Conf-911202--35

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ANL/CP--74996

DE92 005216

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NOVEMBER 1991

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*The effort of SRP was supported by US Department of Energy BES-Materials Science under Contract No. W-31-109-Eng-38. The effort of JMR was supported by the Office of Naval Research under Contract No.N00014-88-F-0019.

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Manuscript to be published in Proceedings of the MRS Symposium on "Structure and Properties of Interfaces In Materials" at the Fall meeting of the MRS, Boston MA, 2-6 December 1991

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RECONSTRUCTION OF A HIGH-ANGLE TWIST GRAIN BOUNDARY BY GRAND-CANONICAL SIMULATED QUENCHING

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ABSTRACT

A formalism for obtaining the zero-temperature structure of mono-component solids by simulated quenching in the grand-canonical ensemble is outlined. The structure of a high-angle twist grain boundary on the (110) plane of an fcc metal is investigated. The lowest energy structure is found to be a twinned structure with a density approximately 20% higher than the structure obtained from canonical-ensemble energy-minimization.

INTRODUCTION

There is a large, ongoing experimental, theoretical and simulational effort to determine the structure and energy of grain boundaries (GBs) in metals.[1] In the simulations, the number of atoms in the computational cell is fixed throughout the simulation, and is determined from an input structure, often obtained from the coincident site lattice (CSL) model. Fixing the number of atoms in the simulation at the outset is a severe restriction, however, since the GB energy might be reduced by the addition of atoms to low-density regions near the grain boundary or by the removal of atoms from high-density regions near the grain boundary. In principle, grand-canonical ensemble (GCE) simulations allow atoms to be added to and removed from a system. Unfortunately GCE simulations of solids have, until now, proved to be essentially impossible because of the prohibitively high initial energy penalty to the addition or removal of atoms.

In this paper, we outline a recently-developed formalism for determining the zero-temperature structure of mono-component solids in the grand-canonical ensemble, which is both straightforward to implement and computationally inexpensive.[2] The new formalism, grand-canonical simulated quenching (GCSQ), is used to determine the equilibrium structure of a high-angle twist grain boundary on the (110) plane of an fcc metal. The lowest energy structure is found to be qualitatively different from that derived from canonical-ensemble simulations based on the CSL structure.

FORMALISM FOR SIMULATIONS OF SOLIDS IN THE GRAND-CANONICAL ENSEMBLE

The heat function, L, in the grand-canonical (μVT) ensemble is

$$L = E - \mu N \quad , \tag{1}$$

where E is the internal energy, μ is the chemical potential and N is the number of atoms. Because it was first introduced by Hill,[3] L is known as the Hill energy.

For mono-component systems the chemical potential is equal to the Gibbs free energy per atom which, at zero temperature and pressure, is just the internal energy. Thus, for a zero-temperature perfect crystal L vanishes. By contrast, for an inhomogeneous system at zero temperature $L>0$.

For a system of atoms in the (μVT) ensemble interacting via a pair potential, $U(r_{ij})$, $r_{ij} = | \mathbf{r}_i - \mathbf{r}_j |$ the Hill energy is:

$$L = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} U(r_{ij}) \; - \; \mu N \quad . \tag{2}$$

To develop a formalism for the simulation of solids in the grand-canonical ensemble, we make two departures from canonical-ensemble simulation schemes:

(i) A solid is considered as being formed from M mobile sites, which may or may not be occupied. These sites may be considered to be merely mathematical points in space, to which atoms can be attached. Thus rather than describing a solid as an N atom system with atom i described by the six position and momentum coordinates ($\mathbf{r}_i, \mathbf{p}_i$), the solid will be described as a system of M sites ($M \geq N$), the ith site being described by its position, $\mathbf{r}_i$, its momentum $\mathbf{p}_i$ and by the number of atoms at the site (the 'occupancy' of the site).

(ii) The occupancy of the each site is taken to be a time-dependent non-integer quantity; the occupancy of the ith site is x_i where $0 \leq x_i \leq 1$.

