Towards quantitative determination of atomic structures of amorphous materials in three dimensions

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Towards quantitative determination of atomic structures of amorphous materials in three dimensions

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Abstract

Amorphous materials such as glass, polymer and amorphous alloy have broad applications ranging from daily life to extreme conditions due to their unique properties in elasticity, strength and electrical resistivity. A better understanding of atomic structure of amorphous materials will provide invaluable information for their further engineering and applications. However, experimentally determining the three-dimensional (3D) atomic structure of amorphous materials has been a long-standing problem. Due to the disordered atomic arrangement, amorphous materials do not have any translational and rotational symmetry at long-range scale. Conventional characterization methods, such as the scattering and the microscopy imaging, can only provide the statistic structural information which is averaged over the macroscopic region. The knowledge of the 3D
atomic structure of amorphous materials is limited. Recently atomic resolution electron tomography (AET) has proved an increasingly powerful tool for atomic scale structural characterization without any crystalline assumptions, which opens a door to determine the 3D structure of various amorphous materials. In this review, we summarize the state-of-art characterization methods for the exploration of atomic structures of amorphous materials in the past few decades, including X-ray/neutron diffraction, nano-beam and angstrom-beam electron diffraction, fluctuation electron microscopy, high-resolution scanning/transmission electron microscopy, and atom probe tomography. From experimental data and theoretical descriptions, 3D structures of various amorphous materials have been built up. Particularly, we introduce the principles and recent progresses of AET, and highlight the most recent groundbreaking feat accomplished by AET, i.e., the first experimental determination of all 3D atomic positions in a multi-component glass-forming alloy and the 3D atomic packing in amorphous solids. We also discuss the new opportunities and challenges for characterizing the chemical and structural defects in amorphous materials.

**Keywords** amorphous solid, atomic structure, 3D reconstruction, atomic resolution electron tomography, short-range order, medium-range order

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1. Introduction

Amorphous materials have a long history and a profound significance in the evolution of civilization and science development [1,2]. The most common amorphous material, glass,
was first discovered and used as weapons and tools by humans no later than 3000 B.C. Amorphous materials include many natural amorphous materials such as natural glasses, ambers, rosins, and natural rubbers, as well as synthetic amorphous materials such as oxide glasses, polymers, plastics, amorphous semiconductors and amorphous alloys. They are ubiquitous in our daily life and have broad applications, ranging from renewable energy [3-5], energy storage [6,7], non-volatile memory [8-10], telecommunication and computer networking [11], high-efficiency transformers [12,13], catalysis [14-16], to biomedical applications [17,18]. Metallic glass (MG), an important type of amorphous materials, was successfully prepared for the first time in 1960s through rapid quenching techniques [19]. It has attracted much attention due to its fancy properties in mechanics, soft magnetics and corrosion resistance [20-26]. MG also has unique phenomena such as special thermodynamic and kinetic processes under thermal transformation and supercooling conditions [27-35]. The origin of the unique properties of such materials is related to the disordered atomic arrangement which has both short-range order (SRO) and medium-range order (MRO), excludes long-range order and periodicity. These local ordered structures were also observed in liquid-to-liquid phase transition and nano-glasses [36].

The nature of glass is one of the biggest unsolved questions in solid state theory and condensed matter physics [37,38], and the three dimensional (3D) atomic arrangement of amorphous materials has become a long-standing problem. Over the years, a number of experimental methods have been employed to explore the structure of amorphous
materials, such as X-ray diffraction (XRD) [39] and neutron diffraction (ND) [40], X-ray absorption fine structure (XAFS) [41], atomic force microscopy (AFM) [42,43], nano-beam and angstrom-beam electron diffraction (NBED and ABED) [44,45], fluctuation electron microscopy (FEM) [46,47], high-resolution scanning/transmission electron microscopy (STEM/TEM) [48-50], nuclear magnetic resonance (NMR) [51] and atom probe tomography (APT) [52]. However, conventional characterization methods currently cannot yield accurate structures at the atomic level. Averaged structures can be obtained in the radial distribution function (RDF) and pair distribution function (PDF) provided by diffraction measurements [53], while the local coordination information got by extended X-ray absorption fine structure (EXAFS) [54] and NMR [55] experiments. However, the knowledge about the 3D atomic structure of amorphous materials is yet limited; the atomic motifs and their connections at medium-range are smeared out. Meanwhile, several computational methods [56-59] such as density functional theory, energy minimization (or relaxation) methods, molecular dynamics (MD) simulations and reverse Monte Carlo (RMC) modeling have been developed and combined with experimental methods to generate plausible 3D structural models of amorphous materials at the atomic level.

Despite all these developments, experimentally determining the three-dimensional atomic structure of amorphous materials remained an unsolved problem until very recently [60,61]. With rapid development in aberration-corrected electron microscopes, advanced detectors, data acquisition methods, iterative 3D reconstruction algorithms and
post-processing methods, atomic electron tomography (AET) has proved to be a powerful technique for atomic-scale structural characterization in 3D and even 4D [62-65]. In principle AET can solve this long-standing problem as it has the ability to resolve the 3D atomic structure of materials without assuming crystallinity. In 2021, Miao and his colleagues advanced AET to experimentally determine the 3D positions of all the atoms in both monatomic and multi-component amorphous solid samples [60,61]. This groundbreaking accomplishment would open a door for quantitative studying of the atomic structures of amorphous materials in 3D. In this review, we summarize various characterization methods applied to the study of atomic structures of amorphous materials in the past few decades, including XRD/ND, FEM, NBED and ABED, high-resolution STEM/TEM, and APT. We introduce the experimental and computational aspects of AET and recent progress in resolving the 3D atomic structure of materials. We highlight the first experimental determination of 3D coordinates in a nanometer-scale MG and the 3D packing of liquid-like monatomic amorphous solid. Finally, we discuss the opportunities and challenges in developing advanced quantitative techniques for amorphous materials structure determination, including the development of faster data acquisition and computation algorithms, identification of all the chemical species in atomic resolution, and combination of multiple techniques. We anticipate AET will open up a new door for studying the structural and chemical defects in glass, exploring unusual materials such as poly-amorphous and structurally anisotropic glasses, and solving fundamental processes such as the amorphous-crystalline phase transition and the glass transition.
2. The exploration of amorphous structures in three dimensions

