ON THE VOLUME DEPENDENCE OF COMPUTED
GRAIN BOUNDARY ENERGY

P. D. Bristowe and A. Brokman*

Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

August 1980

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

MASTER

Prepared for

U.S. Department of Energy
under Contract DE-AS02-78ER05002.A001

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

* Also at Bergman School for Applied Science, Hebrew University of Jerusalem, Israel.

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Fig

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ON THE VOLUME DEPENDENCE OF COMPUTED GRAIN BOUNDARY ENERGY

P.D. Bristowe and A. Brokman[†]
Department of Materials Science and Engineering,
Massachusetts Institute of Technology, Cambridge, MA 02139

I. Introduction

Over the past five years there have been numerous studies of grain boundary structure using the method of computer molecular statics which assume pairwise central potentials for the interatomic interaction (1-6). These studies have focused on the structure of the boundary that result from minimizing the potential energy of a system of interacting point nuclei and relating this structure to various geometrical models of interfaces (7,8) and also to some experimental observations (9-11). In addition to the relaxed configuration the grain boundary energy has been computed and quite often plotted on the familiar cusped curve of energy versus misorientation. In most of these works, it was recognized that the absolute value of the calculated energies is probably only correct to $\pm 40\%$ due to inadequacies in matching the potential to experimental data, artificially terminating the potential at some cut off radius or to unaccounted for kinetic effects. Emphasis is usually placed on relative grain boundary energies but these may still be inaccurate due to various, but related, approximations and constraints implicitly imposed on the calculation--namely central forces, finite model size, fixed border conditions and volume dependent contributions to the energy of the system. It is the purpose of this work to clarify how these particular properties of the model can effect the computed grain boundary energy and demonstrate instances in which the quoted energy has strictly been inaccurate. The implication of these results, especially on how they effect the method of relaxation and the resulting grain boundary structure is discussed. Firstly, however, some important aspects of interatomic potentials are described.

II. Equilibrium vs. Non-Equilibrium Potentials with Respect to Volume Change

The application and validity of the central force approximation in metals and its consequence has been well documented (see e.g. refs. 12, 13). In summary it can be said that in simple metals where the interaction between the electrons and the ions can be represented by a weak pseudopotential, the total energy of the perfect lattice can, to lowest order, be given in two parts

$$E_{\text{total}} = \phi_v(v) + \phi_s(v) \quad (1)$$

where $\phi_v(v)$ is a large volume dependent contribution and characterizes the cohesive energy of the free electron gas, and $\phi_s(v)$ is a structural part which can be written as a central pair potential $\phi(\underline{r};v)$ and in general also depends explicitly on the volume v of the crystal. Although the functional form of ϕ_v cannot be derived easily, it has been represented as a power series so that

$$E_{\text{total}} = \sum_n P_n v^n + \frac{1}{2} \sum_{\underline{R} \neq \underline{R}'} \phi(\underline{R}-\underline{R}';v) \quad (2)$$

where P_n are constant coefficients and $\underline{R}$ are lattice sites. In the limit of small volume changes the pair potential ϕ becomes independent of v and a linear relationship between ϕ_v and v is assumed. Therefore,

[†] Also at Bergman School for Applied Science, Hebrew University of Jerusalem, Israel.

$$E_{\text{total}} = P v + \frac{1}{2} \sum_{\underline{R} \neq \underline{R}'} \phi(\underline{R} - \underline{R}') \quad (3)$$

Under these conditions, it can be shown from lattice stability criteria (14) that the coefficient P is the Cauchy pressure which for cubic crystals is related to the elastic constants, thus

$$P = (c_{12} - c_{44})/2 \quad (4)$$

This pressure represents the pressure of the free electron gas by way of Eq. (1).