By choosing an appropriate number of sites at the beginning of the simulation (i) will allow simulations with a fixed number of sites but an unfixed number of atoms. Also, by allowing the occupancy of any site to be a fractional quantity, changes in occupancy may be made continuously with resultantly small incremental changes in the energy of the system. Moreover, since it is a continuous variable, equations of motion for x_i may be derived. The price that must be paid for this is, of course, that the occupancy of a site is not necessarily an integer. However, as will be seen below, the above assumptions lead to zero-temperature structures in which there are no fractionally occupied sites: each site is either occupied by exactly one atom or is empty.

In postulating fractional occupancy of sites, the constraint $0 \leq x_i \leq 1 \forall\, i$ was assumed. This constraint is easily imposed by making a change of variable from x to a function θ, where

$$x_i = \frac{1}{2} (\cos \theta_i + 1) \qquad . \qquad (3)$$

The total energy function for the system of M sites is given by the heat function plus kinetic-energy terms for the real-space and occupancy-space degrees of freedom:[2]

$$E = \frac{1}{2} Q \sum_{i=1}^{M} \dot{\theta}_i^2 + \frac{1}{2} m \sum_{i=1}^{M} \dot{\mathbf{r}}_i^2 + \frac{1}{8} \sum_{i=1}^{M} \sum_{\substack{j=1 \\ j \neq i}}^{M} (\cos \theta_i + 1)(\cos \theta_j + 1)\, U(r_{ij}) - \frac{1}{2} \mu \sum_{i=1}^{M} (\cos \theta_i + 1) \qquad (4)$$

The Euler-Lagrange equations may be used to derive the equations of motion for θ_i and $\mathbf{r}_i$ from the Lagrangian associated with this energy function They are:

$$Q \ddot{\theta}_i = \frac{1}{4} \sin \theta_i \sum_{\substack{j=1 \\ j \neq i}}^{M} (\cos \theta_j + 1)\, U(r_{ij}) - \frac{\mu}{2} \sin \theta_i \qquad , \qquad (5a)$$

$$m \ddot{r}_{i\alpha} = -\frac{1}{8} \sum_{\substack{j=1 \\ j \neq i}}^{M} (\cos \theta_i + 1)(\cos \theta_j + 1) \frac{\partial U(r_{ij})}{\partial r_{i\alpha}} \qquad . \qquad (5b)$$

There are two stationary solutions to Eq. 5a. They are:

$$\sin \theta_i = 0 \qquad , \qquad (6)$$

and

$$\mu = \frac{1}{2} \sum_{j=1}^{M} (\cos \theta_j + 1)\, U(r_{ij}) \quad , \quad \sin \theta_i \neq 0 \qquad . \qquad (7)$$

The first solution (Eq. 6) leads to two different physical situations. For $\cos \theta_i = +1$ the ith site is occupied ($x_i=1$). For $\cos \theta_i = -1$ the ith site is unoccupied ($x_i=0$). Notice that these solutions are independent of j, i.e., the system may contain a mixture of occupied and unoccupied sites. If all of the sites are unoccupied then there are no atoms in the system. Trivially, this is an energy minimum with L=0. There is a second solution with L=0, which corresponds to a perfect crystal. Depending on the initial choice of the number of sites this may have all or only a fraction of the sites occupied.

Analysis of the second stationary solution (Eq. 7) is only a little more complicated. Recall that the zero-temperature chemical potential is simply the zero-temperature perfect-crystal cohesive energy per atom, U_0. However, the right-hand side of Eq. 7 is the energy of atom i. Thus, the only solution to Eq. 3.3 is that the jth site is occupied by exactly one atom or completely empty, such that the occupied sites form a perfect-crystal lattice.

The stationary solution of Eq. 5b must simultaneously be obtained. For x_i =0 or x_j =0 Eq. 5b vanishes. For x_i = 1 and x_j=1, Eq. 5b yields:

$$\sum_{\substack{j=1\\ j\neq i\\ \text{occ.}}}^{M} \frac{\partial U(r_{ij})}{\partial r_{i\alpha}} = 0 \qquad , \qquad (9)$$

i.e., the net force on each occupied site due to the other occupied sites is zero, which is the usual equilibrium constraint on equilibrium atom positions.

