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## COMPUTER SIMULATION OF THE THERMODYNAMIC PROPERTIES OF GRAIN BOUNDARIES

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Résumé - On présente ici un calcul explicite des grandeurs thermodynamiques d'excès caractéristiques des joints de grain à partir de simulation de dynamique moléculaire. On s'intéresse particulièrement au calcul de l'énergie libre interfaciale en fonction de la désorientation du joint. On observe en outre des transitions de phase dans la structure du joint qui se traduisent par une réorientation spontanée des deux cristaux et/ou l'apparition d'un film quasi-liquide au niveau du joint.

Abstract - Methods are discussed for the explicit calculation of the excess thermodynamic properties of grain boundaries using molecular dynamics simulations in the NPT ensemble. Specific attention is focussed on techniques for the calculation of excess free energies. Results on the variation of interfacial free energy with misorientation are reported. In addition, observations of phase transitions among grain boundary structures are discussed, including grain boundary melting transitions and reorientation phenomena.

## 1. INTRODUCTION

Interest in the structure and physical properties of internal interfaces in solids has spawned the development of a variety of tools, both theoretical and experimental, for their study. One of the approaches that has been employed in a considerable number of studies is atomistic computer simulation, employing almost exclusively molecular statics techniques, using central pair-wise interatomic potentials. The results of such studies are rather difficult to quantitatively evaluate because of the current limitations on resolution of the corresponding experimental methods of probing structure, but some qualitative agreement has, in certain cases, been attained. Several rather severe limitations are inherent in molecular statics simulations in general, and additional limitations arise through the methods with which they have been applied to grain boundaries in particular. The most major intrinsic limitation of the molecular statics method is the obvious one: one accesses, at best, the  $T=0$  structure of the system, and those properties which are functions of instantaneous coordinates only, such as the internal energy of the system. The vast majority of the interfacial properties and processes of interest to materials scientists, such as diffusion, migration and deformation, occur at finite temperatures. To answer even such comparatively simple questions as the relative stability of different interfacial structures becomes impossible in the regimes of interest. In addition to its intrinsic limitations, the molecular statics calculations of grain boundaries have been limited by additional constraints. Often the atomic relaxations that are allowed in searching for local minima in the energy of the system are a severely constrained subset of the conceivable relaxations for an actual grain boundary. Sometimes the excess volume of the grain boundary is constrained to be zero because the interatomic potential functions employed in the simulation are derived for constant electron density.

Many of the intrinsic limitations of molecular statics simulations are relieved by use of dynamical simulation techniques, such as molecular dynamics or Monte Carlo. In this paper we discuss methods of calculating thermodynamic properties of grain boundaries using molecular dynamics. As will be shown, a number of properties are obtained with relative ease, while others, such as entropy, require considerable work. Techniques for calculating interfacial excess entropy will be described and results presented. Our goal is to systematically investigate the phase diagram of a boundary, considered as an independent thermodynamic entity. Because thermodynamic properties of grain boundaries depend on a number of geometrical parameters, in addition to the more typical ones characteristic of bulk phases, the types of phase transitions that a grain boundary may undergo are rich and varied. In this paper we describe two types of grain boundary phase transition that we have observed in our molecular dynamics simulations of two-dimensional Lennard-Jones bicrystals. The first is a melting transition in which a grain boundary which is a well-defined crystalline entity at low temperature is replaced at approximately 80% of the bulk melting point with a disordered liquid-like layer of high mobility. The second phenomena we have observed is the relative reorientation of a bicrystal from one well-defined grain boundary orientation into another as the temperature is changed. Both transitions are reflected in discontinuities in the calculated excess properties of the system.

## 2. GRAIN BOUNDARY PHASE EQUILIBRIA

Before discussing how molecular dynamics techniques are used to calculate excess thermodynamic properties of grain boundaries it is useful to recall how they are defined. Following Gibbs' classical development of surface thermodynamics (1) we can define the excess thermodynamic properties of an interface, or any other defect for that matter. The excess value of any extensive thermodynamic property of a defect is simply defined as the difference between the value of the property in a system containing the defect, in our case a bicrystal, and its value in a reference perfect crystal system. A phase transition of a defect is then defined in terms of discontinuities in the calculated, or measured, excess properties, in regions where the bulk phases are stable.

