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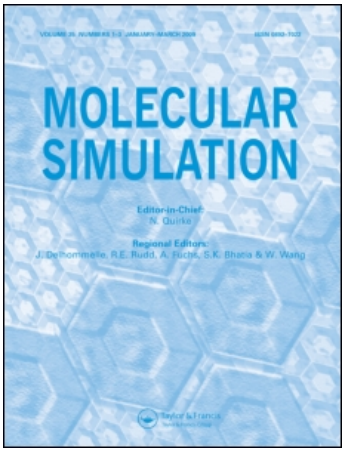

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Stephen J. Cook[a]; Paulette Clancy[a]
[a] School of Chemical Engineering, Cornell University, Ithaca, NY, USA

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SOLUTE TRAPPING AT A RAPIDLY MOVING SOLID/LIQUID INTERFACE FOR A LENNARD-JONES ALLOY

STEPHEN J. COOK and PAULETTE CLANCY*

School of Chemical Engineering, Cornell University, Ithaca, NY 14853, USA

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Non-equilibrium Molecular Dynamics simulation methods have been used to study the trapping of "impurities" in an $A_{85}B_{15}$ Lennard-Jones alloy where the B atoms are 10% bigger in diameter than A. The observation of surface melting in this system is used to calculate an equilibrium interfacial segregation coefficient. Simulations of rapid melting and resolidification were performed for the (100) and (111) orientations at two different substrate temperatures ($0.65\,T_m$ and $0.97\,T_m$) for each orientation. Solute impurity atoms are shown to have been trapped in the solid at greater concentrations than are obtained under equilibrium conditions. An apparent non-equilibrium segregation coefficient is calculated from these results. We observe that segregation of impurities occurs when the interface velocity is below the calculated diffusive speed of impurities away from the interface. Above this velocity impurities are unable to segregate into the liquid and are trapped in the rapidly-growing solid. Partitionless solidification is observed when the regrowth velocity greatly exceeds the diffusive velocity. This result is in agreement with the theoretical predictions of Aziz. The orientation of the crystal is found to have an important effect on the regrowth velocity. As expected, growth on the (111) face is less than half that on the (100) for identical substrate temperatures, but this does not enhance segregation over trapping due to the quite different solidification mechanism involved. Growth at the (111) face is found to proceed by the nucleation of a (111) surface ledge and its subsequent rapid passage. The (111) face is also found to involve a greater undercooling than (100) in agreement with the prediction of White *et al.*

KEY WORDS: Non-equilibrium computer simulation, Molecular Dynamics, crystal growth, impurity segregation, LJ alloys.

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1. INTRODUCTION

Rapid solidification, and other non-equilibrium crystal growth techniques, are of increasing technological importance in the preparation of semiconductors, metals, and ceramic materials. These techniques can produce new materials whose properties (electronic, mechanical and structural) are tailored for specific applications. The location and concentration of impurities has a marked effect on these properties. It is thus of considerable interest to understand the relationship between the nature of the impurity atoms and its response to the rapidly moving solidification front. It is well-known [1,2] that rapid solidification results in orders of magnitude greater incorporation of impurities into the crystal than is expected from equilibrium considerations; this phenomenon is known as "solute trapping". However, this relation-

*Author to whom correspondence should be addressed.

ship between the impurity and the solid/liquid interface is presently not well understood. The mechanism for the incorporation of atoms into the substrate is not known, nor is it understood which characteristics of the impurity are the most important in determining segregational behavior. The two entities (impurities and the interface) are expected to exert a mutual influence over one another but the nature of this influence remains unclear.

In order to try to answer some of these questions we have used a non-equilibrium Molecular Dynamics computer simulation method to follow the rapid melting and subsequent resolidification of a simple atomic system, a Lennard-Jones alloy $A_{85}B_{15}$ where A and B differ only in size. We shall determine the trapping and segregation of B atoms under both equilibrium and non-equilibrium conditions noting any structural or kinetic properties (transient as well as permanent) which may help elucidate the phenomena taking place.

The organization of the paper is as follows. Section 2 briefly reviews past work. Section 3 describes the details of the simulation method. Section 4 presents results for the observed surface melting and its implication for the calculation of the equilibrium segregation coefficient. Section 5 presents results for the non-equilibrium segregational phenomena produced during rapid solidification and the effect of changing the substrate temperature (and hence the undercooling of the system) and the crystal orientation. Finally, section 6 summarizes our findings for this hypothetical alloy.

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2. PAST WORK

The invention of splat cooling and similar large thermal quench techniques led to intense research into rapid solidification processing. The early studies focussed primarily on metallic alloys and especially on the formation of metallic glasses. In the early seventies, numerous groups also began studying the melt and solidification behavior of semiconductors under pulsed laser irradiation. These attempts at the "laser annealing" of silicon resulted from the desire to achieve liquid phase epitaxial regrowth on ion-implantation damage without impurity redistribution. It was later recognized that the rapid solidification technique also allowed non-equilibrium impurity levels to be achieved within silicon, albeit only metastably.

Semi-empirical methods are available [3] to determine the undercooling-interface velocity relationship for laser-inducing melting, but they provide little or no information about the mechanism for the observed kinetics. A considerable volume of theoretical work in this area has concerned the solution of moving-boundary coupled heat and mass diffusion equations. The initial work was performed by Baeri *et al.* [4], but much of the later work has been performed at Oak Ridge National Laboratory by Wood and co-workers [5] to develop a macroscopic description for pulsed laser processing. The theory was applied to silicon and to doped materials with good agreement between experimental and calculated dopant profiles. Studies of the non-equilibrium interfacial segregation coefficient were made to relate it to the interface velocity through simple expressions, again reasonably successful in reproducing experimental data. However, the interfacial segregation coefficient k_i is obtained by *fitting* the calculated theoretical results to experimental values. This work was extended [6] to the study of a variety of nucleation phenomena with the capability to allow phase changes to occur at temperatures other than the equilibrium values, thus allowing undercooling and overheating to be considered. While such numerical

modelling allows experimental results to be matched to phenomenological models, they fail to provide any fundamental information at the atomic level.

The seminal paper describing a theoretical picture of impurity segregation is due to Baker and Cahn [7] who showed that traditional theories of solid/liquid transition were unable to explain the composition of zinc-cadmium alloys obtained by splat cooling. While many theories for solute trapping have been proposed, notably due to Turnbull [8], the most interesting new theoretical treatment in this area is due to Aziz and Kaplan [9] in which, in an extension of Turnbull's work, the steady-state velocity of a planar interface is predicted together with the composition of the growing phase. This so-called Continuous Growth Model theory seems to provide a more quantitatively accurate picture of "solute trapping" than was obtained by other kinetic models. It assumes a sharp solid/liquid interface and that the impurities will not affect the interface morphology. The theory has successfully reproduced experimental results for Bi in Si [22] and for Ni in Cu [23], but the inability of experiments to measure individual parameters within the theory has prevented its complete validation. It is one of the goals of the present work to measure the values of individual parameters within the theory and to comment on its validity using these results.

