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A MOLECULAR DYNAMICS STUDY OF GRAIN BOUNDARY PHASE EQUILIBRIA: THE CASE OF THE $\Sigma = 13$ BOUNDARY

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Computer molecular dynamics simulations of a two-dimensional $\Sigma = 13$ bicrystal, interacting through a Lennard-Jones potential, have been performed. Grain boundary phase equilibria were studied through the temperature dependence of the bicrystal enthalpy. Two phenomena were studied: a transition to a liquid-like layer at approximately 80% of the bulk melting point, and a reorientation of the grain boundary from the $\Sigma = 13$ misorientation of 27.80° to a misorientation of approximately 44°.

1. Introduction

The importance of interfacial phenomena in the understanding of bulk polycrystalline physical properties is well-recognized, and has led to a great diversity of experimental and theoretical work on grain boundaries and other solid–solid interfaces. One area that we feel has received insufficient attention to date, and which is particularly well-suited to atomistic simulation techniques, is grain boundary phase equilibria. In this paper we report the results of a molecular dynamics study of the thermodynamic properties of a two-dimensional bicrystal, the interfacial phase transition it undergoes, and the reorientation of the bicrystal at high temperature.

A thermodynamics of surfaces is well established through the work of Gibbs [1], and its application to the study of solid–solid interfacial equilibrium is straightforward. Excess thermodynamic properties of interfaces are defined with respect to those of perfect bulk reference states. Then, an interfacial phase transition is defined in terms of singularities in interfacial excess properties. For the case of grain boundaries, some evidence, of both experimental and theoretical nature, exists which indicates the presence of what has been called a

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grain boundary melting transition. In this transition, a grain boundary is replaced with a liquid-like layer at temperatures well below the bulk melting point. An example of experimental evidence is the electron microscope study of Glicksmam and Vold [2]. On the theoretical end, Kikuchi and Cahn [3] used a lattice gas model to study a 2D $\Sigma = 5$ boundary and found a gradual melting transition at approximately one half of the bulk melting point. Two groups have applied molecular dynamics methods to the study of this phenomenon. Gicotti, Guillope and Pontikis [4] simulated a $\Sigma = 5$ tilt boundary and observed a gradual onset of a liquid-like boundary layer. In addition, the authors of this paper have been involved in a molecular dynamics study of grain boundary phase transitions in Ar, specifically by examining the behaviour of the grain boundary excess enthalpy with temperature. Preliminary results of this work on a $\Sigma = 7$ bicrystal have already been reported [5]. By calculating enthalpies of single crystal reference systems at the same temperatures we were able to unambiguously determine the grain boundary excess enthalpy.

Grain boundaries are crystalline defects which cannot be present in thermal equilibrium but which, once introduced into a perfect crystal, may be locally equilibrated. Those of the independent geometrical parameters describing the bicrystal which are free to vary will relax to equilibrium values which depend on the values of the constrained parameters. One such relaxation is a change in the relative misorientation between the two grains. Considerable experimental evidence for grain boundary reorientation exists, but it has never, to date, been observed in a dynamic computer simulation.

Our purpose in the present study was to investigate the possibility that the transition we observed earlier would occur in a boundary having a different misorientation, and hence structure, and to more clearly elucidate the nature of the transition. As an additional bonus we shed some light on the relative enthalpy difference of boundaries of differing orientation.

2. Methods

The system studied was a 2D close-packed bicrystal containing a $\Sigma = 13$ tilt grain boundary, as shown in fig. 1. The initial structure is obtained by a rotation of 27.80° about the x direction, followed by the removal of two atoms from the system which overlap too closely. Particles were interacting through a central pair-wise Lennard-Jones potential with parameters chosen to simulate Ar [6] ($\epsilon = 119.79$ K, and $\sigma = 3.405$ Å). Periodic boundary conditions were employed. We used the flexible borders technique of Parinello and Rahmann [7] to carry out the simulations in the NPT ensemble. This technique solves the equations of motion through a Lagrangian formulation developed by Andersen [8]. The cell edges are vectors which are dynamic variables in the formulation allowing the cell size and shape to change in the course of the simulation. The

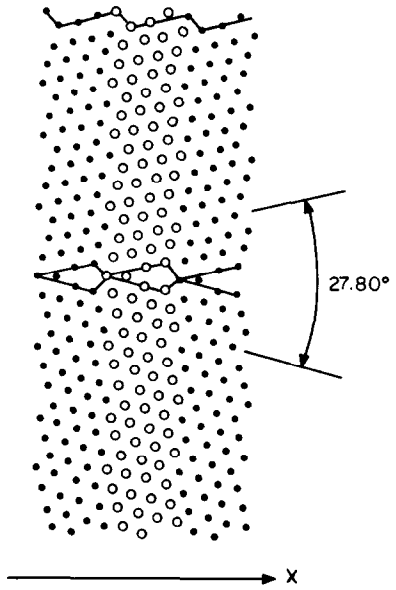

Fig. 1. Initial configuration of the simulation cell of the $\Sigma = 13$ bicrystal with 110 particles. Also shown are two of the simulation cell images in the x direction. Note that one particle has been removed from each grain boundary.

majority of the calculations were performed on a system of 110 particles containing two grain boundaries. The interaction range was chosen to be 1.7σ. Additional calculations on a larger system of 220 particles with an interaction range of 2.6σ were performed.

