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Understanding the limits of pair-distribution functions for nanoscale correlation function measurement

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Abstract

We explore the ability of the pair-distribution function (pdf) to accurately measure medium-range correlation lengths in nanoscale crystalline materials. Through simple computer simulations of disordered fcc metals, we find that the presence of quadratic displacement fields is sufficient to mask topological order (mro) at the medium-range (1–3 nm). This reconciles previous measurements and modeling on amorphous silicon—which showed that paracrystalline structures give pair correlation functions which are almost indistinguishable from random networks—with the wide use of pdfs to measure correlation lengths in nanoscale crystalline materials. Through simple analytical considerations, we identify conditions when the pdf method can be trusted for mro measurements in nanocrystalline materials. We show that while the reliability of the technique is dependent on the nature of materials studied, in general the technique fails for sufficiently small grain size in compact materials. When the pdf method does not work, we have previously shown that fluctuation microscopy is a powerful tool to give information on mro.

1. Introduction

The pair-distribution function, or pdf, can be directly derived from diffraction data and has been widely used in the study of materials (see for example a recent review (Proffen *et al* 2003)). In distorted materials, such as glasses, it is widely known that the pdf dies out quickly at distances beyond several times the nearest neighbor bond distance (Elliot 1983). As a result, while it is very valuable for studying short-range order, the pdf has been far less useful in studies of medium-range order (mro) (1–3 nm). This does not discount the fact that several authors have shown that the pdf can be theoretically sensitive to medium-range order but the effects observed are subtle and not unique (Elliot 1983, Bodapati *et al* 2006).

In contrast, for the study of nanocrystalline materials, the pdf has been shown to be capable of measuring correlation lengths on the nanoscale, which overlaps the regime often thought of as 'medium-range order' (Billinge and Kanatzidis 2004). Since the structure of some amorphous materials has been proposed to be 'paracrystalline', and thus the mro

not so different from nanocrystal correlation lengths, this presents a paradox. For example, simulations have shown that paracrystalline silicon, which is highly topologically ordered, can appear almost indistinguishable from a random network in the pair-distribution function (Voyles *et al* 2001). When is the pdf able to measure mro and when is it not, for nanoscale crystalline or paracrystalline materials? And perhaps more importantly, when no correlations are seen in the pdf beyond a certain distance, does that really mean that there is no ordering beyond that length scale?

In this paper we use computer simulations of disorder in very simple spherical models of single-crystal copper to learn how well the pdf can observe medium-range correlations. The results show that when lattice plane curvature is induced by stress in structures, this can mask in the pdf the existence of medium-range correlations. We generalize this result to discuss conditions in which the pdf might fail, and conclude that it is not very dependent on materials nature, but very strongly dependent on 'grain size'. In fact, when correlation lengths are below ∼2–3 nm, the pdf technique loses sensitivity to order. In that case, methods such as fluctuation microscopy (Treacy and Gibson 1996, Gibson and Treacy 1997) are required to measure medium-range order.

2. Numerical simulation

The pair-distribution function is also known as the 'reduced' radial-distribution function and is given by $G(r) = 4\pi r[\rho(r) - \rho_0]$ (Elliot 1983). This is directly derived by Fourier transformation of x-ray, neutron or electron scattering data.

In order to understand the effect of strain-related disorder on the pair-distribution function, we have carried out simple simulations using a face-centered-lattice with the lattice spacing of copper (3.62 Å). The models were cut as spheres from a perfect lattice, and the results were analyzed for different sphere radii (r_s). The pair-distribution function was corrected for finite model size (Gibson 1978). Ensembles of typically 50 grains were averaged to get better statistics. Several models for strain fields were examined, but only two representative models are presented here:

(a) *Simple Gaussian uncorrelated displacement (Einstein model).* Figure 1 shows a 20 Å radius model with 2880 atoms, and a Gaussian random atomic displacement of 0.1 Å standard deviation, typical of thermal vibration amplitudes.

The pair-distribution function for this model is shown in figure 2:

As pointed out by Levashov *et al* (2005) small Gaussian displacements cause no increased attenuation of the oscillating pdf with increasing r, and so do not mask medium-range correlations.

(b) *However, such attenuation can be induced by a strain gradient.* In its simplest form this means a curvature of the lattice planes. To model this we have used a simple quadratic dependence of the displacement field with distance from the origin of a spherical crystal. Simulations show that shear or compression have qualitatively similar effect on the pdf. Figure 3 shows an example which corresponds to a compression displacement with radius of curvature of 80 Å. (In this calculation, the principal axes of stress were randomly oriented over an ensemble of 30 models, only one of which is shown in figure 4. Also, the Gaussian displacement of (a) was simultaneously included.)

Obviously, the pdf peaks are significantly attenuated with increasing distance. Yet the structure is obviously still well-ordered across the entire sphere as shown in figure 4.