Atomistic computer simulation studies of the dynamics and structure of the solid/liquid interface have been the subject of increasing attention, but these have almost exclusively been concerned with equilibrium studies and with pure substances. Of most relevance here has been the work of Broughton and Gilmer [10] in studying the properties of the equilibrium solid/liquid interface for LJ atoms. Landman and co-workers were the first to study the epitaxial crystallization of an undercooled melt of Lennard-Jones atoms using Molecular Dynamics computer simulation techniques [11]. Subsequent work [12] studied the non-equilibrium simulation of laser annealing for a system of 1500 Lennard-Jones (LJ) atoms, a binary mixture of 90% LJ "argon" and 10% "krypton" atoms, with the "impurity" Kr atoms initially randomly substituted into the fcc lattice. It was claimed that some impurity segregation at the free surface was observed, but this is not clear from the comparison of initial and final impurity distributions. We have developed a similar non-equilibrium Molecular Dynamics (NEMD) method to Landman *et al.*, but incorporating a different method of energy input and a simple method for taking into account the reflectivity change on melting. This NEMD method was used to follow the entire melting and freezing transient behavior of a system of LJ "argon" atoms [13].

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3. SIMULATION PROCEDURE

The configuration for the simulation cell to be used in our studies is shown schematically in Figure 1. The 'dynamic solid' region of the cell is a composite of two parts, a 'doped' section containing impurities and an undoped substrate below. The 'doped' section is made by assigning some of the N atoms to be impurity atoms (here, with a different size), initially distributed randomly on lattice sites among the substrate atoms. An isobaric-isothermal ensemble simulation (fixed NPT) at zero pressure is then run for each part for *at least* 50,000 time steps ($\sim$ 500 ps for a LJ system) in order to equilibrate them sufficiently. The two parts are brought together, a solid/vapor interface is created above the doped section, and several layers of atoms at the bottom of the underlying substrate (spanning a distance greater than the potential cutoff - 4 planes here) are designated as representing the fixed lattice. A heat sink, consisting of

a further three atomic planes, is employed to emulate the presence of an underlying substrate wherein the velocities of the particles are rescaled to maintain the substrate temperature. This configuration is then equilibrated further for 100,000 time steps, or until the interface is stable and immobile.

The positions of the atoms are separated into "layers" for property calculation. A layer is defined as encompassing those "n" atoms separated from the preceeding layer in the simulation cell by a certain distance in z, the height of the box. In the solid, by design, a layer will enclose a single crystalline plane. In the liquid, interlayer spacing ceases to be a meaningful concept. This criterion, however, is maintained in our analysis in order to determine the average composition of the disordered region in an equivalent volume. Progress was monitored by observing the two-dimensional pair correlation function, $g(r)$, diffusion coefficients via mean-square displacement data, the two-dimensional structure factor, $S^2(k)$, and by direct visual inspection via interactive computer graphics [14]. The order parameter is important in defining the width or extent of the disordered layer. The order parameter decreases from a value of 0.8 for the crystalline layers to 0.0 for a completely disordered liquid-like layer. We have decided, arbitrarily, that layers with order parameters above 0.4 (i.e. halfway between the fully ordered and completely disordered values) are designated as ordered and those below 0.4 are designated as disordered. The transition between order and disorder is quite sharp; the uncertainty in our assignation of layers as ordered or disordered is usually confined to one layer.

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The simulation results given here are for a system which contains 3000–3500 particles, depending on the orientation of the exposed crystal. This improves statistics, reduces the effect of the boundary conditions and distances the heat bath from the portion of the substrate affected by the 'laser'. For studies involving more than one component, especially one in low concentration, it is important to consider sufficient particles so that problems arising from poor statistical data be avoided. Even a system of 3500 particles has only 25 impurity atoms per layer on average, so we are repeating these calculations for a system of 7744 particles to study the size dependence of the results. The values of the properties (thermodynamic, etc) are calculated as an ensemble average over the particles in a two dimensional "slice" less than $1\sigma_A$ thick (where σ_A is the LJ collision diameter), so it is particularly important to have sufficient particles for adequate statistics. The procedure for property calculation is described fully in [13]. An impurity concentration of 15% was chosen to ensure planarity of the solidification interface while providing adequate counting statistics for the calculation of system properties relating to impurities. In some semiconductor alloys, a dopant concentration of only 3% could cause the interface to become unstable and lose planarity, although for others, such as As, the interface can tolerate up to a 15% As concentration. This fact contributed to our decision to employ a 15% impurity concentration, though it may well be that for the dimensions of our simulation box ($\sim 12.5\sigma_A \times 12.5\sigma_A \times 20\sigma_A$) the interface would remain planar at far higher concentrations of B. The chosen impurity concentration should not affect our calculation of the segregation coefficient, which has been shown experimentally to be largely independent of the impurity concentration [1].

For the simulation cell shown in Figure 1, we select the type of impurity, its concentration (via the number of impurity atoms), and the maximum depth to which impurities appear. The chosen substrate temperature is maintained with the aid of the heat bath. We select the orientation of the crystal lattice and choose an appropriate energy fluence and pulse duration. Here 'appropriate' is such that the interface

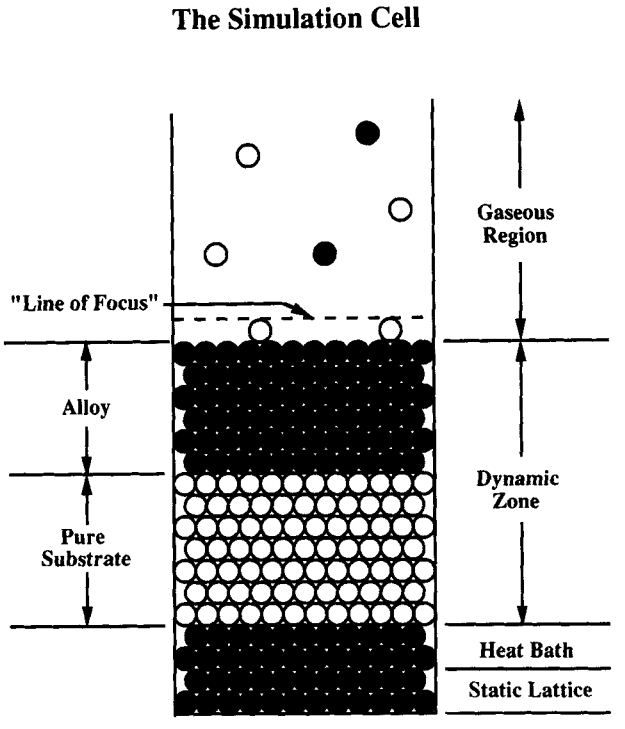

Figure 1 Side view of the simulation cell showing both the doped and undoped sections, as well as the static and thermostatted sections.