2.1 X-ray and neutron diffraction

Amorphous materials present one of the greatest challenges to the experimental characterization techniques. XRD was definitely one of the very first experiment techniques to tackle this problem. It is difficult to overestimate the impact of X-ray crystallography on modern science and technology [66]. Other particles such as neutrons and electrons are also used to produce diffraction patterns. Although electron, neutron, and X-ray interact with matter differently, the resulting diffraction patterns can be analyzed using the same coherent diffraction imaging techniques. We will discuss electron diffraction in the next section separately. Based on the diffraction pattern produced from the periodic structure in crystal solid, X-ray crystallography can determine the mean atom positions, chemical bonding and other various information. It is still a primary method for characterizing atomic structures of materials. Although amorphous materials cannot yield diffraction patterns of regularly spaced spots to determine the atomic positions due to the lack of long-range order structure, however XRD studies have long been used to obtain information (mainly RDF and PDF from diffraction patterns) on the short and medium range structure of amorphous materials. In 1930s, Warren and coworkers pioneered some early work on the XRD in glass and presented a random three-dimensional network in vitreous SiO$_2$[67,68]. In 1960s, Bernal built up a random packing model to represent the structure of liquids using the hard sphere packing and obtained a range of possible atomic geometrical arrangements [69,70]. His random packing model
corroborated with the experimental observation of the split-second peak of the RDF [71]. It has significant impact on the subsequent studying of MG structures [72]. After 1970s, with increasing computational power, the combination of simulation methods such as RMC/MD and XRD/ND patterns became popular [73]. Several review articles have summarized the study of amorphous materials using X-ray and/or neutron diffraction thoroughly [74-77], here we highlight a few recent works due to the length limitation.

In 2006, Sheng et al. combined experimental and computational techniques to resolve the atomic-level structure of MGs [78]. Fig. 1a shows the XRD curve from X-ray scattering and EXAFS spectra of Ni$_{80}$P$_{20}$ MG, which fit well with the 3D atomic configuration (Fig. 1a bottom left) reconstructed using the RMC method. They analyzed the packing of solute-centred quasi-equivalent clusters, e.g. the fivefold symmetry in the cluster connections (Fig. 1a, bottom right). This work allows one to analyze the SRO and MRO of binary metallic glass using a combination of XRD and RMC technique [78]. Similar approaches were applied to ternary and multi-component bulk metallic glass (BMG) by Sheng et al. in 2008 [79]. They analyzed the SRO and MRO of the 3D atomic configuration constructed from ab initio simulation and showed the solute-centered clusters and topology of the SRO clusters (Fig. 1b). In 2007, Sheng et al. applied in situ XRD to monitor the pressure-induced transition between two distinct amorphous polymorphs in a Ce$_{55}$Al$_{45}$ MG [80]. Top panel of Fig. 1c shows the XRD peak positions shift during the compression and decompression experiments. Combined with ab initio MD simulations, bottom panel in Fig. 1c show the strong bonding from the 3D
isosurfaces of the electron charge density in the f-electron delocalized glass. Recently, Lou et al. used \textit{in situ} XRD to study a two-way tuning of structural order in Ce$_{65}$Al$_{10}$Co$_{25}$ MG [81]. They revealed that the MGs have a thermal-driven structural ordering and a reverse disordering process via pressure-induced rejuvenation.

Neutron interact with the nuclei of atoms and can penetrate into deep of bulk materials. Neutron diffraction is widely used in the study of BMG structures [82-86]. \textbf{Fig. 1d} shows typical PDF of glassy Cu$_{64.5}$Zr$_{35.5}$ obtained by Fourier transforming the experimental structure factor $S(q)$ (the inset in \textbf{Fig. 1d}). In 2009, Ma et al. analyzed the X-ray and neutron diffraction experiments results of various MGs and fitted the first peak position in momentum transfer with atomic volumes. The results show that the MROs have the characteristics of a fractal network with a dimension of 2.31. They proposed a new packing scheme, self-similar packing of atomic clusters to described MROs [87]. In 2018, Lan et al. compared the glass-forming ability (GFA) of a series of Zr-Cu-Al MG with ND and high-resolution TEM [88]. Top panels in \textbf{Fig. 1e} show the PDFs of two MGs upon annealing. The peak intensity and position evolution (black arrows) indicate higher coordination shells and the ordering process. The bottom panels show the PDFs for the crystalline products and the as-cast amorphous state of all studied Zr-Cu-Al BMGs. From the exponential decay of the peak height, they characterized the different ordering in all samples. Neutron diffraction PDF analysis provides important information of atomic clustering, showing that the easy connection of short-range clusters at the medium-range length scale would favor the avalanche nucleation.
**Figure 1. X-ray and neutron diffraction.** (a) Structure determination for Ni$_{80}$P$_{20}$ MG by XRD (top) analysis, the insets show the EXAFS spectra. Bottom left is the atom packing model reconstructed by RMC method. Bottom right shows the local cluster and the packing varies of clusters (Adapted from Ref. 78. © 2006, Springer Nature.) (b) (left) The structure factors of the Al$_{89}$La$_6$Ni$_5$ MG from XRD experiment and the inverse Monte Carlo (IMC) simulation, showing a satisfactory match between simulation and
experiments. (right) An atomic slab of Al$_{89}$La$_{6}$Ni$_{5}$ MG obtained from IMC modeling with thickness of 3.5 Å, showing the random distribution of La and Ni atoms mostly surrounded by Al atoms. (Adapted from Ref. 79. © 2008, Elsevier.) (e) (top) XRD pattern of Ce$_{55}$Al$_{45}$ MG obtained *in situ* during the compression and decompression experiments. (bottom) The two-dimensional projections of the 3D isosurfaces of the electron charge density from *ab initio* calculations for the two amorphous states. (Adapted from Ref. 80. © 2007, Springer Nature.) (d) Two reduced PDF $G(r)$ of glassy Cu$_{64.5}$Zr$_{35.5}$ obtained by Fourier transforming the experimental structure factor $S(q)$ (the inset) with two termination values ($q_{\text{max}}$). (Adapted from Ref. 87. © 2009, Springer Nature.) (e) (top) PDFs of Cu-Zr-Al BMGs with different compositions. (bottom) Reduced PDFs for the crystalline products and the as-cast amorphous state of studied Zr-Cu-Al alloys using the exponential function fitting (the dotted lines). (Adapted from Ref. 88. © 2008, Elsevier.)

