Molecular dynamics simulation for pressure-induced structural transition from C$_{60}$ fullerene into amorphous diamond

Akihito Kikuchi and Shinji Tsuneyuki

Institute for Solid State Physics, University of Tokyo,
Kashiwa-no-ha 5-1-5, Kashiwa-shi, Chiba 277-8581, Japan

Abstract

The pressure-induced structural transition in fcc C$_{60}$ fullerene by shock compression and rapid quenching is investigated by a semi-empirical tight-binding molecular dynamics simulation, adopting a constant-pressure scheme and a method of the order N electronic structure calculation. At first, the process of the amorphization of C$_{60}$ is demonstrated. The simulated results indicated that, in the material fabricated after the quenching, the remaining dangling bonds have a large influence on physical properties, such as, the density and the presence of the band gap at the Fermi level. We have furthermore studied the formation of the short-range order, observed as amorphous diamond. In order to form the amorphous diamond phase, the bonding state of sp$^2$ must be turned into that of sp$^3$. The transition process is seriously influenced from the external pressure, the temperature, or the presence of hydrogen. The comparison to the pressure-induced structural transition in the graphite is also executed and a brief discussion on the difference in those carbon crystals is given.
1 Introduction

In the field of high-pressure material science, diverse carbon systems under pressure have been intensively studied with interest in synthesizing new phases. For example, the pressure-induced structural transition from $C_{60}$ fullerene to amorphous diamond is realized by shock compression and rapid quenching\cite{1}. The shock compression and rapid quenching generate the high pressure (50-55GPa) and the temperature (2000-3000K) in a fraction of a microsecond. Consequently the $C_{60}$ fcc crystal transforms into stable transparent glassy chips of $\mu m$ in size, which are confirmed to be an amorphous phase of diamond by electron energy-loss spectroscopy and electron diffractometry\cite{1}. Though this phase has a short-range order similar to normal diamond, it is amorphous. This amorphous phase is characterized by being consisted mostly from sp$^3$ bonding, in contrast with previously reported amorphous carbon which is considered to be a disordered phase of graphite with sp$^2$ bonds\cite{2, 3}. By an investigation of the sample after the shock compression, the fabrication process for the amorphous diamond is postulated in the following way \cite{1}. Once the fcc cell of $C_{60}$ is compressed, the inter-cluster bonding between $C_{60}$ molecules is formed. In other words, the polymerization of the $C_{60}$ clusters occurs there, as was observed in several high-pressure experiments\cite{1, 4, 5}. By the further compression, molecules collapse and change into the amorphous. In the amorphous, the bonding state of sp$^3$ is gradually produced and it forms a short-range order extending up to the volume of the normal diamond unit cell. This high temperature phase is quenched and obtained as the amorphous diamond, in which a greater part of the bonding state turns into sp$^3$ type without the crystal growth in long range.

In fact, there is uncertainty in the understanding of the fabrication process from $C_{60}$ to amorphous diamond, since the postulation for the process is obtained by checking the various
phases of $C_{60}$ remaining after the compression and the quenching and it is not based on direct observation of the reaction. In order to clarify such a transition process, the aid of the computer simulation will be needed. As for the structural transformation in carbon systems, there are a lot of theoretical approaches, from the first principles or semi-empirical way. However, those studies focus on the transformation between graphite and diamond. In the present stage, the theoretical simulation on the pressure-induced structural transformation in $C_{60}$ has not been executed sufficiently. Therefore, the object of the present work is set to be a theoretical understanding of the pressure-induced structural transition in $C_{60}$ crystal. For this purpose, a molecular dynamics simulation is executed using a tight-binding Hamiltonian with model parameters for carbon and hydrogen systems proposed by Winn, Rassinger and Hafner, combined with the constant pressure scheme by Wentzcovotch. The model parameters can reproduce the energy difference and geometries in various carbon systems including hydrogen, such as molecules and reconstructed diamond surfaces, as well as the bulk property of diamonds and graphites. This model parameters also give results consistent with other ab-initio and semi-empirical calculations for liquid carbon phase. In addition, to save computational costs, a part of calculations, involved in the crystal structure optimization, was carried out using the density matrix method, what is called the order N method.

