamond clusters.

Despite obvious experimental and theoretical difficulties (characteristic formation times in the microsecond range, very high pressure and temperature, and large number of atoms), many studies have been carried out in order to investigate the formation process and properties of these nanodiamonds. Among these works, Titov *et al.* have carried out a small-angle x-ray scattering experiment on detonation products, with or without addition of nanodiamonds to the explosive material.³ They conclude that detonation nanodiamonds

FIG. 1. (Color online) Schematic carbon phase diagram proposed by Viecelli and Ree (Ref. 9). CJ conditions for the detonation products of some carbon-rich explosives are represented (blue triangle: nitromethane, red circle: TATB, orange square: TNT). The dashed lines are an approximation to the displacement of the coexistence lines for fixed size carbon clusters.

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TABLE I. Simulation details for the nucleation/growth simulations in vacuum and under pressure, including the carbon density ρ_C and the total density ρ_{tot} for the simulations under pressure. The hybridization distribution, the pressure, and the mean potential energy at the end of each simulation are presented. At $P=0$ GPa, the reference energies per atom in graphite and diamond are -7.25 , and -7.23 eV, respectively.

Simulations in vacuum									Simulations under pressure					
Number of C atoms	400								400					
Number of Ar atoms	...								2975					
Cell parameter (Å)	150		100		70		33		60.0		47.6		37.8	
ρ_C (g/cm ³)	0.002		0.008		0.022		0.222		0.037		0.074		0.148	
ρ_{tot} (g/cm ³)	...		...		...		...		0.95		1.9		3.8	
Temperature (K)	1000	2000	1000	2000	1000	2000	1000	2000	2000	5000	2000	5000	2000	5000
sp fraction	0.52	0.29	0.22	0.27	0.25	0.27	0.51	0.70	0.10	0.45	0.02	0.12	0.30	0.25
sp^2 fraction	0.44	0.63	0.74	0.88	0.67	0.90	0.18	0.28	0.85	0.45	0.95	0.80	0.60	0.65
sp^3 fraction	0.01	0.03	0.03	0.03	0.03	0.00	0.00	0.00	0.05	0.05	0.03	0.08	0.04	0.08
Simulation time (ns)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	0.9	0.5	0.9	0.4	0.4	0.2
Pressure (GPa)	...	...	...	...	...	...	...	...	0.9	2.0	5.2	9.1	148.5	152.7
E_{pot} (eV/atom)	-4.13	-5.72	-6.14	-6.31	-6.38	-6.38	-6.13	-6.18	-6.50	-5.46	-6.44	-5.86	-4.26	-4.33

are formed beyond the CJ point, namely, after the formation of other detonation products (such as CO_2 , N_2 , and H_2O) has been completed. From the theoretical point of view, Raty and Galli used density functional theory to simulate the relative stability of hydrogen stabilized nanodiamonds and buckydiamonds (nanodiamonds with a reconstructed non hydrogenated fullerene-like surface).¹⁰ Their results showed that up to a critical cluster size, atomic hydrogen inhibits the formation of the fullerene layer at the cluster surface, thus stabilizing the sp^3 diamond structure and allowing further aggregation of carbon atoms at the surface. They provided an explanation for the peaked size distribution of detonation diamond by comparing the size dependence of the free energy of both types of nanodiamonds (hydrogenated and reconstructed). Their conclusions suggested that hydrogen could play a key role in the growth mechanism, which is only possible if the nucleation/growth process occurs inside the reaction zone, before the CJ point is reached, a result that contradicts the findings of Titov *et al.*

These results show that although a good understanding of the thermodynamic properties and the mechanism/kinetics of formation of detonation nanodiamonds is important for many applications, information on these issues is still scarce and contradictory. In particular, little is known about the first steps of the nucleation/growth process of clusters in detonation products. Although some theoretical work on the formation of clusters in vacuum from a dilute carbon gas has been reported recently,^{11–14} we are not aware of any study on the influence of the environmental effects such as the pressure imposed by the other gases in the case of detonations. In the latter particular case, the extreme thermodynamic conditions may crucially affect the mechanism and kinetics of the nucleation/growth of carbon clusters.

