Structural characterization of deformed crystals by analysis of common atomic neighborhood

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Abstract

Simulations of crystal deformation and structural transformation may generate complex datasets involving networks with million to billion chemical bonds which makes local structure analysis a challenge. An ideal analysis method must recognize perfect crystal structures, such as face-centered cubic, body-centered cubic and hexagonal close packed, and differentiate structural defects such as dislocations, stacking faults, grain boundaries, cracks and surfaces. Currently a few methods are used for this purpose, e.g., the Common Neighbor Analysis (CNA) and the Centrosymmetry Parameter (CSP). This paper proposes an alternative method based on the calculation of a single parameter that depends on the common atomic neighborhood. We validate the method characterizing local structures in complex molecular-dynamics datasets, clarifying its advantages over the CNA and the CSP methods.

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1. Introduction

The analysis of atomic chemical bonds is widely used to characterize the state of a local crystal structure in simulations of solid materials. Because of the unique atomic arrangement of a given crystal phase its presence within a simulated material can be attested by a topological analysis of the chemical bond network. In such analysis, the structure of a material is considered as a topological network of chemical bonds. Bonds here are typically defined between a pair of atoms, for which Pauling’s bond order has a value larger than a threshold value. Usually though a bond is defined in simulations when the pair distance is less than a cutoff radius. Most local structure analysis methods such as the Common Neighbor Analysis (CNA) and the Centrosymmetry Parameter (CSP) use such abstractions to characterize the local state of solid materials. The popularity of these methods has soared in recent years due to the ever-increasing size and complexity of the chemical networks that are simulated [1]. For such large systems, structural analysis algorithms demand low computational complexity. Large datasets are commonly found in molecular dynamics (MD) simulations, which model materials as a set of atoms. Currently, state-of-the-art MD simulations may involve hundred-billion atoms [2]. Efficient algorithms for structural characterization with near linear scaling are therefore vital for such analysis, especially if the analysis is to be performed in real time during the simulation.

Among the most used methods for structure analysis the CNA, proposed by Honeycutt and Andersen [3], is based on nearest neighbor atoms. It is a generalization of the method proposed by Blaisten-Farojas and Andersen [4], in order to determine the equilibrium structure of small clusters of Lennard-Jones atoms. With that method Honeycutt and Andersen could describe the structural transition in small clusters with increasing size from icosahedral structure, to polyicosahedral to fcc (face-centered cubic). Jonsson and Andersen [5], used the same technique to study the structures produced by cooling Lennard-Jones fluids to below the glass transition. Clarke and Jonsson [6], used a slight different version of the CNA to investigate the...
densification and the icosahedral ordering of hard-sphere packings. Faken and Jonsson [7], used the same version of CNA in combination with 3D computer graphics to study the crystal nucleation in a molten copper slab. The CNA has been useful in the investigation of several other systems such as the microstructure of liquid and amorphous Ni [8], small Au clusters [9,10], metallic nanocontacts [11], grain boundaries [12,13], dislocation processes in nanocrystalline aluminum [14], liquid and supercooled tantalum [15], liquid and supercooled copper [16], and metallic glasses [17].

Another frequently used method for structure analysis is the CSP which is based on the spatial arrangement formed by the nearest neighbor atoms. Different from the CNA the CSP is however well defined only in a centrosymmetric crystal such as fcc and bcc (body-centered cubic). The CSP method was originally proposed by Kelchner, Plimpton, and Hamilton [18] to identify dislocations and stacking faults created during indentation of gold surface and to distinguish them from purely elastically deformed regions. A slightly different version of the CSP was proposed by Li [19,20] and implemented in a 3D computer visualization package. The CSP was applied successfully to address different problems such as the scaling of small indentation results in Au to the experimental range [21], incipient plasticity during indentation [22], deformation of metallic nanowires during compressive and tensile loading [23,24], impact dynamics of copper clusters [25], deformation in nanocrystalline metals [26,27], dislocation nucleation close to copper interfaces [28], shock deformation of metals [29], and defaceting phase transitions in grain boundaries [30]. The calculation of the CSP has also been included in molecular dynamics standard codes such as the SPaSM [31].

Apart from the popular CNA and CSP methods a few other techniques have been used to distinguish among atomic structures and identify the location and type of different structural defects [32–38]. This paper proposes an alternative method that could be used in place of the CNA and CSP methods. It is in one hand of simple implementation and interpretation, like the CSP method, because it is based on a single parameter calculation. On the other hand it is well defined in non-centrosymmetric crystals and it has a broad range of possible applications, like the CNA method. In the next section details of these two approaches—CNA and CSP—are briefly reviewed and the alternative method presented and analyzed.

