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A generalized crystal-cutting method for modeling arbitrarily oriented crystals in 3D periodic simulation cells with applications to crystal–crystal interfaces

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ABSTRACT

A Generalized Crystal-Cutting Method (GCCM) is developed that automates construction of three-dimensionally periodic simulation cells containing arbitrarily oriented single crystals and thin films, two-dimensionally (2D) infinite crystal–crystal homophase and heterophase interfaces, and nanostructures with intrinsic N-fold interfaces. The GCCM is based on a simple mathematical formalism that facilitates easy definition of constraints on cut crystal geometries. The method preserves the translational symmetry of all Bravais lattices and thus can be applied to any crystal described by such a lattice including complicated, low-symmetry molecular crystals. Implementations are presented with carefully articulated combinations of loop searches and constraints that drastically reduce computational complexity compared to simple loop searches. Orthorhombic representations of monoclinic and triclinic crystals found using the GCCM overcome some limitations in standard distributions of popular molecular dynamics software packages. Stability of grain boundaries in β-HMX was investigated using molecular dynamics and molecular statics simulations with 2D infinite crystal–crystal homophase interfaces created using the GCCM. The order of stabilities for the four grain boundaries studied is predicted to correlate with the relative prominence of particular crystal faces in lab-grown β-HMX crystals. We demonstrate how nanostructures can be constructed through simple constraints applied in the GCCM framework. Example GCCM constructions are shown that are relevant to some current problems in materials science, including shock sensitivity of explosives, layered electronic devices, and pharmaceuticals.

1. Introduction

Molecular dynamics (MD) and related particle-based simulation methods are indispensable tools in the study of crystal anisotropy [1–10], surfaces [10–13], defects [14–19], and crystal–crystal interfaces such as grain boundaries [20–27] and heterophase interfaces [28–30]. Many of these studies [14–24,27,29,30] have focused on materials with comparatively 'simple' and highly symmetric (*e.g.*, cubic) packing structures, including atomic crystals of metals, ceramics, and traditional semiconductors such as gallium arsenide. However, a wide range of technologically relevant molecular materials, including pharmaceuticals [31,32], high explosives [33–36], and organic semiconductors [37,38], exhibit packing structures with significantly lower symmetry and often crystallize in monoclinic and triclinic forms. Low-symmetry crystal systems, especially the monoclinic and triclinic systems, can complicate the construction of simulation cells that involve oriented thin films, grain boundaries, and crystal–crystal interfaces. Examples from materials science range from engineering layered electronic devices [3,22,26,29,30] to predicting the shock response and detonation sensitivity of explosives [5,6,8,28]. We present here a Generalized Crystal-Cutting Method (GCCM) that enables and practically automates facile construction of simulation cells containing oriented crystalline thin films and crystal–crystal interfaces.

Many MD simulations of crystals employ three-dimensional (3D) periodic boundary conditions (PBCs), which lead to simulation geometries corresponding to infinite stacks of thin films or 'bulk' material. An implicit requirement for the use of PBCs in crystal simulations is that the simulation cell exactly preserves the crystal translational symmetry. For this reason, low-symmetry crystals with monoclinic and triclinic Bravais lattices are often modeled in non-orthorhombic parallelepiped-shaped simulation cells. This

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requirement also places enormous constraints on translational-symmetry-preserving rotations of the underlying crystal in a given simulation cell. One generally *cannot* arbitrarily rotate a crystal in a simulation cell with 3D PBCs to orient some direction in the crystal along another direction in the lab frame while preserving translational symmetry. Such requirements complicate studies that involve oriented crystals and can make it incredibly difficult to simultaneously model two or more different oriented crystals that satisfy PBCs in a single simulation cell. This severely hinders simulation studies of many anisotropic properties, grain boundaries, and crystal–crystal interfaces between different polymorphs and materials.

Literature sources include some reports of 3D periodic cells containing oriented crystals [1,2,4–6] and (at least apparent) orthorhombic representations of monoclinic [28] and triclinic [12,28] crystals. We are also aware of one report [28] using cells containing two-dimensionally (2D) infinite interfaces with triclinic crystals and a recently developed method [39] for constructing interfaces in graphene. However, in most of these cases there is little to no discussion as to *how* the cells were constructed; where extensive discussion is given, the approach is not generalized for all Bravais lattices. These constructions appear to have been handled largely on a case-by-case basis.

In this report we develop a mathematical formalism and search-and-construction algorithms for the GCCM to facilitate the systematic construction of 3D periodic simulation cells containing arbitrarily oriented single crystals and thin films. The GCCM circumvents problematic (or impossible) crystal rotations by defining new simulation cells constructed by cutting inscribed crystals in a symmetry-preserving manner. As the GCCM is designed to preserve the translational-symmetry of all Bravais lattices, it can be applied to any crystal described by such a lattice irrespective of the complexity of the atomic or molecular structure or the symmetry of the space group. A simple formalism for defining constraints is employed that facilitates searches for possible orthorhombic representations of monoclinic and triclinic crystals and can be used to generate constituents of more complicated constructions, such as nanowires and nanoparticles. The GCCM formalism is readily extended to find commensurate 2D infinite crystal–crystal grain boundaries and interfaces that can be modeled in a single cell with 3D PBCs. Carefully ordering loop searches and application of constraints greatly reduces the computational complexity for finding commensurate crystal–crystal interfaces using the GCCM formalism and is necessary to make the calculation tractable.