The contents of this paper are as follows. At first the process of the pressure-induced amorphization of $C_{60}$ will be presented. According to the simulation presented here, the $C_{60}$ fcc crystal is easily and speedily transformed into the amorphous by the compression, going through the path postulated by the experiment as above, since the $C_{60}$ structure is constructed by bondings of distorted sp$^2$ type and it has potentiality in the transition to sp$^3$
type bondings. However, in the simulated result, the amorphous phase itself is far from the state which should be classified as "amorphous diamond", especially just after the transition from C$_{60}$, since the collapsed C$_{60}$ fcc crystal includes a number of dangling bonds which have not yet turned into sp$^3$ bondings. Therefore, the present work will furthermore pursue the transition from sp$^2$ to sp$^3$ in the amorphous phase through the compression, which will gradually reduce the number of the dangling bonds and drive the system towards the "amorphous diamond" phase of randomly packing sp$^3$ bondings. The details of those dynamical effects, such as the dependence on the temperature and the pressure, are not necessarily clarified by the experiment alone. Finally, the present paper will give a comparison of the structural transition in C$_{60}$ to the pressure-induced graphite-diamond transition by the simulation. It will explain the reason why C$_{60}$ fcc crystal shows the transition to amorphous diamond phase and why graphite directly turns into perfect cubic diamond.

2 The simulation scheme

In the present work, the simulations are executed in the following way.

1) The initial external pressure is set to be 0GPa and the pressure is gradually raised to the desired value.

2) Then the simulation is executed at a stationary pressure in sufficiently long time.

3) To simulate the process of the rapid quenching, the optimized structure at 0GPa and 0K is finally obtained, by letting down the applied pressure.

In the present stage, we do not have the detailed information on the physical quantities in the sample through the shock-compression, such as, the variation in the pressure and the temperature related to the propagation of shock waves. For example, the temperature is not
preserved and rapidly escapes from the compressed system while the pressure is kept to be high. Thus, in some calculations, the temperature is also given as a parameter independent of the pressure. In the electronic structure calculation, a periodic boundary condition is applied to the fcc unit cell containing four C$_{60}$ molecules and the summation over k-space is estimated at the Γ point alone.

3 Amorphization from the C$_{60}$ fcc crystal

3.1 Compression at 0K

At first, the C$_{60}$ fcc crystal was optimized at the pressure of 50-100GPa, keeping the temperature at 0K. The C$_{60}$ fcc structure is stable in this pressure range. The initial cubic cell parameter including four C$_{60}$ molecules is set to be 14.15Å. For example, a compression at 50GPa changed the cell into smaller one, in which the cell parameter shrinks to 13.6 Å. In the compressed cell, the relative positions of atoms are still preserved, while the covalent bonds are formed between C$_{60}$ molecules. This is a kind of the polymerization, but not the amorphization.

3.2 Compression at finite temperature

Obviously, the reason why the C$_{60}$ crystal is stable in such a high pressure is that the simulation is executed in an unphysical condition, i.e., keeping the temperature at 0 K. In the experiments for fabricating the amorphous diamond, the temperature rapidly rises from the room temperature to the range no less than 2000-3000 K. Then the collapse of the crystal will become drastic owing to the active movements of atoms, as can be expected from the phase diagram of carbon[11]. Therefore, in this section, the simulation is executed with the condition that the temperature of the system can vary. To do this, the equation of motion is
solved in the constant pressure scheme of molecular dynamics[8] without any scaling of the kinetic energy.

Figure 1 shows the snapshots of an example of the amorphization. In this case, the pressure is linearly increased from 0GPa to 65GPa in the first 0.45ps and kept constant after that. The temperature is set to be 300K in the beginning and spontaneously increases to 2000-3000K by compression partly because this is adiabatic compression and partly because of recombination of C-C bonds. In the early stage, the stacking structure of the fcc crystal is still preserved. The C_{60} molecules come to show deformation and polymerization, if the inter-cluster distance becomes much closer to the intra-cluster atomic distance, as was observed in the compression study by Duclos et al.[12]. By further compression, amorphization occurs and it results in the destruction of the molecular structure in the whole cell. At the same time, the sp^{2} bonding gradually transforms into the sp^{3}.

The structural change in Fig.1 is also quantitatively checked. Figures 2 and 3 show the change in the pair-distribution function and the bond-angle distribution, which correspond to the snapshot of the transition process in Fig.1. The initial fcc C_{60} crystal has already turned into the amorphous phase in the first 1000 MD steps (1.0ps), as can be seen from these figures. The initial bond-angle distribution has two peaks at 108 degrees and 120 degrees, which mean bond-angles in five- and six-membered rings. As the time goes by, these two clear peaks become more and more broad and finally merge into one peak around 110 degrees. This indicates the vanishing of the molecular structure of C_{60}.

