The Problem with Determining Atomic Structure at the Nanoscale

Simon J. L. Billinge and Igor Levin

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Simon J. L. Billinge[1]* and Igor Levin[2]

Emerging complex functional materials often have atomic order limited to the nanoscale. Examples include nanoparticles, species encapsulated in mesoporous hosts, and bulk crystals with intrinsic nanoscale order. The powerful methods that we have for solving the atomic structure of bulk crystals fail for such materials. Currently, no broadly applicable, quantitative, and robust methods exist to replace crystallography at the nanoscale. We provide an overview of various classes of nanostructured materials and review the methods that are currently used to study their structure. We suggest that successful solutions to these nanostructure problems will involve interactions among researchers from materials science, physics, chemistry, computer science, and applied mathematics, working within a "complex modeling" paradigm that combines theory and experiment in a self-consistent computational framework.

The "structure problem" can be stated straightforwardly: Given a new material, what is the atomic arrangement inside it? Having this knowledge is a prerequisite to further theoretical understanding of the material's properties. For the case of crystals, there are robust and quantitative solutions to this problem, as far as the average atomic positions are concerned. In many cases, it is possible to put a crystal on a computer-controlled x-ray diffractometer (XRD) and have the computer retrieve the structure. This is not so for nanostructured materials, such as nanoparticles, mesoporous materials, and bulk crystals with short-range structural fluctuations. What emerges from the XRD when a sample of nanoparticles, for example, is loaded is not a structural model but a broad and continuous intensity distribution that is not amenable to a crystallographic structure solution. The need to determine atomic arrangements in nanostructured materials, quantitatively and with high precision, is what we call the "nanostructure problem." A number of powerful probes exist for studying local and nanoscale structures, but in general we have no widely applicable solution to the nanostructure problem.

Solving the crystal structure problem was far from trivial, the history of which is dotted with Nobel prizes. The reason is the "phase problem": the inherent loss of information that occurs when scattered intensities are measured. The challenge is to reconstruct the lost phase information from the intensity data. In most cases, this is done by solving a large, nonlinear, global optimization problem, where the degrees of freedom are the unknown phases, or atomic coordinates, and where the constraints come from the data (Bragg

peak positions and intensities). Such a problem is solvable in principle if there are more constraints than degrees of freedom and solvable in practice if this condition is matched with suitable algorithms. Crystal structure problems are usually well conditioned because thousands of Bragg peaks are measured to determine hundreds of atom positions in the unit cell (in the case of protein crystallography, these numbers are larger), and the existing algorithms work well.

This global optimization approach is completely generic and presents to us a road map for solving the nanostructure problem. First, we need to ensure that the particular nanostructure problem is well conditioned: We have more constraints from data, and other prior knowledge, than degrees of freedom in our model. Second, we need algorithms that can reconstruct the three-dimensional (3D) structure from the information at hand. In the case of nanostructures, both aspects present substantial challenges.

Many techniques exist for probing nanostructured materials. Some are inherently local, such as transmission electron microscopy (TEM) and scanning probe microscopies. Others are bulk average probes that are sensitive to local structure, such as the atomic pair distribution function (PDF) method or extended x-ray absorption fine structure (EXAFS) analysis. The principal difficulty with the application of these methods to solving the nanostructure problem is that, in general, any one technique does not contain sufficient information to constrain a unique structural solution. A coherent strategy is required for combining input from multiple experimental methods and theory in a self-consistent global optimization scheme: something that we refer to as "complex modeling."

Types of Nanostructure

Many crystals are now being made and studied that have local atomic arrangements substantially different from those inferred from the crystallog-

raphy ([1]). We refer to these as nanostructured bulk materials, and an example is shown in Fig. 1A. In these materials, domains of local structural order exist whose correlations extend over nanometer-length scales without destroying the average lattice. There is a growing realization that this behavior is not rare but widespread and can be extremely useful. For example, the most desirable ferroelectrics for transducers are relaxors with polar nanodomains ([2]); the most promising bulk thermoelectrics have nanoscale phase separations perfectly tuned to scatter heat-conducting long-wavelength phonons ([3], [4]); and nanoscale phase separation, possibly an intrinsic property of the electronic system, is thought to be essential for obtaining colossal responses in advanced electronic materials such as colossal magnetoresistant (CMR) manganites and high-temperature superconductors ([5]).