The study of phase equilibria of crystalline defects is considerably enlivened by the functional dependence of their properties on various geometrical parameters. The fact that the thermodynamic properties of grain boundaries depend on these geometrical parameters raises the possibility of interesting classes of phase transitions that have no direct analogy in the corresponding bulk phases. These geometrical parameters are involved in the idealized description of the creation of the defect. For the case of a planar crystalline interface they are 10 in number. Four describe the transformation, such as rotation, reflection or inversion which generates one crystal from the other. Three more describe any relative rigid body translation between the two crystals, and three are required to specify the exact location of the interface plane. All of these parameters, with the exception of the parameter describing the chirality of the transformation operation, will, in general, undergo relaxations. Experiment or theory will usually fix the values of some of the parameters, allowing the others to relax to constrained equilibrium values. Under certain conditions changes in the geometrical parameters will mark the occurrence in interfacial phase transitions. The types of transitions that can, in principle, occur are rich and varied. Facetting transitions involve changes in the parameters describing the location of the boundary plane (2). A boundary plane orientation that is stable under certain conditions may be replaced by two or more differing orientations as the conditions are varied. Another phenomena that can occur involves changes in the parameters which describe the relative misorientation between the two crystals. Similar changes can occur in the parameters describing the rigid body translation between

the two crystals. Of course there is also the possibility that interfacial phase transitions occur which do not involve changes in the geometrical parameters, though this will be the exception rather than the rule. Such transitions can include grain boundary melting transitions, which have been observed in a variety of studies, or displacive interfacial phase transitions.

The dependence of the thermodynamic properties of grain boundaries on the geometrical parameters also causes symmetry arguments to become extremely powerful in the study of phase equilibria of such defects. In particular, through knowledge of how the symmetry changes with the geometrical parameters one is able to locate positions on the grain boundary free energy surface which must, by symmetry, be extrema (3). These symmetry dictated extrema, then, serve as logical starting points for computer simulation studies of grain boundary properties.

The evidence that exists to date concerning grain boundary phase transitions is somewhat skimpy. There have been a number of theoretical studies which indicate that low  $\Sigma$  tilt boundaries undergo a transition to a melted layer. These include a lattice gas study (4), and several molecular dynamics studies (5-7). On the experimental side, there is the TEM study of Glicksman and Vold, in which certain boundaries are observed to be replaced by liquid layers (8). Recently, Watanabe and co-workers have seen interesting indications of a grain boundary phase transition through measurement of the activation energy as a function of temperature for grain boundary sliding for well characterized bicrystals (9). In this paper we will present results on molecular dynamics studies in which both melting and reorientation transitions are observed.

### 3. MOLECULAR DYNAMICS CALCULATIONS OF THERMODYNAMIC PROPERTIES

In this section we briefly describe how molecular dynamics techniques are used to calculate excess thermodynamic properties of defects in general, and of interfaces in particular. As was pointed out in the previous section, excess thermodynamic properties of a defect can be unambiguously defined through the use of perfect crystal reference states. Therefore it will be important to establish the thermodynamic properties of the bulk.

We begin by recalling what molecular dynamics is. Molecular dynamics is a computational technique whereby the classical mechanical equations of motion of a system of molecules or atoms are solved numerically. Given initial coordinates and velocities of each atom, and an interatomic potential function, the trajectories of each atom in time are calculated. The constraints imposed on the system, such as periodic or fixed border conditions, constant pressure or constant volume vary from simulation to simulation. The output of a molecular dynamics run is the coordinates and velocities of each atom at each time step. Our task is to calculate the properties of the system from these quantities.

Many thermodynamic properties are directly obtainable from a MD simulation. These are those properties which are defined in terms of instantaneous coordinates and/or velocities, and thus are defined at each time step. This category of properties includes internal energy, pressure, enthalpy, temperature, and density. The thermodynamic value of such a property, then, is simply the time average value. Clearly one will only be able operationally to calculate such an average if the system is at least metastable, and remains in the state of interest for sufficiently long times.