Compressions in the pressure higher than 65GPa accompanies more temperature increase and it turns C_{60} into amorphous. On the other hand, if the maximum pressures are lower than 50GPa, and if the simulation starts at the room temperature, the fcc C_{60} crystal does not
collapse completely, probably because the final temperature (1000-2000K) is not sufficiently high. However, if the initial temperature is set to be sufficiently high, as high as in the order of 1000K, the amorphization proceeds even at about 50GPa.

4 Formation of amorphous diamond

To gain the frozen phase after the rapid-quenching, we execute the crystal structure optimization firstly at the high pressure and finally obtain the optimized structure at 0GPa, gradually letting down the pressure. In the actual process of the shock compression and rapid quenching, the high-temperature phase is frozen into the system owing to the rapid decrease in the temperature, while the high pressure is still kept.

Figures 4(a) and 4(b) show the results of the crystal structure optimization, where the maximum compression pressures are set to be 65GPa and 125GPa, respectively. (In both cases, the optimized structures at 0GPa are obtained after the MD simulations continued as long as about 10ps, so that the property of the finally fabricated material shall not seriously be affected by the finiteness of the simulation time.) In these structures, the short-range order, formed in the high temperature and the high pressure, remains almost unchanged. The pair distribution function (not shown here) shows the peaks around 1.5Å and 2.5Å, which correspond to the contributions from the first- and next-nearest neighboring atoms, as is seen in that of the high temperature phase. However, only from the location of the peaks, it is difficult to determine whether the short-range order comes from a diamond-like structure or not. It may be likely that the peaks are attributed to the fragments of the C₆₀, since the distances from one atom to the first- or next-nearest neighboring atoms are of the same extent both in diamond and in a single C₆₀ molecule. Thus the distribution of the
azimuthal angle, as is defined in Fig.5(a), was checked. Here the azimuthal angle is defined to be the relative angle of the two planes, respectively spanned by two bonds, when these two plane share one common bond. This distribution gives the information on the networking structure of the tetrahedron of sp$^3$, and it will have peaks around 60 degrees or 180 degrees for cubic diamond and around 140 degrees for the C$_{60}$ structure. (The pairs of six- and five-membered rings in C$_{60}$ form the angle of about 140 degrees.) In Fig.5(b), for the case of the compression at 65GPa, there are no prominent peaks around 60 or 140 degrees. It means that the cage structure of C$_{60}$ vanishes, while the diamond-like short range order is not clearly formed. On the other hand, in the structure compressed at 125GPa, there is a prominent peak near 60 degrees in Fig.5(c). The cubic-diamond-like short-range order, extending up to the third-nearest neighbors, is much more developed there, since this structure compressed by the larger pressure has much more number of sp$^3$ bonding.

In fact, the networking structure of bonds is not necessarily confined to cubic diamond phase alone, since the energy difference between cubic and hexagonal diamond phase is little. Several local bonding structures similar to that of hexagonal diamond are found in the simulated results. In perfect hexagonal diamond structure, the azimuthal angle with respect to a bond on an atom parallel to the c-axis takes 0 and 120 degrees. On the other hand azimuthal angles with respect to other three bonds on an atom take 60 and 180 degrees, which is the same as cubic diamond. Therefore, even in perfect hexagonal diamond phase, the contributions to the distribution of azimuthal angles at 0 and 120 degrees is weak and it is one third of those at 60 and 180 degrees. Thus contribution from hexagonal-diamond like short range order around 0 or 120 degrees is hidden due to the randomness in amorphous.

The density in the structure compressed by the maximum pressure 65GPa [Fig.4(a)] is
estimated to be about 2.7 g/cm³. On the other hand, the density is 3.5 g/cm³ after the compression at the maximum pressure 125GPa [Fig.4(b)], which is comparable to the experiment. In the actual amorphous diamond, the density is estimated to be larger than 3.3 g/cm³[13].

