Chapter 13

Concluding Remarks

As we mentioned in the preface to the second edition, and throughout the book, the world of PDF has changed enormously in the 10 years since the first edition of this book, to the point where it is unrecognizable. Historically, radial distribution function methods were used almost exclusively for glasses and amorphous materials where crystallography was powerless. In the period beginning in the early 1990s, they began to be applied to the study of disorder in crystalline materials with many surprises and new insights emerging from these studies. The methods developed and became more powerful and this period was summarized in the first edition of this book in 2003. In the 10 years since that time, the field has exploded with much more powerful experimental methods, modeling and rich and broad experimental applications beyond physics, which was the original field of application in the early 1990s, to materials science, chemistry, nanoscience, geology, and all the way to pharmaceuticals, and the examples described in this book are but an appetizer for what has been done by many people.

For a long time since the development of the X-ray diffraction technique in the early twentieth century, determining the atomic structure of a solid has meant determining the crystal structure, by carrying out a diffraction measurement and analyzing the data with crystallographic methods. If one occasionally ran into a glass, the structure would be termed "amorphous," that is, structureless, and the analysis would be practically abandoned there. However, sophistication in materials development brought about a major class of materials that are neither perfectly crystalline nor totally amorphous. Such a material, a crystallographically challenged material, would fall right into the gap of the existing techniques of structural analysis. And yet the details of the atomic structure usually have profound effects on their properties. In this book, we discussed how to determine the structure of such a complex material, mainly borrowing from the method of structural analysis for glasses and liquids. Compared to glasses and liquids, however, the systems have much stronger local atomic order. In order to characterize such short- and medium-range order quantitatively, the data have to be collected with high accuracy and the analysis has to be carried out

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with great care. But when it is executed properly, the power of the method is remarkable. Now with the advent of nanoscience and nanomaterials, this need has taken on new dimensions, especially because of the "nanostructure problem," the fact that the power crystallographic methods on which we rely to solve structures of crystals break down for nanostructures.

The purpose of this book is to introduce the readers to the technique of PDF analysis of amorphous, nanocrystalline, and disordered crystalline materials by starting from scratch and getting into some practical details. As many of us are familiar with the conventional methods of crystal structural analysis that is done in reciprocal space, the notion of using the PDF method for the structural study of a crystal may appear strange in the beginning. Actually, the PDF is a much more intuitive way to characterize the structure than in reciprocal space, particularly because we, at least most of us, live in real space! It simply represents the bond lengths and other interatomic distances, and by combining these distances in 3D, the total structure can be reconstructed.

An important factor that differentiates the PDF method from conventional methods is the inclusion of diffuse scattering. The presence of diffuse scattering in the data may not be obvious, particularly for the powder diffraction data. But it is always present, at least in the form of thermal diffuse scattering. In the case when the crystal lattice is not perfect, additional diffuse scattering is produced by the defects and it provides important information regarding the nature and spatial distribution of the defects. In some crystals, such as the crystals with polarons, or the emphanitic appearance of fluctuations in PbTe, these defects arise not because of lattice imperfections but are intrinsic, for example, due to the interaction of the lattice with electrons. For nanomaterials, there are few approaches for determining the 3D structure, but PDF is providing crucial structural information and insights.

The importance of the local structure is well recognized in some fields, for example, in the EXAFS and solid-state NMR communities. However, these spectroscopies provide information on only the very shortest lengthscales with emphasis on the nearest neighbors. On the other hand, the intermediate or nanoscale structure is equally important in determining the properties of the system. The PDF method is a unique probe that provides the information on such intermediate-range structure. While the measurement and the data analysis of this method are not trivial, with proper training anyone can practice this method, and as the tools to collect, analyze, and model the data get better, it is rapidly opening up to a much wider group of users. Our hope is that this book will spark interest in this method and will play an educational role of introduction into the field of local structural research using the PDF method. By presenting the theory and data analysis equations in some detail, we hope too that it will become a point of reference on the subject, though these technical chapters and appendices may make grueling reading.

As more pulsed neutron and synchrotron radiation sources and dedicated and optimized PDF beamlines are constructed, the opportunity to practice this

method is growing rapidly, the more so with the introduction of electron PDFs. We hope this method will continue to impact our understanding of materials, from condensed-matter physics and solid-state chemistry through earth science to biology and biomedical materials science.