In this paper we present a theoretical study of the first steps of the nucleation/growth mechanism of clusters from a dilute carbon gas, both in vacuum and under rare gas pressure. In particular, we investigate the influence of the thermodynamical conditions (temperature, pressure, and density) on the topology and the growth kinetics of the clusters. We examine the situation proposed by Titov *et al.*³ and assume that the formation of carbon clusters occurs after the CJ

point. In that case the detonation products interact with the excess carbon species only as a nonreactive heat and pressure reservoir. By doing so we neglect the possible influence of atomic hydrogen on the growth process as suggested by Raty and Galli.¹⁰ This paper is organized as follows: in Sec. II we give the computational details of our simulations, then in Sec. III we present our results on the nucleation/growth of carbon clusters in vacuum. In Sec. IV we present our simulations under pressure, and we comment the results in Sec. V.

II. METHODS

We have performed molecular dynamics simulations by means of the computer code STAMP developed at CEA, in the canonical ensemble using a Nosé–Hoover thermostat with a characteristic mass of 10^{-18} kg. We used the LCBOPII potential developed by Los *et al.*¹⁵ to model the carbon-carbon interaction. The equations of motion were integrated with a Verlet algorithm, using a time step of 0.1 fs.

A. Simulations in vacuum

As in Ref. 14, our starting configuration was a cubic box containing 400 carbon atoms. Their initial positions were defined as follows: first, a simple cubic grid of 512 starting positions ($8 \times 8 \times 8$) was built in the simulation box, then the 400 carbon atoms were distributed on this grid in a random fashion. By adjusting the box size, five initial densities were studied, ranging from a very dilute carbon gas up to densities close to diamond and graphite in standard conditions (see Table I).

B. Simulations under rare gas pressure

As discussed above, we assumed that the detonation products interact with the excess carbon species only as a nonreactive heat and pressure reservoir that we mimic by means of a rare gas (argon). The simulation box was chosen to obtain a total density range relevant for detonation product applications (0.95, 1.9, and 3.8 g/cm³) as follows: first 3375 argon atoms were placed on a $(15 \times 15 \times 15)$ simple cubic

FIG. 2. Time evolution of the nucleation/growth mechanism for a 400 atom box at $\rho=0.022 \text{ g/cm}^3$ and $T=2000 \text{ K}$.

grid, then 400 of these atoms were transformed into carbon in a random fashion and the box size was adjusted to obtain the desired density (see Table I).

We modeled the argon-argon and carbon-argon interactions with Lennard–Jones (LJ) potentials. We used the parameters from Ref. 16 for the Ar/Ar interactions and calculated the parameters for the C/Ar interactions with the usual Lorentz–Berthelot rule and the parameters from Ref. 17. We changed the value of $\sigma_{\text{C/Ar}}$ to $5 \text{ \AA}$ to avoid the insertion of argon atoms inside the carbon clusters. A test with the original $\sigma_{\text{C/Ar}}=4 \text{ \AA}$ was performed to check that this approximation did not influence the growth/nucleation mechanism. The value of the LJ cutoff distance was set to $10.5 \text{ \AA}$, a distance slightly shorter than the cutoff used in the cell method¹⁸ applied for the parallelization scheme ($10.6 \text{ \AA}$).

III. NUCLEATION/GROWTH PROCESS IN VACUUM

We used molecular dynamics to follow the nucleation/growth process of carbon clusters in vacuum for 2 ns. As detailed in Table I, we considered five densities (0.002 , 0.008 , 0.022 , 0.2 , and 2.2 g/cm^3) at 1000 and 2000 K .

A. Nucleation/growth mechanism

To illustrate the growth mechanism, we present the initial evolution of the 0.022 g/cm^3 system at 2000 K (Fig. 2). At these thermodynamic conditions the simulation yields a single sp^2 structure close to a complex fullerenelike arrangement. A careful observation of the first frames (up to 50 ps) shows that the nucleation of small carbon clusters is a rather homogeneous process, with a spatial distribution of short chains and rings containing up to 20 atoms. Then for times up to 100 ps , these small clusters tend to aggregate to form larger clusters (few tens of atoms) which transform into fullerene structures after about 150 ps . To check the possible influence of the size of the simulation box, we present in Fig. 3 a similar simulation with a larger box ($10\,800$ atoms) at the same density. At this length scale one sees that the nucleation process remains very homogeneous, yielding a spatial distribution of small fullerene structures containing a few tens of atoms each, with only a few carbon chains or rings remaining. The homogeneity of the nucleation/growth process is an interesting feature as these processes are often thought of as

FIG. 3. Same as Fig. 2 for a $10\,800$ atom box.

being heterogeneous: most growth models are based on the assumption that a large cluster grows by accumulation of surrounding atoms or smaller clusters. Our results suggest that this picture is not adequate, at least for the first nanoseconds of growth, since at any time the system contains a homogeneous spatial distribution of clusters with a rather narrow size distribution: accordingly larger cluster sizes should be formed by merging several clusters of similar (smaller) sizes. Note that the comparison between the small and large simulation boxes illustrates the importance of investigating size effects when forming structures containing a number of atoms close to the total number of atoms in the box.