Figures 6(a) and 6(b) show the density of states of the finally fabricated material (frozen phase) after the compression at the maximum pressure 65GPa and 125GPa. These electronic structures are quantitatively different from that of the initial C_{60} fcc crystal, which is given in Ref.[14]. The difference between Fig.6(a) and 6(b) results from the number of dangling bonds. In these figures, the contribution to the DOS from threefold carbon atoms is compared to the total DOS. Owing to the contribution from dangling bonds, the gap between the conduction and valence bands vanishes. In case of the compression at 65GPa[Fig.6(a)], the ratio of atoms with dangling bond amounts to 50 %, while in case of the compression at 125GPa[Fig.6(b)], the ratio of such atoms deceases to about 10%. Therefore, in the latter case, the conduction and valence bands are distinguished by a reduction of the DOS near the Fermi level, which is featured as a shaded zone in the figure. This reduction in the DOS is interpreted to be an analogous of the wide gap in the perfect diamond structure. In Fig.6(a), a narrow gap at the Fermi level is formed in the dangling bond states and it separates the occupied and unoccupied states. This is because the presence of a gap, even if it is narrow, makes the system more stable.

Comparing the results corresponding to the compression at 65GPa and 125GPa, the latter case, compressed at the larger pressure, is considered to be a better simulation, since the actual amorphous diamond has a transparent optical property similar to the normal diamond and it will have an electronic structure with a large gap near the Fermi level. In
our simulations, at the pressure above 100GPa and the temperature above 5000K, the ratio of threefold carbon atoms decreases to 10–20%, and the valence and conduction bands tend to be distinguished by a wide range reduction in the DOS near the Fermi level, owing to the decrease of the dangling bonds. In the experimentally obtained amorphous diamond, the number of the dangling bonds will also be reduced, possibly more than in this simulation. (It is certain that the dangling bonds still remain in the actual amorphous diamond, as was indicated by the EELS spectrum in Ref.[1].)

5 An analysis for the dynamical process in the transition

After the rapid amorphous transition, it takes a long time until the short range order is formed again. In this section, the dynamical process in the reaction, especially related to the pressure and the temperature, is investigated. Figure 7 shows the results by a simulation where the external pressure is increased from 0GPa to 65GPa, and after that, the pressure is furthermore increased to 125 GPa, in order to check the pressure dependence. Figures 7(a)-(d) show the time dependence of the external pressure, the temperature, the mean square of the displacement, and the ratio of carbon atoms with fourfold coordination. The increase in the ratio of carbon atoms with fourfold coordination stands for the transition from $sp^2$ to $sp^3$, and it reflects on the reconstruction of the short-range order. In the amorphous phase, $sp^2$-type bonding is gradually transformed into $sp^3$-type, while the transition speed, in other word, the speed of the short-range order formation is going down. However, at least in the order of the picoseconds, the system has not yet arrive at the stationary state. The figure furthermore shows the dependence of the reaction on the external pressure. When the
external pressure is raised again, the number of the sp³ bonding grows much more, since the
transition is accelerated by the higher temperature and the higher density. The density in
the high temperature phase amounts to about 3.0g/cm³ at 65GPa and increases to about
3.5g/cm³ at 125GPa.

The simulated result supports the postulations for the amorphous diamond formation
process from the experimental data[1]. We should stress here the importance of the following
phenomena. Since the high temperature is generated through the reconstruction of the
bonding, the reaction is enhanced so that the system can cross the potential barrier and
transform its structure. (The system obtains work by the compression and the temperature
increases to some extent, but it is not enough to speed up the reaction furthermore.) As
an example, figure 8 shows the results of the two simulation where the external pressure is
increased to 125GPa. In the first case, denoted as (A), there is no restriction to the variation
of the temperature. On the other hand, in the second case, denoted as (B), the temperature
is set to be 2500K after 0.5ps. The transition from sp² to sp³ is apparently hindered in the
case of (B), since the movement of atoms is inactive because of the lower temperature, in
contrast with the case (A). For the same reason, the compression at 0K, shown in the previous
section, cannot turn C₆₀ to the amorphous. These simulations also suggest that there are
possibly innumerable quasi-stable configurations by which the system is easily trapped. The
amorphous diamond phase can also be regarded as one of such quasi-stable transient phases
located in the reaction path from C₆₀ to the bonding state of sp³ in whole crystal, i.e. perfect
diamond phase. (In fact, the shock compression applied to lower-grade C₆₀ exhibited the
entire transition to the diamond crystallite, probably because of the easier crystal growth in
the presence of defects and impurities.) Since shock compression process continues as long as
nanoseconds, it is possible that the actual amorphous diamond phase has a structure much closer to perfect diamond, compared to the present simulation whose time-scale is at most picoseconds order. In the actual shock compression, a large fluctuation in the pressure and the temperature through the shock-wave propagation will fabricate variously altered phases, as are classified in several states\[1\], ranging from the slightly compressed fcc structure to the amorphous diamond.