By definition, soft materials produce a large response to a mechanical load. The emerging nanostructured bulk materials can be thought of as hard materials that are electronically or magnetically (or in some other regard) soft. They have locally correlated domains of order that can be easily flipped or switched, producing a large response ([5]). Because the structure is scale-dependent, the response also depends on the length and time scales of the probing excitation. Understanding the formation of nanostructures in (and their effects on the properties of) these materials is a complex problem because the different scales cannot necessarily be considered independently from each other. Multiscale modeling is a major frontier in computational materials science ([6]). The same could be said for multiscale studies in the experimental materials domain.

Mesoporous materials, illustrated in Fig. 1B, are bulk materials that contain porosity with nanometer-scale dimensions. They have a wide range of uses, including catalysis, chemical separation, waste remediation, hosts for hydrogen storage, passivation of reactive species, as well as hitherto unforeseen applications. Just about every bulk material is a candidate for being manufactured in mesoporous form, but most progress has been made in covalent network systems, such as alumino-silicates ([7]), carbon ([8]), and silicon ([9]). Attention has recently been focused toward making narrow band-gap semiconducting materials in the mesoporous form ([10]). The internal pores of these materials can also be functionalized with molecules to modify their reactive properties.

Structural questions are twofold in these systems: What is the structure of the framework, and what is the structure of species intercalated inside the pores? These are also multiscale problems. The performance of the material is not only sensitive to pore sizes (1 to 100 nm) and connectivity, but also to access to the pore network that depends on particle size (1 to 100 μm) and morphology. Except in the minority of crystalline

[1]Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824, USA. [2]Ceramics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899–1070, USA.

*To whom correspondence should be addressed. E-mail: billinge@pa.msu.edu

cases, such as the zeolites, noncrystalline methods are needed. In general, the intercalated species are not arranged periodically in space, so noncrystallographic nanostructure methods are required to solve their structure.

Starting in the late 1980s, chemists began synthesizing nanoparticles: nanometer-scale crystals of semiconducting and metallic materials (Fig. 1C) (11). The synthetic ingenuity has developed rapidly, so that there is now enormous control and breadth of composition, size, shape, polydispersity, and self-assembly. Some nanoparticles even have their own substructure. Nanoparticles have already found application, for example, as nonquenching fluorescent tags for biological molecules. Assemblies of nanoparticles offer an entirely new and hardly explored frontier for applications.

The physical properties of the nanoparticles are modified as a result of their finite size that modifies the electronic structure through quantum confinement (11). However, equally important is the modification of the local atomic structure resulting from a substantial proportion of the sample being associated with a surface. The surface itself relaxes, but the presence of surface strains also can modify the "bulk" structure and the nature of stable extended defects (12). The nanoparticle structure can also depend on the chemical environment in which the nanoparticle resides and the nature of the passivating surfactant layers (13). However, because of the nanostructure problem, most structural studies have been semiquantitative at best and often rely on extrapolations from the bulk material. When considering discrete nanoparticles, it is also

important to consider the true nature of the material and to formulate the pertinent structural question; for example, is the sample an ensemble of identical particles, a statistical distribution of similar particles, or a single nanoparticle in a device?

Experimental Methods for Nanostructure Elucidation

Experimental probes of nanoscale structure fall into a number of categories. Such probes can yield direct or indirect information about the atomic arrangement. XRD is an example of the former and Raman spectroscopy the latter. They can be methods that probe small, nanometer- to micrometer-sized regions of samples or bulk average probes of local structure. In general, methods from different categories provide highly complementary information and are much more powerful when used together. In Table 1, we list and categorize the different techniques described below.

One standard approach to crystal structure solution involves reconstructing the phase, as well as the known intensity, of each Bragg reflection. Lost phase information can also be reconstructed from nonperiodic systems in a process known as diffraction imaging (14, 15). The experimental requirement is a highly coherent x-ray beam with a cross-sectional area that is more than two times that of the nanoparticle under study. The nanoparticle or particles are mounted on a nonscattering (or weakly scattering) support. Powerful algorithms exist for reconstructing the lost phase information when the area illuminated by the coherent beam is more than twice that of the

nanoparticle. This allows for a direct Fourier transform to reveal the density distribution, which is an image of the sample (16). The first successful experimental demonstration used soft x-rays to image 100-nm-diameter gold spheres arranged as letters (17). Currently, these techniques have not demonstrated atomic-scale resolution from x-ray measurements and show more promise in the short term as a nanoscale imaging method. In principle, with a probe of sufficiently short wavelength, individual atoms could be imaged, and this approach could be used for structure determination. Atoms on a carbon nanotube have already been imaged in this way by means of electron diffraction (18).

