

Fraction crystalline from electron powder patterns of unlayered graphene in solidified carbon rain

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Elemental carbon at low (e.g. ambient and lower) pressure sublimates to vapor near 4000K, but liquid carbon is reported after laser ablation [1,2]. Some meteoritic carbon particles, whose isotopes fingerprint s-process nucleosynthesis and likely formed in or near red giant star photospheres, show an “unlayered-graphene” core/graphite-rim structure [3-5] (with HRTEM evidence for faceted pentacones [6]). The cores likely result from super-cooled carbon droplets that nucleated graphene sheets on randomly oriented 5 and 6 member rings. Similar core-rim particles result from slow cooling of carbon vapor in the lab [7], albeit with graphene sheets having smaller coherence widths.

The Debye scattering equation [8] allows one to calculate the interference effect of small randomly-oriented crystalline clusters on otherwise diffuse atomic scattering from a specimen. It is ideal for working with oddly-shaped clusters (like unlayered graphene sheets, and faceted carbon pentacones) because molecule shape effects (like the high-frequency tails on powder diffraction peaks from atom-thick sheets [9]) are automatically taken into account in its predictions.

Electron powder diffraction (and HRTEM) observations of presolar onion cores suggest an average graphene sheet size of about 40Å coherence width, or $N \approx 612$ atoms per cluster. Diffraction from the labgrown cores instead suggest sheets with only 12Å coherence width, or $N \approx 60$ atoms per cluster. This is not surprising since the small size of our oven interior suggests that condensed particles impact an oven wall within about 10 milliseconds, while containerless cooling of carbon condensate in a red giant photosphere might take place over much longer times (limited only e.g. by radiation pressure ejection).

One way to estimate the fraction crystalline at each peak is to measure three heights at the peak frequency on a model "100%-crystalline" Debye system with comparable peak width, namely the *total peak height* s_2 , the *estimated background height* s_1 beneath the peak, and the *"diffuse-scattering baseline" height* s_x . Then on an "experimental profile" measure the observed *total peak height* h_2 and the corresponding *peak background* h_1 beneath the peak.

One can infer the *experimental baseline height* h_x by assuming that the incoherent baseline position is where the model predicts i.e. $(h_x-h_1)/(h_2-h_1) = (s_x-s_1)/(s_2-s_1)$, so that $h_x = h_1 + (h_2-h_1)(s_x-s_1)/(s_2-s_1)$. The *non-crystalline background component* h_o may then be inferred by assuming that the crystalline-component peak shape follows the prediction i.e. $(h_x-h_o)/(h_2-h_o) = s_x/s_2$ so that $h_o = (h_1s_2-h_2s_1)/(s_2-s_1)$, where any combination of subscripts 1, 2 and x may be used in place of subscripts x and 2 here. Finally, the *fraction crystalline* f_x may be estimated if one divides the inferred crystalline-component baseline by the experimental baseline, i.e. $f_x \approx (h_x-h_o)/h_x = ((h_2-h_1)s_x)/((h_2-h_1)s_x+h_1s_2-h_2s_1)$.

This fraction crystalline will be less than one provided that the total peak to (peak-background) height ratio is less in the experimental sample i.e. $h_2/h_1 < s_2/s_1$, and hence that the non-crystalline background

height h_0 is positive. By measuring this f_x value on a given profile at more than one peak, one might report a mean and a measure of uncertainty as well. For the experimental (Fig. 1) and model (e.g. Fig. 2) pattern profiles, the fraction of atoms in unlayered graphene sheets about 600 atoms in size (presolar) and 60 atoms in size (homegrown) is estimated to be about 40% and 12%, respectively.

The "time at temperature" (e.g. in the 3000K range) needed to rearrange liquid atoms, so that nearly half of them are in graphene sheets about 600 atoms in size, would tell us both about the way that carbon atoms on earth were condensed and ejected from red giant atmospheres, and about the challenges we might face in trying to create similar materials on earth e.g. for their potentially-interesting diffusion barrier properties. The ratio between crystalline fraction f_x and the number of atoms per sheet also be used to tell us the number of sheets per atom (or per cc, or per gram, for a given density), and (depending on whether they are nucleated on pentagonal or hexagonal loops) the number of sheet nuclei which have managed to seed growth to the average final size during the cooldown process. These numbers in turn are being compared with ab-initio and semi-empirical predictions of loop formation in a solidifying carbon melt [10], with the goal of refining cluster-kinetic and analytical models of nucleation and growth in the days ahead.