It appears that the speed of increasing pressure may have some influence on the reaction. For example, if the response of the crystal inner stress cannot catch up with the rapid increase of the pressure, the decaying process of the crystal will become more drastic. The response of the inner stress is related to the cell deformation and it is dependent on the fictitious mass assigned to the cell deformation, as well as the external pressure and the inner stress in the constant-pressure scheme. We would like to avoid such dependence of the simulation on the artificial degree of freedom as possible. For this purpose, we adjusted the fictitious mass heavy enough so that the fluctuation of the "kinetic energy" assigned to the cell deformation is kept to be very small and the almost "isenthalpic" simulation becomes possible at a stationary pressure. The speed of raising the applied pressure is set to be sufficiently slow in such a way that the inner stress shall rise parallel with the external pressure. By doing so, the system property is almost determined by the the current pressure, and scarcely dependent on the kinetic contribution from the cell deformation. For example, in figure 7 and 8, where the pressure is raised to 125GPa in two different ways, the final system properties, such as the temperature and the bonding order, are similar.
6 Discussions

In the electronic structure of the finally fabricated material after the compression, the contribution from dangling bonds is not negligible. If the contribution of this kind appearing between the valence and conduction band is large, the fabricated material will lose the transparent optical property and it will not be qualified to be called amorphous diamond. As we have seen, the contribution from dangling bonds will be reduced after the compression at sufficiently higher temperature and pressure. In fact, there may be other mechanism that will reduce the contribution from dangling bonds. For example, it is well-known that the presence of hydrogen atoms reduces the number of dangling bonds in case of amorphous silicon. The DOS after the shock-compression in presence of hydrogen atoms are given in Fig.9. A comparison between Fig.9(a) and Fig.6(a), which are the DOS after the compression at 55GPa and 65GPa, shows that the DOS is apparently reduced around the Fermi level in the presence of the hydrogen, even if the pressure is somewhat lower. However, there is no clear gap between the valence and conduction band in Fig.9(a). Such a situation is not improved so much at higher pressure, as in Fig.9(b). In addition, according to the simulation like this, even in the case when much more numbers of the hydrogen atoms are included, dangling bonds not terminated by hydrogens are still left. This will be because the reactivity and the mobility of bonds are weakened by the presence of many hydrogen atoms and the formation of the short range order of sp\(^3\) will rather be hindered.

In case of the compression of C\(_{60}\), there are number of quasi-stable configurations in amorphous phase, and such a transient phase will easily be frozen by the quenching. This will be the major difference to the pressure-induced structural transition from graphite to diamond. Figure 10 shows the transition of the bonding state from sp\(^2\) to sp\(^3\) in the com-
pression of the graphite. In the figure, the rapid increase in the ratio of fourfold carbon atoms after 1000fs stands for the transition from graphite to diamond. The transition speed is far faster than the cooling speed of the temperature in the shock compression experiment which is estimated to be from $10^6$ to $10^{10}$ K/s\cite{17}. Graphite and diamond phases are located in very close configurations in the potential surface and there is no stable transient state in the transition path from graphite to diamond. Since graphite rapidly transforms into the cubic diamond without being trapped by any quasi-stable structure, perfect diamond phase remains alone after the quenching and amorphous diamond phase will not be obtained\cite{18}.

It should be noted here that, in comparison with ab-initio theory, there are less accuracy and less transferability in the tight-binding models, in spite of the fact that the model parameters succeed in reproducing the bulk property of certain carbon crystals. This is because the tight-binding model parameters are obtained by the fitting to the ab-initio results for several crystal structures. In order to check the model parameter dependence of our simulation, we have executed additional calculations using another model parameter by Xu et al. \cite{19} and compared the results to those given in the previous sections. According to the results obtained by the Xu’s parameters, if the initial condition and the applied pressure are the same, the electronic and structural properties, such as the transition rate from sp$^2$ to sp$^3$ and the increase in the temperature, are of the same extent, compared to those given in the previous sections. For example, when the compression is executed above 100GPa, the ratio of atoms with dangling bond decreases to $10 - 20 \%$ and the DOS shows the reduction near the Fermi level, as well as the result in the previous section.

