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Seeking Ways to Break Energy Storage Limits

by William D Mattson, Brian C Barnes, and Betsy M Rice

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An ongoing scientific question is whether a system can contain more energy than the free atom limit (FAL), the amount of energy that can be stored in a chemically bound system. In this study, we proposed guest-host complexes based on compressed xenon encompassed by fullerenes of different sizes that we hypothesized might exceed the FAL based on simple geometric principles. Geometry optimizations using both density functional theory and classical atomistic potential energy models were performed to test the hypothesis, but we were unable to prove our hypothesis with the system sizes that we simulated.

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density functional theory, guest-host structures, carbon nanotubes, free atom limit, geometry optimizations

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1. Introduction

An ongoing scientific question is whether a system can contain more energy than the free atom limit (FAL), a postulate promoted by Lindsay and Fajardo[1] as a hard-upper limit for the amount of energy that can be stored in a chemically bound system. This postulate is based on a simple covalent bonding view of simple acyclic molecular systems. However, a simple bonding view may not be consistent with the great complexity of attainable molecular systems, such as highly strained systems involving rings, cages, or guest-host complexes. While this limit was first postulated in the 1950s,[1] there has been no further demonstration of the validity of the postulate, although there has been no system shown to violate it.

Typically, the FAL argument is made assuming a superposition of bonding energies within a 1-D view of atom pair energies, each having a minimum energy at a specific bond length (Fig. 1), with the system energy reaching a maximum at infinite atomic separation as seen at the right side of the figure (hence the name *free atom limit*). However, the strong repulsive wall on the left side of the figure is not taken into consideration for these systems. The reason for this is that in order to compress the bonds sufficiently to drive the energy significantly up the repulsive wall an external structure constraining the system must undergo an equally sufficient tensile strain, increasing the energy by sampling the attractive tail of the potential energy, which cannot exceed the FAL. Atom pair contributions from a massive container (such as a diamond anvil cell) will have a cumulative contribution to the system energy far below the FAL and it is assumed that the compressed interior sample would not be sufficiently large enough to compensate for the contribution of the container.

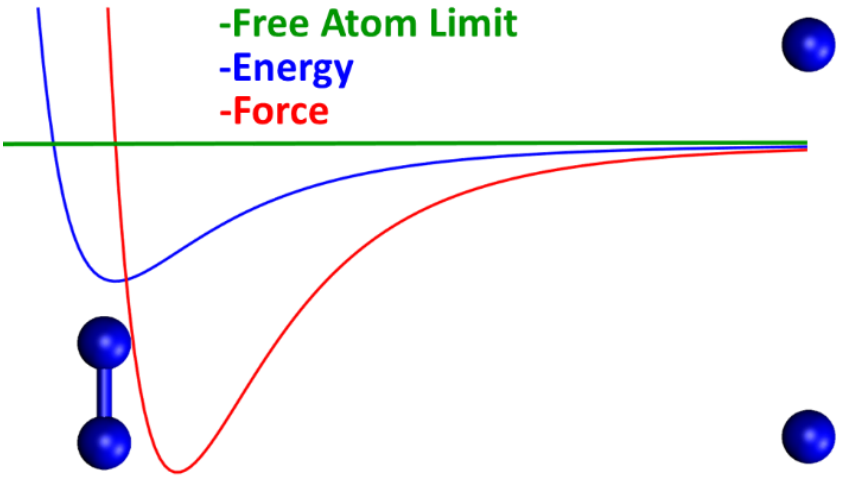

Fig. 1 Schematic of typical potential energy and forces for a covalent bond as a function of interatomic separation

We proposed a multidimensional guest-host complex that we hypothesized might exceed the FAL based on simple geometric principles. To get away from the 1-D view of molecular system energies, we considered guest-host complexes in which the guest material is under extreme compression and experiencing completely repulsive interactions (i.e., higher energy than the FAL), encompassed by a host structure with a strength that could withstand the pressure imposed by the guest material but with a mass that was not large enough to overwhelm the contribution of the repulsive energy of the guest. This host structure would then be under significant tensile strain, also increasing its energy well above the minimum energy structure. Finally, depending on the guest-host interaction, there would be either an additional energy increase or a decrease in energy.

Considering the geometric nature of such a guest-host system, the energy contributions from the guest system are proportional to the system volume, while the energy contributions from the host system are proportional to its surface area. Figure 2 demonstrates this proportionality. Thus, for a stable guest-host structure, the ratio of the energy increase due to compression of the material relative to the tension of the host will rise proportionally to the size of the system. At some system size, the energy from the compressed material will dominate the system energy and exceed the FAL.