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extends into the substrate to a depth at least that of the maximum impurity depth, aiming at melting close to half the substrate. A description of the method we have developed to model for the energy transfer process is given fully in [13]. Thus, the conditions of our simulation closely emulate experimental conditions, and avoid many of the assumptions made by other theoretical attempts to model this phenomenon. For example, we *predict* (rather than fix in advance) the overheating and undercooling arising from the simulation of the physical set-up and processing conditions. We are also able to study both the melting and resolidification processes, whereas most other simulation studies focus on the resolidification alone. Although the resolidification is clearly the more important of the two, the study of melting under far from equilibrium conditions has intrinsic interest of its own.

4. RESULTS: SURFACE MELTING

Simulations performed at a reduced temperature, T^*, $= 0.4$ indicate that the crystal-vapor interface for both the (100) and (111) surfaces is characterized by simple termination of the bulk, with a small expansion (7.5%) in the interplanar spacing between the last two atomic planes at the vapor interface. The situation at the higher reduced temperature, $T^* = 0.6$, however, is dramatically different: All simulation variables clearly indicate the existence on both crystal faces of surface disordering

Table 1 Comparison of surface melting at the fcc (100) and fcc (111) faces of a Lennard-Jones $A_{85}B_{15}$ alloy.

*Layer number**	*Structure factor, S^2*		*In-plane diffusion coefficients/cm^2 s^{-1}*	
	(100)	*(111)*	*D (100)*	*D (111)*
1	0.19	0.06	3.7×10^{-5}	2.7×10^{-5}
2	0.40	0.40	2.7×10^{-6}	2.6×10^{-6}
3	0.67	0.67	8.6×10^{-7}	1.0×10^{-8}
4	0.8	0.8	8.4×10^{-8}	~ 0

*The lower the layer number, the closer to the vapour interface.

which has been called "surface melting" by previous workers. Although these disordered layers do not form a true bulk liquid phase, the properties of the two topmost layers are very much liquid-like, exhibiting diffusion coefficients of 10^{-5} cm^2/s and translational structure factors near zero. Table 1 demonstrates the nature of the interface formed by these surface-melted regions.

These surface-melted regions, furthermore, show an impurity segregation phenomenon characteristic of an equilibrium solid-liquid interface. At the beginning of the equilibration of the crystal/vapor interface there are approximately equal numbers of impurities in each layer. As the equilibration proceeds and the surface-melted layers become manifest, it can be observed that the impurity atoms prefer to reside in the liquid-like region. This segregation of impurity atoms into the surface-melted layers proceeds until steady-state values of x_S and x_L are obtained, as can be seen in the time-history shown in Figure 2. It is observed, in both cases, that the surface-melted region "strips" impurities out of the solid, but this effect is much more

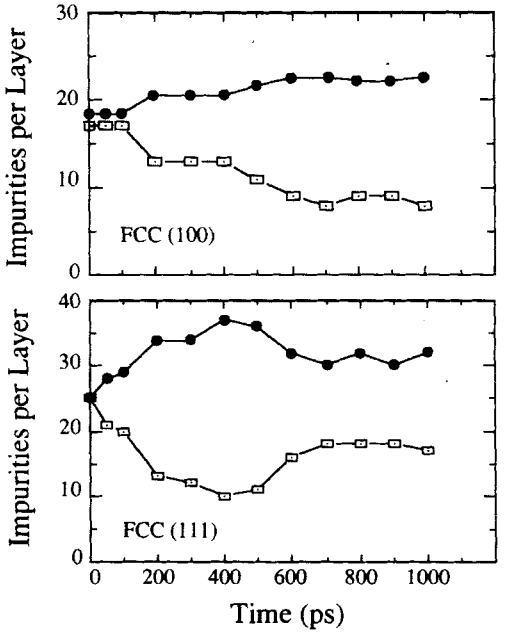

Figure 2 Time history of segregation phenomenon into the surface-melted region, shown here for both crystalline orientations studied.

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pronounced on the (100) face. It should be emphasized that this occurs only because we are measuring the *interfacial* segregation coefficient, k_i^e. The quantity obtained in most laser melting experiments is the *bulk* equilibrium segregation coefficient, k^e, which is a property of the bulk phases alone and is not affected by orientation. The alloy shows somewhat more disordering (on either face) than a pure LJ system (i.e. equivalent here to $A_{100}B_0$). Broughton and Gilmer [16] studied surface melting in a pure LJ system and found one layer to be disordered at this temperature. Our results for a pure LJ system at $T^* = 0.6$ using the order parameter criterion described earlier also concur that one layer is disordered. This observation, that the presence of impurities increases surface melting effects, is well-known experimentally. Indeed, the experimental studies for pure lead [17] which appear to show surface melting are still contested as being due to the presence of impurities.

Our major interest in this phenomenon is that a surface-melted region should represent a reasonable estimate of the equilibrium interfacial segregation coefficient, k_i^e defined as

$$k_i^e = \frac{x_S}{x_L}$$

where x_S and x_L are the mole fractions of the impurity in the solid and liquid respectively. Since, as mentioned earlier, the surface-melted region is not a bulk liquid phase but a thin film, we are in the process of simulating a static solid/liquid interface for this system in which the extent of the liquid phase is large enough to constitute a bulk liquid phase. The value of k_i^e thus calculated will be compared to that obtained from the surface-melted region. The advantage of using the surface melting to calculate k_i^e is that the surface melting is obtained as a by-product of the equilibration (i.e. it is a computationally-free "extra") for the non-equilibrium studies and does not involve a separate simulation.

Using data for the average impurity occupation of each "layer", we estimate the equilibrium interfacial segregation coefficient, k_i^e to be 0.30 for the (100) face and 0.61 for the (111) surface. These values are reasonable for systems in which the two components are not greatly dissimilar in size. Arsenic and phosphorus in silicon, for example, have k^e values of 0.30 and 0.35, respectively [18], although values for the interfacial segregation coefficient are experimentally inaccessible. Since a larger liquid region could be expected to enhance this segregation, the estimates obtained are most likely upper bounds on the true values of k_i^e.

5. RAPID SOLIDIFICATION RESULTS

A well-equilibrated solid with a reduced temperature of 0.4 (approximately 0.65 T_m) exposing a (100) face was subjected to a gaussian energy pulse of density 25 mJ/cm^2 over a period of 15 ps. A melt front initiated at the surface of the system and penetrated approximately $7.4\sigma_A$ (25Å) into the solid, well into the pure substrate underlying the doped region of the simulation cell. The temperature of the solid-liquid interface fell from a maximum of $T^* = 0.70$ through the equilibrium melting point ($T^* \sim 0.62$) to a steady-state temperature of 0.53, i.e. a 16% undercooling (almost identical to the undercooling produced by a pure LJ system). Very rapid melting was followed by rapid solidification through the pure material at 42 ms^{-1}. As the interface approached and entered the "doped" region, however, we observed a decrease in the

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interfacial velocity. This effect, which has been observed experimentally [19], occurs due to the change in the undercooling of the interface brought about by the difference in melting points of the two "materials". Although the temperature of the interface is constant across this boundary, the melting point of the LJ alloy is slightly lower than the melting point of the pure LJ material, leading to a smaller undercooling, and hence providing less of a driving force for solidification. As the temperature of the interface continued to drop due to the conduction of energy into the heat bath, the undercooling increased and the interface once again established a steady-state solidification velocity, 21 ms^{-1}, in the doped region. This velocity was maintained until the regrowth process was complete.

