

Computer Simulation of Grain Boundary Structures in Minerals

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Summary

We report important preliminary results from atomistic simulations of grain boundaries in minerals. The recently developed parallel PCMD (polycrystal molecular dynamics) program was used to perform structural optimization. In particular, we have simulated the {310}/[001] symmetric tilt grain boundary of MgO as a function of pressure. The simulation cell containing about 55,000 atoms was used. Visualization of the atomic position-time series data show that the structure changes dramatically on compression from a simple open-structure at zero pressure to a highly dense structure containing high coordination state and a screw-like dislocation at high pressure, consistent with previous atomistic simulations. Our future directions include the study of more grain boundaries in this and other minerals. With knowledge about various candidate structures for a given boundary, we will optimize them further using the first-principles molecular dynamics method based on density functional theory.

Introduction

Real materials such as minerals and ceramics are, in general, polycrystalline and as such, their physical properties are strongly influenced by grain boundaries and structures. For instance, mechanical deformations of rocks are directly dependent on grain size and processes such as creep. Before attempting simulation of a complex multigrain system, it is important to understand atomic structures of individual grain boundaries, which are known to act as barriers to dislocation motion and as nucleation sites for corrosion, precipitation and fracture. They can form a network of highways on which transport is faster than through the crystal grain. The atomistic simulation offers a unique opportunity to understand the boundary structures [1-3], which can now be compared with the direct observation of the atomic positions using high-resolution transmission electron microscopy [4,5]. We have recently initiated the investigation of grain boundaries in MgO for several reasons: First, MgO represents a prototype oxide with a wide stability field and it is one of the widely studied materials. Second, it is an important mineral since the MgO+FeO+SiO₂ system makes about 90% of the Earth's mantle. The polycrystalline properties under high pressure and temperature are crucial in interpreting rich seismic data of the deep interior. Third, while the single-crystal properties of MgO have widely been studied previously, our knowledge about its polycrystalline structure and properties is still limited. Atomistic simulations were pre-

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viously performed to investigate the pressure-induced structural transitions [2,3] and vacancy migration [6] in [001] tilt grain boundaries. Here, we report preliminary results from molecular dynamics simulation of MgO bicrystal containing {310}/[001] symmetric tilt grain boundary as a function of pressure. Our simulations have used much larger cells containing atoms in tens of thousands, compared to previous simulations involving a few hundred atoms.

Polycrystal Molecular Dynamics (PCMD) Method

We have recently developed the parallel PCMD program to simulate a system, which is composed of multiple grains [7]. The van der Waals and repulsive contributions to the pair-wise interactions between atoms are given by

$$V_{vdwr} = \sum_{i < j} \left[(B_i + B_j) \exp \left(\frac{A_i + A_j - r_{ij}}{B_i + B_j} \right) - \frac{C_i C_j}{r_{ij}^6} \right]$$

The parameters A , B , and C in the units of Å, Å and Å³kcal^{1/2}/mol^{1/2}, respectively, are as follows [8]: For Mg atom, $A = 1.0133$, $B = 0.052$, $C = 0.0$; and for O atom, $A = 1.7600$, $B = 0.150$, $C = 26.3996$. Ewald method is used to compute the long-range Coulomb interactions. The PCMD algorithm has been parallelized using the spatial decomposition approach and dynamic management of distributed linked cell list [9,10]. The physical system is divided into P subsystems, $P_x \times P_y \times P_z$, in the x , y , and z directions, and each subsystem is assigned to a processor. Each processor p thus stores arrays containing the positions r_i ($i = 1, \dots, N_p$), velocities v_i ($i = 1, \dots, N_p$), species s_i ($i = 1, \dots, N_p$) of atoms, and grain numbers g_i ($i = 1, \dots, N_p$) in which the atoms reside, where N_p is the number of atoms residing in the P^{th} subsystem. When time-stepping procedure updates the atomic positions, some atom i in subsystem P may have moved out to a neighboring subsystem P_n . This atom is ‘migrated’ to processor P_n , i.e., the information, r_i , v_i , s_i , and g_i is removed from processor P and sent to processor P_n , where it is appended to position, velocity, species and grain arrays. Performance tests using up to 512 processors have shown that with increasing the number of atoms, the execution time initially increases rapidly and then more gradually showing a linear-scaling behavior when the number of atoms becomes large (two millions or more) [7].