Calculations of entropy, and hence such quantities as free energies, however, are not obtainable in so simple a fashion. This is because they are not expressible as ensemble averages and require knowledge of the partition function of the system. There are several techniques by which molecular dynamics methods

may be used to estimate free energies. The simplest approach that we have used to estimate free energies is due to Hoover (10). It consists of a direct evaluation of the canonical partition function within the quasi-harmonic approximation. Under this approximation, the total potential energy of the system can be written as a quadratic form in the particle displacements,  $u_i$  :

$$U = U_0 + 1/2 \sum_{i,j} k_{ij} u_i u_j$$

Carrying out the integration of the partition function one finds the partition function to be proportional to the inverse square root of the determinant of the matrix of the force constant coefficients  $k_{ij}$ . The proportionality constant is a function of the static lattice potential  $U_0$ , temperature, volume and number of particles. For a system under periodic boundary conditions the determinant vanishes due to the existence of displacements for which no restoring forces are involved, such as translation of the crystal. This motion is then constrained by pinning one particle in the system. The new determinant will be the determinant of a matrix built from the original force constant matrix by removing rows and columns corresponding to the fixed particle. The force constant matrix is calculated from an average structure generated in a MD simulation. Clearly this method has limitations intrinsic to the quasi-harmonic approximation, and is not useful except at low temperatures.

We have used a second, more generally applicable method called computer calorimetry (11) to calculate free energies. The crux of this method is that one is able to express ratios of partition functions, between the system of interest and a reference system, as an ensemble average. This allows us to compute differences in free energies. The reference system differs from the system of interest in its interatomic potential function. If we choose a reference system of known free energy, we are then able to calculate explicit values for the free energy of the system of interest.

In our grain boundary studies the system of interest is characterized by a Lennard-Jones potential,  $U_1$ , and the reference system is characterized by a Hooke's law type potential,  $U_0$ . We then construct two normalized distribution functions  $h_0(x)$  and  $h_1(x)$  in the independent ensembles generated by  $U_0$  and  $U_1$  :

$$h_0(x) = \int \delta(U_0 - U_1 - x) \exp(-U_0/kT) d\mathbf{r} / \Delta_0$$

$$h_1(x) = \int \delta(U_0 - U_1 - x) \exp(-U_1/kT) d\mathbf{r} / \Delta_1$$

Here  $\Delta_i$  is the isothermal-isobaric partition function of system  $i$ , and  $\delta$  is the Dirac delta function. These functions,  $h_i(x)$ , can be estimated in a molecular dynamics simulation by compiling a histogram of the frequency of occurrence of states with potential energy difference  $U_0 - U_1$  between  $x - dx/2$  and  $x + dx/2$ . The free energy difference is then given by:

$$\exp[-(G_0 - G_1)/kT] = \Delta_0 / \Delta_1 = \exp(-x/kT) [h_1(x) / h_0(x)]$$

When the two distributions overlap completely or partially, any point  $x$  in the overlapping region can be picked, and the free energy difference obtained from the above expression. When no overlap occurs but the histograms are significantly broader than  $kT$  and separated by a gap not much broader than the histograms themselves, extrapolation of the two functions  $\ln h_0(x) + x/2kT$  and  $\ln h_1(x) - x/2kT$  gives good estimates of  $G_0 - G_1$ . When no overlap occurs, and the gap is large, a multistage sampling must be used, in which one invokes intermediate potential functions to bridge the system to the reference system.

When the techniques described above are applied to calculate the excess properties of crystalline defects additional work is involved. We must establish also the thermodynamic properties of the bulk reference system including any number and shape dependence. Then the excess thermodynamic properties of the defect are found by taking the difference in those of the defected system and the perfect crystal reference system.

#### 4. RESULTS OF OUR MD SIMULATIONS

The molecular dynamics technique we used is based on an extension due to Parinello and Rahmann (12) of a Lagrangian formulation due to Andersen (13). In this so-called flexible borders technique, the simulation cell edges are dynamic variables, allowing the cell to change both size and shape in the course of the simulation. This technique is extremely important for the study of phase transitions, which can often be prevented from occurring if one has a fixed cell.