2. Structural analysis methods

2.1. The Common Neighbor Analysis (CNA)

In the original CNA method proposed by Honeycutt and Andersen [3] a structure is represented by diagrams. Starting with a pair of atoms, $\alpha$ and $\beta$, the diagram is classified by a set of four indexes: (i), (ii), (iii), and (iv), where

(i) with values 1 or 2 indicates that $\alpha$ and $\beta$ are nearest-neighbors ($i = 1$) or not ($i = 2$);
(ii) indicates the number of nearest neighbors shared by the ($\alpha$, $\beta$) pair (common neighbors);
(iii) indicates the number of bonds among the common neighbors;
(iv) differentiates diagrams with same (i), (ii), and (iii) indexes and different bonding among common neighbors.

Here two atoms are nearest neighbors if the distance between them is less or equal to a cutoff distance, which is in general defined as the first minimum in the pair distribution function [39]. Fig. 1(a)–(d) shows diagrams for a few selected crystal structures, and exemplify the four indexes CNA classification. Fig. 1(a) shows the 1421 diagram, present in the fcc structure, formed when a pair of nearest neighbors atoms share 4 common neighbors, which have two bonds. Fig. 1(b) shows the diagram 1422 which is present in the hcp (hexagonal close packed) structure in the same amount as the 1421 diagram. Fig. 1(c) and (d) shows the 1441 and 1661 diagrams which are found in the hcp and bcc structures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 1. Illustrations of diagrams constructed from the classification of local structures defined in the CNA method. Brown ($i$) and yellow ($j$) atoms indicate one pair of nearest neighbor atoms, light-blue ($k$) atoms are common neighbors of the brown-yellow pair. (a) shows a 1421 diagram, indicating that brown ($i$) and yellow ($j$) atoms are nearest neighbors, have 4 common neighbors ($k$) which in turn have two bonds. The 1421 is the only diagram present in the fcc structure. (b)–(d) show the 1422, 1441, and 1661 diagrams which are found in the hcp and bcc structures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
neighbor atoms pairs forming 1441 diagrams while the rest 4/7 forming 1661 diagrams.

2.2. The Centrosymmetry Parameter (CSP)

The CSP method proposed by Kelchner, Plimpton, and Hamilton [18] quantifies local deviations from centrosymmetry in a given centrosymmetric structure such as fcc and bcc. Based on that, defects are effectively identified and distinguished from elastically deformed regions. The calculation of the parameter exploits the fact that a centrosymmetric material will remain centrosymmetric under a homogeneous elastic deformation. In such materials each atom has a certain number of pairs of opposite bonds formed by the nearest neighbor atoms. Fig. 2 (a)–(c) show the opposite pairs in the fcc, bcc, and hcp structures. In an fcc structure, Fig. 2(a), each atom has 6 pairs of opposite nearest neighbor atoms, and therefore 6 pairs of opposite bonds. In a bcc structure the first and second shell of nearest neighbors are close so we consider both as a single shell. Together this combined shell has 7 pairs of opposite neighbors, see Fig. 2(b). Under deformation or on a defect these bonds will change in length and direction and that change is quantified in a parameter. For an fcc structure the CSP is defined as follows:

\[ P = \sum_{i=1,6} |\mathbf{R}_i + \mathbf{R}_{i+6}|^2, \]

where \( \mathbf{R}_i \) and \( \mathbf{R}_{i+6} \) are bond vectors corresponding to the six pairs of opposite nearest neighbors. In a perfect undeformed structure the calculation is trivial. However, in a deformed structure the 12 vectors \( \mathbf{R}_i \) for each atom must be determined by finding those neighbors with vectors close in distance to the undistorted nearest neighbor vectors. Each, equal and opposite, pair of vectors is added together, and the sum of the square of undistorted nearest neighbor vectors. Each, equal and opposite, by finding those neighbors with vectors close in distance to the

\[ R_i = 0 \]

where the index \( j \) goes over the \( n_i \) nearest neighbors of atom \( i \), and the index \( k \) goes over the \( n_{ij} \) common nearest neighbors

An alternative CSP definition was proposed by Li [19,20] and implemented in the “Atomeye” visualization package. This definition follows

\[ c_i = \frac{\sum_{j=1}^{m_i} D_k}{\sum_{j=1}^{m_i} |\mathbf{R}_j|^2}, \]

where \( c_i \) is the centrosymmetry parameter for the \( i \)th atom, \( m_i \) the number of its neighbors, \( \mathbf{R}_j \) are bond vectors and the function \( D_k = |\mathbf{R}_k + \mathbf{R}_k'|^2 \) is minimized by the bond \( \mathbf{R}_k' \). This parameter is dimensionless with a maximum value of 1. In one perfect fcc structure, for example, atoms at an intrinsic stacking fault has \( c_i = 0.0416 \). This implementation has the advantage of finding dynamically the best opposite pairs of atoms as it is required for a real time analysis of an arbitrary structure being visualized.

