

## Nucleation of C<sub>60</sub> Clusters

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We have examined the nucleation of C<sub>60</sub> clusters via molecular-dynamics simulations. We find that it is possible to nucleate a "buckminsterfullerenelike" cluster with no symmetry-, or volume-imposed constraints from a "hot plasma" of carbon atoms. The growth sequence for buckminsterfullerene is dominated by the nucleation of long carbon chains in the initial phase. As the nucleation process proceeds, these chains branch and form polycyclic rings. We find an abrupt onset of ring formation at a temperature which corresponds to the melting point of graphite.

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Understanding the nucleation process by which the buckminsterfullerene molecule forms is a formidable undertaking [1-5]. The molecule possesses complete symmetry in that each of its sixty carbon atoms resides in an identical environment. It is hard to envision a process for the nucleation of such a highly symmetric molecular system of such size. We determine that it may be possible to form C<sub>60</sub> directly from a "hot carbon plasma" without invoking a preexisting nucleation subunit.

For systems of more than a dozen atoms, it is not possible to examine dynamics via direct quantum-mechanical calculations, except for extraordinarily short time spans. A common practice in such cases is to replace quantum-mechanical interactions by "classical interactions" which are derived from interatomic potentials [6,7]. The implementation of "classical" interatomic potentials may result in orders-of-magnitude reduction of the computational effort for dynamical simulations. For solids composed of open-shelled species, the issue of generating accurate potentials is unresolved. Some workers have suggested that such potentials are of limited utility, at best, as *many-body* interactions, by definition, are strongly dependent on the local environment. We have found that this need not be the case, provided some care is taken in choosing the database from which the interatomic potentials are constructed. For example, in the case of silicon [8], we employed two divergent data sets: (a) the high-pressure phases of silicon which contain "overcoordinated" silicon atoms, i.e., atoms with more than four bonds, and (b) clusters of silicon which contain "undercoordinated" species. Our goal was to build these divergent bonding configurations into our potential. We succeeded in this endeavor to the extent that we were able to predict "magic" numbers for the reactivity of small silicon clusters and, more recently, to predict an isomeric transformation of silicon clusters [9].

Here we focus on constructing a potential for carbon which will be applicable to modeling the nucleation of buckminsterfullerene. Unlike silicon, carbon can exist with multiple bond formation, and, as a consequence, is more challenging. Our starting point will be to consider

our silicon potential [8] and make modifications to reflect the inherent differences between silicon and carbon. To construct a carbon potential, we rescaled our silicon potential so that the potential yielded an accurate bond length and energy for carbon in the diamond structure. We then compared the energy of various other polytypes to quantum-mechanical total-energy calculations [10].

Our bulk carbon potential is given by

$$E[\{\mathbf{R}\}] = \sum_{i,j,i < j} \left[ \frac{A \exp(-\beta_1 R_{ij}^2)}{R_{ij}^2} - \frac{g_{ij} \exp(-\beta_2 R_{ij}^2)}{R_{ij}} \right]. \quad (1)$$

$R_{ij}$  is the interatomic distance between  $i, j$  and the many-body interactions are contained within the factor  $g_{ij}$ .  $g_{ij}$  is constructed to be large for covalent, open-structure systems (structures with large bond angles such as diamond or graphite) as compared to metallic, close-packed systems. We define  $g_{ij}$  as

$$g_{ij} = g_0 + g_1 S_{ij} S_{ji}, \quad (2)$$

where

$$S_{ij} = 1 + \langle \cos(3\theta_{ijk}) \rangle,$$

$$\langle f(\theta_{ijk}) \rangle = [f]/[1],$$

$$[f(\theta_{ijk})] = \sum_{k, k \neq i, j} f(\theta_{ijk}) \exp(-\lambda_1 \theta_{ijk}^4) \exp(-\lambda_2 R_{ijk}^4),$$