The extension of this two-body potential formalism to non-simple metals (e.g., transition or noble metals) is not easily justified but some success has been achieved especially when the pair potential ϕ has been derived empirically. The use of empirical pair potentials representing non-simple metals in simulations of crystal defects, especially point defects and more recently grain boundaries, has met with some surprising success considering the number of arbitrary assumptions made. Assuming that the coefficient P does not change in deformation, then the defect formation energy is given by

$$\gamma = P v_F + \frac{1}{2} \sum_{\underline{D} \neq \underline{D}'} \phi(\underline{D} - \underline{D}') - \frac{1}{2} \sum_{\underline{R} \neq \underline{R}'} \phi(\underline{R} - \underline{R}') \quad (5)$$

where $\underline{D}$ are the defect lattice sites and v_F is the defect formation volume equal to $v_D - v$. Calculations have shown that for point defects the term $P v_F$ is far from negligible and can be a major contribution to the formation energy (15). There is, however, a special case when $P v_F$ is always zero and that is when the Cauchy relation $c_{12} = c_{44}$ holds. When an empirical potential is matched (erroneously) to the elastic constants so as to obey the Cauchy relation then the Cauchy pressure and hence the volume dependence of the potential is zero. This simplifies the calculation since only the pair potential contributes to the total formation energy but the procedure, which effectively neglects free electron contributions, is a severe approximation. An example of such a potential is the Johnson α -iron cubic polynomial potential (16) which, because of its stability with respect to volume changes, is called an equilibrium potential. Examples of empirical non-equilibrium potentials of the polynomial type are given in (3) for copper and nickel. A non-equilibrium pseudopotential for aluminum often used in grain boundary simulations is given in (17). Another situation in which the $P v_F$ term becomes negligible is when the formation energy of a defect is calculated at constant volume or more properly when the average volume per atom remains constant.

III. Volume Changes in Bicrystal Systems

In recent atomistic calculations of grain boundary structure and energy equilibrium and non-equilibrium potentials have been used in which the crystal volume has usually been kept constant (2-5) but which has sometimes been varied (1,6). These studies have calculated the relaxed grain boundary energy and also some important structural features such as the in-plane translation between grains and the local expansion or excess volume of the boundary. All of these parameters are now, at least for some special boundaries, experimentally measurable quantities (9, 10). Ideally, when modelling a grain boundary perfectly flexible (i.e., unconstraining) border conditions should be applied in every direction since in general the relaxation between the grains is expected to be large. In practice fixed borders parallel to the grain boundary plane in a constant volume model have been used which undoubtedly confines the relaxation normal to the boundary. It is recognized that with these borders a compressive strain is induced in the crystal far from the boundary as the boundary structure expands and will lead to spurious (usually excessive) results for the grain boundary energy and possibly an incorrectly constrained boundary structure.

There are two ways of reducing or even eliminating this effect while still retaining the fixed borders: either keeping the crystal volume constant and using an extremely large computational cell in the direction perpendicular to the boundary plane or using a relatively small cell and changing continuously the bicrystal volume until the minimum in energy is obtained. In either method the elastic energy density in the model caused by a local volume expansion at the boundary is proportional to the square of the strain normal to the boundary from which it is not difficult to show that the total elastic energy is inversely proportional to the size of the model in that direction and directly proportional to the square of the volume change. Therefore, either stretching the model or increasing the model size by adding extra layers will reduce the elastic

strain energy. So far we have only considered ϕ_s in Eq. (1). The volume change in ϕ_s causes in turn changes in ϕ_y , i.e. in order to be self consistent, the effect of the expansion on the electron gas should be considered in the case of the non-equilibrium potential. We report here the use of both these expansion methods on tilt and twist boundaries using equilibrium and non-equilibrium potentials and demonstrate how the results differ from those already published.

IV. Computed Results

In Figure (1) the variation of the grain boundary energy with volume expansion is plotted for two bcc [001] tilt boundaries ($\Sigma=5$ and $\Sigma=25$) using the equilibrium Johnson potential representing iron. In this calculation it is assumed that the Cauchy pressure remains constant, and identically zero, when the defect is introduced and when the crystal volume is increased. In such a case the boundary energy simply consists of the pair potential contribution and for each boundary reaches a quadratic minimum for a particular separation of the grains. The Figure is analogous to that of Figure (5) in reference (1) for the $\Sigma=3$ twins. The starting configuration used was that of ref. (5) and it is seen that upon allowing a volume relaxation perpendicular to the boundary plane the energy can reduce by up to 12%. A similar and slightly larger effect occurs for a $\Sigma=5$ [001] twist boundary using the same potential as seen in Figure (2).