2.3. A Common Neighborhood Parameter (CNP)

The way the CNA and CSP methods characterize structures makes them suitable for specific kinds of applications. The CNA characterizes by using the statistics of diagrams formed from a given arbitrary local atomic configuration. That is a powerful method but it may be intricate to implement and to interpret. The CSP on the other hand gives a measure of the deviation from the centrosymmetry in the vicinity of a given atom. It is of easy implementation and interpretation but it is only defined in a centrosymmetric crystal. The advantages of these two methods can be put together through the definition of a parameter \( Q_i \), for each atom \( i \) in the structure, which will be called from here on as the Common Neighborhood Parameter (CNP). The definition of \( Q_i \) follows

\[ Q_i = \frac{1}{n_i} \sum_{j=1}^{n_i} \left| \sum_{k=1}^{n_{ij}} (\mathbf{R}_{ik} + \mathbf{R}_{jk}) \right|^2, \]

where the index \( j \) goes over the \( n_i \) nearest neighbors of atom \( i \), and the index \( k \) goes over the \( n_{ij} \) common nearest neighbors.
between atom $i$ and atom $j$, $\mathbf{R}_{ik}$ is the vector connecting atom $i$ to atom $k$, see Fig. 3.

For instance, in perfect fcc and bcc structures $Q_i = 0$. Table 2 shows CNP $Q_i$ values compared with values from the two CSP methods discussed.

While the CNA method analyze the nearest neighbors of an atom $i$ and the configuration of their common neighbors the CSP monitor the state of the bonds formed by opposite nearest neighbors. The vectors (bonds) formed to the common neighbors do not form opposite vectors but their sum depends on the state of the local structure and can be used to characterize the local environment. The CNP explores this intrinsic characteristic of the common neighbors with the advantage of not requiring explicit knowledge about what are the opposite neighbor pairs. The only information the CNP method requires is the nearest neighbor list for each atom, which is usually known beforehand in a simulation.

3. Discussion

The application of the CNP may be advantageous in several situations over the application of CNA or CSP methods. One example is shown in Fig. 4 (a)–(d), which compares the ability of the CNA and CNP methods to describe the defect distribution created on a copper nanowire subjected to a high tensile strain rate of $1.5 \times 10^{11}$ s$^{-1}$. Strained atomic configurations at $\varepsilon = 0.13$ and $\varepsilon = 0.39$ are visualized with atoms colored following the values of CNA and CNP methods.

With CNA analysis one can distinguish atoms in fcc and hcp regions by calculating the statistics of diagrams formed from the nearest neighbors of each atom and comparing it with those previously known from standard crystals, e.g., fcc, bcc, etc. Fig. 4 (a) and (b) shows atoms in fcc and hcp local regions that were selected by the presence of 1421 and 1422 CNA diagrams. Atoms with only 1421 diagrams are in fcc regions and those atoms with 50% 1421 and 50% 1422 diagrams are in hcp regions. All atoms with other kinds of diagrams were eliminated. While powerful this analysis needs attention in the calculation and interpretation of the statistics of diagrams distribution along the system. The CNP analysis needs similar information about the phases, but use instead a simpler procedure with the calculation of a single parameter for each atom what provides a direct interpretation. The fcc crystal can be identified when CNP values are close to 0 Å$^2$, see Table 1. Values around 4.4 Å$^2$ indicate atoms in hcp local crystals.

In Fig. 5 (a)–(c) part of a simulated copper crystal, at 10 K, is visualized showing a dissociated dislocation, which is formed by two partial dislocations surrounding a stacking fault. Visualized atoms in Fig. 5(a) are colored by coordination number (number of bonds per atom), which indicates the presence of the partial dislocations delimiting the intrinsic stacking fault. Fig. 5 (b) and (c) shows the same structure with atoms colored by the CSP (Li) and CNP atomic values. As can be seen by using the CNP method one can obtain a higher resolution than by using CSP. Atoms at the intrinsic stacking fault and partial dislocations can be better identified and distinguished. In Fig. 5(c) CNP values around 10 Å$^2$ indicate atoms in dislocations which have coordination 11 and 13. The stacking fault which has a CNP value around 4.4 Å$^2$ is better identified than in Fig. 5(b) using the CSP. One of the reasons for the better accuracy of the CNP method over the CSP is the need to always find the correct opposite neighbors in the later, which in a dynamic simulation of a deforming structure are not accurately defined. In the case of the hcp crystal that can be further complicated because the three not opposite pairs may cause trouble in finding the best opposite pairs, see Fig. 2(c).

4. Summary

In summary an alternative method for structural characterization based on the common atomic neighborhood is proposed for the analysis of complex data sets of deformed simulated materials. The method is compared to the Common Neighbor Analysis and the Centrosymmetry Parameter methods. The efficiency of the proposed method is validated and its advantages are clarified. For instance the method combines the advantages of the CNA and CSP methods. It is of easy implementation and interpretation and may be applied in an arbitrary crystal. It is...
sensitive to structural deformations and can be used to characterize in real time local structures of undeformed and elastically deformed crystals as well as to distinguish defects such as stacking faults, dislocations, disordered regions, surfaces, etc.

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