with  $R_{ijk} = (R_{ij} + R_{ik})/2$ . This form represents a very short-ranged function which has sharp angular and radial cutoffs. The factor  $S_{ij}$  ranges from 0 for metallic structures with small bond angles to 2 for covalent systems. Also, for  $\theta_{ijk} < \pi/3$  ( $> 2\pi/3$ ) we saturate  $\cos(3\theta_{ijk})$  so that  $\cos(3\theta_{ijk}) = -1$  ( $+1$ ). Values for the parameters are  $A = 45.59 \text{ eV \AA}^2$ ,  $\beta_1 = 0.80 \text{ \AA}^{-2}$ ,  $\beta_2 = 0.35 \text{ \AA}^{-2}$ ,  $g_0 = 1.33 \text{ eV \AA}$ ,  $g_1 = 6.09 \text{ eV \AA}$ ,  $\lambda_1 = (2/\pi)^4$ , and  $\lambda_2 = 0.961 \text{ \AA}^{-4}$ .

This potential yields accurate energies and bond lengths for carbon in the diamond and graphite structures. For diamond, the calculated cohesive energy is 7.3 eV/atom and the bond length is 1.53 \AA; the experimental

values [11,12] are 7.37 eV/atom and 1.54 Å. The bulk modulus is also in good accord with experiment: 4.4 Mbar for the calculated and 4.42 Mbar for the measured value [13]. With respect to graphite, we find the cohesive energy is about 0.03 eV/atom lower than diamond versus a value of 0.02 eV/atom from experiment [14]. The intraplanar bond length from our calculation is 1.45 Å versus 1.42 Å as measured [15]. Surprisingly, given the absence of an explicit van der Waals interaction, we find that the calculated  $c/a$  ratio for graphite is accurately given by our potential: It is about 4% smaller than measured.

If we use our potential in Eq. (1) to examine buckminsterfullerene, we find that this structure is not dynamically stable. We find that  $C_{60}$  will be more energetically favorable as a fragment of the diamond crystal, i.e., each atom tends to be fourfold coordinated and “puckered” sixfold rings are prominent. Our potential contains no information on isolated carbon rings, or graphitic sheets, as will be important for modeling buckminsterfullerene. In order to remedy this flaw, we modify the potential interactions as extracted from the crystalline polymorphs. We strengthen the bonds in buckminsterfullerene and we include an additional angular factor which insures that isolated graphitic sheets will not be stable in a planar geometry, but will prefer to “buckle.” The form of this modification is taken from our silicon work [8] and fixed by a comparison to total-energy calculations [16,17] for solid-state buckminsterfullerene [18].

To strengthen the buckminsterfullerene bonds, we introduce a “dangling-bond vector”  $D_i$ . This vector is defined as

$$D_i = - \sum_{j,j \neq i} \mathbf{R}_{ij} \exp(-\lambda_3 R_{ij}^2) / \sum_{j,j \neq i} \exp(-\lambda_3 R_{ij}^2). \quad (3)$$

This vector vanishes for the crystalline polymorphs, but will be present for systems which do not possess a local inversion center such as buckminsterfullerene. We define an angular term as

$$Q_{ij} = 1 + z D_i \sin[\alpha(\theta_{ij} - \pi/3)]. \quad (4)$$

We combine this term with the dangling bond to modify our  $g_{ij}$  term. We take

$$\Delta g_0/g_0 = \mu(Q_{ij}Q_{ji} - 1)\exp(-\beta_2 R_{ij}^2). \quad (5)$$

This form assures us two desirable features. The buckminsterfullerene bonds will be stabilized versus the diamond fragment and the angular term will facilitate “buckling.” We note two features of this potential that differ from silicon [8]. The range of the bond strengthening term is longer than silicon, i.e., we implement a Gaussian weighting in Eq. (3). The range of this term should exceed one hexagonal ring to ensure that ordering between fivefold and sixfold rings is possible. Also, we do not weaken the bulk angular terms in Eq. (5), i.e., alter  $g_1$ , as we did for silicon. Unlike carbon, small silicon