Thus, at zero temperature GCSQ results in a structure which is an energy minimum and has each site either occupied by exactly one atom or completely empty. The applicability of this method has been verified by performing GCSQ on systems initially containing point defects.[2]

ZERO-TEMPERATURE RECONSTRUCTION OF A HIGH-ANGLE GRAIN BOUNDARY

In the simulations described below, the atoms interact via a Lennard-Jones (LJ) potential parameterized to copper (ε=0.167eV,σ= 2.315Å), shifted smoothly to zero and cut off between the fourth and fifth neighbor shells at 2.33σ. The mass of the atoms is 63.5 amu. For this potential and these parameters the zero-temperature lattice constant, a = 3.616Å, and cohesive energy per atom, E_0 = -1.0378 eV. The chemical potential has the value $\mu = E_0$ = -1.0378 eV. The grand-canonical simulated quench to zero temperature was performed by removing a small fraction (0.125%) of the kinetic energy in the real-space and occupancy-space degrees of freedom at every 'time' step.

As an initial model geometry we choose a point-defect free GB derived from the coincident-site-lattice (CSL) rotation of two perfect semi-inifinite crystal lattices relative to each other about the plane normal. The (110) θ=31.59° (Σ27) GB employed here is obtained by rotating one perfect semi-crystal relative to another by an angle of 31.59° about the (110) plane normal. The system is oriented with the planar normals along the z-axis and, consequently, the x-y-plane is parallel to the GB plane. Because of the interface there is no periodicity in the z-direction. However, in the x-y-plane, the structure is periodic. The (110) θ=31.59° (Σ27) GB has a rectangular planar repeat unit with an area which is Σ=27 that of the corresponding primitive planar unit cell (Σ=1) on the (110) plane in a perfect single crystal.

The zero-temperature structure and energy of this grain boundary have been previously determined in the canonical ensemble by iterative energy minimization ("lattice statics") using a Region I-Region II scheme to simulate an isolated grain boundary. In this scheme, the computational cell is periodic in the x-y plane, but the GB region is embedded in the z-direction between two rigid block of atoms.[4,5] The number of atoms in the system remained fixed throughout the simulation, but the dimensions of the unit cell in the z direction were allowed to relax. A substantial volume expansion at the grain boundary was observed and the grain boundary energy was found to be 1052 Jm^{-2}. [6] This GB structure will be denoted the V-structure hereafter.

A Region I- Region II scheme similar to that used in the canonical-ensemble simulations was used for the GCSQ. The unrelaxed grain-boundary structure with no volume expansion was chosen as an initial structure. Since this has an excess atomic density over that of the canonical-ensemble relaxed structure described above, we expect that atoms will be removed from, rather than added to, the system when the number of atoms is allowed to vary. Therefore, the initial sites were arranged to be coincident with the locations of the unrelaxed atoms and no additional sites were added.

The lowest energy configuration (designated here as the N-structure) obtained in the GCSQ had energy 1019 Jm^{-2} which is 33 Jm^{-2} less than that of the V-structure. The 'temporal' evolution of the total number of atoms in the system and the Hill energy during the course of this simulation are shown in Fig. 1. Of the 54 (2 × 27) atoms in the two planes adjacent to the grain boundary 16 were removed during the GCSQ. Lattice-statics simulations at zero stress in the z-direction for this N-structure resulted in a small volume contraction and a further reduction of the GB energy to 992 Jm^{-2} (the NV-structure) which is 60 Jm^{-2} (or 6 percent) less than that of the V-structure.