It should also be mentioned that the model Hamiltonian used here does not include van der Waals interactions and is not quantitatively sufficient for the initial C$_{60}$ fcc structure.
formed by van der Waals force. However, the purpose of the present work is the investigation in a compressed carbon system. Since the van der Waals force is much weaker than covalent bonds between atoms, it will be negligible in the simulation, especially after the transition into the high-density amorphous. In other words, the model parameters adopted here will be a good, even if not the best, description for the physical process of the pressure-induced structural transition from the C\textsubscript{60} fcc crystal into the amorphous diamond.

7 Conclusion

We have investigated the amorphization of C\textsubscript{60} fcc and the formation of amorphous diamond phase. The electronic property of amorphized phase of C\textsubscript{60} just after the transition is far from so-called amorphous diamond, since the amorphized C\textsubscript{60} contains a number of dangling bonds which have not yet turned into sp\textsuperscript{3} type bonding. Amorphous diamond phase is being gradually formed through the change in the bonding structure from sp\textsuperscript{2} to sp\textsuperscript{3} under high pressure and high temperature. If dangling bonds are sufficiently reduced, the valence and conduction bands are distinguished and a transparent optical property is observed in amorphous diamond phase as well as perfect cubic diamond. Amorphous phase is interpreted as one of quasi-stable phases in the transition path from C\textsubscript{60} to diamond phase under pressure. If the temperature and the pressure are not sufficiently high, the reaction will be interrupted before forming amorphous diamond phase, probably because there are many quasi-stable phases between C\textsubscript{60} and diamond and the system is liable to be trapped by such phases. This is in contrast with pressure-induced graphite-diamond transition. Since graphite and diamond phase are located in very near configurations in the potential surface, the transition from graphite to diamond proceeds rapidly without passing through any stable transient
phase. From this reason, the formation of amorphous diamond phase is characteristic in the compression of C\textsubscript{60} and such a phase is not obtained in the compression of graphite.

References

[1] H.Hirai, K.Kondo, N.Yoshizawa, and M.Shiraishi, Appl.Phys.Lett.\textbf{64} 1797(1994); H.Hirai and K.Kondo, Phys.Rev.B\textbf{51}, 15555(1995);

[2] C.S.Yoo and W.H.Nellis, Science \textbf{254}, 1489(1991).

[3] T.Sekine, Proc.Jpn.Acad.Ser. B\textbf{68}, 95(1992).

[4] Y.Iwasa et al., Science \textbf{264}, 1570(1994).

[5] A.M.Rao et al., Science \textbf{259}, 955(1993).

[6] M.O’Keefe, Nature \textbf{352}, 674(1991).

[7] M.D.Winn, M.Rassinger, and J.Hafner, Phys.Rev.B\textbf{55}, 5364(1997).

[8] R.M.Wentzcovitch, J.L.Martins, and G.D.Price, Phys.Rev.Lett.\textbf{70}, 3947(1993);
   R.M.Wentzcovitch, W.W.Schulz, and P.B.Allen, ibid.\textbf{75}, 3389(1994).

[9] Y.Tateyama, T.Ogitsu, K.Kusakabe, and S.Tsuneyuki, Phys.Rev.B\textbf{54}, 14994(1996).

[10] X.-P.Li, R.W.Nunes, and D.Vanderbilt, Phys.Rev.B\textbf{47}, 10891(1992).

[11] F.P.Bundy, J.Chem.Phys.\textbf{38}, 618(1963), \textit{ibid.}\textbf{38}, 631(1963)

[12] S.J.Duclos, K.Brister, R.C.Haddon, A.R.Kortan, and F.A.Thiel, Nature \textbf{351}, 380(1991).

[13] H.Hirai and K.Kondo, Kagaku \textbf{50}, 368(1995), in Japanese.

[14] S.Saito and A.Oshiyama, Rhys.Rev.Lett.\textbf{66}, 2367(1991).

[15] H.Hirai,K.Kondo, and T.Ohwada,Carbon \textbf{31}, 1095(1993).
In the compression with the presence of hydrogen, the temperature grows more than that does in the case without hydrogen, since the combination energy between C and H is released together with that between C and C. However the transition speed itself is not raised so large.