clusters are known to be close-packed structures [8]. Our potential yields accurate diamond and graphite structures, and a dynamically stable buckminsterfullerene with the “correct” bond length and energy as extracted from total-energy calculations [16,17]. Our bond lengths for the buckminsterfullerene molecule are 1.42 and 1.49 Å for the bond shared between fivefold and sixfold rings and the bond shared between sixfold rings, respectively. This compares very well with the theoretical values [16,17] of 1.40 and 1.47 Å for solid-state buckminsterfullerene [18]. The difference in energy between solid-state buckminsterfullerene and carbon in the diamond structure [17] is  $\sim 0.4$  eV/atom. This value can be compared to 0.43 eV/atom, which is the difference in energy from our potential between buckminsterfullerene and the diamond structure. The potential parameters for Eqs. (3)-(5) are  $\alpha = 2.25$ ,  $z = 0.132/\text{Å}$ ,  $\lambda_3 = 0.0361 \text{ Å}^{-2}$ , and  $\mu = 4.0$ .

To simulate the nucleation of buckminsterfullerene, we consider an initial configuration consisting of a “large” box of sixty carbon atoms. These atoms are not allowed to interact significantly. Specifically, we consider a cube of 12 Å on a side and deposit the atoms randomly within this box. We impose one constraint: The atoms are not allowed to be within 2 Å of one another. This allows us to contain the sixty atoms, yet not have them overly “biased” by the initial configuration [8]. We chose an initial temperature for the atoms to be 7000 K. This temperature is chosen to be well above the melting point of solid carbon [19]. Our initial condition corresponds to a “hot, chaotic plasma” of weakly interacting carbon atoms. Using the interatomic potentials given above, and a Langevin molecular-dynamics simulation [8], we quench this system. There are two goals to our simulation. First, we wish to observe what sort of structures form as we rapidly cool this system. Second, we will modify this simulation process in an attempt to nucleate the lowest-energy structure possible.

With respect to the first goal, we quench the system as with our silicon cluster work [8]. The time step for the integration of motion is 2 fsec with a total simulation time of 20 psec. During this time, the box temperature is reduced from 7000 to 1000 K. Initially, short chains are formed as illustrated in Fig. 1(a). At sufficiently high temperatures, it is clear that entropic considerations dominate the structural properties of the “plasma.” For a given number of atoms, a chain will be favored by entropy over a ring. This is consistent with earlier work which suggested that chains would be stable at high temperatures [20,21]. It is surprising, perhaps, that these chains grow to fairly long units, e.g., over ten atoms in length. However, our carbon potential and presumably the “real” carbon interactions favor large angles in the chain growth which inhibits ring closure [Fig. 1(b)]. At moderately high temperatures ( $\sim 5000$  K) enthalpic considerations begin to influence the quench and the chain structure begins to change. The chains form branches and eventually