The chronology of the growth process is confirmed by the time evolution of the hybridization distribution of the 400 atom system presented in Fig. 4. It shows that in the first 100 ps , atomic carbon is consumed to produce mainly short-lived dimers ($\sim 50 \text{ ps}$) and carbon chains (dimers and sp curves, respectively). The formation of sp^2 structures appears only when a sufficient density of carbon chains has been achieved and is clearly responsible for the decay of the sp fraction. After 250 ps the sp^2 fraction is predominant with a substantial sp residue. We observed a very similar pattern for the large simulation box. The steepness of the sp/sp^2 transitions observed at $t=150\text{--}200 \text{ ps}$ and $t=600 \text{ ps}$ indicates that the formation of fullerenes from carbon chains is a sudden and fast process: as a matter of fact, rather than the appear-

FIG. 4. (Color online) Time evolution of the hybridization distribution of the $\rho=0.022 \text{ g/cm}^3$ and $T=2000 \text{ K}$ simulation (400 atoms). Blue crosses: isolated atoms. Green circles: dimers. Orange squares: sp chains and rings. Red diamonds: sp^2 structures. Purple triangles: sp^3 structures. Notice the hybridization jumps from sp to sp^2 at $t=150\text{--}200 \text{ ps}$ and $t=600 \text{ ps}$.

FIG. 5. Topology of the carbon clusters obtained at the end of the nucleation/growth simulations in vacuum. Left column: simulations at 1000 K. Right column: simulations at 2000 K. The total simulation time is 2 ns for all cases.

ance of trifurcates,¹⁴ the first step to the formation of fullerene structures is the nucleation of short rings (five to seven carbon atoms) from several branched carbon chains. These rings appear to be very stable since the reverse process was never observed in our simulations. The nucleation of the short rings is entropically slow since it corresponds to constrained configurations, but it seems to activate the second step which is the formation of the full fullerene structure from the surrounding carbon chains. This second step is very fast and yields the characteristic stepwise patterns observed in Fig. 4.

B. Influence of temperature and density on the topology of the clusters

In Fig. 5 we present the end-of-simulation topologies obtained after 2 ns, for the 400 atoms and over the whole ranges of thermodynamical conditions considered. These topologies are strongly dependent on density and much less on temperature. At densities close to graphite (2.2 g/cm³), highly disordered (amorphous) structures are obtained. When decreasing the density by one order of magnitude, three dimensional (3D) graphitic and highly porous structures are obtained. For densities ranging from 100th to 1000th of graphite, fullerenelike clusters are formed: a single large and

irregular structure at $\rho=0.022$ g/cm³, and a collection of small and nearly spherical clusters at $\rho=0.008$ g/cm³. At low temperatures, these small clusters tend to aggregate without merging completely. At the lowest density $\rho=0.002$ g/cm³, a collection of *sp* rings containing up to a few tens of atoms are formed, as well as one isolated fullerene structure with a regular shape.

These results show that the nucleation of carbon clusters from a dilute atomic gas in vacuum yields mainly *sp*² derived topologies with a strong dependence on density (from graphitic networks at high densities to very small fullerene-like structures at low densities). This preference for graphitic structures is in good agreement with the previous works of Bogana *et al.*^{11,12} and Yamaguchi *et al.*^{13,14} Although less thermodynamically stable than graphite or diamond (on average, the value of the cluster energy is generally 1 eV higher than graphite or diamond, as shown in Table I), these structures are very likely to form because (1) low pressures favor the formation of graphitic structures over diamond, (2) the formation of fullerene structures minimizes the surface energy of the cluster, and (3) the presence of structural defects in the grown graphitic sheets tend to bend them, making it configurationally easier to close up to form fullerene structures.