The remainder of the article is organized as follows. The mathematical formalism and key algorithms for the GCCM are developed in Section 2, with constructions involving single crystals discussed in Section 2.1, extensions for 2D infinite crystal–crystal interfaces derived in Section 2.2, and strategies for constructing nanostructures with N-fold crystal–crystal interfaces presented in Section 2.3. Benefits and demonstrations of the GCCM for MD simulations are described in Section 3, namely computational advantages of using orthorhombic representations of low-symmetry crystals in Section 3.1, a comparison study of energetics of grain boundaries in a monoclinic molecular crystal in Section 3.2, and results from simulations of silver nanowires and icosahedral nanoparticles exhibiting five-fold twins in Section 3.3. Potential applications of the GCCM to systems including energetic materials, organic semiconductors, and pharmaceuticals are described with corresponding constructions in Section 4. Conclusions are drawn in Section 5. All of the GCCM software source code for constructing simulation cells of arbitrarily oriented single crystals and crystal–crystal interfaces is provided as Supplementary Material (see Appendix A).

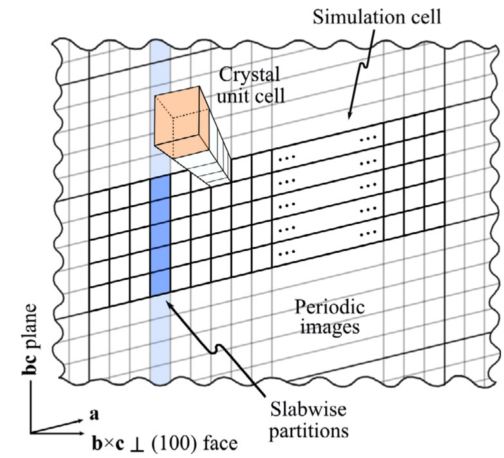

Fig. 1. A simulation cell constructed by translating the crystal unit cell has faces that coincide with the (100), (010), and (001) crystallographic faces. 2D periodic, 'infinite' slabwise partitions (see blue shaded region) can only be defined if the normal vector for the slab is parallel to the normal vector of one of the faces of the simulation cell, which in this case is also the normal of the (100) crystal face. Analogous slabwise partitions can be defined in this simulation cell with normal vectors parallel to the (010) and (001) face normal vectors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Generalized Crystal-Cutting Method (GCCM)

2.1. Constructing simulation cells of oriented single crystals

Here we derive a mathematical formalism for the GCCM for systematic construction of 3D periodic simulation cells of arbitrarily oriented single crystals. The GCCM comprises two algorithms. The first algorithm determines commensurate crystal cuts that preserve translational symmetry of the lattice and define the edges of new 3D periodic simulation cells. The second algorithm populates a chosen cell with atoms and/or molecules. These two algorithms serve as a basis to construct cells for many kinds of single-crystal simulations and for more complicated constructions such as crystal–crystal interfaces.

Consider a crystal with a Bravais lattice of arbitrary symmetry class with lattice vectors **a**, **b**, and **c** and an arbitrary set of basis atoms for the unit cell. The respective lattice vector lengths are a, b, and c and the angles between the lattice vectors are $\alpha\angle\mathbf{bc}$, $\beta\angle\mathbf{ac}$, and $\gamma\angle\mathbf{ab}$. Given 3D PBCs, simple unit cell translations can be used to trivially create simulation cells with surfaces normal to the crystal faces (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, and $(00\bar{1})$. (Recall that the (ijk) and $(\overline{ijk})$ faces are equivalent for centrosymmetric crystals.) Fig. 1 shows one such simulation cell suitable for probing properties along the normal to the (100) face. It is clearly seen that the (100) face normal vector is exactly perpendicular to **b** and **c**, but is not parallel to **a** (*i.e.*, lattice direction [100]) for crystals with monoclinic or triclinic symmetry. A crystal face (ijk) normal vector is in general parallel to lattice direction $[ijk]$ only for cubic crystals.

A critical feature of the simulation cell construction in Fig. 1 is that the periodic boundaries allow for 'infinite' 2D slabwise partitions, highlighted by shading, whose normal vector is exactly parallel to the normal of the (100) face. Clearly, analogous slabs can be defined in this cell with normal vectors parallel to the normals of the (010) and (001) faces. It can also be seen that it is impossible to use this cell to define smooth-faced infinite 2D periodic slabs with different orientations, such as those with normal directions [100] or perpendicular to (110). However, defining infinite 2D slabs in the cell is desirable, or necessary, for many types of simulations. For instance, simulations of supported shock waves often use a 2D infinite rigid piston (or momentum mirror) with a normal vector

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