Periodic boundary conditions were employed. Particles in our system were interacting through central pair-wise interatomic potentials. Most of the calculations were done with a Lennard-Jones potential:

$$V(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6]$$

with parameters chosen to simulate argon ( $\epsilon = 119.79$  K and  $\sigma = 3.405$  Å). However a Hooke's law type potential,

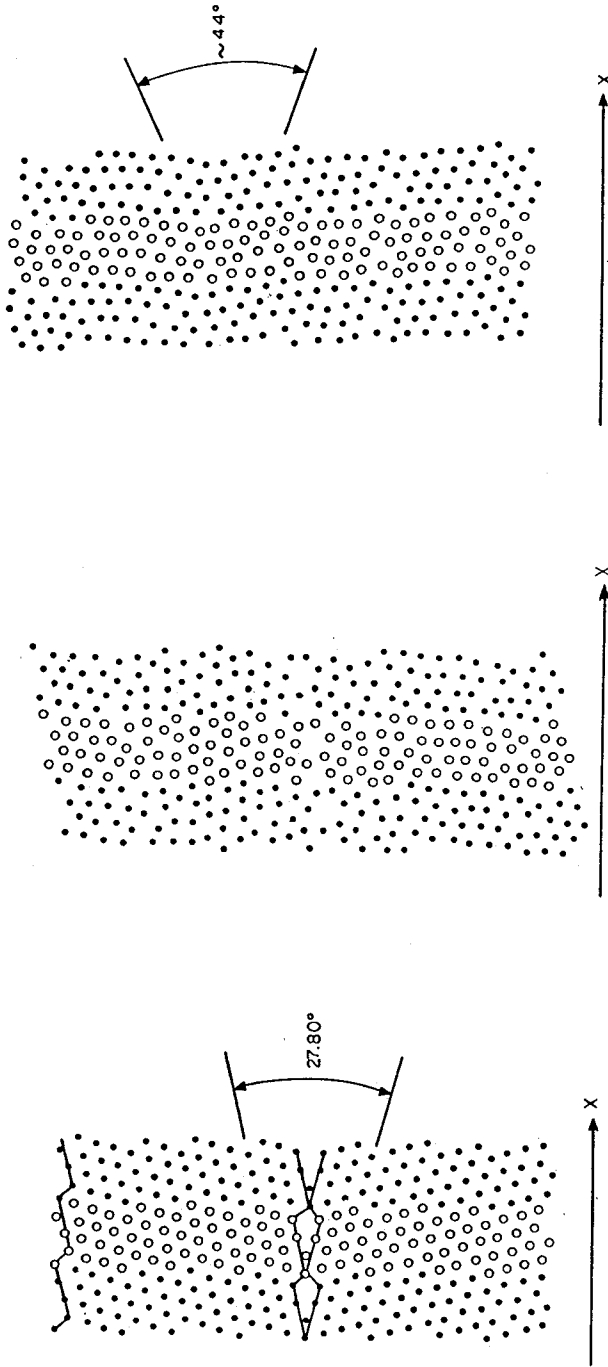
$$V(r) = \epsilon / \omega^2 [r - (\sigma + \omega)]^2 - \epsilon$$

with  $\omega = (2^{1/6} - 1)\sigma$  was utilized as reference system for the free energy calculations. The equations of motion were solved by the finite difference method.

##### 4.1. Grain Boundary Phase Transitions:

We investigated a two-dimensional  $\Sigma = 13$  ( $\theta = 27.80^\circ$ ) tilt boundary with 110 particles using the flexible borders technique with Lennard-Jones interactions between first neighbours. Enthalpy and density of the system were calculated over a wide range of temperatures and at a reduced hydrostatic pressure  $P^* = P\sigma^2/4\epsilon$  of 0.4936. In order to decrease the energy of the rigid system, one particle in the boundary overlapping too closely with its neighbours was removed. The relaxed structure, shown in Fig. 1, was obtained by holding the system at low reduced temperatures  $T^* = T/4\epsilon = 0.01$  for long times and calculating the time-averaged atomic coordinates. Heating the bicrystal to 80% of the bulk melting point and cooling it back down to  $T^* = 0.01$  gave an identical enthalpy value confirming that this relaxed structure is a well-defined local minimum.