In the presence of such strong lattice plane curvature, the pdf is much less able to see the medium-range topological order that is present. As the curvature increases, the attenuation shown in figure 3 becomes more severe.

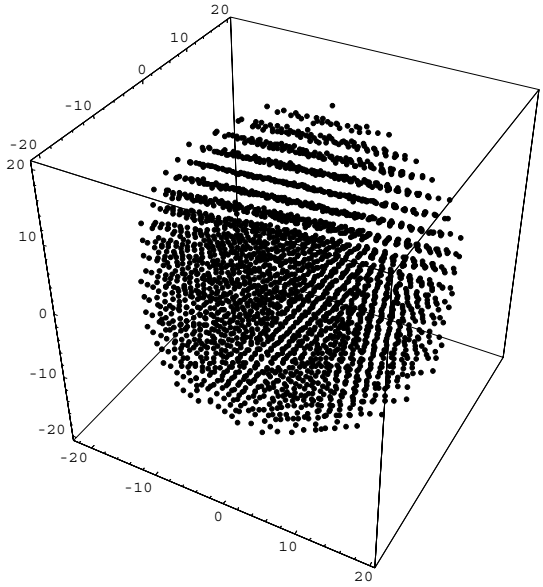

Figure 1. Atomic model of a Cu nanocrystal with Gaussian displacements.

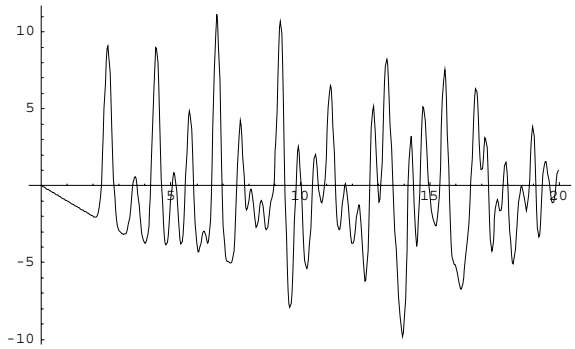

Figure 2. Pair distribution function calculated from an ensemble of models such as figure 1.

A number of other types of disorder were studied, including sinusoidal modulations. Further calculations suggest that more complex strain fields present in real grains would attenuate the pdf even more than the simple model of lattice curvature. However, it seems that the key to decay of the oscillation amplitude in the pdf is the existence of curved lattice planes.

3. Analytical modeling

One can simply understand the attenuation of the pdf in the presence of quadratic displacement fields as being due to a progressive increase in the width of peaks in the pdf $G(r)$ as the distance r increases. Approximate peak widths increase like $r^3/4R^2$ as a function of distance r, with radius of curvature R. For the model above R is about 80 Å, which at 25 Å distance predicts a ∼0.6 Å peak width in the pdf, sufficient to greatly reduce peak amplitudes due to overlap of

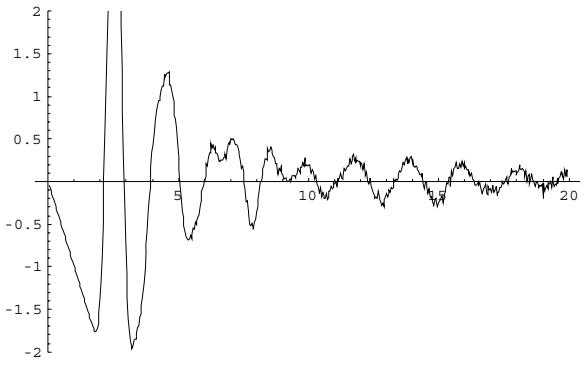

Figure 3. Pair distribution function calculated from an ensemble of Cu nanocrystals with quadratic displacements.

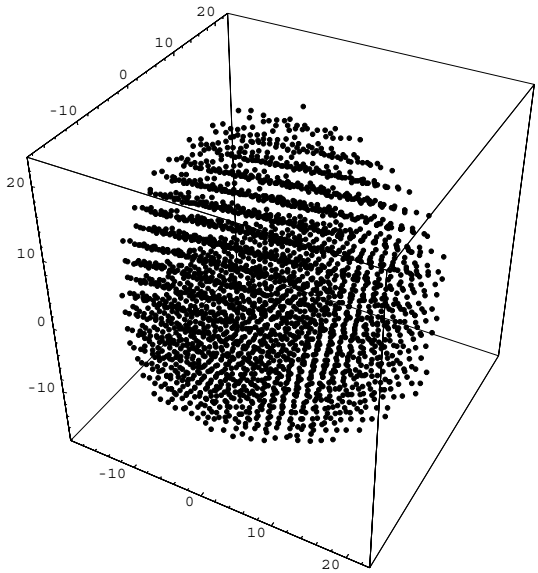

Figure 4. A representative Cu nanocrystal with quadratic displacements used to calculate figure 3.

adjacent peaks. This is as we observe in the simulation (b) (figure 3). In contrast, Gaussian broadening (a) (figure 2) does not cause a peak width change with r, and so does not attenuate the pdf.