The tendency to form large single clusters rather than distributions of smaller even-numbered ones—as observed in time-of-flight-mass spectra experiments^{19,20}—could be related to the cluster density which is always superior to 1 per 10⁶ Å³ in our simulations, a value much larger than the experimental one of 1 per 10⁸ Å³ estimated by Yerezian *et al.*²¹ Experimental evidence for the formation of large fullerene clusters can be found elsewhere.^{21–23}

It should be noted that our strong topological dependence on density rather than temperature does not agree with the results of Yamaguchi *et al.* who used a tight binding molecular dynamics (TBMD) scheme and found a strong temperature influence on the topologies, but little influence of the density: for similar starting configurations at 1000 K, they obtained a density-independent mixture of *sp* and *sp*² structures consisting mainly of flat graphitic “flakes” connected by carbon chains. Their graphitic flakes were only curved at higher temperatures, which allowed the formation of large fullerene structures. This difference appears to be mainly kinetic since we obtained qualitatively similar topologies during the fullerene formation process at smaller simulation times (typically 0.2 ns). Thus the kinetics with LCBOPII appears to be faster than with Yamaguchi’s tight-binding scheme, roughly by a factor 2–5.

C. Kinetics

In order to evaluate the kinetics of the growth process, we show in Fig. 6 the time evolution of the average cluster size for all densities and temperatures. The growth evolution can be modeled by a succession of exponential laws characteristic of two main growth regimes. The first regime corresponds to the formation of carbon dimers and is characterized by a substantial increase in the growth velocity with density and temperature. The second regime corresponds to

FIG. 6. (Color online) Time evolution of the average cluster size (logarithmic scale) for the simulated densities (black circles: 0.002 g/cm³, blue squares: 0.008 g/cm³, green diamonds: 0.022 g/cm³) and temperatures (full symbols: 1000 K, empty symbols: 2000 K). The single carbon atoms are not included in the average calculation. For each simulation, a succession of linear regimes can be observed indicating typical exponential growth laws Ae^{Bt} . The evolution of the 0.022 g/cm³ case is very fast and was not represented here for convenience.

the formation of chains, rings and higher hybridization structures, and is characterized by a slower growth velocity.

For all densities and temperatures, we fitted the growth evolution of the second regime data with an exponential law Ae^{Bt} with A and B given in Table II. This table also gives an extrapolation of the time required to form 4 nm clusters containing 50,000 atoms (the characteristic peak size of the nanodiamonds formed in detonation products). In Table II, $t_{50,000}$ ranges from 4 to 15 ns. This is about three orders of magnitude shorter than the experimental estimates suggested recently.³ It is then clear that simulating the growth of carbon clusters in vacuum is not appropriate to understand the behavior of carbon compounds in detonation products: the effect of the environment, in particular, the extreme pressures undergone by the carbon atoms, should be accounted for to improve this description.

IV. NUCLEATION/GROWTH PROCESS UNDER PRESSURE

The nucleation/growth process under pressure was simulated for total densities of 0.95, 1.9, and 3.8 g/cm³ and temperatures of 2000 and 5000 K. These ranges correspond to those obtained in detonation products for explosives such as nitromethane (total density at the CJ point: 1.5 g/cm³, excess carbon density of 0.053 g/cm³, temperature of 3500 K and pressure of 12.3 GPa). Since the number of atoms in the system is much larger than for the vacuum case (3375 atoms against 400), shorter calculation times have been reached, depending on the density.

A. Nucleation/growth mechanism

The nucleation/growth trajectory of the $\rho=1.9$ g/cm³ and $T=2000$ K system (case C in Fig. 9) is presented in Fig. 7. As for the vacuum process, the mechanism involves first the formation of short carbon chains, then rings and branched carbon atoms (sp^2) are formed, leading to small graphite sheets and fullerenes with rather regular topologies. One striking difference with the growth in vacuum is the

TABLE II. Fitted parameters for the exponential growth laws plotted in Fig. 6. Only the slowest regime of each case is considered. Extrapolations to the time $t_{50,000}$ needed to grow detonationlike carbon clusters (4 nm, $\sim 50,000$ atoms) are given.