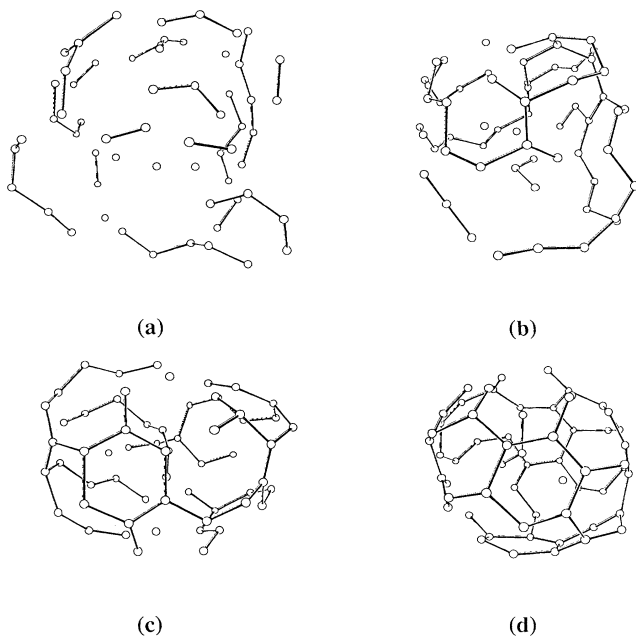


FIG. 1. Structures illustrating the nucleation process for a cluster of sixty carbon atoms. (a) The cluster is at 6000 K. Short chains appear. (b) The cluster is at 5000 K. Longer chains are formed which start to branch. (c) Hexagonal rings begin to form at 4000 K. (d) A spheroidal cluster is formed with sixfold rings formed (2000 K).

hexagonal rings start to appear near 4000 K [Fig. 1(c)]. This suggests that one may not be able to nucleate buckminsterfullerene above this temperature. It also suggests that the solid state, i.e., graphite, may not be nucleated above this temperature. This finding is consistent with estimates [19,20] of  $\sim 4000\text{--}5000$  K for the melting point of carbon. The ring structure is maintained to lower temperatures [Fig. 1(d)].

In order to examine the evolution of the ring structure in more detail, we determined the percentage of atoms in the system which reside in sixfold rings as the system is quenched. This is illustrated in Fig. 2 where we also indicate the average binding energy as a function of the quench temperature from (1). At high temperatures, few atoms exist in rings. As the temperature is lowered a strong onset of ring nucleation occurs near  $\sim 4800$  K. This "first-order" change is replicated in the binding energy and is consistent with the melting point of graphite.

Although our anneal is not sufficiently slow to produce a highly symmetric structure, it is apparent that the lowest-temperature structure in the anneal corresponds to a "spheroidal" cluster with a number of linked hexagonal rings. The energy of this structure is somewhat removed from the energy of an ideal buckminsterfullerene molecule. The energy we calculate for this structure is  $\sim 6.7$  eV/atom as contrasted with the energy of the ideal buckminsterfullerene of  $\sim 7.0$  eV/atom. Because our quench is quick, we often find atoms trapped in the interior of the

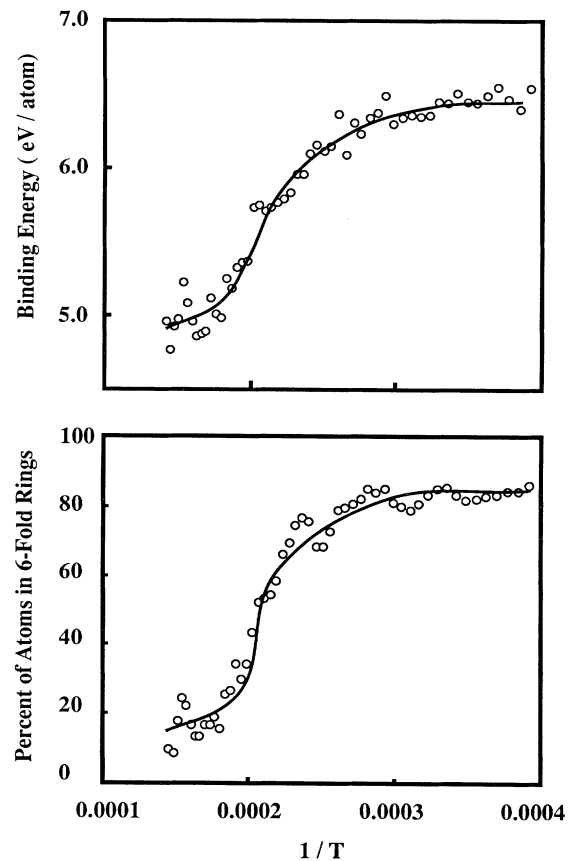


FIG. 2. Binding energy per atom (top) and the percent of atoms in sixfold rings (bottom) as a function of the quenching temperature. Notice the abrupt onset of ring formation below  $\sim 5000$  K.

spheroid cluster.