2.2 Fluctuation electron microscopy and nano-beam/angstrom-beam electron diffraction

Since electron diffraction was discovered in 1927, electron has become a powerful source used in material characterization. Similar to X-ray and neutron diffraction, average distance information of atoms is also provided in electron diffraction. FEM is an electron microscopy technique sensitive to nanometer-scale structures or MRO in disordered materials [89]. The theory of FEM has been developed since 1993 by Treacy and Gibson [90-92], and the details of both TEM and STEM experiments were carried out by Voyles...
et al. in 1999 and 2002, respectively [93,94]. Since then, FEM has been widely employed to study a variety of disordered materials, such as amorphous semiconductors [95,96], MGs [97-100], oxide materials [101] and amorphous alloys [102-104]. FEM rests on the statistical analysis of the scattering from nanoscopic volumes of the sample, which can be realized by dark-field TEM imaging, micro-diffraction or dark-field STEM imaging with a thin annular detector (TAD) [105]. In either case, the measurements are performed at deliberately low image resolution (typically 0.5~5.0 nm), resulting in a position-resolved map of the diffracted intensity. For homogeneous disordered samples, a map with low variance is expected, whereas heterogeneous samples with randomly oriented ordered clusters lead to a map with high variance.

In 2012, Hwang et al. proposed a new model for the atomic structure of Zr$_{50}$Cu$_{45}$Al$_5$ BMG based on hybrid RMC simulations with the combination of SRO from an empirical potential and MRO from FEM data [106]. The model contains a significant fraction of crystal-like atomic clusters. The crystal-like clusters in the BMG samples were transformed into icosahedral-like clusters through structural relaxation upon annealing (Fig. 2a). In 2018, Zhang et al. reported a Ni$_{60}$Nb$_{40}$ alloy vitrified from face-centered cubic (fcc) Ni and body-centered cubic (bcc) Nb by cold rolling and rapid solidification [107]. Comparing to the as-spun sample with a two-step crystallization reaction, the as-rolled alloy has a lower crystallization onset temperature with a single crystallization reaction (Fig. 2b). In 2019, Perking et al. carried out an in situ nano-beam electron diffraction experiment and combined experiment results with MD simulation to analyze
the change of the SRO and MRO during the formation of a shear band of Cu_{46}Zr_{46}Al_{8} BMGs (Fig. 2c). They observed a spatially resolved reduction of order prior to shear banding due to increased strain [108]. Reducing the diameter of the electron beam down to sub-nanometer size, distinct diffraction spots appear while the halo rings in select area electron diffraction (SAED) fade. These distinct diffraction spots provide important information in understanding SRO and MRO in MGs (Fig. 2d top right). In 2011, Hirata et al. combined NBED and computational techniques in modeling the SRO and MRO structure of MG [44]. Bottom panel in Fig. 2d shows the edge-sharing of a polyhedron corresponding to a local atomic cluster in a glassy Zr_{66.7}Ni_{33.3} thin foil. The simulated NBED pattern from the cluster model agrees with the experimental one, confirming the face-sharing configuration of the super-cluster. This was the first work that applied NBED technique with ab initio dynamic simulation to determine the SRO and MRO in amorphous materials. In 2013, Hirata et al. applied a coherent electron beam with a diameter of 0.36 nm for ABED measurement. They compared the measured ABED patterns with simulated ones and found experimental patterns partially match those of the five-fold orientations (Fig. 2e top panel). The most common ABED patterns were found to originate from the distorted icosahedra by searing all possible on-axis diffraction patterns predicted by the MD simulation (Fig. 2e middle panel). The correlation between a local fcc symmetry and a distorted pentagon of icosahedral order is shown in bottom panel of Fig. 2e [109]. This work provides important information in geometric frustration of local icosahedral order in MGs.
Figure 2. Fluctuation electron microscopy and nano-beam/angstrom-beam electron diffraction. (a) Normalized variance $V(k)$ from the as-quenched and annealed Zr$_{50}$Cu$_{45}$Al$_5$ MGs. (Adapted from Ref. 106. © 2012, American Physical Society.) (b) Top panel shows DSC traces (left) and XRD curve (right) of as-spun and as-rolled Ni$_{60}$Nb$_{40}$ MGs. Bottom panel shows the variances from FEM measurements and the HRMC
simulated models of Ni$_{60}$Nb$_{40}$ MGs. (Adapted from Ref. 107. © 2018, Elsevier.) (c) (top) Annular dark field image taken before, during and after in situ deformation of BMG sample. (bottom) The NBED was performed in the green dashed box with the scale bar of 150 nm. Three patterns show two-fold (orange), four-fold (blue) and zero (yellow) symmetries in different regions. (Adapted from Ref. 108. © 2019, Springer Nature.) (d) (top left) Schematic shows the experimental procedure of ABED on an icosahedral cluster with a coherent electron beam with a diameter of 0.36 nm. (top right) Examples of the nano-beam size dependence of electron diffraction patterns. (bottom) Experimental (bottom left) and simulated (bottom middle) NBED pattern including two sets of possible rectangle diffraction patterns. (bottom right) Two face-sharing ⟨0 2 8 1⟩ polyhedra with a common on-axis orientation for Bragg diffraction. (Adapted from Ref. 44. © 2011, Springer Nature.) (e) (top) Experimental (left) and simulated (middle) ABED patterns of an ideal icosahedron model (right) in 5-fold direction. (middle) The experimental (left), simulated (middle) ABED pattern and distorted icosahedron model (right) from Zr$_{80}$Pt$_{20}$ with six diffraction spots. (bottom) The correlation of distorted icosahedron with local fcc symmetry. (Adapted from Ref. 109. © 2013, American Association for the Advancement of Science.)

