Calculation of Excess Volume and Width Histograms

Prior to performing detailed analyses of width histograms, we performed an analysis of premelting behavior based on the temperature dependence of the excess volume. The excess volume was calculated by time averaging over values for single configurations, computed as follows. For a single snapshot the excess volume was computed from the distance between two lattice planes, one in each grain. These planes were chosen in each grain such that they were far from the boundary and the free surfaces. The volume of material that would lie between the two planes in a perfect crystal can be computed by counting the total number of atoms between the two planes (including half of the atoms in each of the two planes) and multiplying that number by the volume per atom of the bulk crystal at the same temperature (and zero pressure). The difference between the actual volume and the expected bulk volume, divided by the area of the boundary, is the excess volume. A slight linear dependence of this measured excess volume on the distance between the planes was found, presumably the result of the numerical error in the lattice constant at high temperature. However, any consistent choice was adequate for our purposes here, as the excess volume results were used mainly to determine the qualitative nature of the premelting behavior, as discussed below. The specific planes chosen for the excess volume were 1/4 and 3/4 of the way through the simulation cell.

In order to compute equilibrium grain-boundary width distributions, $P(w, T_i)$, for a given interface temperature T_i, we proceeded as follows. For each snapshot the grain-boundary width w was determined using a scheme developed by Hoyt et al. [40] for the analysis of solid-liquid interface capillary fluctuations. In this approach each atom is assigned a structural order parameter, $\phi_i = \frac{1}{12} \sum_j \mid \vec{r}_{ij} - \vec{r}^{\,c}_{ij} \mid^2$, where r_{ij} are the actual positions of the 12 nearest neighbors of atom i and r^c_{ij} are the atom sites for the corresponding neighbors in the perfect crystal. The ϕ_i values are then averaged in bins along the direction normal to the boundary and the point of inflection in the average order parameter profile is taken as the position of the grain boundary. In the case of grain boundaries two separate profiles are required. The first uses r^c_{ij} for the crystal orientation of one of the two grains in the bicrystal, and for the second r^c_{ij} is chosen based on the other grain. After these two order