Density (g/cm ³)	Temperature (K)	A	B 10^{-5} ps^{-1}	$t_{50,000}$ (ns)
0.002	1000	2.9	1.1	9.0
	2000	6.6	0.9	9.8
0.008	1000	5.5	2.2	4.2
	2000	22.7	1.5	5.3
0.022	1000	148.0	0.4	15.0
	2000	110.0	0.6	9.6

increased velocity of formation over the first 100 ps: after only 10 ps, clusters containing up to 20 atoms are formed, including rings and some branched chains involving sp^2 carbon atoms: these structures were only observed after 50 ps in the vacuum case. After 100 ps, almost all carbon atoms are involved into sp^2 structures, mainly fullerenes with topologies resembling the vacuum case at 250 ps. After 250 ps, both pressure and vacuum cases present similar topologies.

The reason for the increased kinetics during the first 100 ps is that the surrounding rare gas acts as a third body, increasing the efficiency of the C–C collisions by dissipating the excess kinetic energy formed in the C–C bond-making process. After 100 ps, the surrounding gas slows down the diffusion of the fullerene structures with respect to the “vacuum” mechanism. As for the vacuum case, the overall nucleation/growth mechanism seems to be rather homogeneous with a smooth spatial distribution of clusters of similar sizes at all simulation times. Again the formation of large clusters is obtained by merging several clusters of comparable size rather than agglomerating small clusters or carbon atoms on a large structure, a result contradictory with the usual picture of a heterogeneous nucleation and growth mechanism.

The time evolution of the distribution of hybridization fraction shown in Fig. 8 illustrates the very efficient and fast kinetics of formation of the sp^2 fullerene structures, with a percentage close to 95% reached over less than 200 ps of simulation. The sp^3 fraction remains less than 5% and the sp^3 atoms are not connected.

FIG. 7. Time evolution of the nucleation/growth mechanism under pressure for $\rho=1.9$ g/cm³, $T=2000$ K, and $P=5.2$ GPa (case C of Fig. 9). The small black dots represent the rare gas atoms.

FIG. 8. (Color online) Same as Fig. 4 for the $\rho=1.9$ g/cm³ and $T=2000$ K simulation with argon.

B. Influence of temperature and density on the topology of the clusters

Snapshots of the end-of-trajectory structures, as well as the pressure and the total integration time, are presented in Fig. 9. The results show clearly that fullerene-like structures are formed at all densities and temperatures, except for low pressure and high temperature (case B) where the final structure is a liquid droplet. Contrary to the vacuum cases, the average cluster size decreases when density and pressure increase, illustrating the difficulty for growing clusters to diffuse and aggregate at high densities. At low density and low temperature (case A), a single and very irregular cluster is obtained, whereas at intermediate density (case C) smaller

FIG. 9. Snapshots of the simulation box at the end of each trajectory. The small black dots represent the rare gas atoms. Left column: simulations at 2000 K. Right column: simulations at 5000 K. The pressure and the total integration time are specified in each case.

TABLE III. Estimation of the critical pressure required to activate a fullerene/diamond transition for different cluster sizes. U_s is the difference in potential energy between diamond and fullerene, V_f and V_d are the volumes of the fullerene and the diamond clusters, respectively, and P_c is the critical pressure, as defined in Eq. (3). Units: U_s in eV, V_f and V_d in Å³, and P_c in GPa. The reference structures for fullerenes up to 100 atoms are taken from Yoshida's fullerene library (Ref. 24). For $N=400$, the reference is the cluster obtained at the end of our simulation at $\rho=1.9$ g/cm³ and $T=2000$ K.

N	U_s	V_f	V_d	P_c
20	22.9	215.6	113.3	35.7
30	21.5	362.0	169.9	17.9
40	39.5	509.7	226.5	22.3
50	47.5	661.7	283.2	20.1
60	72.2	1492.9	339.8	10.0
70	59.2	1657.2	396.4	7.5
80	84.9	1816.4	453.0	10.0
90	110.8	2047.8	509.7	11.5
100	99.9	2348.9	566.3	9.0
400	86.3	2500.0	2265.2	58.8

clusters are formed (30–50 atoms) and tend to aggregate without merging completely on the timescale of our simulations. Higher densities (cases E and F) yield collections of small clusters (5–25 atoms and 5–40 atoms, respectively).

