Comment on "Nucleation of C_{60} Clusters"

A recent Letter [1] describes a carbon interatomic potential which leads to structures similar to buckminsterfullerene on quenching a group of sixty carbon atoms in molecular-dynamics (MD) simulations. It is not clear, however, that the simulations plausibly model the nucleation of buckminsterfullerene in real experiments. The cooling rate assumed is many orders of magnitude too large, and this affects the nucleation process.

The simulations proceed from an initial state where sixty carbon atoms are confined to a cube of side length 12 Å. The temperature falls from 7000 to 1000 K in 20 ps. The resulting structures are roughly spherical and a high percentage of the atoms reside in sixfold rings.

Experimentally, fullerenes have been made by vaporizing graphite, either with a laser [2] or using resistive heating [3], in an inert atmosphere of helium. Nucleation takes place from the hot vapor, cooled by expansion and heat exchange with the surroundings. The crucial comparison to be made is between the cooling rates used in the simulations and estimated real cooling rates.

In laser evaporation a 30-mJ laser pulse is incident upon a graphite plate [2]. The following model is not entirely realistic in its neglect of the heating and pressurization of the helium caused by the passage of a shock wave, but it is probably adequate in providing a rough estimate of the vapor expansion rate. With this neglect, the rate of work done by the expanding vapor on the helium is $p_0\dot{V}$, where p_0 is the helium pressure and $\dot{V}$ is the vapor volume expansion rate. Considering the kinetic energy gained by the helium around an expanding sphere, and using the continuity equation, the radial expansion velocity can be estimated to be $(2p_0/3\rho_0)^{1/2}$, where ρ_0 is the helium density. This is about 82% of the speed of sound in the helium and is about 635 ms^{-1} at 20 °C. The expansion continues until the pressure of the vapor bubble has fallen to ambient.

If the work done on the helium were the only energy loss, and assuming the ideal gas law is adequate for the latter stages of the expansion, the pressure p and the volume V of the vapor would satisfy $(p+p_0/3)V=2E_0/3$, where E_0 is the initial energy. Assuming $p_0=10^4$ Pa and $E_0=30$ mJ, the volume after pressure equilibration is 1.2 cm^3 and the temperature about $\frac{3}{5}$ the initial value T_i. Using the estimated expansion velocity, this yields a cooling rate from 10000 K of about 6×10^8 Ks^{-1} and an expansion time of 10 μs.

However, radiative energy loss is likely to dominate. The integrated loss is equal to $\int 4\pi r^2\sigma T^4 dt$, using an emissivity of unity, where r is the radius of the vapor bubble and σ is the Stefan-Boltzmann constant. The fastest possible purely radiative cooling with $T=T_i$ would lead to a final volume not less than $\dot{r}E_0/\sigma T_i^4$ which for the previously given parameters is 3.4×10^{-8} m^3. $\dot{r}$ is the assumed constant radial expansion velocity. The cooling takes approximately 3 μs at a rate of 3×10^9 Ks^{-1}.

The evolution of the vapor would require more complicated modeling to be realistic, but it is clear that experimental cooling rates are about 10^5 times smaller than the rate of 3×10^{14} Ks^{-1} used in the MD simulations. Indeed, the author of Ref. [1] realizes some of the temporal problems with rapid quenches and attempts to modify defective final structures by further annealing. However, with realistic cooling rates, MD simulations starting from a hot, dense initial state would lead to the rapid dispersal of the atoms, which would qualitatively change the nucleation mechanism from a bulk freezing phenomenon to an accretion process.

The simulations are interesting studies of the way fullerene structures may be favored by the form of the carbon interatomic potential. They do not, however, model the real nucleation process which is likely to be dominated by the addition of monomers or dimers to a growing cluster. This can depend on kinetics as well as equilibrium free-energy considerations (e.g., Ref. [4], where the influence of energy-exchange collisions on the nucleation of liquid droplets is studied). Studies of the effect of geometry on the cluster binding energy, e.g., Ref. [5], together with detailed modeling of the cooling of the carbon vapor and the accretion process [6] would offer the best insights into the nucleation of buckminsterfullerene.

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