INTERFACIAL FREE ENERGY OF A TWO-DIMENSIONAL BICRYSTAL

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The grain-boundary free energy of a two-dimensional $\Sigma = 7$ bicrystal has been estimated by combining a quasiharmonic method based on evaluation of the partition function, with Monte Carlo energy sampling.

Free energies are fundamental to understanding the thermodynamics of solids [1]. Grain-boundary phase transformations in polycrystalline solids can be characterized in terms of the excess free energy per unit length associated with the different grains [2]. The determination of equilibrium grain-boundary structures at finite temperatures requires minimising constrained free energies, though frequently only the potential energy is minimised [3].

Computer simulations are efficient methods for sampling the configuration space of many-particle systems. These techniques have two advantages over static calculations [3]. Dynamical mechanisms can be followed, and thermal effects, including entropy and pressure, are included, thus providing estimates of the Gibbs or Helmholtz free energies [4]. In this letter we describe a general approach to calculating bicrystal grain-boundary free energies as a function of temperature, by combining lattice dynamics with Monte Carlo energy measurements. These methods can be applied to any bicrystal boundary with a stable quasiharmonic energy minimum. We use a piecewise-linear nearest-

neighbor force law. These results have interesting implications, and the methods used can be applied to other, two- or three-dimensional, solid interfaces.

We consider four different crystal sizes all of the shape shown in fig. 1. Each bicrystal contains a $\Sigma = 7$ (38.21°) coincidence boundary, with repeat length of $\sqrt{7}$ times the equilibrium interatomic spacing d. The interatomic potential leads to piecewise-
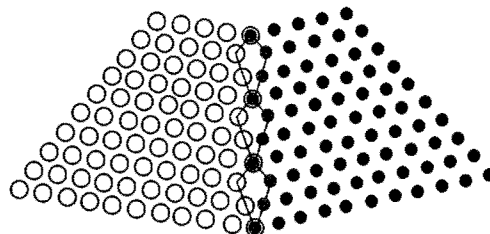

Fig. 1. A $\Sigma = 7$ (38.21°) bicrystal with $N = 150$ atoms and a grain-boundary length of $L = 3\sqrt{7}d$. The system can be converted to a 10 × 15 atom parallelogram by connecting the two sides after a relative out-of-plane rotation.

linear forces:

$$\phi(r) = \frac{1}{2}\kappa(r-d)^2 - \kappa w^2 , \qquad r < d+w ,$$
$$= -\frac{1}{2}\kappa(r-d-2w)^2, \qquad d+w < r < d+2w ,$$
$$= 0, \qquad d+2w < r .$$

For this potential the crystal bulk and surface properties have been characterized by Huckaby and others [5]. Here we illustrate the free energy calculation for the width parameter $w = 0.15\,d$. First, relaxed crystal structures were obtained by solving damped equations of motion, $m\ddot{q} = F - \alpha\dot{q}$. Five thousand time steps provided energy minima with machine (sixteen-digit) accuracy and forces less than $10^{-14}\,\kappa d$.

The classical canonical partition function can be evaluated at low temperatures, in the quasiharmonic approximation,

$$\exp(-A/k_B T) = Z_{QH}$$
$$= V(2\pi r)\,(\pi k_B T)^{N-1.5}(\mathrm{Det})^{-0.5}/\lambda^{2N} ,$$

where λ is the thermal de Broglie wavelength, $h(2\pi m k_B T)$, and Det is the determinant of a $(2N-3) \times (2N-3)$ symmetric matrix constructed by fixing particle 1 at the origin, $(x_1, y_1) = (0, 0)$, and placing particle 2 on the x-axis at a distance r away, $(x_2, y_2) = (r, 0)$. The matrix is the N-particle, $2N \times 2N$ force-constant matrix, with the 3 rows and columns, corresponding to x_1, y_1, y_2, removed [6].

By comparing the grain-boundary energies and entropies with those of perfect crystals, in our case parallelograms of 4×7, 7×11, 10×15, and 13×19 atoms, the energy and entropy data shown in table 1 were obtained. Plotting these data versus the reciprocal grain-boundary length gives the infinite-crystal

Table 2
Energies obtained by Monte Carlo sampling for constrained parallelogram and grain-boundary crystals with $N = 77$. Values shown are for 50 000 moves at each temperature (the last figure is uncertain). Bulk melting temperature is about $0.012\ \kappa d^2/k_B$.

$k_B T/\kappa d^2$	$\Phi_p/\kappa d^2$	$\Phi_{gb}/\kappa d^2$
0.003	−4.19	−4.06
0.006	−3.93	−3.79
0.009	−3.60	−3.43

quasiharmonic grain-boundary free energy,

$$\Delta A_{QH}/L = 0.0225\ \kappa d - 0.430\ k_B T/d ,$$

where L is the grain-boundary length. Earmme et al. found a grain-boundary entropy of $1.3\ k_B$ per atomic area for a $\Sigma = 5$ face-centered cubic model of aluminum [7]. Hashimoto et al. found similar results for the $\Sigma = 5$ case and considerably smaller entropies in the case of $\Sigma = 11$ [8].

To estimate the magnitude of *anharmonic* contributions (of order T^2 and higher) we performed Monte Carlo calculations of the energies of the 77 particle systems, grain-boundary and perfect crystal. System configurations were sampled with each particle constrained to lie within a circle of radius $d/2$ centered at its minimum energy position, and data up to 3/4 of the bulk melting temperature were obtained. Table 2 shows the results for the 77 particle systems. The difference between the Monte Carlo results and those of table 1 is the anharmonic contribution to the internal energy. Assuming this follows a T^2 variation we can integrate the energy difference to obtain an estimate of the coefficient of the T^2 contribution to the free energy. For the 77 particle grain-boundary system one finds the interface free energy per unit length to be

Table 1
Parallelogram and grain-boundary energies for two-dimensional crystals. Energy and entropy differences are tabulated. I is the moment of inertia. Infinite size extrapolations are also given.

N	I_p/md^2	I_{gb}/md^2	$\Phi_p/\kappa d^2$	$\Phi_{gb}/\kappa d^2$	$\Delta\Phi/\kappa dL$	$\Delta Sd/k_B L$
4×7	147	152.34	−1.4175	−1.3605	0.021559	0.54330
7×11	1078	1104.4	−4.4100	−4.2936	0.022005	0.48932
10×15	4037.5	4110.8	−9.0225	−8.8460	0.022165	0.46942
13×19	10868	11024	−15.2550	−15.0196	0.022244	0.45964
∞					0.0225	0.430

$$\Delta A/L = \Delta A_{QH}/L - 120(k_B T)^2/\kappa d^3 .$$

The anharmonic free energy shift is seen to be relatively large, such that the quasiharmonic approximation could be in error by a factor of two near melting.

The methods illustrated here should be equally effective with other potentials and three-dimensional systems. The simple size dependence, with corrections to $\Delta A/L$ of order $d k_B T/L$, found here suggests that extrapolating a series of small crystal calculations increases the accuracy of the estimated free energies. The determinant method for quasiharmonic free energy evaluation is orders of magnitude faster than the corresponding matrix diagonalisation. If necessary, quantum corrections can be included. The use of simulation techniques to estimate free energy of defect solids deserves further attention.

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