H. Hirai and K. Kondo, Science 253, 772 (1991).

Even in the pressure-temperature range where the C_{60} turns into the amorphous, the graphite is stable, while being somewhat compressed along c-axis. The simulation, however, shows that the compression at a sufficiently high pressure and a high temperature distorts the graphite sheets and causes the fluctuation where the weak inter-layer bridging is being formed. If such a fluctuation can grow large enough, the global transition to the diamond will start. This accounts for the time-lag between the raise of the pressure and that of the ratio of sp^3[Fig.10]. Such inter-layer bridging in the fluctuation easily vanishes and does not remain after the decrease in the pressure and the temperature.

C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho, J. Phys. Condens. Matter 4, 6047 (1992).
Figure captions

- Figure 1: Snapshots of the transition from C_{60} fcc crystal to amorphous are given. The pressure is increased from 0GPa to 65GPa in 0.45ps and kept to be 65GPa after that. The pictures show the system cut out into a $15 \times 15 \times 15\text{Å}^3$ cube, which does not stand for the unit cell.

- Figure 2: Pair distribution function in each MD step, which corresponds to the compression given in figure 1.

- Figure 3: Bond-angle distribution in each MD step, which correspond to the compression given in figure 1. Although the structures, characteristic to C_{60}, remain at first, they have almost vanished in 0.5ps and the system turns into the amorphous.

- Figure 4(a): The structure fabricated after the compression at the maximum pressure at 65GPa.

- Figure 4(b): The structure fabricated after the compression at the maximum pressure at 125GPa.

- Figure 5(a): Definition of azimuthal angle.

- Figure 5(b): Distribution of the azimuthal angle after the compression at 65GPa, in the structure of figure 4(a).

- Figure 5(c): Distribution of the azimuthal angle after the compression at 125GPa, in the structure of figure 4(b).

- Figure 6: Density of states corresponding to figure 5. The solid line shows the total DOS, and the dotted line shows the contribution from threefold carbon atoms.

- Figure 6(a): DOS after the compression at 65GPa.

- Figure 6(b): DOS after the compression at 125GPa.

- Figure 7: An example of the dynamical effect caused by changes in the pressure through the compression is given here. Pressure is raised from 0GPa to 65GPa, and after that, again raised to 125GPa. The early stage of this simulation, where the pressure is confined in the range from 0GPa to 65GPa, corresponds to the snapshot given in figure 1. These figures show the very slow reconstruction process of the short-range order in the amorphous at the high pressure and temperature.

- Figure 7(a): The change in the applied pressure.

- Figure 7(b): The variation in the temperature. By raising the pressure again, the temperature increases again.

- Figure 7(c): The mean square of the displacement. By raising the pressure again, the atomic movement becomes more active.

- Figure 7(d): The ratio of fourfold carbon atoms. The increase in this ratio means the formation of the sp^3 bonding. By raising the pressure again, much more numbers of the sp^3 bonding are generated.

- Figure 8: Another example of the dynamical effect caused by change in the temperature through the compression is given here. The pressure is raised from 0GPa to 125GPa.
In the path, denoted as (A), there is no concentration on the temperature. In the path (B), the temperature is scaled at 2500K after 0.5ps.

- Figure 8(a): The change in the applied pressure.
- Figure 8(b): The variation in the temperature.
- Figure 8(c): The mean square of the displacement. In the path (B), owing to the lower temperature, the atomic movement becomes more inactive.
- Figure 8(d): The ratio of fourfold carbon atoms. In the path (B), owing to the lower temperature, the transition speed from sp\(^2\) to sp\(^3\) decreases.
- Figure 9: The density of states with the presence of hydrogen. The solid line shows the total DOS, and the dotted line shows the contribution from threefold carbon atoms. The cell includes hydrogen atoms at 12.5% in number. Figure 9(a) shows the DOS after the compression at the maximum pressure 55GPa. The contribution from threefold C atoms is about 40% in the total DOS. Figure 9(b) shows the DOS after the compression at the maximum pressure 125GPa. The contribution from threefold C atoms is about 20% in the total DOS.
- Figure 10: This figure shows the ratio of fourfold carbon atoms in the pressure-induced structural transition from graphite to cubic diamond. The transition from sp\(^2\) to sp\(^3\) in the whole crystal can be seen in the rapid increase in that ratio, changing from 0 to 1. In this simulation, the unit cell includes 240 carbon atoms. The pressure is raised from 0GPa to 150GPa in initial 0.15ps and kept constant. The temperature is scaled to be 5000K throughout the simulation. The graphite directly turns into the stable perfect cubic diamond, taking a reaction path similar to that demonstrated in a first principles simulation[9].
Figure 1: Snapshots of the transition from C_{60} fcc crystal to amorphous are given. The pressure is increased from 0GPa to 65GPa in 0.45ps and kept to be 65GPa after that. The pictures show the system cut out into a 15 \times 15 \times 15\text{Å}^3 cube, which does not stand for the unit cell.