The results of the study of the variation of bicrystal enthalpy and volume with temperature are plotted in Fig. 2. The low temperature grain boundary is a well-defined periodic entity. Above  $T^* = 0.16$  the entire system melts. In the range of temperatures  $T^* = 0.14 - 0.15$ , where a discontinuity in bicrystal enthalpy and density occurs, two phenomena are observed.

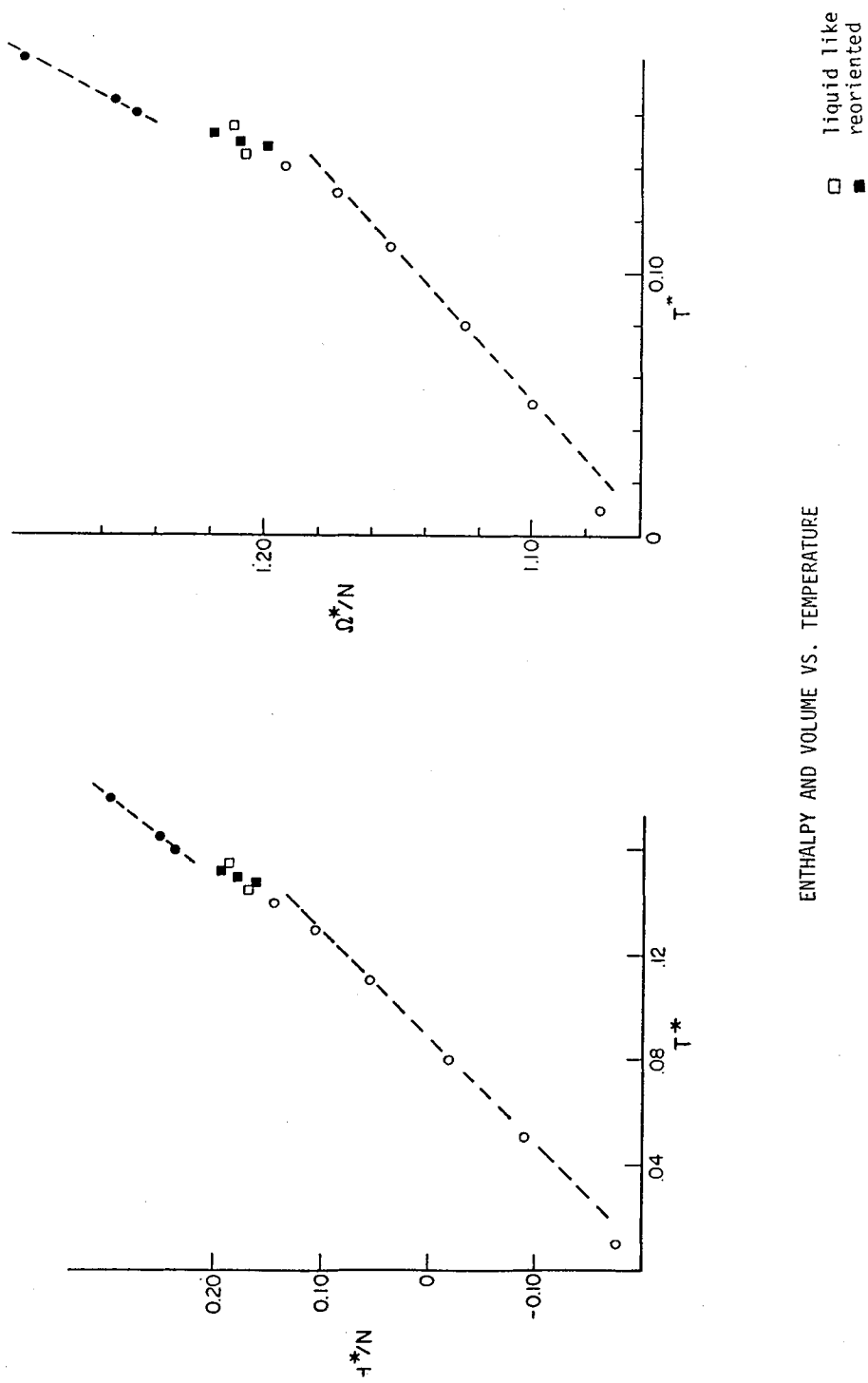


REORIENTED BICRYSTAL

"LIQUID LIKE" GB

GB  $\Sigma=13$

Fig. 1. Structures assumed by the  $\Sigma=13$  bicrystal. The open circles represent particles inside the simulation cell, while the black dots represent two of the eight image cells. a) The time-averaged low T relaxed structure. b) Structure of the liquid-like layer after the transition. c) The reoriented structure.