2.3 Transmission electron microscopy

TEM has proved one of the most efficient and versatile tools for the characterization of matter [110-112]. Recent successes in aberration correction allow us to image atoms at
sub-angstrom resolution with much-improved contrast [113-116]. Aberration corrected electron microscopy both in TEM or STEM mode along with the fast Fourier transform (FFT) can provide convincing and supportive direct images of amorphous structures, which has been extensively used in amorphous materials characterization [117-121]. With the rapid development in fast detector and in situ microscopy techniques, TEM not only provide a static image from one structure, but also monitor some important dynamic processes.

In 2011, Wang et al. directly observed the crystallization of Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ glass-forming liquid through HRTEM [122]. They found there exists a metastable state prone to forming icosahedra-like atomic clusters (Fig. 3a left panel). The imperfect 2D type order packing in the right panel Fig. 3a is considered to be short-range ordered atomic clusters which could hurdle further crystal nucleation due to the pinning effect caused by lattice mismatch. Zhong et al. employed in situ TEM to vitrify monatomic metallic liquid through ultrafast quenching [123]. Fig. 3b shows the HRTEM image of a Ta MG after an extremely high cooling process. FFT confirms a fully amorphous region connecting two body-centered cubic (bcc) nano-tips. The glass-crystal interfaces were identified as being atomically rough and diffuse (right panel in Fig. 3b).

In 2018, Luo et al. reported an ultrastable Zr-based MG formed on substrates with a temperature of 0.43$T_g$, taking the advantages of high contrast in HRTEM and high-angle annular dark-field STEM mode (HAADF-STEM), more homogeneous structures are observed in the ultrastable glass comparing to ordinary glass (Fig. 3c) [124]. Early
aberration-corrected STEM micrographs of amorphous structures can go back to 2004, Shibata et al. showed direct images of dopant atoms in amorphous films. Despite some atom dots look slightly stretched and jittering due to the thermal stability, the Z-contrast STEM images of atoms (Fig. 3d) clearly show heavy atom La preferentially segregate to the amorphous-crystalline interfaces [125]. In 2019, Wu et al. reported a general synthesis approach for amorphous noble metal nanosheets. Fig. 3e shows the aberration-corrected HAADF-STEM image of amorphous Ir nanosheets. The inset shows the amorphous halo from SAED pattern [126]. In 2020, Toh et al. synthesized free-standing monolayer amorphous carbon. HRTEM image in Fig. 3f reveals the monolayer carbon lacks long-range periodicity and possesses a connected distorted structure with a wide distribution of five-, six-, seven- and eight-member rings [127]. More recently, Lan et al. explored the medium-range structure motifs between amorphous and crystalline Pd-Ni-P alloy. The spherical aberration-corrected TEM image in Fig. 3g shows the amorphous-crystalline interface at [115] direction. From the HAADF-STEM images combined with synchrotron PDF analysis, they illustrate the six-membered tricapped trigonal prism cluster (6M-TTP) structure (Fig. 3g). They believe these findings will shed light on the structure of amorphous materials at extended length scales beyond SRO [128].
Figure 3. TEM and STEM for high resolution imaging of amorphous materials. (a) Typical localized atomic ordering observed during nanocrystallization of the supercooled liquid. The circles highlight the atomic configurations from an amorphous region with icosahedral-like clusters. Scale bar 1 nm. (Adapted from Ref. 122. © 2011, American Physical Society.) (b) Ta MG vitrified via an ultrafast liquid-quenching approach. (left) An amorphous Ta nano-tips is formed between two bcc Ta crystals. Bottom left shows the corresponding FFT from the upper images. (right) Atomic image of glass-crystal interfaces. The cyan dotted lines show the gradual breakdown of the long-range order. (Adapted from Ref. 123. © 2014, Springer Nature.) (c) HRTEM images and SAED (left) and HADDF-STEM images (right) of the ultrastable ZrCuAl MGs. (Adapted from Ref.
124. © 2018 Springer Nature.) Scale bar 5 nm. (d) Magnified HADDF-STEM (left) and reconstructed images (right) of the interface between the oxynitride amorphous intergranular film and the prismatic surface of the La doped $\beta$-Si$_3$N$_4$ grain. La atoms are denoted by red arrows (left) and the predicted La potions are shown by white circles (right). (Adapted from Ref. 125. © 2004 Springer Nature.) (e) Aberration-corrected HAADF-STEM image of amorphous Ir nanosheets. The insert image shows the SAED pattern. (Adapted from Ref. 126. © 2019, Springer Nature.) (f) Monochromated HRTEM image of monolayer amorphous carbon and the corresponding Fourier transform of the selected region (inset). (Adapted from Ref. 127. © 2020, Springer Nature.) Scale bar 1 nm. (g) HADDF-STEM image of the Pd-Ni-P alloy containing both cube phase and amorphous region with [111] zone axis (left). Magnified image of cube phase (right top) and amorphous phase (right bottom), compared with simulated images and the 6M-TTP cluster model. (Adapted from Ref. 128. © 2021, Springer Nature.)