Calculation of the impurity densities and mole fractions as a function of position in the simulation cell indicated that the regrowing solid had the same composition as the liquid immediately preceding the passage of the solidification front. This solute trapping phenomenon is known as "partitionless solidification". Its appearance under these circumstances is consistent with the large solidification velocity observed. The maximum diffusive speed of the impurities, v_D ($= D_B/\lambda$ in [9]), can be approximately calculated by dividing the diffusion coefficient for a typical liquid close to the melting point, 1×10^{-5} cm^2/s, by the average spacing between atomic planes, $0.8\sigma_A$ or 2.74×10^{-8} cm for Ar. We obtain an estimate for v_D of 3.5 ms^{-1}, which is one-sixth the speed of the growing interface, indicating that the impurities had little opportunity to avoid being incorporated into the growing solid.

The interface morphology for the (100) face was studied throughout the duration of the simulation by observation of the 2-D pair correlation function, diffusion coefficients, the 2-D translational structure factor and via computer graphics. It was found that the growing (100) interface for this mixture was somewhat diffuse, representing a smoothly varying transition between a well-ordered solid and the liquid state, extending for ~ 3 "planes". This smooth structural transition, which can be observed in the layer-by-layer traversal through the interface shown in the photographs comprising Figure 3, has the effect that a new crystalline layer will begin to form before the layer beneath it is fully annealed. Impurities in the liquid, then, "feel" the influence of the growing solid long before they are incorporated into a region which possesses significant solid-like character. There seems to be no nucleation center from which growth has proceeded; rather, it appears that growth proceeds in a continuous manner where atoms are incorporated into the solid upon assuming available lattice sites. The growth does not appear to require an initial nucleation and so is quite rapid.

This simulation was repeated on the (111) face under identical conditions of the energy pulse as were used for (100). The interfacial undercooling here was found to be greater than for the (100) face, the steady-state temperature being $T^* = 0.47$ (i.e. a 25% undercooling). This agrees with the prediction of White *et al.* [1]. Although a larger undercooling usually yields a larger solidification velocity for a given face, the solidification velocity in the doped region for (111), 15 ms^{-1}, was smaller than the velocity obtained on (100) at a lesser undercooling, providing evidence that the (111) face solidifies via a different mechanism than the (100) face. This finding is consistent with experimental results for silicon as well as simulation studies of both pure Lennard-Jones atoms and the Stillinger-Weber model of silicon [20,24,25]. Examination of the interface using computer graphics, shown in Figure 4, also shows that the interfacial morphology is different than for (100). Whereas growth on the (100) face features a non-coherent growth of solid-like regions, the (111) interfacial region is

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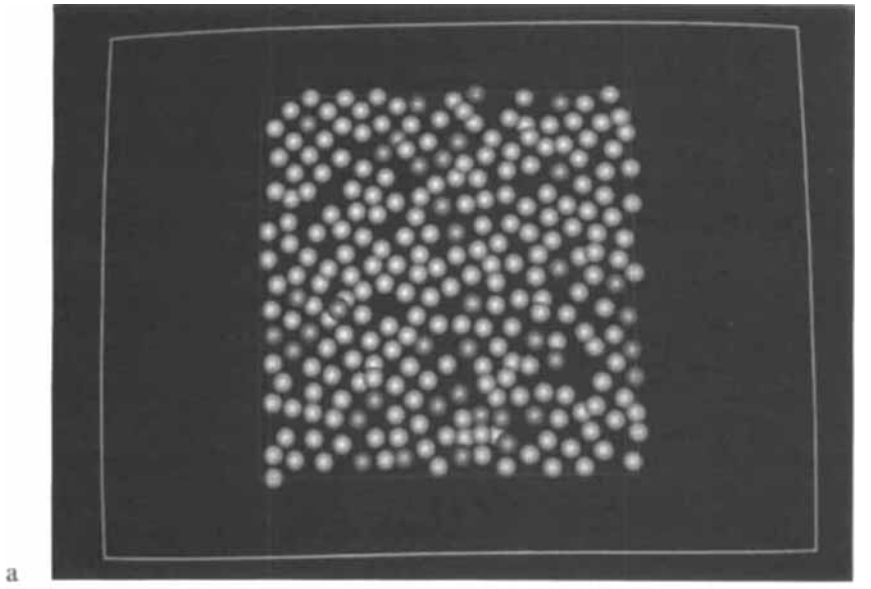

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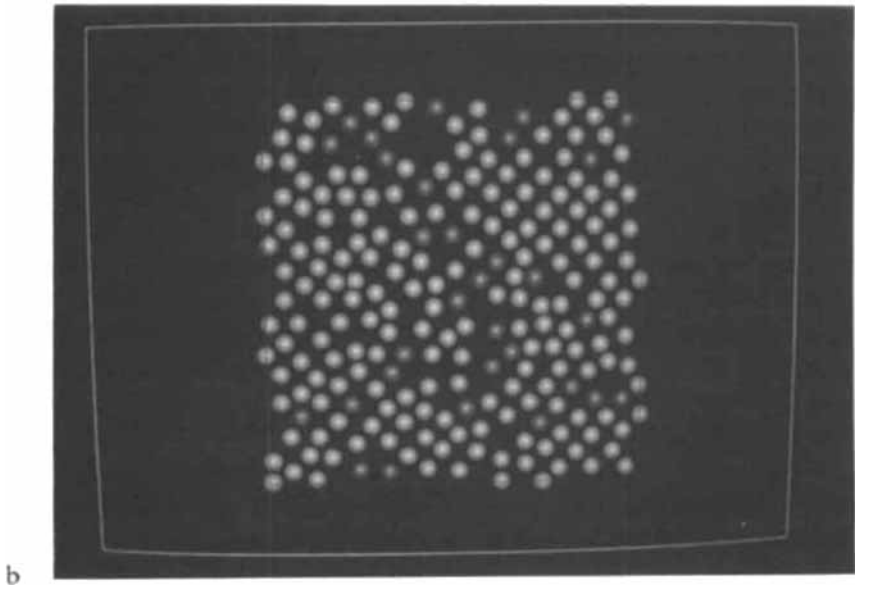

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Figure 3 (*See* colour plate I) Computer graphics snapshots of the interfacial region for rapid growth on (100) after 105 ps. Notice that the last defects to anneal are isolated point defects, a vacancy and an interstitial. Colour key: Blue planes are judged to be solid, magenta planes are interfacial and red planes are liquid. Impurity atoms are always coloured green.