Nanostructures can also be solved from conventional diffraction data by computer modeling. For some time, it has been possible to extract nanoscale structure with the use of total scattering data that includes both Bragg (where it is present) and diffuse scattering intensities (1, 19). Such data yield the local and intermediate range structure and are often probed by Fourier-transforming to real space, yielding the atomic PDF (19). This function gives a measure of the probability of finding pairs of atoms separated by some distance. For example, a strong peak in the PDF can be seen at the nearest-neighbor distance between atoms, then another at the second neighbor, and so on. Where a well-defined structure exists, peaks are observed at intermediate and long ranges, beyond 30 nm in some cases.

Total scattering data are rich in nanoscale structural information. The scattering pattern in reciprocal space and the PDF in real space are readily calculated from a model atomic configuration. The model can then be updated by moving atoms (or other parameters) until a good agreement is obtained between the calculated and measured patterns: a process called structure refinement. The diffuse scattering from nanostructured regions of single crystals can be studied with x-rays and neutrons (20); however, quantitative analysis of the data is a challenging computational problem that is under active development. Greater progress has been made with modeling the isotropic scattering from powders. When the analysis is carried out in reciprocal space, the model often consists of many atoms that are moved around with the use of a simulated annealing approach known as reverse Monte Carlo (21). This approach is widely used for extracting structural configurations from more highly disordered materials, such as glasses and liquids, with little a priori knowledge of the structure. Disorder in crystals is frequently modeled in real space in an approach that is similar to Rietveld refinement of regular powder x-ray or neutron diffraction data (22) but which yields the local structure because it is the PDF that is being fit (23, 24). The optimization method can be a local downhill-search method (24), such as Newton or Levenberg-Marquardt, or a global search method, such as Monte Carlo (25): the
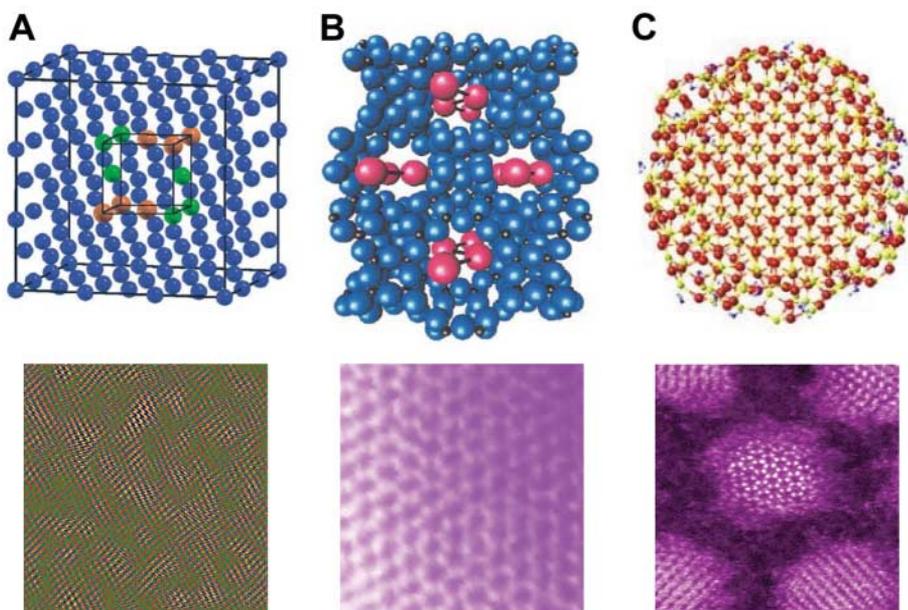
Fig. 1. Examples of nanostructured materials. (**A**) Nanostructured bulk materials. (**B**) Intercalated mesoporous materials. (**C**) Discrete nanoparticles. In each case, ball-and-stick renditions of possible structures are shown on the top, and TEM images of examples are shown on the bottom. Ball-and-stick images were reproduced with permission {in (A) and (B) from the American Physical Society [from (52) and (53), respectively] and in (C) [from (13)]}.

former being much faster but requiring the initial guess to be rather close to the actual solution. There is sometimes benefit to fitting jointly in real and reciprocal space (25).