2.4 Atomic probe tomography

Atom probe tomography (APT) is capable of providing both 3D imaging and chemical composition information at sub-nanometer resolution [129,130]. This technique is widely used in metallurgy since its invention. With the development of laser pulsing and specimen preparation, APT has expanded its applications to semiconductors [132], ceramic and geologic materials [132] and even biomaterials [133]. APT is suitable for MG characterization with 3D distribution of element composition. Many studies have
been done since 2002 [134,135].

In 2016, Schnabel et al. studied ultrastrong Co-based MG thin films using a combinatorial approach. APT images of the CoZrTaB thin film are presented including the iso-concentration surfaces of 50.0 at% for Co and 28.3 at% for Zr (Fig. 4a top panels). They observed Co and Zr-rich phases with size of nanoscale (Fig. 4a bottom panels) [136]. In 2019, Du et al. reported the observation of a reentrant glass transition in MGs [137]. The reentrant glass transition has been observed in colloid systems earlier [138,139]. The reentrant glass transition transforms an MG from its as-quenched state to an ultrastable state, mediated by the supercooled liquid of the as-quenched state. APT analysis shows the uniform elementary distribution in the sample (Fig. 4b). In 2019, Jia et al. reported a non-noble and multi-component MG catalyst for organic dye removal. Fig. 4c shows APT reconstruction of a reused ribbon catalyst. The reused ribbon presents a distinct hierarchical gradient structure with Fe elements concentrated in the matrix and S/O elements mainly distributed on the top layer of the ribbon [140]. In 2021, Orava et al. reported a recent work about in situ phase evolution in a prototype Cu-Zr-Al MG at an annealing rate ranging from $10^2$ to $10^3$ K·s$^{-1}$ during cooling [52]. They employed APT to reveal the compositions of different formed phases. Fig. 4d shows the Al precipitation in a multi-component MG. The 1D profile shows the concentration of each element varies in different precipitation areas.
Figure 4. Atom probe tomography. (a) APT images of the CoZrTaB MG with average B-contents of 29.6 at% (top left) and 27.0 at% (top right) along the film growth direction. The concentration profiles for Co, Zr, Ta and B are obtained from the APT reconstructions (bottom panels). (Adapted from Ref. 136. © 2016, Elsevier.) (b) 3D APT reconstruction (top) and corresponding concentration profiles (bottom) of the ordered Pd$_{42.5}$Ni$_{42.5}$P$_{15}$ MG, showing that no phase separation with partitioning of chemical composition after the phase transition. (Adapted from Ref. 137. © 2020, Elsevier.) (c) 3D APT images of reused ribbons of Fe-based amorphous catalysts. (Adapted from Ref. 138. © 2019, Wiley-VCH GmbH.) (d) APT volume rendering of Al in a Cu-Zr-Al MG showing the Al precipitation. (Adapted from Ref. 52. © 2021, Springer Nature.)
3. Quantitatively determining the atomic coordinates of amorphous materials

3.1 Atomic resolution electron tomography: principle and progress

TEM has proved a very powerful tool for imaging amorphous materials as summarized in Sections 2.2 and 2.3, however, it only provides 2D projections from 3D structures which could give deceptive structural information due to the overlap of critical features. Electron tomography (ET) which reconstructs 3D structural information from a tilt series of 2D TEM/STEM images has been proved to be a valuable tool to determine unique 3D structures without assumptions of crystallinity or averaging [141-143]. Many efforts have been made to resolve 3D periodic structures at atomic resolution using prior knowledge and assumptions [144-147]. Atomic electron tomography (AET) is a powerful technique which can resolve the 3D atomic structure of materials combining high-resolution tomographic tilt series with advanced iterative algorithms [148,149]. **Fig. 5a** illustrates the schematic layout of AET. (i) The sample is usually rotated along a tilt axis; and a series of high-resolution (typically atomic resolution) projected images of one sample is measured at different viewing angles. (ii) After the data acquisition, the tomographic tilt series need to be processed properly to get rid of noise, image drift and scan coil distortion etc. The processed tilt series is then precisely aligned with center of mass, cross-correlation and/or common-line methods to achieve atomic resolution tomography reconstruction. (iii) A 3D volume of the sample is computed from the aligned tilt series using reconstruction algorithms. To overcome the “missing wedge” problem (*i.e.* specimens cannot usually be tilted beyond ±70° [150,151]), iterative reconstruction
algorithms such as algebraic reconstruction technique (ART) [152], simultaneous ART (SART) [153], simultaneous iterative reconstruction technique (SIRT) [154-156], equal slope tomography (EST) [150,157-160], generalized Fourier iterative reconstruction (GENFIRE) [62,161] and real space iterative reconstruction (RESIRE) [60,61] were developed to retrieve the 3D information of the samples. (iv) After a 3D reconstruction volume has been obtained, the last step is to trace the coordinates and classify the chemical compositions of all the atoms.