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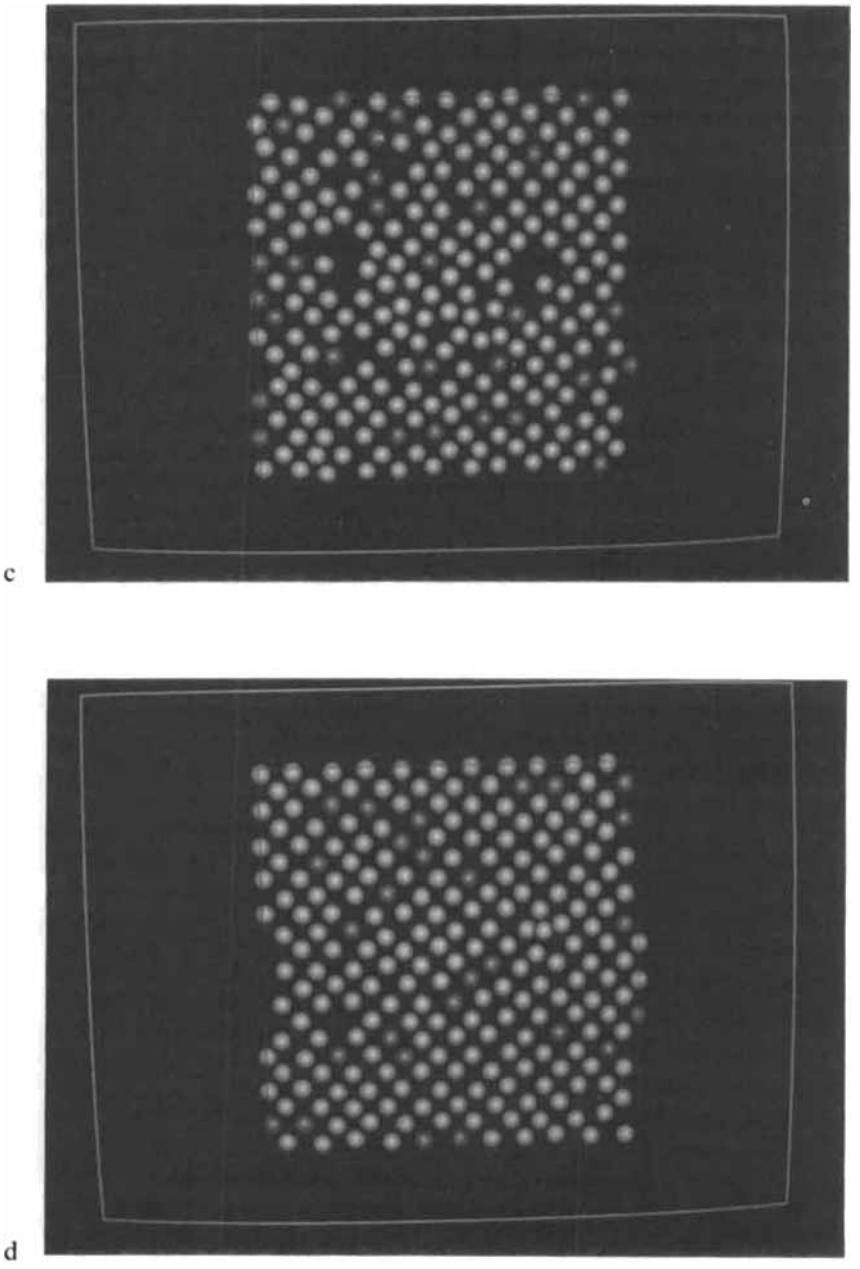

Figure 3 (*Continued*) (*See* colour plate II).

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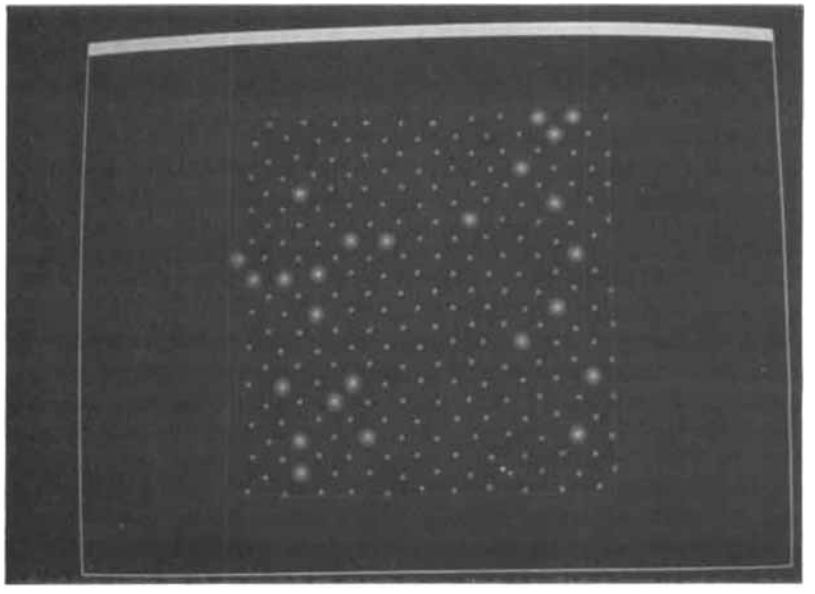

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Figure 3 (*Continued*) (*See* colour plate III).

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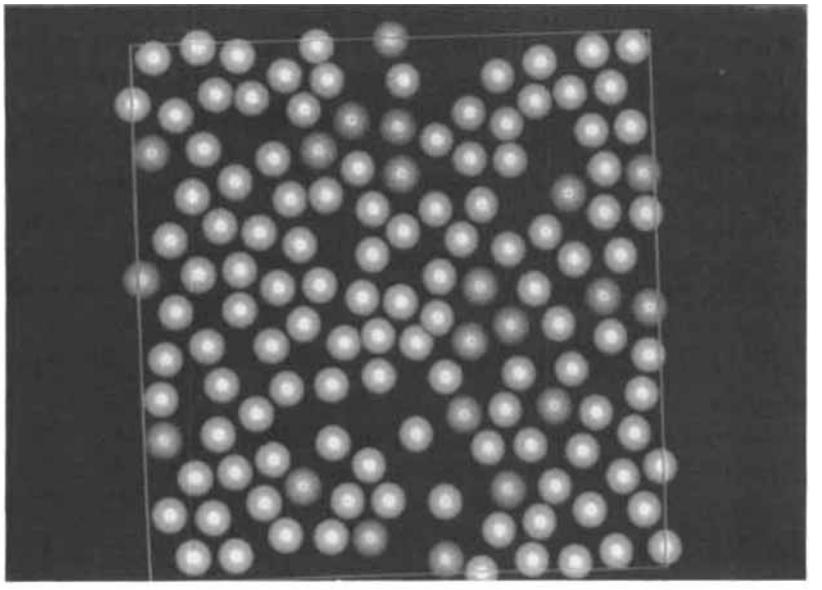
characterized by the nucleation of a (111) ledge which grows laterally to complete the plane. This can be seen clearly in Figure 4, and more dramatically in Figure 5. Further analysis showed that the regrown alloy contained numerous stacking faults. Burke *et al.* [20] have observed similar behavior in the growth of the (111) surface for pure LJ and suggested that the (111) surface grows as individual atoms find lattice positions in either the fcc and hcp arrangement which then serves as a template for the completion of the layer. It appears that the presence of impurities has not dramatically altered this situation (at this concentration, at least!), but the number of stacking faults has increased, presumably due to the extra interfacial stress brought about by the presence of the bigger impurity atoms.