None of the above approaches allows for the ab initio solution of unknown nanoparticle structures from well-ordered nanoparticles (i.e., the case where a specific solution exists). However, by means of a recently developed algorithm, the 3D structure of C_{60} was determined from PDF data alone (26). In this case, the information content of the data (18 distinct atom-pair distances and their multiplicities) was enough to give a unique 3D reconstruction of the 60-atom buckyball, as illustrated in Fig. 2. The case of C_{60} proved to be well conditioned, though it was not obvious a priori that this would be the case. In general, total PDF data will have to be augmented with information from other sources such as EXAFS, nuclear magnetic resonance (NMR), TEM, or chemically resolved PDFs obtained from differential measurements making use of the different scattering strengths of isotopes (neutrons) or resonantly scattering elements (x-rays). The local structural methods described here are beginning to be applied to study excited-state structures of materials with the use of time-resolved pump-probe experiments (27, 28). Developments in nanostructure determination can therefore be quickly extended to excited-state structures in the future.

X-ray and neutron small-angle scattering, nanoscale tomographic imaging, and reflectivity measurements are widely used to study nano-structured systems. They do not yield atomic-resolution information but provide important ancillary data (for example, about the homogeneity of the sample) that will be important in constraining the proper atomic-scale structural solution. Similar highly complementary 3D information about materials, with atomic resolution and chemical specificity but not quantitative bond-length information, is also available by

means of the destructive atom probe tomographic technique (29).

EXAFS is a bulk probe that carries information about near-neighbor distance distributions, coordination numbers, and, less directly, bond angles. EXAFS probes only the first few coordination shells and therefore does not reveal nanometer-scale structure. However, it contains crucial chemical-specific local structural information and is sensitive to dilute species. Thus, it is a natural complement to the nanoscale, but chemically unresolved, PDF data. EXAFS is a widely applied local structural technique. Simultaneous quantitative analysis of diffraction and EXAFS data sets, currently rather rare (30), will certainly grow in importance in the future.

X-ray absorption near-edge structure (XANES) also reveals information on inter-atomic distances and coordination numbers but is substantially more sensitive to bond angles than EXAFS. XANES commonly serves as a fingerprint for the coordination type and oxidation state of a given chemical species, but it can also provide such structural details as the magnitudes of local metal displacements and chemical short-range order parameters (31) in transition metal oxides. Unlike EXAFS, the agreement between calculated and experimental XANES in many cases is still only semiquantitative, though the theory is rapidly developing (32). Full quantitative fitting will allow direct incorporation of this important information into nanostructure problems.

Raman spectroscopy in solids exploits the inelastic scattering of light by optical phonons. As such, it is an indirect probe of structure; however, Raman spectra are extremely sensitive to local deviations from the average periodicity, making this a valuable probe of local structure. Interpretation of Raman spectra requires accurate assignment of Raman peaks to specific vibrations from an independent preknowledge of the structure. Although group theoretical analyses provide

initial insight into the nature of Raman-active modes, first-principles calculations are essential for a reliable peak assignment. First-principles calculations of Raman intensities are feasible (33) but still scarce, even for ideal crystals. Currently, Raman spectra serve as fingerprints for phase identification in nanostructures, providing important constraints for the correct structural model. Considering the broad availability of Raman spectroscopy and its sensitivity to local structural details, this technique has a potential to become a standard laboratory tool for rapid local structure analysis. Full access to the rich local structural information contained in Raman spectra necessitates development of theoretical models and efficient computer algorithms in systems that are distorted from the ideal structure.

Solid-state NMR (34) and related techniques, such as Mössbauer and muon spectroscopies, are other spectroscopic methods that are sensitive to local structure. They yield information about the local symmetry and coordination of the probe atom or site and can also be valuable for establishing and quantifying phase separation where it exists.

Advanced TEMs provide a multitude of complementary diffraction, imaging, and spectroscopic techniques—all available in a single instrument—that enable quantitative, atomically resolved, structural and chemical information over scales ranging from a micrometer to an angstrom. Real-space structural imaging from thin sections of material in high-resolution TEM (HRTEM) and scanning TEM (STEM) modes provides information on the nature of nanocrystals and nanostructures in bulk materials. Diffraction patterns are also available from these small areas.