Many efforts have been made to pushing the limitation of AET [64,65,162-167]. EST had made significant progress in determination of 3D structure of grain boundaries and dislocations in nanoparticles at atomic resolution even without using aberration corrected electron microscopy [168,169]. After combining aberration corrected electron microscopy with EST, in 2015, Xu et al. successfully located 3D coordinates of more than three thousands of individual atoms in a tungsten tip (Fig. 5b) [170]. They showed the ability of AET to determine the 3D coordinates of individual atoms in materials and to identify point defects in three dimensions. In 2017, an iron-platinum binary metallic nanoparticle with more than twenty thousands of atoms has been characterized via AET [62]. Fig. 5c shows the experimental coordinates and chemical species of all the Fe and Pt atoms. This work demonstrates AET could resolve complex nanostructures with chemical order/disorder. Another important breakthrough has been made to observe early nucleation in an ex-situ AET experiment. By adding a new dimension (time) to AET (i.e. 4D-AET), Zhou et al. captured small nuclei can undergo growth, fluctuation and
dissolution (Fig. 5d) [63], showing a never-before-seen view of atom-by-atom nucleation. This work not only represents for the first time the experimental demonstration of determining the structure and dynamics of materials at 4D atomic resolution, but also opens the door to study many fundamental problems such as atomic diffusion, grain boundary dynamics, interface motion, defect dynamics, phase transitions and surface reconstruction.

**Figure 5. AET principle and recent progresses.** (a) A schematic layout of AET, showing how AET works from data acquisition, image pre-processing, reconstruction to atom tracing model. (b) 3D positions of individual atoms in a tungsten needle sample revealed by AET. Atoms in different layers are colored differently. (Adapted from Ref. 160. © 2015, Springer Nature.) (c) Overview of the 3D positions of individual atomic species with Fe atoms in red and Pt atoms in blue. 6,569 iron and 16,627 platinum atoms are classified in this work. (Adapted from Ref. 62. © 2017, Springer Nature.) (d)
Capturing 4D atomic nucleation with AET. Growing (top), fluctuating (middle) and dissolving (bottom) nuclei are tracked at different annealing times. (Adapted from Ref. 63. © 2019, Springer Nature.)

3.2 First determination of 3D atomic positions in a glass-forming alloy

The successes of AET with crystals have naturally raised up the conjecture that the 3D atomic structures of amorphous materials can be determined with this powerful technique. In principle AET has the ability to solve the atomic structures of amorphous materials using similar approach to crystals as no crystalline assumption or prior information is needed. It has been demonstrated that amorphous structures could be reconstructed using multi-slice STEM simulations [151], although tomography of crystalline materials is considered to be inherently easier than tomography of amorphous materials [171]. However, amorphous materials are usually less stable under the electron beams, successful acquisition of a full intact tilt series from an amorphous material with durable signal-to-noise ratio (SNR) become more critical and urgent. In 2021, the first published experimental 3D atomic structures of amorphous materials are obtained from an amorphous glass-forming nanoparticle alloy and an amorphous film [60]. This groundbreaking work was done by a collaborative group led by Jianwei Miao from UCLA. Fig. 6a shows the experimental projection image of the glass-forming nanoparticle prepared using carbothermal shock technique [172] and the amorphous halo from average 2D power spectrum of 55 experimental images (top panel), and two 2.4-Å-thick slices of
the 3D reconstruction along different viewing directions (bottom panel). Some crystalline features are present but most regions from the slices show disorder atomic structures. The AET is currently sensitive enough to classify the multiple elements in the alloy into three different types according to their contrast depending on atomic number [60]. Fig. 6b shows the experimental 3D atomic model of this glass-forming nanoparticle. In addition, as proof of principle, in this work, they determined another atomic structure from a CuTa binary amorphous film Fig. 6c shows the discontinuous amorphous film prepared by physical vapor deposition (top panel), atomic resolution projected image and the amorphous halo (bottom panels) of CuTa film. The 3D model of the CuTa thin film has a total of 1,808 Cu (gold) and 12,774 Ta (blue) atoms (Fig. 6d). It is notable that in those two amorphous materials with completely different sample preparation methods, suitable protection from electron beam damage and optimized electron dose are pivoting to the successful tilt series acquisition. Voyles emphasized the importance of this work as “fulfilling a decades-old dream for glass scientists” [173].
Figure 6. Determining 3D atomic positions in a glass-forming alloy. (Adapted from Ref. 60 © 2021, Springer Nature.) (a) (top left) Representative experimental projection image, where some crystalline features are visible. Scale bar, 2 nm. (top right) Average 2D power spectrum of 55 experimental images, showing the amorphous halo. (bottom) Two 2.4-Å-thick slices of the 3D reconstruction in the x-y (left) and y-z (right) plane, where the majority of type-3 atoms (bright dots) are distributed in the second coordination shell. (b) Experimental 3D atomic model of the glass-forming nanoparticle. (c) (top) Large-field-of-view image of amorphous CuTa film. Scale bar, 30 nm. (bottom left) Magnified image of the region in the corresponding white square. Scale bar 2 nm. (bottom right) Average 2D power spectrum of all the experimental images. (d) 3D atomic model of a portion of the CuTa thin film with a total of 1,808 Cu (gold) and 12,774 Ta (blue) atoms.
3.3 3D atomic packing of monatomic amorphous solids

It is worth mentioning that the same group from UCLA also resolved the 3D atomic structures of monatomic amorphous solids (PVD amorphous Ta film and chemical synthesized Pd particle) using AET technique and the data was published subsequently [61]. Fig. 7a shows the experimental 3D atom models of Ta thin film (left) and two Pd nanoparticles (middle and right) with surface crystal nuclei in grey and average 2D power spectra of the experimental images in the insets, respectively. Fig. 7b shows a slice through the Ta thin film (left) and two Pd particles (middle and right) with the local mass density heterogeneity overlaid with polytetrahedral packing. They combined AET experiment result with MD simulation, provide a fundamental sight into the 3D atomic packing of monatomic amorphous materials and liquids.
**Figure 7. 3D atomic positions and atom packing in monatomic amorphous solids.**