ENTHALPY AND VOLUME VS. TEMPERATURE

FIG. 2. Reduced bicrystal enthalpy and volume per particle versus reduced temperature. The open circles represent the low T behaviour of a perfect  $\Sigma=13$  bicrystal. The black squares represent the bulk liquid system. The open and black squares stand respectively for a liquid-like interface and a reoriented bicrystal.



The first is the replacement of the boundary by a liquid-like layer, which is visible in Fig 1b. This is the phenomena that we call the melting transition. It is similar to the melting transition observed previously on a  $\Sigma = 7$  grain boundary (5). From our data we estimate the grain boundary melting temperature to be 80% of the bulk melting point.

The second phenomena we observe in the high temperature region, but below the bulk melting, is the reorientation phenomena. The misorientation characterizing the bicrystal changes from 27.80 to approximately 44°. This structure is shown in Fig. 1c. The small width of the cell may make the reorientation transition easier to effect, because of coupling between the cell and its images, but it has no effect on the relative stability of the initial and final phases. This reorientation transition was not observed in the study of the  $\Sigma = 7$  bicrystal, and, in fact, has not been observed in any previous study.

#### 4.2. Free Energy Calculations

The two techniques to calculate free energies were tested on 2d close-packed perfect crystals with different sizes and geometries. The determinant technique was applied on both Lennard-Jones and Hooke's law type crystals to compute their Helmholtz free energies. Gibbs free energies of the Lennard-Jones crystals were estimated by computer calorimetry using the previous Hooke's law type crystals as reference systems.

Systems having 52, 104 and 208 particles with first neighbour interactions were investigated at reduced temperatures which were low but high enough to be above the Debye temperature ( $T^* = 0.04$ ) so that they are in the classical limit. The free energy and entropy results obtained by the two techniques are in good agreement: within 5% for the entropy and less than 3% for the free energies. The results are tabulated in Table 1.

General trends besides the expected temperature dependence of free energies and entropy can be extracted. The looser the system is, the higher (in absolute value) the free energies and entropy are, a narrow well potential and bulk shape system making a crystal stiffer. The data we gathered have not enabled us to establish quantitatively the number dependence of the thermodynamic properties. Meanwhile, qualitatively, whatever the potential is, energies and entropies increase (in absolute value) with the number of particles simulated. We studied the effect of second neighbour interactions on thermodynamic properties of the Lennard-Jones crystals. Second neighbour interactions make the systems stiffer and therefore lower the entropy, while the energies are decreased due to more potential energy.

Similar results were observed on  $\Sigma = 7$  and  $\Sigma = 13$  bicrystals, and are given in Table 3. Direct evaluation of the force constant matrix was not possible due to grain boundary migration. We then employed a biased method consisting of artificially expanding to match the volume at the desired temperature an average structure generated at lower temperature where migration does not occur. This pseudo determinant technique unfortunately yields relatively high discrepancy with computer calorimetry entropies, which are more reliable.

Excess thermodynamic properties per unit length of grain boundary were calculated from the computer calorimetry and determinant technique data respectively in the case of first and second neighbour interaction. The results are given in Table 4, which also lists the reference perfect crystals. The  $\Sigma = 7$  grain boundary has a slightly lower excess energy and higher excess volume than the  $\Sigma = 13$  boundary. The entropies, however, differ by a factor of 10 in favour of the  $\Sigma = 7$ , at the temperatures studied, qualitatively due to a looser boundary

structure. The free energy of the  $\Sigma = 7$  is lower than that of the  $\Sigma = 13$ . We expect that in the series of close-packed 2d CSL boundaries entropy will decrease with the excess volume. Further calculations of a close-packed  $\Sigma = 19$  boundary will be made to investigate this phenomena.