The dynamical nature of the electron scattering means that HRTEM images contain all the phase information as well as the amplitudes of diffracted beams, which should facilitate ab initio crystal structure determination; however, the image contrast also depends on nonstructural factors such as sample thickness, lens aberrations, and imaging conditions. Only for sufficiently thin samples, as encountered in the studies of nanoparticles, can Fourier restorations of the electron wave at the exit surface of a sample enable direct interpretation of phase contrast in terms of the crystal potential. The power of this approach is highlighted in determinations of the chirality of single-walled carbon nanotubes (SWNTs) (35) and atomic arrangements in 1D semiconductor crystals (36). The phase information contained in HRTEM images can be combined with the amplitude information from electron diffraction patterns to solve the structure in a manner similar to the direct methods of x-ray crystallography (37). Despite considerable promise, ab initio solutions of the nanostructure problem with the use of HRTEM and electron crystallography are far from routine, and atomic arrangements are more commonly found by matching a computed phase contrast for a trial structure to the experimental images.

Table 1. Experimental probes of nanoscale structure categorized as direct versus indirect measures of structure and whether they probe the whole sample (bulk probe) or a small part of it (local probe).

Probe	Direct (D)/indirect (I) measures	Bulk (B)/local (L) probes
Total scattering/PDF	D	B
Diffuse scattering from single crystals	D	B
EXAFS	D	B
XANES	I	B
Raman spectroscopy	I	B
NMR/Mössbauer/μSR	I	B
Small-angle scattering*	I	B
Tomographic imaging*	I	B
Diffraction imaging	D	L
TEM/electron diffraction	D	L
Atom probe tomography	D	L
STM/AFM	I	L
X-ray/neutron reflectivity*†	I	L

*A direct measure of structure at low resolution that gives information that could be used indirectly in a nanostructure solution.
†Local in the sense that it only probes surfaces and interfaces.

Annular dark-field STEM images, recorded by means of electrons scattered to large angles, exhibit a so-called Z contrast with the image intensity being approximately proportional to the atomic number, Z, squared. Atomic-resolution Z-contrast images carry both structural and chemical information that, in many cases, can be inferred directly from the image without computer simulations. Z-contrast imaging is often combined with electron energy-loss spectroscopy (EELS)—a technique analogous to soft x-ray absorption spectroscopy—to obtain additional element-specific chemical and structural information on the atomic scale. The Z-contrast/EELS combination is particularly useful for determination of nanoscale chemical and charge ordering (38) and the location of dopant atoms (39). Recent dramatic advances in TEM instrumentation in the form of lens spherical-aberration correctors substantially improve the merits of both HRTEM- and STEM-based techniques for determination of local atomic arrangements, subject to sample limitations and radiation damage. Direct HRTEM imaging of oxygen atoms (40), a 3D-like HRTEM imaging of SWNTs (41), and depth-resolved STEM imaging of a single-impurity atom (42) are just a few examples that illustrate the potential contributions of aberration-corrected TEM to solutions of nanostructure problems.

Electron diffraction is a highly sensitive tool for the detection of diffuse intensity (43) because electrons are scattered by matter 1000 to 10,000 times more strongly than x-rays or neutrons. As with x-rays, the diffuse intensity encodes nanoscale structural information that can, in principle, be modeled to yield nanostructure, though fully quantitative analysis of the data is difficult. Precession methods that make the electron scattering more kinematical in nature (44) would help to make these analyses more quantitative, though this kind of analysis is in a fledgling state. Electron nanodiffraction in a STEM mode also contains structural information from nanometer-sized regions and can be used directly (45), or combined with STEM imaging in hybrid methods such as fluctuation microscopy (46), to determine medium-range structural correlations. As with the x-ray case, time-resolved measurements of excited-state structures are also possible with electrons and are especially apropos for nanoparticles (47).

In the world of nanostructures, TEM-based methods are positioned to play a critical role by providing single-crystal structural models that can be used in subsequent refinements by means of powder scattering and spectroscopic tools. Simultaneous quantitative analysis of TEM and other types of structural data (e.g., PDF and EXAFS) should greatly facilitate the determination of local atomic arrangements but will require the development of suitable computer software.