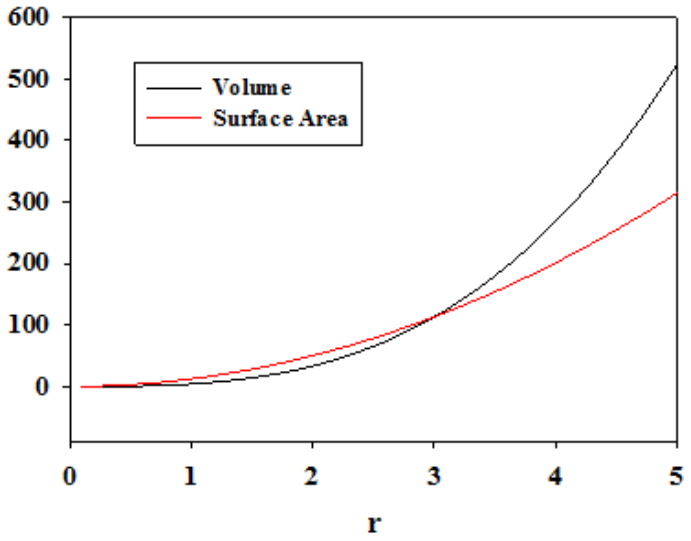

Fig. 2 Volume grows at a rate faster than surface area, proportional to system size

To explore this hypothesis, we chose a guest-host structure based on compressed xenon encompassed by fullerenes of different sizes. The choice of fullerenes is due to their known high-tensile strength, while the choice of xenon is due to size; its interactions are almost always completely repulsive inside fullerenes at high

density. Furthermore, the interaction between the xenon cluster and the fullerene cage would be repulsive.

2. Xenon-Buckminsterfullerene (Xe-C_{60})

The question "How many rare gas atoms can be placed into a fullerene cage until the pressure becomes large enough to break the C_{60} framework?" was explored by Tonner et al.[2] In this study, they use quantum mechanical methods to determine the number of a variety of rare gas atoms that could be encapsulated within a C_{60} molecule without rupturing the shell. They report that only 6 xenon atoms could be encapsulated without destabilizing the system. We performed a geometry optimization of this structure using the CP2K[3] suite of quantum mechanical software with the Perdew-Burke-Ernzerhof (PBE)[4,5] generalized gradient approximation density functional theory. CP2K employs a highly efficient hybrid Gaussian and plane wave basis set. The Gaussian basis set was MOLOPT TZVP[6] for PBE, with the plane wave cutoff set to 1000 Ry. Electron exchange was treated with the generalized gradient approximation, using the PBE functional and Grimme's D3 van der Waals correction.[7] The calculations were run with the overlap transform method.[8] The results indicate that the energy of this structure is well below the FAL.

We also attempted calculations in which 19 xenon atoms were placed within a C_{60} molecule during the geometry optimization simply to raise the energy and see if, at the level of theory we assumed, the shell would rupture. It did not rupture; instead, xenon atoms began to diffuse through the C_{60} wall (see Fig. 3 for snapshots). The geometry optimization was stopped after the eighth step, since the system energy reached a point below the FAL at this time.

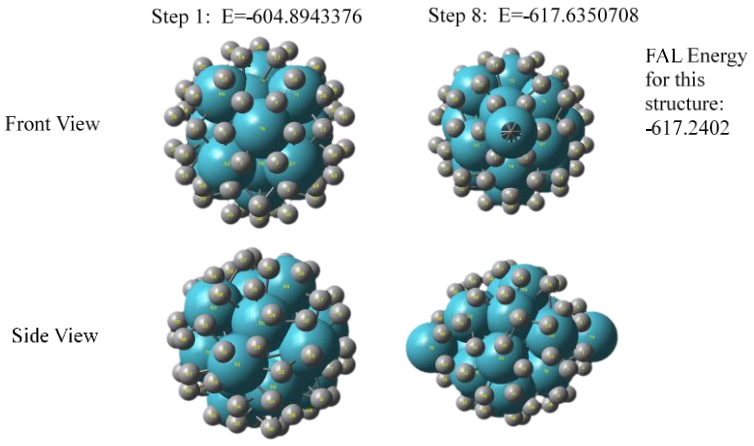

Fig. 3 Structures of a C_{60}-Xe_{19} guest-host complex at the beginning (Step 1) and end (Step 8) of our calculations to optimize the geometry of this structure. Energies are given in hartrees.

3. Xe-C_{980}

We attempted to determine the limit of how many xenon atoms could be placed into a larger fullerene cage, composed of 980 carbon atoms; the choice of this fullerene size was due to the availability of a proposed structure found to be stable through theoretical calculations.[9] The results of our calculations were inconclusive. We were unable to identify a structure that could accommodate a high density of xenon atoms without rupturing the shell. The smallest number of xenon atoms that we attempted to place within the fullerene whose initial energy was above the FAL was 538; however, the shell ruptured (Fig. 4). Additionally, the energy decreased to below the FAL during the geometry optimization, before the shell ruptured.