N	GEO	PO	T*	V*/N	H*/N	DET			CC		
						S*/N	F*/N	G*/N	S*/N	F*/N	G*/N
52	8x7	h	0.055	1.071	-0.104	0.100	-0.638	-0.109	-	-	-
52	8x7	h	0.060	1.071	-0.094	0.260	-0.638	-0.110	-	-	-
52	8x7	h	0.065	1.071	-0.083	0.439	-0.640	-0.111	-	-	-
52	8x7	LJ	0.055	1.089	-0.102	0.856	-0.687	-0.149	0.883	-0.668	-0.151
52	8x7	LJ	0.060	1.093	-0.091	1.054	-0.694	-0.154	1.093	-0.696	-0.157
52	8x7	LJ	0.065	1.098	-0.077	1.241	-0.699	-0.157	1.307	-0.703	-0.161
104	8x14	h	0.055	1.071	-0.105	0.186	-0.644	-0.115	-	-	-
104	8x14	h	0.060	1.071	-0.094	0.397	-0.646	-0.117	-	-	-
104	8x14	h	0.065	1.071	-0.083	0.558	-0.648	-0.119	-	-	-
104	8x14	LJ	0.055	1.089	-0.102	0.971	-0.693	-0.156	0.935	-0.691	-0.154
104	8x14	LJ	0.060	1.092	-0.092	1.179	-0.702	-0.163	1.158	-0.701	-0.161
104	8x14	LJ	0.065	1.097	-0.079	1.386	-0.710	-0.169	1.382	-0.710	-0.169
104	4x28	h	0.055	1.071	-0.103	0.279	-0.647	-0.118	-	-	-
104	4x28	LJ	0.055	1.090	-0.101	1.018	-0.695	-0.157	1.055	-0.697	-0.159
208	8x28	LJ	0.055	1.089	-0.104	1.520	-0.725	-0.188	-	-	-

Table 1.

Perfect crystal thermodynamic data calculated by molecular dynamics, the determinant technique, and computer calorimetry, in the case of first neighbour interactions. GEO stands for the geometry of the system and is expressed in reduced units ( $r^* = r/\sigma$ ). PO stands for potential; LJ for Lennard-Jones and h for Hooke's law type potential.

N	GEO	PO	T*	V*/N	H*/N	DET		
						S*/N	F*/N	G*/N
52	8x7	LJ	0.055	1.076	-0.171	0.638	-0.738	-0.206
52	8x7	LJ	0.060	1.080	-0.160	0.876	-0.744	-0.212
52	8x7	LJ	0.065	1.084	-0.147	1.061	-0.751	-0.216
104	8x14	LJ	0.055	1.075	-0.174	0.718	-0.744	-0.214
104	8x14	LJ	0.060	1.079	-0.162	0.952	-0.751	-0.219
104	8x14	LJ	0.065	1.083	-0.150	1.149	-0.759	-0.225

Table 2. Perfect crystal thermodynamic data, for the case of second neighbour interactions.

N	GEO	PO	T*	V*	H*	DET+'DET'			CC		
						S*	F*	G*	S*	F*	G*
112	$\Sigma=7$ 6x21	h	0.055	121.65	-5.99	35.48	-67.98	-7.94	-	-	-
112	$\Sigma=7$ 6x21	LJ	0.005	124.63	-7.23	125.25	-75.63	-14.11	137.94	-76.33	-14.81
110	$\Sigma=13$ 4x30	h	0.055	119.59	-8.14	32.24	-68.94	-9.91	-	-	-
110	$\Sigma=13$ 4x30	LJ	0.055	121.50	-8.42	104.18	-74.12	-14.15	117.70	-74.86	-14.89

N	GEO	PO	T*	V*	H*	'DET'		
						S*	F*	G*
112	$\Sigma=7$ 6x21	LJ	0.055	122.80	-15.42	101.63	-81.62	-21.01

Table 3. Bicrystal thermodynamic data. 'DET' means that a biased determinant technique was used.

	L	PO	T*	V <sup>e</sup> /L	H <sup>e</sup> /L	S <sup>e</sup> /L	F <sup>e</sup> /L	G <sup>e</sup> /L	
$\Sigma=7$	5.925	LJ	0.055	0.427	0.695	3.331	0.301	0.512	1 <sup>st</sup> neighbor
$\Sigma=13$	4.036	LJ	0.055	0.390	0.675	0.339	0.460	0.653	1 <sup>st</sup> neighbor
$\Sigma=7$	5.901	LJ	0.055	0.407	0.700	3.598	0.301	0.502	2 <sup>nd</sup> neighbor

Table 4. Excess thermodynamic quantities of  $\Sigma=7$  and  $\Sigma=13$  grain boundaries.