Figure (3) demonstrates the effect of keeping the crystal volume constant in the model but performing the simulations for various model sizes perpendicular to the boundary plane. Figure 3(a) is for the bcc $\Sigma=5$ [001] tilt boundary already given in Figure (1) and shows how the boundary energy reduces to the same value when the model size is increased. The same effect is seen to occur, as seen in Figure (3)b and (c), for $\Sigma=5$ [001] and $\Sigma=3$ [110] twist boundaries using a non-equilibrium potential for copper. The percentage drop in energy in these two cases, however, is somewhat smaller than for the tilt boundary.

When the crystal volume was increased by less than two percent using a non-equilibrium potential the boundary energy was found to decrease linearly as the volume expanded and the slope of the curve equaled the Cauchy pressure. This result was found for the $\Sigma=5$ [001] and $\Sigma=3$ [110] copper twist boundaries and also in cases not shown here for twist boundaries and single crystals in nickel (3) and also in twin boundaries in tungsten and molybdenum (1). Clearly this approach is not suitable for determining the least constrained structure as the potentials by their very nature will not reveal equilibrium configurations with respect to volume change. One way of determining this structure in such a situation is to perform the volume expansions/contractions and calculate the strain far from the boundary. When this is zero the volume dependent term can be calculated and included in the total energy.

V. Discussion

From the above results it can be stated that many relaxed grain boundary energies calculated thus far by computer simulation seem to contain inaccuracies due to neglect of volume relaxation especially when relatively small model sizes are used in a constant volume crystal. The energy differences that occur when eliminating the long range compressive strain in the model are comparable, in some instances, to the difference in grain boundary energy between alternative in-plane translated boundary structures. It can be speculated that the relaxation methods used to date for grain boundaries which do not allow in some way for a free relaxation of the excess grain boundary volume will produce questionable results, especially for the grain boundary energy. This has certainly been shown to be the case in some recently computed work on bcc tilt boundaries (5) and might also be the case in some earlier studies (2,4). Examination of the local boundary structure that results when the long range strains are released have shown that, in some cases, small changes can occur and will, therefore, be important in choosing the minimum energy structure.

In view of the last point, we examined further some of the computed grain boundary structures. The local tilt boundary structures studied in (5) did not change greatly upon allowing a volume expansion despite a significant lowering in the grain boundary energies. The same kind of marginal effect on the location of atoms near the boundary was found for several of the twist boundaries. We believe that the lattice distortion at the boundary due to the interaction between the two grains is much stronger than that arising from the fixed border condition and thus leads to the insignificant change in structure. We also conclude that the fixed border condition causes a long range stress field ($1/N$) while the grain boundary interaction is relatively short range. (This last observation is reflected in the fact that the grain boundary width has often been found to be small--see for example, Ref. 11). Therefore, the expansion correction is mainly of importance for the energy calculation rather than the structure simulation.

An important feature of Figure 1 is that the expanded boundary energy can be treated as a two-body interaction between grains; if the non-expanded relaxed coordinates of crystal 1 and 2 are R_1 and R_2 respectively and after expansion the relaxed coordinates are given by R'_1 and R'_2 , then the energy of the expanded boundary is

$$E' = \sum_{R'_1 \neq R'_2} \phi(R'_1 - R'_2) \quad (6)$$

Because of the regular analytic form of the curves in Figure (1) we can write this as

$$E' = f(\Delta v) \sum_{R'_1 \neq R'_2} \phi(R'_1 - R'_2) = f(\Delta v) E \quad (7)$$

where Δv is the value of the volume expansion. The function of $f(\Delta v)$ is regular, analytic, with one minima, i.e., it can represent the intergrain interaction potential.