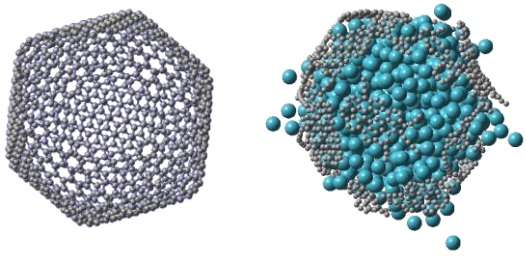

Fig. 4 Optimized structure of C_{980} (left) and ruptured C_{980}-Xe_{536} (right) resulting from a geometry optimization

Attempting to include only 484 atoms produced a complex that dropped to an energy below the FAL at the initial stages of the geometry optimization. Due to the high computational resources required to perform these calculations, we were unable to perform additional calculations.

4. Xe-Carbon Nanotube (CNT)

Because of our inability to attain guest-host complexes that would achieve energies in excess of the FAL assuming more spherically shaped geometries, we explored cylindrical geometries having lower curvature of the carbon shell. Using this geometry for large systems, the overall surface tension could be significantly reduced, therefore stabilizing the carbon shell and perhaps better withstanding the pressure due to the highly compressed guest material. As the radius of the CNT is increased, the system more closely approximates graphene, which is known to have exceptional mechanical properties. We performed molecular dynamics simulations of CNTs filled with xenon using the classical reactive force field, ReaxFF,[10] as implemented in the Large-scale Atomic/Molecular Massively Parallel Simulator molecular simulation software.[11] In these simulations, an infinitely long nanotube was created through the use of periodic boundaries with a cylindrical slice. The

force field used for the nanotube was an open literature parameterization created for CNT simulations. The xenon force field was a simple Lennard-Jones model, with geometric cross terms for Xe-C interactions. The goal of these calculations was to establish whether a cylindrical nanotube small enough to be easily validated through quantum mechanical calculations would provide evidence against the FAL postulate. This requires construction of a cylindrical nanotube with enough xenon inside to exceed the FAL, but not enough that the nanotube ruptures. No evidence against the FAL was found. In all systems tested, the CNT ruptured, typically after the total energy of the system was already below the FAL. It may be that significantly larger cylindrical nanotubes provide evidence against the FAL; but those systems would likely be so large that validation with QM methods would be intractable. In Fig. 5, we provide an example result from this approach.

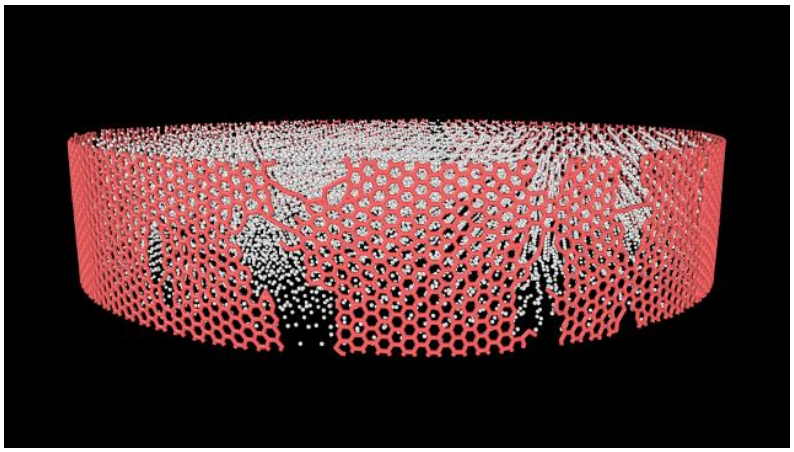

Fig. 5 Structure of a 5200-atom CNT containing 16318 Xe atoms resulting from an isothermal isochoric molecular dynamics simulation at 300 K

In this snapshot, the cylindrical nanotube has ruptured, despite being below the FAL when the rupture began to form. This system was composed of a (100, 100) CNT containing 5200 carbon atoms, initially having a 67.6-Å radius, which was briefly relaxed and then filled with 16318 xenon atoms (initially in a face-centered cubic lattice). After filling with xenon, the system was equilibrated at constant number, volume, and temperature using a velocity rescaling thermostat at 300 K (in order to ensure slow relaxation xenon forces against the nanotube wall). In the simulation shown in Fig. 5, ruptures began to form after approximately 4.2 ps.

5. Summary and Conclusions

We were unable to prove our hypothesis with the system sizes that we simulated; however, larger system sizes should demonstrate that these complexes will exceed the FAL. Future work should explore the relationship between size and point of rupture, which might show trends regarding the proportion of xenon to fullerene carbon that would be required to exceed the FAL.

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List of Symbols, Abbreviations, and Acronyms

1-D	one-dimensional
C	carbon
C_{60}	buckminsterfullerene
CNT	carbon nanotube
FAL	free atom limit
PBE	Perdew-Burke-Ernzerhof
Xe	xenon

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