We now briefly compare the NV-structure with the V-structure. A measure of the density of a system containing a grain boundary is the volume excess per unit area , $\delta V/A$, of a system containing an interface over a perfect crystal with an equal number of atoms. For the V-structure $\delta V/A = 0.179a$;[6] for the NV-structure $\delta V/A=0.149a$; that is the NV-structure is 20% more dense than the V-structure. That there are also significant qualitative differences in the NV- and V-structures at the atomic level is illustrated in Fig. 2, which shows edge-on views of the two grain-boundaries. For clarity, each individual atomic plane is denoted by a different symbol. The V-structure is symmetric about the GB-plane but has no atoms at the GB plane. The NV-structure is qualitatively different from the V-structure in that there is a plane of atoms (denoted by crosses) at the GB-plane; i.e., the grain boundary has a twinned structure.

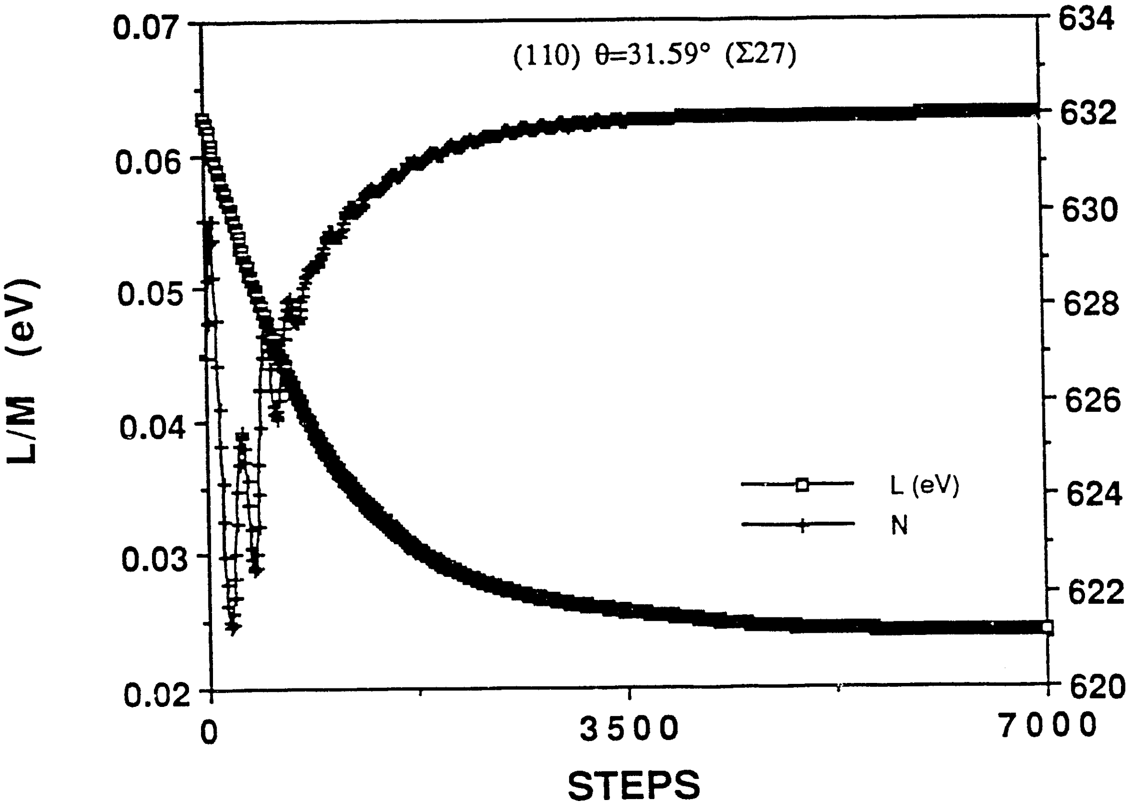

Fig. 1 Number of atoms (N) and Hill energy per site (L/M) as a function of the number of 'time' steps for a 648 site system initially containing a (110) θ=31.59° (Σ27) grain boundary. The non-zero final value of the Hill energy corresponds to a grain boundary energy of 1019 Jm^{-2}.