A main problem in any computation which involves a volume change is, as was implied, the change in energy due to the change in volume. The problem arises from the fact that on one hand the interatomic potential is constructed for a certain volume associated with a given lattice parameter while on the other hand the programs are calculating the minimum in energy due to change in configuration r (involves forces) and not volume v (involves pressure). We can present the total change in energy as:

$$dE = \nabla E \cdot dr + \frac{\partial E}{\partial v} dv \quad (8)$$

The first right hand term is the "force term" and is calculated by the program while the second term is the "pressure" one, and should be added to the computed energy. In view of equation (3) this term is simply Pdv , i.e., the correction that should be made to the energy is given by $\Delta E = +P\Delta v$. This point clarifies some of the confusion appearing lately in the literature (6,1).

VI. Conclusion

In conclusion it has been shown that to avoid inaccurate boundary energies completely free and unconstrained borders should ideally be applied. The degree of freedom along the direction in which the boundary structure is not periodic is especially important. Alternatively if fixed borders are used, models large enough so that the compressive strains have a negligible effect on the boundary energy and structure must be used. In small models and changing the volume care should be taken in calculating the total energy correctly. When using non-equilibrium potentials this procedure is strictly invalid since the total energy should be minimized not just the pair contribution. In this case the free electron contribution Pdv has to be added to the expanded structure energy. The procedure is doubtful when the volume changes become large and the linear approximation breaks down.

Acknowledgement

This work was supported by the National Science Foundation (P.D.B.) under Grant DMR-78-12804 and also the Department of Energy (A.B.) under Contract Number DE-AS02-78ER05002.A001. The authors wish to acknowledge the use of computer codes developed at AERE Harwell and the University of Surrey. They also wish to thank Professor R.W. Balluffi for useful comments on the manuscript.

References

1. P.D. Bristowe and A.G. Crocker, Phil. Mag., 31, 503 (1975).
2. D.A. Smith, V. Vitek and R.C. Pond, Acta Met., 25, 475 (1977).
3. P.D. Bristowe and A.G. Crocker, Phil. Mag., A 38, 487 (1978).
4. R.C. Pond, D.A. Smith and V. Vitek, Acta Met., 27, 235 (1979).
5. V. Vitek, D.A. Smith and R.C. Pond, Phil. Mag., A 41, 649 (1980).
6. K.W. Ingle and A.G. Crocker, Phil. Mag., A 41, 713 (1980).
7. M.F. Ashby, F. Spaepen and S. Williams, Acta Met., 26, 1647 (1978).
8. R.C. Pond, D.A. Smith and V. Vitek, Scripta Met., 12, 699 (1978).
9. R.C. Pond and V. Vitek, Proc. R. Soc. Lond A, 357, 453 (1977).
10. R.C. Pond, J. Micro., 116, 105 (1979).
11. P.D. Bristowe and S.L. Sass, Acta Met., 28, 575 (1980).
12. N.W. Ashcroft, Interatomic Potentials and Simulation of Lattice Defects, Plenum Press, New York 91 (1972).

13. V. Vitek, A.P. Sutton, D.A. Smith and R.C. Pond, ASM Materials Science Seminar on Grain Boundary Structure and Kinetics, Milwaukee, Wisconsin (1979)
14. M. Born and K. Huang, The Dynamical Theory Crystal Lattices, Clarendon Press, Oxford (1954).
15. A.G. Crocker, M. Doneghan and K.W. Ingle, Phil. Mag. A 41, 21 (1980).
16. R.A. Johnson, Phys. Rev. 134, 1329 (1964).
17. L. Dagens, M. Rasolt, and R. Taylor, Phys. Rev. (B) 11, 2726 (1975).

Fig. 1 Variation of grain boundary energy with volume expansion for two bcc [001] tilt boundaries. The values obtained in Ref. 5 are given by $\otimes$.

Fig. 2 Variation of grain boundary energy with volume expansion for a bcc [001] twist boundary.

Fig. 3 Variation of grain boundary energy with increasing model size for (a) a bcc [001] tilt boundary where $\otimes$ is the value obtained in Ref. 5 (b) a fcc [001] twist boundary where $\boxplus$ is the value obtained in Ref. 3 (c) a fcc [110] twist boundary where $\odot$ is the value obtained in Ref. 6.