Surface imaging probes, such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM), also provide valuable nanoscale information. They often have atomic resolution and can also give spectroscopic information on the nanoscale (48). Nanoscale-resolution x-ray imaging probes are under development and will give bulk projections and, with the use of tomographic methods, will yield 3D reconstructions of nanostructures. These methods yield similar information to diffraction-based lensless imaging techniques described above and currently have similar resolutions. X-ray imaging probes do not have atomic resolution, but combining the information with other atomic-resolution data is a powerful way to extract complex multiscale structures: Knowing the nanoscale morphology of the material can act as a constraint for other higher-resolution probes. In exceptional cases, it may be possible to get a multiscale structure solution by this approach, as has been demonstrated in the solution of virus structures by combining low-resolution cryogenic electron microscopy (cryo-EM) images with atomic-resolution structures of the individual proteins making up the viral capsid (49). A distribution of discrete but identical viral capsids that are frozen on a substrate in random orientations is imaged in the microscope, and software is used to reconstruct the low-resolution structure of a representative capsid. If the structure of the folded proteins making up the capsid has been solved by means of protein crystallography, then those protein structures can be superimposed on the low-resolution electron density map from the cryo-EM to give a more complete solution.

The Future: Complex Modeling

The complex nature of the nanostructure problem means that the solution will require a coordinated response from researchers with a broad range of scientific expertise. This currently happens but in an incoherent way: Multiple groups work independently on the same problem and interact through the literature and conferences. Coherence requires that experimental data are collected, to the extent possible, on the same or same-batch samples, and the data are shared in a common computational global optimization framework. The distinction between theory (predicting outcomes) and experiment (measuring outcomes) becomes blurred because both contribute to our state of knowledge of the system and can be used to regularize the problem. For example, theory can inform us of the presence of physically unreasonable structural solutions that are, nonetheless, consistent with data in an otherwise underconstrained situation. In principle, theoretical calculations can be included in the regression cycle, where approximations in the model are considered as degrees of freedom. Direct energy minimizations and data fitting in the form of χ^2 minimizations can be combined in the global optimization framework. This concept is not new: In crystallography, theoretical constraints (such as positivity of intensities) and prior knowledge from other methods (such as the amino acid sequence of a protein) are crucial in finding structural solutions. However, despite some initial efforts (50, 51), the approach is not being systematically exploited in materials science. Great strides toward more robust and widely applicable quantitative solutions to the nanostructure problem will be made as we learn how to combine the results of experimental methods and theory more effectively.
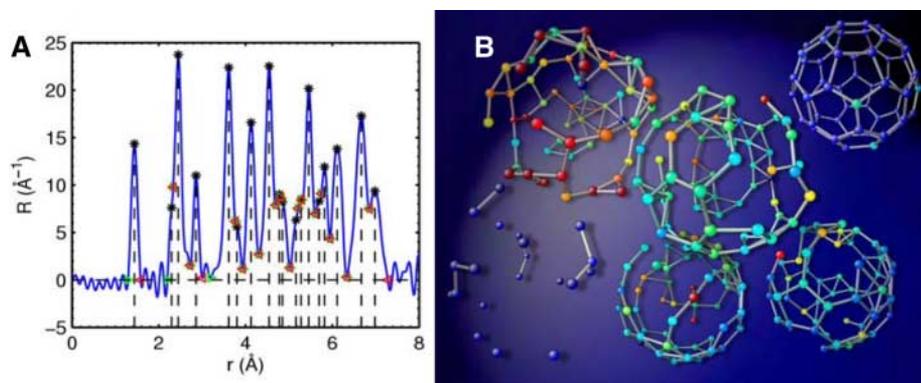

Fig. 2. Example of ab initio nanostructure determination with the use of PDF data and the "Liga" algorithm (26). (**A**) The PDF data are used to extract interatomic distances and multiplicities. This information is used by the algorithm to build up clusters that are consistent with that information, to backtrack by removing atoms in poorly performing clusters, and then to rebuild until a good solution is found. R is the radial distribution function, and r the interatomic distance. Black asterisks indicate the positions of PDF peak maxima and shoulders used to determine interatomic distances present (shown as dashed lines). Red and green triangles indicate the integration limits used to determine peak intensities and therefore multiplicities of those distances. The procedure is illustrated in (**B**) where a number of intermediate clusters are shown on the way to a successful reconstruction of C_{60} (top right corner). The colors of the spheres indicate the amount of error contributed to the atom at that position. It is a continuous color scale from dark blue (low error) to dark red (high error). Images were reproduced with permission [from (26)].

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Reviews: "The problem with determining atomic structure at the nanoscale" by S. J. L. Billinge and I. Levin (27 Apr. 2007, p. 561). The reference to the source article for the TEM image of nanoparticles in Fig. 1C was omitted. The image was adapted from a figure in J. R. McBride, T. C. Kippeny, S. J. Pennycook, S. J. Rosenthal, *Nanoletters* **4**, 1279 (2004).