We obtained the low temperature relaxed structure of the system by holding the system at $T^* = T/4\epsilon = 0.01$ for 23,000 time steps and calculating the time averaged atomic coordinates over the time range after which the system had equilibrated. As an additional check we heated the system to $T^* = 0.13$, which is approximately 80% of the bulk melting point and recooled slowly to $T^* = 0.01$, obtaining identical values for the enthalpy. This gave us confidence that the relaxed structure does indeed represent a well-defined local minimum at temperatures below the grain boundary transition region. This relaxed structure was used as a starting configuration for a variety of runs at many temperatures, for which the bicrystal enthalpy and density were calculated.

3. Results and discussion

Simulation results on the bicrystal of 110 particles at constant reduced hydrostatic pressure of $P^* = P\sigma^2/4\epsilon$ are plotted in fig. 2 and tabulated in table

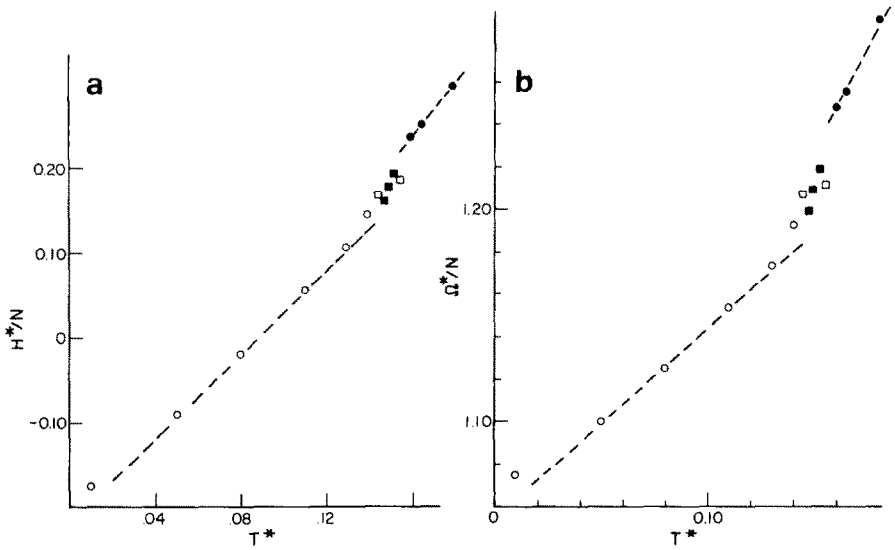

Fig. 2. Variation of enthalpy (a) and area (b) per particle with temperature for the system. Open circles are the low T grain boundary phase, closed circles are the liquid phase, open squares are the liquid-like boundary phase and closed squares are the reoriented bicrystal. The deviation from linearity at low temperatures is expected because of the rapid decrease in heat capacity below the Debye temperature.

1. At low temperatures, up to $T^* = 0.13$, the grain boundary structure remains stable and the temperature dependence of the enthalpy and density of the bicrystal are similar to the preliminary results calculated on the $\Sigma = 7$ boundary.

Table 1
Reduced values of enthalpy and volume per particle as functions of reduced temperature

Temperature	Volume/N	Enthalpy/N
0.01	1.0745	−0.1777
0.05	1.100	−0.09182
0.08	1.1251	−0.0200
0.11	1.1532	0.0545
0.13	1.1727	0.1056
0.14	1.1927	0.14282
0.145	1.2073	0.1667
0.1475	1.1987	0.1593
0.15	1.2105	0.1766
0.1525	1.2190	0.1922
0.155	1.2112	0.1856
0.16	1.2473	0.2356
0.165	1.2554	0.2484
0.18	1.2809	0.2960