Results and Discussion

An important issue related to simulation of grain boundaries is the generation of input configuration that represents realistic grain structures and sizes. For instance, a polycrystalline aggregate contains multiple grains with/out texture and the Voronoi construction method [11] can be used to generate such system, e.g. [12]. In the present study, we are dealing with a simple case of grain boundary – a single symmetric tilt grain boundary of MgO, i.e., a bicrystal containing two grains with a high symmetry interface. In particular, we create an initial configuration for

the $\{310\}/[001]$ tilt boundary by putting face to face the $(3\bar{1}0)$ and (310) surfaces (Figure 1). Since the lattice positions are mirrored about the boundary plane, this is a symmetric boundary. The $\{310\}$ -tilt boundary is called $\Sigma 5$, where the angle between boundaries is 36.9 degrees. Thus created planar boundary passes through the middle of the simulation cell. Since we use the periodic boundary conditions, two outside surfaces of the cell, which are parallel to the $[001]$ plane, form a second grain boundary. The simulation cell thus contains two-grain boundaries pointing in opposite directions, one of which passes through the center of the cell and other is split across the cell. Two cell sizes are used in the simulation; *small cell* containing 6960 and *large cell* containing 58560 atoms.

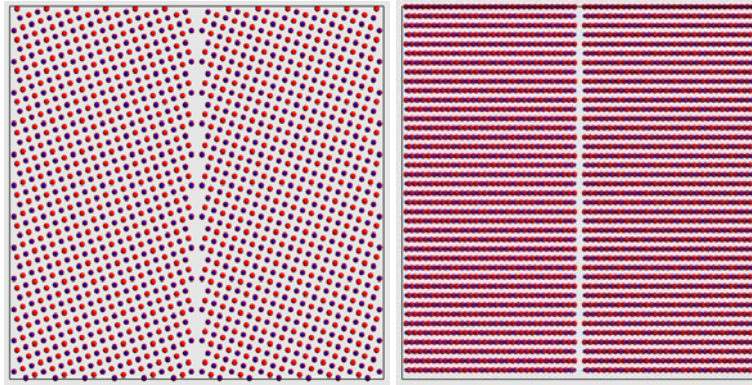


Figure 1: Top (xy) and side (xz) views of the initial configuration used for simulation with *large cell*. Small blue and large red spheres represent Mg and O atoms, respectively.

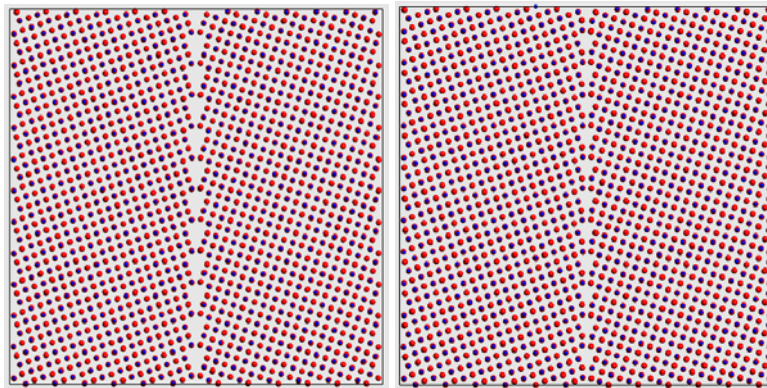


Figure 2: Top (xy) views of the boundary structure at zero pressure (left) and 30 GPa (right).

We have simulated the $\{310\}/[001]$ symmetric tilt grain boundary of MgO as a function of pressure up to 150 GPa at 300 K. The resulting atomic position-time

series datasets are visualized to gain insight into the structural properties. Our preliminary results show that the atomic arrangement at the grain boundary is highly sensitive to pressure. At zero pressure, during the simulation, the initial $(3\bar{1}0)$ and (310) surfaces moved relative to each other so that ions align with opposite charges across the boundary (Figure 2, left). In other words, Mg atoms on one side of the boundary plane are directly facing O atoms on the other side, and vice versa. The resulting grain boundary can be viewed as a series of dislocation pipes showing a well-defined channel structure. In the core of the boundary, the average coordination number of atoms is reduced and the average bond density is changed compared to the single crystal structure (or bulk region). The Mg and O atoms at the boundary show five-fold coordination, compared to six-fold coordination of the bulk atoms. The boundary has an excess free volume, with density significantly less than the bulk value. The predicted structure is found to be insensitive to the size of the simulation cell used. Results from both the *large* and *small* simulation cells agree with each other as well as with a previous MD study [3]. The open structure of the grain boundary is expected to affect the physical and chemical properties. For instance, previous calculations [6] showed that the boundaries are regions of high diffusivity.