(Adapted from Ref. 61. © 2022, Springer Nature.) (a) Experimental 3D atomic model of an amorphous Ta film (left) and two Pd nanoparticles (Pd1; middle, Pd2; right) with surface crystal nuclei in grey. The three insets show the average 2D power spectra of the experimental images for the Ta film and two Pd nanoparticles, where the amorphous halos are visible. Scale bars, 2 nm. (b) A slice through the Ta film (left) and two Pd nanoparticles (Pd1, middle; Pd2, right) shows the local mass density heterogeneity (color) overlaid with polytetrahedral packing (black). Scale bar, 2 nm.

**3.4 SRO and MRO analysis with experiment atomic coordinates**

The most important structure features in amorphous materials are the local atomic configuration including SRO and MRO [174]. Elliott studied structural order of amorphous solid over both short and medium length scales, defining SRO in the range of 2-5 Å, and MRO reaching to 20 Å [175]. Comparing to the statistical structural information from RDF obtained by high-resolution diffraction or plausible structures obtained from simulation methods, the atomic amorphous structures determined from experiment provides direct models with unprecedented 3D detail. It will raise the fresh insight into the structures of disordered solids.

Several SRO analysis methods including RDF/PDF analysis [176], bond-orientation order (BOO) analysis [177-179], Voronoi tessellation [180] and Delaunay triangulation [181] can be applied to the atomic coordinates obtained from the amorphous materials,
yielding quantitative picture of local disordered environment around a single atom. The RDF and PDF can be calculated from the 3D atomic model. From the histogram of atom pair distances in spherical shells with a certain thickness, one can calculate the density of atom pairs as a function of the pair distance. After scaling to one at large pair distances, all the PDF/RDF can be obtained. Fig. 8a shows the PDFs obtained from the multi-component nanoparticle and monatomic amorphous solids. A weak second-peak splitting is observed in the amorphous glass-forming nanoparticle. The ratios of the second, third, fourth and fifth peak positions in Fig. 8a to that of the first peak are 1.74, 1.99, 2.64 and 3.51, respectively, are in good agreement with those of MGs (1: $\sqrt{3}$: $\sqrt{4}$: $\sqrt{7}$: $\sqrt{12}$) [182,183]. The partial PDF can be obtained from different sub sets of atom pair as shown in Fig. 8b, indicating the flexibility of calculating partial PDFs from experimental coordinates. Fig. 8c show the RDF curves of liquid like amorphous solids (Ta films and Pd nanoparticles), in which the peak and valley fit well with those from the simulation PDF of Ta liquid. Local bond orientational order (BOO) parameters [178,179] can be used to distinguish between the amorphous and crystal structures. Using a criterion that the normalized BOO parameter is greater than or equal to 0.5, one can identify the exact fraction of disordered atoms in a single particle. Fig. 8d shows local BOO parameters for all atoms in seven nanoparticles with experimental coordinates, whether the nanoparticle being crystalline, polycrystalline or amorphous becomes straightforward [60].
Figure 8. PDF and BOO analysis. (a) The PDF curve among all atoms in amorphous nanoparticles. The dashed lines point out the ideal peak positions of MG structure according to the theoretical analysis, which fits well in this specimen. The inset shows the second-peak splitting with a double Gaussian fit. (Adapted from Ref. 60. © 2021, Springer Nature.) (b) The PDF curves between two types of atoms in an amorphous alloy NP, as listed in the legend. The curves emphasize the irregular behavior of the curve type 33. (Adapted from Ref. 60. © 2021, Springer Nature.) (c) The PDF curves of three monatomic amorphous solids and one theoretical simulation structure. (Adapted from Ref. 61. © 2022, Springer Nature.) (d) The BOO analysis of all atoms in seven amorphous alloy nanoparticles separately. Cu$_{65}$Zr$_{35}$ simulated model analysis is presented as a reference. The red dashed lines show the criterion that divides the amorphous and crystal
Voronoi tessellation identifies the nearest-neighbor atoms around each central atom to form a Voronoi polyhedron by calculating a Voronoi index, \( n_3, n_4, n_5, n_6 \), where \( n_i \) denotes the number of \( i \)-edged faces. Fig. 9a shows several represented Voronoi polyhedra in nanoparticles. Voronoi tessellation emphasizes the neighboring environment of a single atom, showing local symmetry distribution and coordination number. In previous studies of MG [78,175,184], the icosahedra were popular including Voronoi indices \( 0,0,12,0 \), \( 0,1,10,2 \), \( 0,2,8,2 \), etc. However, from the analysis of experimental coordinates [56,57], the most abundant Voronoi polyhedra are shown in the histogram in Fig. 9b, only 7.03% of all the Voronoi polyhedra are distorted icosahedra, suggesting this nanoparticle has poor glass-forming ability. Five-edged faces are the most abundant in both multi-component nanoparticles and monatomic amorphous solids. Most of the atoms in monatomic amorphous solids form tetrahedra packing. Fig. 9c shows the tetrahedra can form different motifs by sharing faces, such as triplets, quadrilateral, pentagonal and hexagonal bipyramids. The fraction of each motif is presented in Fig. 9d.
Figure 9. The local SRO. (a) The most popular Voronoi polyhedra in the multi-component particle. \((0,0,12,0)\) represents an icosahedron. (Adapted from Ref. 60. © 2021, Springer Nature.) (b) The histogram shows the fraction of the ten most popular Voronoi polyhedra. (Adapted from Ref. 60. © 2021, Springer Nature.) (c) The four populated motifs (triplets, quadrilateral, pentagonal and hexagonal bipyramids) in monatomic amorphous solids. (Adapted from Ref. 61. © 2022, Springer Nature.) (d) Distribution of the four atomic motifs, showing that pentagonal bipyramids are the most abundant atomic motif. (Adapted from Ref. 61. © 2022, Springer Nature.)
MRO in amorphous materials is usually defined as the next level of structural organization beyond SRO [185], showing the packing and connectivity of the local atomic motif structures. Several models have been proposed to describe MRO, such as solute-centre clusters packing model [186], quasi-equivalent clusters packing model [78], fractal model [87], and flow unit model [187]. These models provide significant insights to many scientific problems including the formation mechanism, glass forming ability, stability, property of amorphous materials. The general applicability of all the models is still being debated [74,78,186]. Precise MRO can be measured through experimental coordinates from the multi-component nanoparticles and monatomic amorphous solids.