## 5. DISCUSSION

The results of our molecular dynamics studies to date are intriguing, but they deserve more intensive study in the future. The method of calculating excess thermodynamic properties explicitly through the use of perfect crystal reference systems has the advantage that it allows us to pinpoint an interfacial phase transition unambiguously. However, it offers in itself little knowledge of the nature of the transition. Clearly an important task is to characterize the structure of the liquid-like layer after the transition and its variation with temperature more thoroughly and quantitatively. The quasi-experimental problems of assessing the structure of this layer are non-trivial because of its high mobility. The situation in fact mimics the experimental scenario when one tries to probe atomic structure of well-prepared bicrystals at elevated temperatures and the boundary leaves the bicrystal during the course of the experiment. However this is a computational inconvenience that can and will be overcome through the use of more imaginative though time-consuming computational techniques. To a large degree this is one of a large class of problems which arise due to the small sizes of our simulation cells, a problem that will be alleviated, but not eliminated, in the course of time as computational power increases. In the absence of the possibility of macroscopic scale simulation cells we must continue to try to systematically evaluate the dependence of the properties of the system on the size and geometry of the cell chosen.

A large unsettled question is the mechanism and kinetics of the reorientation transition. A detailed study of this phenomenon is planned for the  $\Sigma=13$  boundary and for others.

In the area of free energy calculation a large amount of work remains to be done. We are now capable of quantitatively evaluating the relative stability of different interfaces at finite temperature. Both the techniques for calculating free energies, however, have their annoying aspects. The determinant technique is limited in its validity to low temperatures. The computer calorimetry technique has its own intrinsic limitations. Both systems have to be defined on the same configuration space which means that we cannot use it to evaluate directly free energy differences between different boundary structures. We are then obliged to calculate explicitly the free energy of each structure, through the use of a reference system of known free energy. If our reference system has a limited range of applicability, as our quasi-harmonic reference does, then we will be limited severely in the regimes where we can effectively use computer calorimetry. It is clear that additional techniques for evaluating free energies of our systems will have to be developed.

It is our intention now to systematically evaluate the effect of grain boundary phase transitions on the physical properties of the interfaces. The properties we have chosen for particular attention are the grain boundary mechanical properties.

## 6. CONCLUSIONS

The conclusions we can draw from our study are the following. A transition, which we call a melting transition, occurs in the 2d tilt boundaries we have studied. The transition occurs at approximately 80% of the bulk melting point, and is reflected in discontinuities in the calculated bicrystal enthalpy and density. The transition is characterized by the replacement of a well-ordered periodic grain boundary with a liquid-like layer of high mobility. In one of our boundaries, the  $\Sigma=13$ , we observe another phenomena. The boundary orientation of  $\theta=27.80^\circ$ , which is stable at low temperatures, is replaced at higher temperatures with an orientation of approximately  $44^\circ$ . Details of the mechanism of this reorientation are currently unclear.

We have successfully developed techniques for calculating free energies of grain boundaries. We are thus now able to address for the first time the question of the relative stability of different grain boundary phases at finite temperature. Both techniques, the determinant technique, which invokes the quasiharmonic approximation, and the computer calorimetry technique have been applied to the study of the  $\Sigma=7$  and  $\Sigma=13$  grain boundaries and to their perfect crystal reference systems. We found the  $\Sigma=7$  boundary to be stable with respect to the  $\Sigma=13$  boundary at the temperatures studied due to its significantly larger entropy. The techniques for free energy calculation need to be expanded and improved.

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#### DISCUSSION

D.R. Clarke: Do your results reveal any evidence of faceting?

G. Kalonji: No. If one considers, though, the geometrical constraints artificially imposed on the system by the periodic boundary conditions, which may, in fact, mimic nature in the limit of small grain size, one can only conclude that the possibility of studying faceting depends directly on the computer budget. Wait a few months.