A striking result here is the absence of sp^3 structures even at pressures as high as 150 GPa where the most stable allotrope of carbon is diamond: the maximum fraction of sp^3 carbon is 8% (see Table I) and no connectivity is found between these atoms. Since the “bulk” energies of a fullerene, graphite and diamond are comparable, a reason for the absence of diamond clusters may be related to the “creation” of surface energy during the transition from fullerenes to diamond. As a matter of fact, fullerenes have negligible surface energies with respect to diamond clusters since in the fullerene structures all the carbon atoms are fully sp^2 coordinated while the surface of diamond clusters have defective coordinations. Then under pressure, a fullerene/diamond transition can occur when the variation of work of the pressure forces compensates the creation of diamond surface energy, as

$$U_s = P_c(V_f - V_d) \Rightarrow P_c = \frac{U_s}{(V_f - V_d)}, \quad (1)$$

where U_s is the surface energy of the diamond cluster, P_c is the critical pressure at the transition, and V_f and V_d are the volume of the fullerene and diamond clusters, respectively. Rough estimates of the critical pressure are presented in Table III for clusters up to 400 atoms. For a N -atom fullerene/diamond cluster the surface energy U_s was estimated from the difference in potential energy between a relaxed spherical diamond cluster and an ideal fullerene structure of similar size (we used the optimized geometries of Yoshida for fullerenes²⁴). The volume of the fullerene structures was approximated by fitting the three main radii of an ellipse to the latter structures, while the volume of the diamond cluster was taken as $N \times v_d$ where v_d is the specific volume of bulk diamond. For the 400 atom structure, we used the configuration obtained at the end of our $\rho = 1.9$ g/cm³ and $T=2000$ K simulation. Our estimates of the

FIG. 10. (Color online) $\log(P_c) = f[\log(N)]$ plot of the data from Table III. Black dots: fullerene structures of Yoshida (Ref. 24), red cross: structure from our simulation at $\rho = 1.9 \text{ g/cm}^3$ and $T = 2000 \text{ K}$. Note the increase in pressure when changing from the optimized fullerene structures to the non-ideal structures grown in our simulations.

critical pressure for $N=20$ to $N=100$ decrease from 35 to $\sim 10 \text{ GPa}$. This decrease in the pressure with increasing cluster size can be explained by the dependence on N of the U_s , V_f , and V_d contributions. For the diamond cluster, V_d scales as N and as r_d^3 (where r_d is the radius of the diamond cluster), then r_d scales as $N^{1/3}$. U_s is proportional to the surface of the cluster which scales as r_d^2 , then U_s scales as $N^{2/3}$. For the fullerene cluster, the surface scales as N and as r_f^2 (where r_f is the radius of a spherical fullerene structure of equivalent size), then r_f scales as $N^{1/2}$. Since V_f scales as r_f^3 , then it also scales as $N^{3/2}$. Overall, one can write

$$P_c \sim \frac{N^{2/3}}{(N^{3/2} - N)}, \quad (2)$$

which rewrites as

$$P_c \sim \frac{1}{N^{1/3}(N^{1/2} - 1)} \sim N^{-5/6}. \quad (3)$$

The logarithmic plot of P_c as a function of N from Table III is presented in Fig. 10: a linear fit of these data yields a slope equal to -0.84 , in good agreement with the ideal value of $-5/6 = -0.83$ of Eq. (3). A striking feature is the strong increase in the critical pressure when considering a nonideal fullerene structure grown in our simulations instead of an optimized hollow cluster (for $N=400$, 58.8 GPa against an extrapolated ideal value of 2.5 GPa). The main reason for such a change is that the volume decreases substantially when switching from an ideal spherical fullerene to the actual structure obtained in our simulation (see Fig. 9), while the specific surfaces remain similar in both cases (all atoms are located at the surface). Therefore, since P_c is inversely proportional to $V_f - V_d$, a small decrease in V_f leads to a large increase in P_c . Note that for pressures higher than 100 GPa, very small clusters are formed and all the atoms are at the surface: this prevents the formation of sp^3 topologies.

These results suggest that neither the critical pressure nor the critical fullerene size needed to start the fullerene/diamond transitions are achieved in our simulations. Clearly, pressures of several tens of gigapascals are necessary when starting from nonideal fullerene clusters of up to 400 atoms.

FIG. 11. (Color online) Same as Fig. 6 for the simulated densities (green circles: 0.95 g/cm^3 , red squares: 1.9 g/cm^3 , blue diamonds: 3.8 g/cm^3) and temperatures (full symbols: 2000 K, empty symbols: 5000 K). The growth velocity has been evaluated using linear regressions. The parameters are given in Table IV.