The ramifications of this type of growth at a (111) face on impurity segregation are important. An impurity in a (100) environment, with its small sub-regions of order surrounded by disorder, has a greater ability to diffuse back into the liquid region than an impurity atom in the (111) case where impurities in the vicinity of the laterally-advancing ledge will only be able to escape capture by moving in the direction of the retreating disordered region. It is expected, therefore, that solute trapping will occur on the (111) face more readily than at the (100) face at similar regrowth velocities. Solute trapping of the impurities was complete on the (111) face, as determined from density profiles at locations immediately before and after solidification, although no comparison can be made with regrowth on (100) at this temperature, as complete trapping was seen on both faces due to the large regrowth velocities involved.

The simulations were repeated for both crystal faces at a higher reduced temperature, $T^* = 0.6$, approximately 97% of the melting point of this mixture. An estimate of the melting point, T_m (NEMD) $= 0.625$, was found from the intercept at



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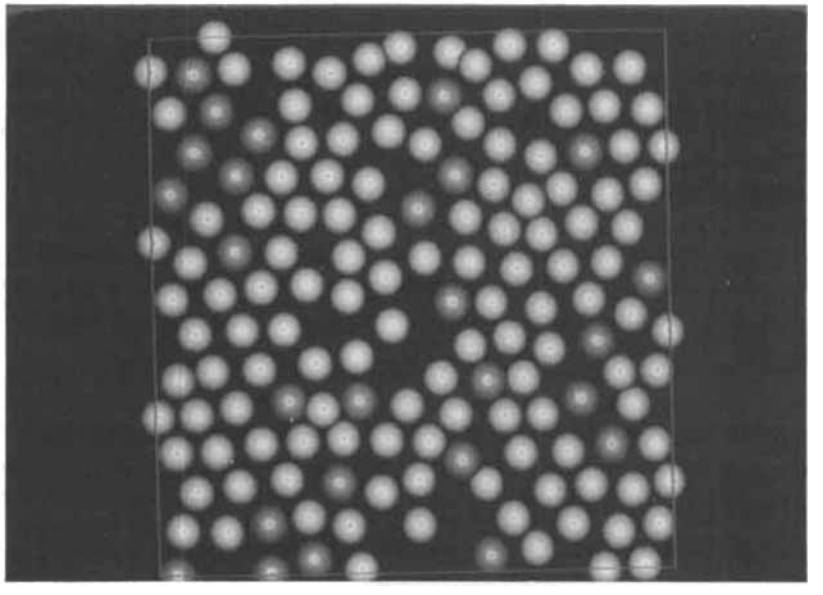

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Figure 4 (*See* colour plate IV) Computer graphics snapshots of the interfacial region for rapid growth on (111) after 150 ps. Nucleation 'proceeds, by lateral' annealing of the plane, evidenced by the extended vacancy region which finally ends in dislocation. Colour key as for Figure 3.

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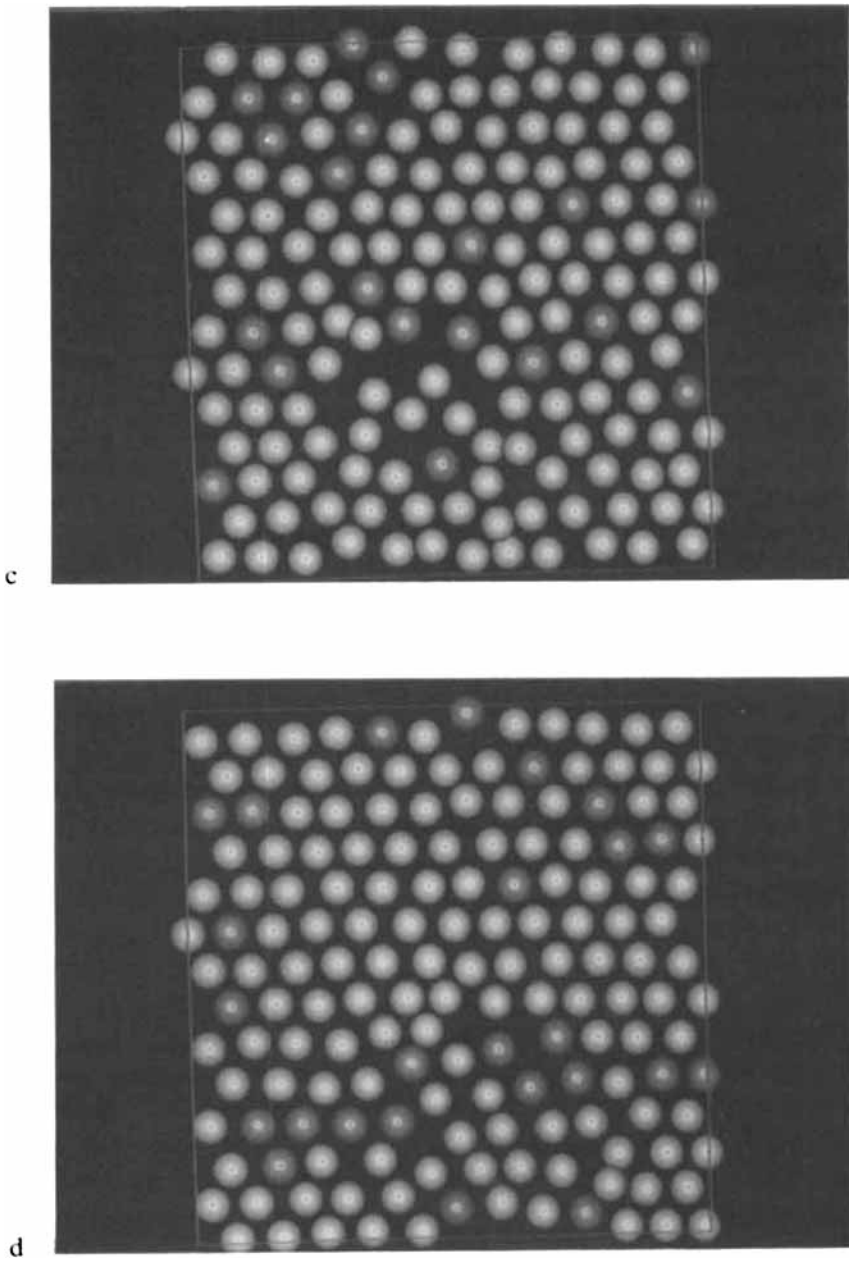

Figure 4 (*Continued*) (*See* colour plate V).