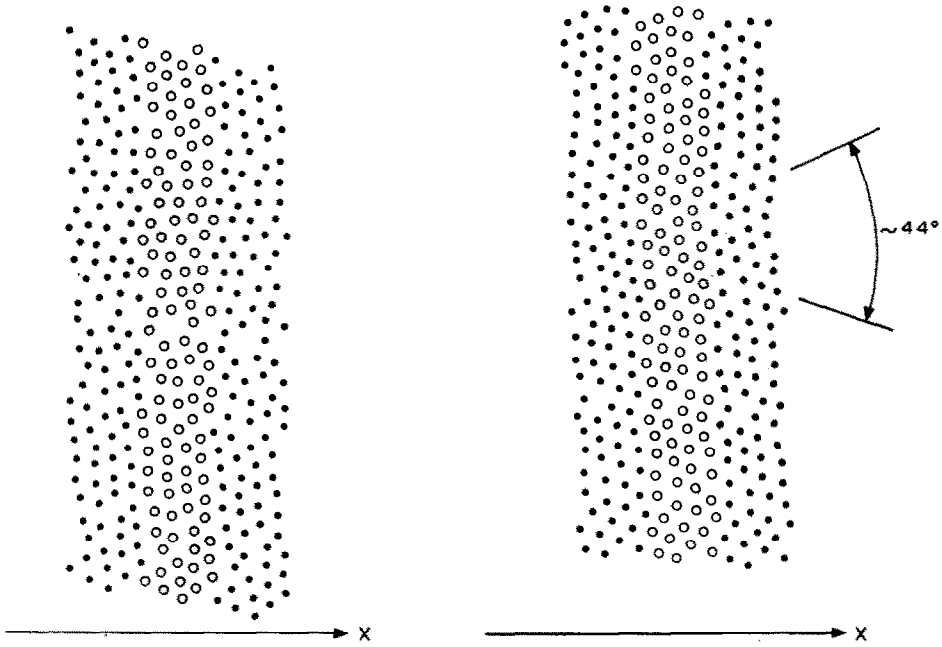

Fig. 3. Snapshot of the simulation cell showing the "liquid-like" phase at $T^* = 0.14$.

Fig. 4. Snapshot of the simulation cell showing the reoriented structure at $T^* = 0.15$.

However, at high temperatures we observed a transition of the grain boundary either to a "liquid-like" structure similar to that of the $\Sigma = 7$ grain boundary studied earlier, or to another bicrystal with a completely different misorientation than that of the $\Sigma = 13$ bicrystal. The misorientation angle in the reoriented bicrystal was approximately 44.0°. Because of the gradual nature of these transitions and the fact that our system size is small, it is difficult to pinpoint the temperature at which these structural transition occur. At $T^* = 0.165$, the previously determined bulk melting point, the entire system melts.

The behaviour of the $\Sigma = 13$ boundary when it undergoes the transition to the liquid-like structure is qualitatively similar to that of the $\Sigma = 7$ boundary we studied earlier. In both systems the periodic, highly ordered boundary structure remains stable up to relatively high temperatures. Also, in both systems the high T grain boundary structure is extremely disordered and "liquid-like". A typical snapshot of the structure in this region is shown in fig. 3. Structural characteristics of the high T grain boundary phase deserve more attention than they have recieved to date, and will be the object of future study.

The reorientation phenomena of the $\Sigma = 13$ bicrystal at high temperatures was not observed in the $\Sigma = 7$ grain boundary. A typical snapshot of the

reoriented structure is shown in fig. 4. To be sure that this structure is not a lower energy structure than the $\Sigma = 13$ bicrystal structure at constant reduced hydrostatic pressure of $P^* = 0.4936$ we cooled down the reoriented structure from $T^* = 0.15$ to $T^* = 0.01$. The enthalpy of the system was found to be approximately 4% higher than that of the $\Sigma = 13$ bicrystal at the same temperature. This proves, ignoring the entropy contribution difference at this very low temperature, that indeed the $\Sigma = 13$ is the more stable boundary at low temperature. From our limited data we are not able to say whether the reoriented bicrystal also undergoes a phase transition to a liquid-like layer before complete melting of the system.

Another object of this work was to calculate relative enthalpy differences between the two boundaries studied to date. Again, these boundaries differ by the characteristic misorientation involved in their construction. Because the interaction range employed in the two studies was not always identical, we are able to compare the grain boundary excess enthalpy values only at one temperature, $T^* = 0.11$. At this temperature the excess enthalpy of the $\Sigma = 7$ boundary is 1.21 per grain boundary length, whereas the excess enthalpy of the $\Sigma = 13$ boundary is 1.19, a difference of approximately 2%. This difference is within the accuracy of our data.

The conclusions we are able to draw from this study are the following. The $\Sigma = 13$ grain boundary in a 2D Ar bicrystal undergoes a transition qualitatively very similar to that previously observed in a $\Sigma = 7$ grain boundary also in Ar. While it is not possible to pinpoint precisely the transition temperature in either case it has certainly occurred by approximately 80% of the 2D bulk melting point. The low temperature grain boundary structures for both systems are well-ordered crystalline structures. The high temperature structures are qualitatively characterized by a high amount of disorder, with the appearance that the grain boundary has been replaced by a liquid-like layer of higher mobility than the low temperature grain boundary phase. More quantitative characterization of this high temperature grain boundary phase remains to be accomplished.

It is appropriate to point out that the effect of system size on both the melting and reorientation transitions deserve more systematic study. Qualitatively it seems clear that increasing system size should inhibit the reorientation transition. However, when we doubled the system size, we observed a reorientation to the same angle. A series of experiments is planned to quantitatively assess the number dependence of the excess thermodynamic properties of the boundary and to assess the effect of system size on reorientation kinetics.

In conclusion, we believe that our results indicate that this type of grain boundary phase transition may be common in many grain boundaries at elevated temperatures. It is also clear that the effect of such transitions on the high temperature physical properties of polycrystalline systems would be profound.

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