It should be noted that these evaluations do not account for the entropy effects or the energetic barriers along the fullerene/diamond transition: these contributions enhance the fullerene stability with respect to diamond because (1) the available configurational space is larger for the more deformable sp^2 structures and (2) overcoming energetic barriers along the transition path requires larger pressures. These effects may also contribute substantially to the low sp^3 fractions observed in our simulations.

C. Kinetics

As for the vacuum case, we present in Fig. 11 the time evolution of the average cluster sizes. We found that the kinetics of the growth process under pressure is linear and appears to be faster than the growth in vacuum during the first simulation steps ($t < 100 \text{ ps}$). This result may be explained in terms of the efficiency of the carbon/carbon collisions. Under pressure, the collisions with the surrounding gas allow an efficient evacuation of the excess kinetic energy (the so-called third-body effect) and improve the yield of the dimer formation. In vacuum such third-body collisions are very rare, therefore most collisions are followed by the dissociation of the formed dimer. The third-body effect vanishes for the collision of larger clusters because the internal degrees of freedom of the colliding clusters allow an efficient evacuation of the excess energy. Accordingly for times larger than 100 ps the growth velocity increases sharply in vacuum, while it remains stable under pressure as the motion of the clusters is hindered by the surrounding gas.

A linear fit of the simulation data under pressure was performed. The calculated slopes (equivalent to a growth rate) and the extrapolated times needed to reach the characteristic size of detonation nanodiamonds are given in Table IV. The estimations range from a few tens of nanoseconds for the most dilute case for up to $1 \mu\text{s}$ for high density, therefore the order of magnitude is up to three times larger than our evaluation in vacuum, and in much better agreement with a recent experimental estimate.³ Although there is no guarantee that the growth rate is linear for times larger than a

TABLE IV. Calculated growth rates and extrapolated times needed to form a 50,000 atom detonation carbon cluster.

Density (g/cm ³)	Temperature (K)	Growth rate (atom/ps)	$t_{50,000}$ (ns)
0.95	2000	0.60	83.3
	5000	1.90	26.3
1.90	2000	0.30	166.7
	5000	2.60	19.2
3.80	2000	0.05	1000.0
	5000	0.11	455.5

few nanoseconds, this result confirms that pressure is an important ingredient of the nucleation/growth mechanism.

V. DISCUSSION

We used molecular dynamics simulations based on the empirical bond order potential LCBOP-II to study the nucleation and growth mechanism of carbon clusters from a dilute carbon gas in vacuum and under pressure.

Our results in vacuum show that the topology of the formed clusters depends mainly on density, with a marked preference for sp^2 structures ranging from 3D carbon networks to small regular fullerene cages. The growth mechanism is homogeneous and involves the successive formation of smooth spatial distributions of carbon chains, rings (sp), and fullerene clusters. Accordingly, the kinetics of formation obey a succession of exponential laws corresponding to these different regimes. Our evaluation of formation rates of a few nanoseconds do not agree with the experimental estimates ($\sim 1 \mu\text{s}$) which suggests that simulations in vacuum cannot account for the mechanism of formation of detonation nanodiamonds.

In order to mimic the environment of the carbon clusters during detonation, we simulated the nucleation/growth process under pressure using rare gas atoms described by LJ potentials. We considered density, pressure and temperature ranges close to the usual detonation conditions (1.5–2.5 g/cm³, several tens of gigapascals, and a few thousands of kelvin). While we found that the external pressure does not affect the topology of the formed clusters, our estimated growth rates reach ranges in good agreement with the experimental values.

We did not observe any substantial formation of sp^3 carbon, either in vacuum or under pressure, and we suggest that sp^3 hybridization may occur only beyond a critical pressure or cluster size. We relate this critical size to an equilibrium between the applied pressure and the amount of surface energy that is created during the fullerene/diamond transition. Our estimate of the critical pressure for a nonideal fullerene structure containing 400 atoms ranges above 50 GPa, thus

much larger than the actual pressure achieved in our simulations. This critical pressure should be lower for larger clusters since their fullerene/diamond transition yield lower specific surface energy.

Our results for the topologies in vacuum are in good qualitative agreement with several bond order¹³ and tight-binding¹⁷ studies, although we found that LCBOP-II yields faster kinetics than the tight-binding scheme of Yamaguchi *et al.*¹⁴

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