Our second goal is to search for the "global" minimum structure, i.e., the ground-state structure. Such a search is notably "doomed" from the start. For any system of modest size, finding the phase space occupied by the ground-state structure is usually beyond our computational capability using standard techniques. For such a highly symmetric structure as buckminsterfullerene, the possibility of a successful search is remote. We seek a more limited objective. Namely, we hope to find a low-energy structure which "resembles" buckminsterfullerene.

We attempted the following algorithm. We take our quenched structure in Fig. 1(d) and "prepare" a new starting configuration for further annealing. To prepare the new starting configuration, we remove all the energetically unfavorable atoms from the cluster. We define "unfavorable" to include atoms whose binding energy is more than 1 standard deviation removed from the average binding energy in the cluster. For a structure such as the one in Fig. 1(d), about 10–15 atoms are involved. These higher-energy atoms are then randomly placed

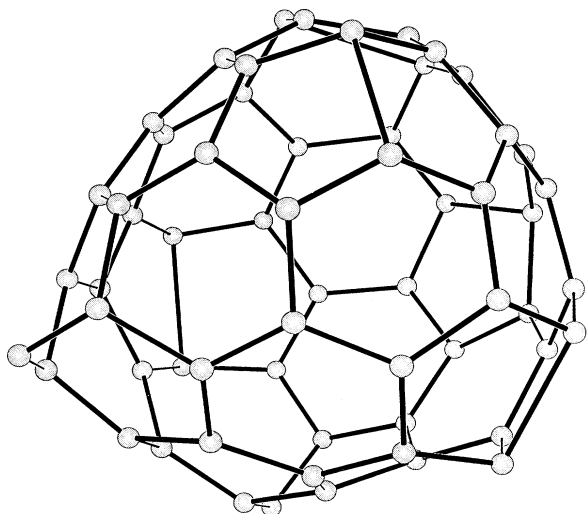


FIG. 3. Lowest-energy structure formed from the annealing simulation. Note the presence of both fivefold and sixfold rings. This structure contains elements in common with buckminsterfullerene; however, defects still dominate the structure.

within the annealing cube with two constraints. The new position of these atoms cannot be within  $2 \text{ \AA}$  of an existing atom, nor can they be placed within  $2 \text{ \AA}$  of an original site which was found to be a high-energy one. These constraints insure that the "prepared" structure is topologically distinct from the previous one. We then repeat the annealing process, i.e., we take an initial temperature of 7000 K and rapidly quench to 1000 K. By repeating this process, we were able to find a lower-energy structure which contained no atoms within the interior of the cluster. This cluster was annealed for a longer period, i.e., approximately 0.1 nsec, from 6000 to 300 K. The lowest-energy structure we found is displayed in Fig. 3. The energy of this structure is comparable to that of the ideal buckminsterfullerene to within  $\sim 0.05 \text{ eV/atom}$ . The structure contains no interior atoms and is dominated by sixfold and fivefold rings.

Two prominent defects occur when compared to the ideal buckminsterfullerene. First, the pentagonal rings share a common base. The bond length corresponding to the shared base is  $\sim 10\%$  longer than the other bond lengths of the pentagon. The shared pentagons may also be considered to form an eight-membered ring with a weak "bridging bond." This configuration is shown in the top part of Fig. 3. Another common defect is for two fivefold rings to share a common base and have the base length increased so that an atom bridges the base and forms two "puckered" sixfold rings. Similar defects have been suggested on the basis of recent quantum-chemistry calculations [22] and semiempirical tight-binding calculations [23]. As an additional check, we constrained our simulation to two dimensions. We obtained a sheet with large portions replicating "ideal" graphitic subunits. The

binding energy of this sheet was  $\sim 0.5 \text{ eV/atom}$  less than the binding energy of our lowest-energy structure in three dimensions (Fig. 3).

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