The use of a quadratic displacement field may seem particular, but in fact it is a general feature that comes from any stress gradient, such as would be associated, for example, with dislocations at a grain boundary. The quadratic term in the displacement is equivalent to the linear term in the strain field, which would be present in the power expansion of any localized stress source. And of course, higher-order terms would almost certainly create similar effects—we have simply chosen the lowest order (quadratic displacement) term that is needed for the effect.

Let us approximate very simply the displacement curvature associated with grain boundaries in a nanocrystalline material. Assuming an array of dislocations characterizes a

grain boundary, and that the average high-angle grain boundary angle is about $\sim\pi/3$ radians, we expect an average grain boundary dislocation density of approximately one every three planes. This predicts an average dislocation number per spherical grain of $\sim 2\pi d/3b$, where b is the dislocation's burger's vector.

The shear stress field of a screw dislocation parallel to the z-axis goes as $\tau_{yz} = -\mu bx/2\pi(x^2 + y^2)$. Converting to a displacement field and expanding to obtain the effective radius of curvature as a function of grain size, gives $R = \frac{\pi d^2}{2b}$. This leads to an effective radius of curvature (adding all the dislocation strain fields in quadrature) of $R = \sqrt{\frac{3\pi}{8}}\frac{d^{\frac{3}{2}}}{\sqrt{b}}$. Equating this to the critical radius of curvature of approximately 80 Å in our simulation of figure 3 leads to a prediction for the minimum grain size in which the pdf method would work. Using $b = a/2[110]$ gives this critical size as $d = 25$ Å. Although this is a crude estimate, it is not unreasonable. Note that as d decreases below this critical level, the blurring of peaks in the pdf would lead to attenuation of any sensitivity to mro on the 1–3 nm length scale. Even though our model is simple, the super-linear functional dependence on d is key to the effect and would be independent, for example, of the type of dislocations at the grain boundary. It would also be quite insensitive to the elastic constants of the material, or grain boundary structure.

Our result assumes a compact of grains, and would be quite different for free standing clusters, where one would not expect to see curved lattice planes. (Surface energy effects on a free cluster would lead to a uniform internal stress to first order, which would not blur the pdf, at least for monodisperse clusters.) Some solid materials where the grains are spaced by an amorphous intergranular material might also show clearer pdf signatures, acting like free clusters. However, in the solid-state a compact nanocrystalline material should be vulnerable to quadratic lattice plane bending for small grain sizes.

Our analysis is obviously not exhaustive, but the results are sufficient to signpost important concerns about the use of the pdf to determine mro. Further analysis of peak shapes and decay rates in pdfs may allow more reliable results to be obtained with the simpler and more widely applicable pdf method. This will be the subject of future study. At present we recommend fluctuation microscopy (Treacy and Gibson 1996) as the most reliable method to prove the absence of mro.

Note that the simple models in this paper obviously apply to crystalline materials with nanoscale grain size. We have shown already that amorphous semiconductors which show medium-range order can be thought of as topologically similar—paracrystalline (Voyles *et al* 2001). The question as to whether medium-range order can exist in amorphous materials and not necessarily be associated with topological crystallinity is not addressed in this paper, but is indeed an interesting one.

4. Conclusion

Our analysis shows that for small highly curved crystalline grains in a compact material, the pdf may be unable to reliably measure the grain size for sufficiently small grains. In general, we argue, there is a critical 'grain size' in topologically ordered crystalline materials, below which the pdf is not a reliable indicator of the absence of medium-range order, and thus not a reliable tool for measuring nanoscale correlation lengths. Evidence for this effect may be detectable due to an increased broadening of pdf peak widths for the first, second and third peaks (which is typically seen in 'amorphous' materials but can be present in small-grained crystalline materials also). Further work is needed to allow the pdf to be unambiguously used in the measure of nanoscale correlation lengths, but also we point to the usefulness of fluctuation microscopy in resolving issues about medium-range order in nanoscale crystalline materials.

A question may be raised—who cares? If the material is heavily strained, does it matter whether the underlying topological order is detected? We argue that it does. For example, it is well known that defects in materials are determined by topology, and defects directly influence mechanical, electrical, optical and even magnetic properties. Thus we would like to know the detailed nature of topological order, but the pdf may not reliably tell us.

While we have chosen a rather arbitrary model for these simulations, we believe that the conclusions are quite independent of the model chosen. The results can be interpreted as revealing a barrier (or an 'inverse window') in the ability of simple diffraction to determine ordering on the medium-range. Short-range (<1 nm) and long-range (>3 nm) order are adequately visualized by diffraction techniques, such as the pdf, but there is a blind spot in the mro region. This is a symptom of the weakness of pair-correlations. Techniques such as fluctuation microscopy are sensitive to higher-order correlation functions (Treacy and Gibson 1996) (up to four atom distribution functions) which open up this 'window' to view.

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