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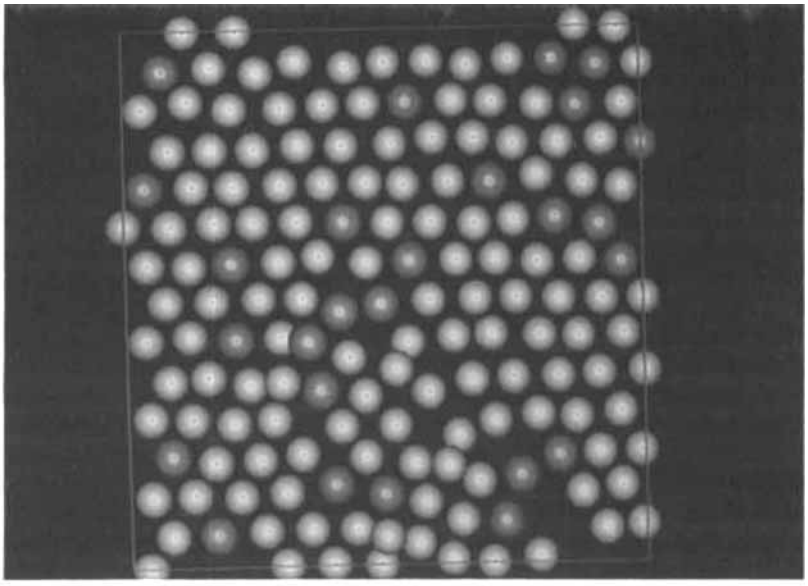

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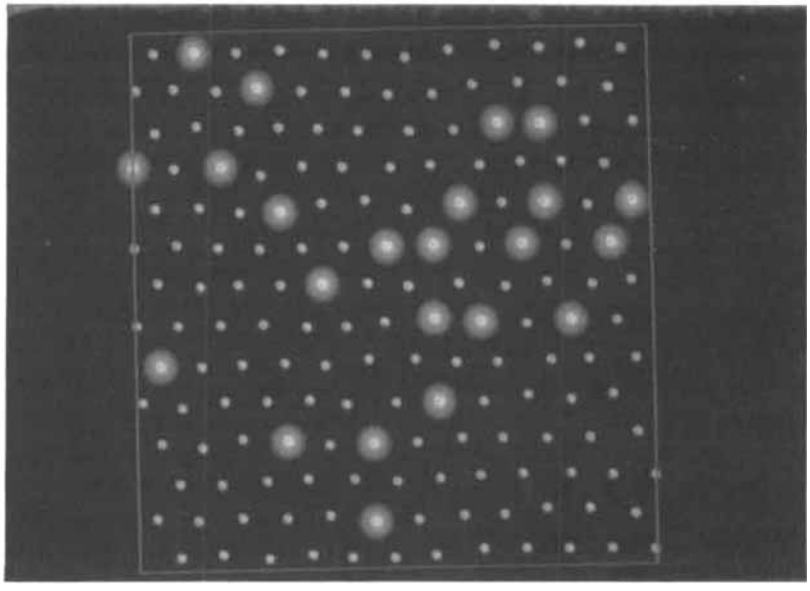

f

Figure 4 (*Continued*) (*See* colour plate VI).

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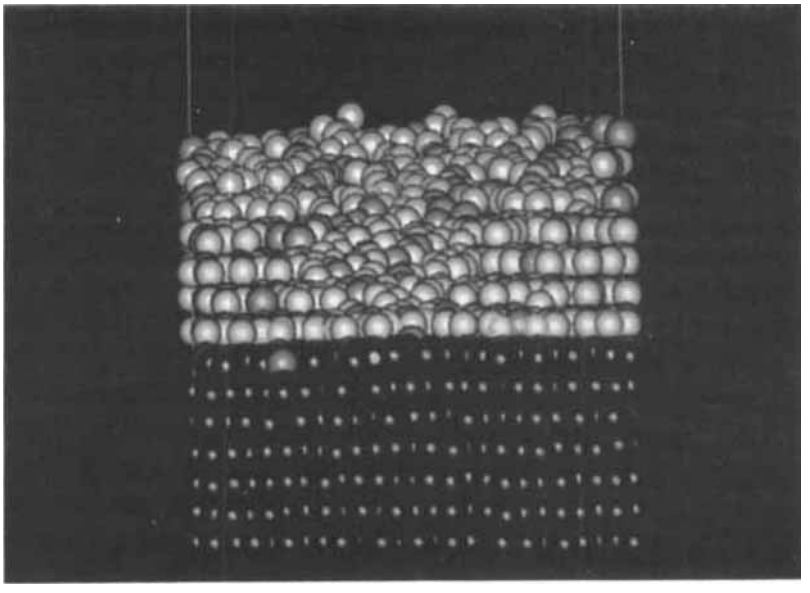

Figure 5 (*See* colour plate VII). Side view of the simulation cell during resolidification on the (111) face. Note that there is a V-shaped wedge of disorder in the center of the interfacial region, flanked on both sides by more ordered regions. Colour key as for Figure 3.

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zero velocity on the interface velocity - interface temperature plot using the non-equilibrium simulation procedure described in [13]. Equilibrium simulations of the NVT crystal/vapor interfacial system were performed at temperatures increased in 0.01 T^* steps from 0.60 to verify this result. These simulations indicate that the true melting point is actually $T^* = 0.62$. The melting points from the two routes thus agree to within 0.005 in T^*, which is quite good agreement. It was expected that much smaller resolidification velocities would be produced here than for the simulations performed at $T^* = 0.4$ due to the proximity to T_m. Thus our chances of observing segregational behavior over trapping should be enhanced.

The equilibrated configurations were subjected to an energy pulse identical to that used for the lower temperature simulations. Melting and regrowth on the (100) face proceeded in a manner similar to that seen for the lower temperature work, with one exception. As the solidification front emerged from the pure LJ section into the alloy region, the temperature of the interface was only slightly below the melting point of the mixture, causing the interface to slow to a speed of approximately $2\,\mathrm{ms}^{-1}$ for a period of time lasting no longer than 100 ps. There is some evidence of impurity segregation during that period, from observation of the density profiles. The atomic planes grown during this period have exactly the same number of impurities as were left in the uppermost solid plane is contact with the surface-melted region during sample equilibration. Figure 6 shows the presence of a large concentration of impurities in the liquid region immediately preceding the interface, where impurities diffusing into the initially pure material are being excluded from the regrowing solid in this region. As the undercooling increased due to heat conduction, the solidification

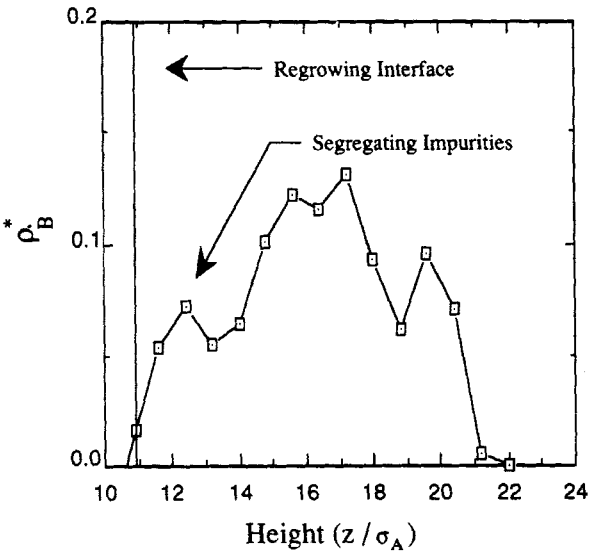

Figure 6 The density profile for impurities during regrowth on (100) after 150 ps at a reduced substrate temperature of 0.6. As the interface (shown by the vertical line) slows while moving from the undoped to doped region, modest segregation produces an excess of impurities in the liquid preceding the regrowing interface.