References:

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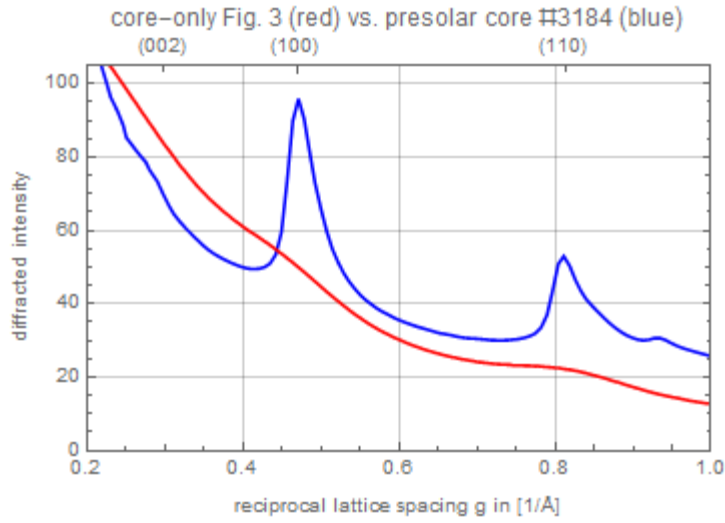


Figure 1. Presolar (blue) vs. homegrown (red) diffraction profiles, showing the almost complete absence of graphite (002).

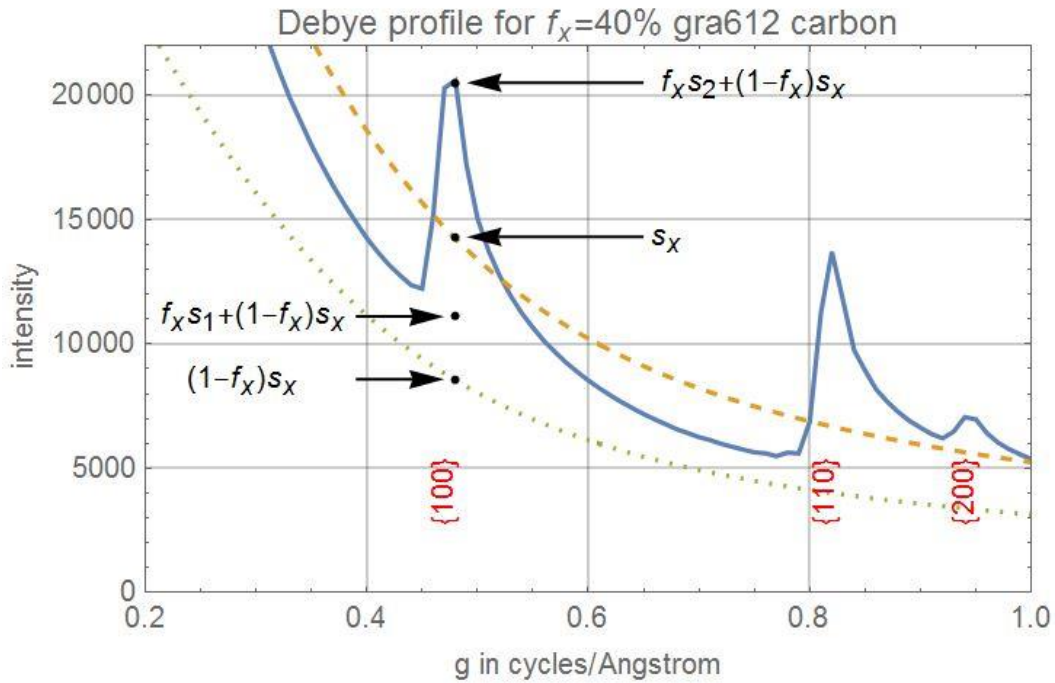


Figure 2. Debye profile for 40% crystalline graphene 612, with a dashed baseline.