(a) 0.0ps/0Pa: Initial structure
(b) 0.5ps/65.0Pa: Polymerized phase

(c) 1.0ps/65.0GPa: Amorphous phase
Figure 2: Pair distribution function in each MD step, which corresponds to the compression given in figure 1.
Figure 3: Bond-angle distribution in each MD step, which correspond to the compression given in figure 1.
Figure 4(a): The structure fabricated after the compression at the maximum pressure at 65GPa.

Figure 4(b): The structure fabricated after the compression at the maximum pressure at 125GPa.
Figure 5(a): Definition of the azimuthal angle
Figure 5(b): Distribution of the azimuthal angle after the compression at 65GPa, in the structure of figure 4(a).

Figure 5(c): Distribution of the azimuthal angle after the compression at 125GPa, in the structure of figure 4(b).
Figure 6: Density of states corresponding to figure 5. The solid line shows the total DOS, and the dotted line shows the contribution from threefold carbon atoms.

Figure 6(a): DOS after the compression at 65GPa.

Figure 6(b): DOS after the compression at 125GPa.
Figure 7: An example of the dynamical effect caused by changes in the pressure through the compression is given here. Pressure is raised from 0GPa to 65GPa, and after that, again raised to 125GPa. The early stage of this simulation, where the pressure is confined in the range from 0GPa to 65GPa, corresponds to the snapshot given in figure 1. These figures show the very slow reconstruction process of the short-range order in the amorphous at the high pressure and temperature.

Figure 7(a): The change in the applied pressure.
Figure 7(b): The variation in the temperature. By raising the pressure again, the temperature increases again.
Figure 7(c): The mean square of the displacement. By raising the pressure again, the atomic movement becomes more active.
Figure 7(d): The ratio of fourfold carbon atoms. The increase in this ratio means the formation of the sp$^3$ bonding. By raising the pressure again, much more numbers of the sp$^3$ bonding are generated.
Figure 8: Another example of the dynamical effect caused by change in the temperature through the compression is given here. The pressure is raised from 0GPa to 125GPa. In the path, denoted as (A), there is no concentration on the temperature. In the path (B), the temperature is scaled at 2500K after 0.5ps.

Figure 8(a): The change in the applied pressure.
Figure 8(b): The variation in the temperature.
Figure 8(c): The mean square of the displacement. In the path (B), owing to the lower temperature, the atomic movement becomes more inactive.
Figure 8(d): The ratio of fourfold carbon atoms. In the path (B), owing to the lower temperature, the transition speed from sp\(^2\) to sp\(^3\) decreases.
Figure 9: The density of states with the presence of hydrogen. The solid line shows the total DOS, and the dotted line shows the contribution from threefold carbon atoms. The cell includes hydrogen atoms at 12.5% in number. Figure 9(a) shows the DOS after the compression at the maximum pressure 55GPa. The contribution from threefold C atoms is about 40% in the total DOS. Figure 9(b) shows the DOS after the compression at the maximum pressure 125GPa. The contribution from threefold C atoms is about 20% in the total DOS.
Figure 10: This figure shows the ratio of fourfold carbon atoms in the pressure-induced structural transition from graphite to cubic diamond. The transition from sp² to sp³ in the whole crystal can be seen in the rapid increase in that ratio, changing from 0 to 1. In this simulation, the unit cell includes 240 carbon atoms. The pressure is raised from 0 Pa to 150 GPa in initial 0.15 ps and kept constant. The temperature is scaled to be 5000 K throughout the simulation. The graphite directly turns into the stable perfect cubic diamond, taking a reaction path similar to that demonstrated in a first principles simulation[9].