Recently, crystal-like MROs were located in the multi-component nanoparticles using experimental coordinates. The particle consists of 8 elements which are classified into three types based on the Z contrast (Fig. 6b) [60]. The PDF of type 33 atom pairs shows the highest peak at a position 1.5 times higher than the nearest-neighbor peak (Fig. 8b), suggesting type-3 atoms are surrounded by other two types of atoms. Fig. 10a shows five solute-centre clusters connect with each other by sharing different numbers of atoms (one to five). Instead of forming a uniform crystal-like structure MRO, four types of MRO (fcc-, hcp-, bcc- and sc-like) coexist in the nanoparticle (Fig. 10b). No icosahedral-like MRO is observed in this sample; and it proves a poor glass forming ability of the sample. The 3D distribution of MROs shows less MROs are observed in the central region [60].
Figure 10. MROs in the glass-forming nanoparticle. (Adapted from Ref. 60, © 2021, Springer Nature.) (a) Representative pairs of solute-centre clusters connected with each other by sharing one to five atoms. (b) 3D atomic packing of four crystal-like stacking MROs. Large red spheres are the solute centers in fcc- (top left), hcp- (top right), bcc- (bottom left) and sc-like (bottom right) MROs. The solvent atoms have been removed and the solute centers are orientated along the fcc, hcp, bcc and sc zone. axes to better visualize the crystal-like MROs. (c) Distribution of the four types of MRO with eight solute-centre atoms or more.

The MROs in monatomic amorphous solids are different from those of multi-
component nanoparticles. The basic motifs connect with each other to form networks which could extend to nanometre scale. Pentagonal bipyramids are the most abundant motif in monatomic amorphous solids, and they connect with each other by sharing four or five atoms with their neighbours to form MROs (named as Pentagonal bipyramid network, PBN, Fig. 11a). Fig. 11b shows the size and length distribution of PBNs. The largest PBN consist 135 pentagonal bipyramids formed by 165 Ta atoms with an end-to-end length of 2.83 nm (Fig. 11c). Most of the PBNs assemble only partial icosahedra. Fig. 11d show a PBN containing five partial icosahedra. All these experimental coordinates enables the analysis of the SRO and MRO at single-atom level, showing the ability of studying amorphous materials quantitatively at atomic level [61].

![Graphical representation of PBNs](https://engine.scichina.com/doi/10.1360/nso/20220048)
4. Future challenges and opportunities

In this review we summarize many characterization techniques for amorphous materials. With enormous efforts putting in disclosing the structural mystery underneath the disordered amorphous materials since early last century, many techniques such as X-ray/neutron diffraction, electron diffraction and FEM, transmission electron microscopy and APT have provided significant insights in the atomic structure and component distribution of amorphous materials. We also introduce the principles and recent progresses of AET, and highlight the most recent groundbreaking feat in determining amorphous atomic structures. AET has demonstrated the ability to directly determine the 3D atomic positions in amorphous materials in the last few years. Now we can quantitatively analyze SRO/MRO of amorphous materials using experiment atomic structures. This could expand our understanding of amorphous materials and provide
insights that aid the development of general description of disordered structures.

Further research brings up more challenges and opportunities in solving fundamental problems relevant to amorphous materials. First challenge is to experimentally identify all the chemical species of complex amorphous materials with multiple elements. AET is currently sensitive to elements with enough Z differences, but could not resolve two elements which being close in the periodic table e.g. Ni and Co. Atomic elemental mapping [188,189] could be one of the promising way to provide complementary information. The second challenge is to determine enough atomic structures of different amorphous materials to establish an amorphous structural databank similar to crystal. Building the databank needs more efforts be to done in many fields to establish high throughput analysis platform for amorphous materials, such as rapid automated data acquisition, big data interpretation [190] and fast computation [191], new reconstruction algorithm [192] and machine learning [193]. Third challenge and opportunity are to implement and combine several novel techniques to AET to improve the capabilities, such as 4D-STEM[194,195], ptychography[196-199] and TEM reconstruction[200]. These methods could in principle get much higher electron efficiency than conventional STEM adopted in current AET, yielding high SNR projection with less electron damage to more beam-sensitive materials. Finally, multimodal microscopy combining AET with multiple complementary experiment techniques such as diffraction and APT may provide comprehensive chemical, structural, and functional information, particularly for heterogeneous amorphous-crystalline samples.
Advanced characterization techniques promise substantially advance amorphous material science. We anticipate the recent breakthrough in experimental determination of amorphous materials will open up a new door for our fundamental understanding in many classic but “holy grail” problems in physics and chemistry, such as the crystallization of amorphous materials and the glass transition.

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