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velocity increased to approximately 4 ms^{-1} and solidification proceeded to completion with complete trapping of the remaining impurities.

At $T^* = 0.6$, the velocity at the (111) face slowed considerably relative to its value at 0.4, eventually reaching a steady-state velocity of only 1.7 ms^{-1}. This velocity was slow enough to allow modest segregation ($k_i' \sim 0.8$), although the high value of k_i^e of 0.6 prevented any dramatic effects such as zone refining. Figure 7 clearly shows that the impurity concentration profile was altered as the solidification interface (marked by the vertical line) proceeded through the liquid. Impurities are continuously swept out of the interfacial region into the remaining liquid. Of particular interest is the impurity profile at 700 ps, near the end of the regrowth period. Although the segregation effect was not dramatic, it is quite apparent from this profile than an excess of impurities have been pushed into the surface region, including solute atoms which had previously diffused into the bulk liquid away from the near-surface region.

6. SUMMARY

For an $A_{85}B_{15}$ LJ alloy, the following conclusions have been reached for a system of 3500 particles:

1. An estimate for the equilibrium interfacial segregation coefficient, k_i^e, was obtained from the surface disordering at $T^* = 0.6$ (i.e. 0.97 T_m). Its value was shown to be 0.3 and 0.6 on the (100) and (111) faces respectively.
2. For a rapidly-moving solid/liquid interface, the presence of the B atoms altered the

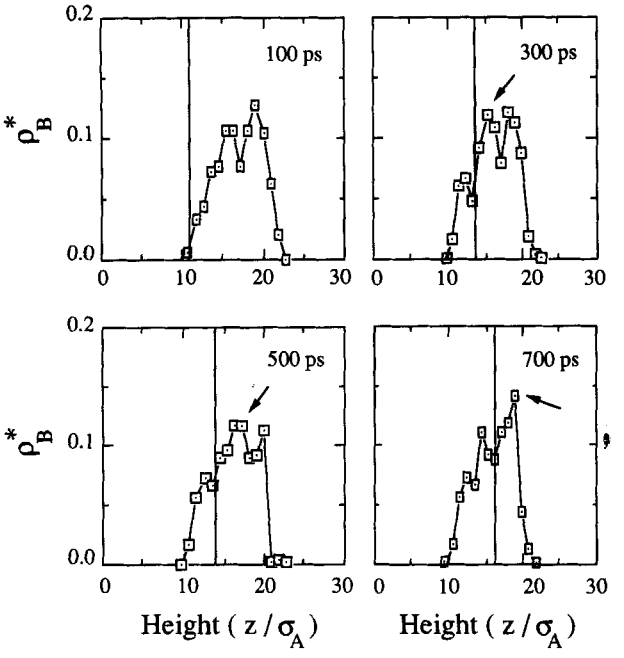

Figure 7 The density profile for impurities during regrowth on (111) at a reduced substrate temperature of 0.6. Regrowth here at 1.7 ms^{-1} allowed segregation of impurities during the entire regrowth process. The impurities segregated into the liquid are marked with an arrow and the solidification interface is marked by the vertical line.

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morphology of the solid/liquid interface. This fact is important in verifying the assumption made in theories such as the Continuous Growth Model of Aziz and Kaplan that the solid/liquid interface is sharp. Here the impurities reduce the extent of the interface from 5–6 planes for a pure LJ "Ar" system to 2–3 planes for the LJ alloy.

3. The mechanism for rapid solidification was quite different at the (100) and (111) faces. The (100) regrew in a continuous manner as atoms reached their proper lattice positions, while the (111) face regrew as individual planes nucleated and then annealed laterally. These mechanisms for growth in the alloy are quite similar to those found for pure Lennard-Jones atoms [20]

4. Observation of the initial, transient and final impurity concentrations as a function of position in the simulation cell shows that complete solute trapping is achieved when the steady-state resolidification velocity is above a critical value, shown here to be the diffusive velocity as calculated by Aziz and Kaplan, $v_D = D_B/\lambda$. This is, to our knowledge, the first confirmation of the principle tenet of the theory, namely, that the factor which mediates between segregation and trapping is the speed of the interface relative to the diffusive speed of the impurities away from it. For a substrate temperature, $T^* = 0.4$, the resolidification velocity was 21 and 15 ms^{-1} on the (100) and (111) faces respectively, and complete solute trapping was observed. Impurities are found to segregate into the liquid only when the interface

velocity is sufficiently slow ($< 2\,ms^{-1}$). At $T^* = 0.6$, this appears to have occurred for a brief period during solidification at the (100) face, before the steady-state velocity reached a value of $4\,ms^{-1}$. Growth at the (111) face at this temperature shows segregation consistent with the observance of a low resolidification velocity of $1.7\,ms^{-1}$. These results indicate that the critical velocity for segregation over trapping is $< 2\,ms^{-1}$ for this particular LJ alloy, at least. This value is in good agreement with the calculated value for v_D ($< 3.5\,ms^{-1}$), corroborating the suggestion of Aziz [15].

Although we are encouraged by our current ability to provoke both solute trapping and impurity segregation under different processing conditions, there are still issues to be resolved. For example, the original arrangement of the simulation cell employed an alloy placed on top of a region of pure material. This was done to mimic the way in which laser processing experiments are carried out in the laboratory. Although this has allowed us to observe the effect of a rapid change in undercooling on the interface velocity through the reduced melting point of the alloy, it causes a diffusive flux of impurities into the previously undoped material in a direction which hinders motion away from the growing interface, leading to less segregation than might otherwise be observed. We are now performing a simulation where the material consists of the alloy alone with the expectation of greater segregation. Another problem is that the segregation observed at the (111) face at $T^* = 0.6$ involved a non-dramatic change of the segregation coefficient ($k_i^e = 0.6 \rightarrow k_i = 0.8$). We are now attempting to design a material for which the k_i^e value is very low so that any non-equilibrium-induced changes will be easier to observe. One possible way to achieve this would be to increase the concentration of B atoms, assuming that the phase diagram for this alloy is qualitatively similar to Haymet *et al.*'s density functional theory results for the same alloy [21], and that the solidification front remains planar (as mentioned earlier). The other remaining question, that of system size, is a recurrent problem in this type of work. We are currently pursuing this question in spite of the tremendous investment of computer time required. One complete run (comprising material preparation, equilibration and rapid thermal processing) takes 120–200 hours of CPU time for 7744 atoms on an IBM 3090–600E or twice that on a Convex C210 which we also use. We are repeating the work reported here for a system containing 7744 atoms (i.e. more than twice as many atoms) and with higher concentrations of impurities in order to determine the effect of size-dependence and improve statistical uncertainties. Preliminary results suggest that the mechanisms for growth at the two faces and the segregational phenomena observed remain essentially unchanged from those reported here.

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