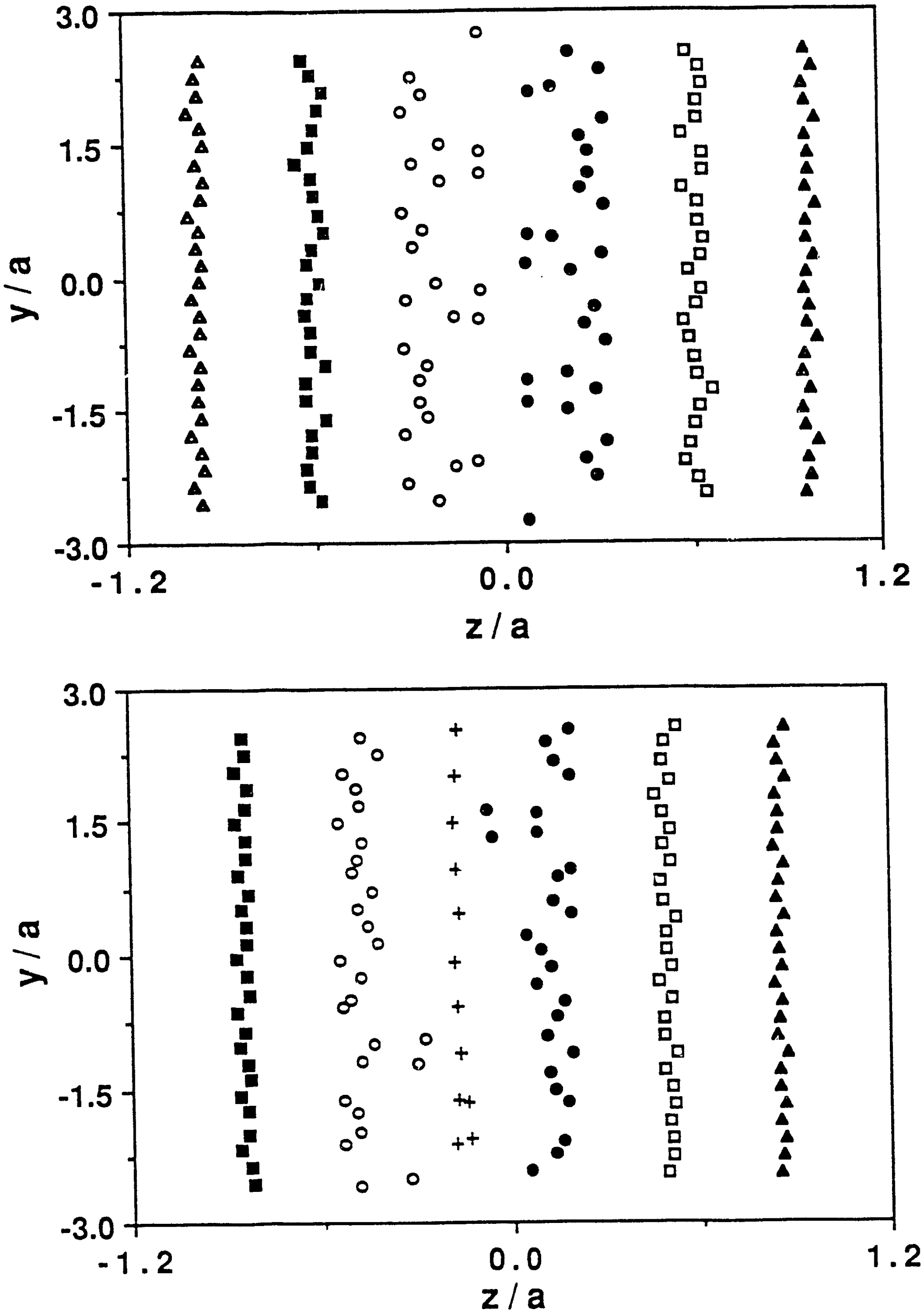

Fig. 2 Top: Grain boundary structure generated using canonical-ensemble energy minimization under zero stress in the z-direction, parallel to the GB normal (the V-structure). The energy of this structure is 1052 Jm^{-2}. Bottom: Grain-boundary structure generated using grand-canonical simulated quenching, followed by canonical-ensemble energy minimization under zero stress in the z direction (the NV-structure). The energy of this structure is 992 Jm^{-2}

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