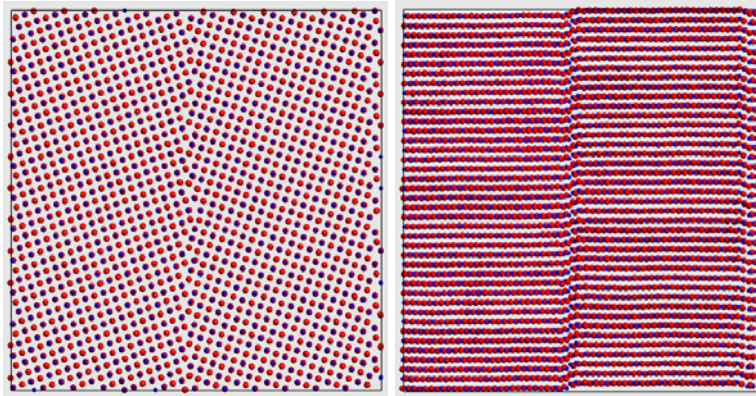


Figure 3: Top, xy (left) and side, zx (right) view of the boundary structure at 60 GPa.

As pressure increases, the open space at the boundary gets squeezed and the boundary gets more distorted and the channel structure starts to collapse. The bond-density increases with more boundary atoms becoming six-fold coordinated. The animation of the position-time series data implies a phonon mode in which the boundaries tend to move independently relative to each other. Corresponding soft phonon mode was previously predicted [2]. The associated shearing mode is stable at 30 GPa thereby preserving the open structure to a great extent (Figure 2, right). However, at 60 GPa, this mode becomes unstable so that the grain boundaries tend to shift permanently along the boundary plane along the y -direction (Fig-

ure 3, left). As a result, the open structure almost disappears and it does not show any well-defined dislocation cores. Moreover, the boundaries also shift along the z -direction (Figure 3, right), however, no such shift has been seen in the case of *small* simulation cell.

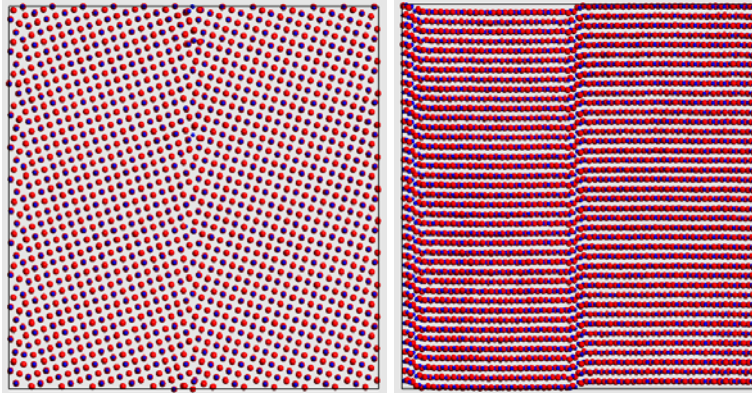


Figure 4: Top and side views of the boundary structure at 100 GPa from the *large* cell.

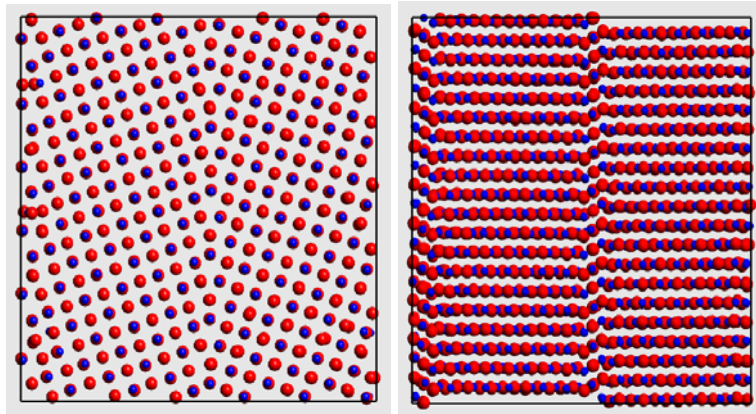


Figure 5: Top and side views of the boundary structure at 100 GPa from the *small* cell.

At very high pressures of 100 and 150 GPa, the boundary structure becomes highly dense. Bonding appears to be complete along the full length of the boundaries (Figure 4). The coordination defects now include not only lower coordination state of five but also include higher coordination state of seven. As a result, the averaged coordination number at the boundary is the same as the bulk coordination number. When viewed orthogonal to the $[001]$ axis, the shift of the two grains relative to one another appears to be very similar to that at 60 GPa. However, on

side-view, planes are offset either of the boundary by almost about 1/2 of a lattice spacing, giving a spiral dislocation structure along the [001] direction. We have also found that the high-pressure boundary structure is sensitive to the size of the simulation cell. The results from the *small* simulation cells used in this and previous [2] studies are found to be different from those from the *large* simulation cell. For instance, see the top and side views of the boundary structure at 100 GPa, as shown in Figure 4 and 5. However, the structure seen in the *small* simulation cell at 100 GPa starts to appear in the *large* simulation cell at 150 GPa (not shown here).

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