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Transition layer in a lattice-gas model of a solid-melt interface

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The equilibrium solid-melt interface in a lattice-gas model of a single-component system is shown to be isomorphous with a earlier calculation of an interface between ordered and disordered structures. When the surface is parallel to a plane that is not close packed, the solid structure changes smoothly into the liquid structure. For the close-packed surface direction, a layer of an intermediate structure is found. In the intermediate layer, atomic planes parallel to the solid surface become liquidlike (i.e., disordered), while the density alternates between high and low from plane to plane. This two-stage interface corresponds to the one reported by Landman *et al.* in their molecular-dynamics calculations.

INTRODUCTION

In a recent simulation of molecular dynamics, Landman *et al.*[1-3] have studied the solid-melt interface of a rare gas during rapid crystallization perpendicular to a close-packed direction. They found an interfacial structure that indicated two stages in the gradual loss of solidity as one moves from solid to melt. Successive layers of atoms became more disordered, until there were disordered layers of atoms parallel to the interface that were clearly distinct layers. Then with still increasing distance from the solid the layers become less distinct, as the oscillatory density that characterized the layers became the uniform liquid density. The processes of two-dimensional disordering of the layers and the merging of the layers occurred in two distinct stages that characterized the moving interface.

In their most recent communication,[3] the calculation was continued until equilibrium was reached. The equilibrated interface retained the layered structure with density oscillations extending far into the liquid. In Fig. 1 of their paper,[3] the quantity O_4 is a parameter representing the transverse orientational order. It is a measure of the probability that three neighboring atoms form a right angle. Its value is high in the fcc structure parallel to the (001) and is normalized to vanish in the liquid. In the interface calculation [see Fig. 1(c) of Ref. 3] it became zero at a reduced distance $Z^* = 1.3$ well inside the interface, not only well before the average density has converged to the liquid density but also well before the density oscillations have damped out. If anything, the transition to two-dimensional melting could be located more clearly in the equilibrated than in the moving interfaces. In this recent calculation, however, an alloy of two rare-gas species was used. This might have been a factor in the results.

The structure of interfaces between a solid and a fluid has been the subject of many studies.[4,5] When the fluid is a dilute vapor, there is little ambiguity about which phase a given atom is in, and one can describe the interface as smooth or rough and one can, for example, speak of a roughening transition. Under some conditions the interface can even lower its energy by forming a melted layer. Such a layer would occur close to the triple point, if the solid-vapor interfacial free energy exceeded the sum of the solid-liquid and liquid-vapor interfacial free energies.

For solid-melt interfaces there is considerable ambiguity about the location of the interface on an atomic scale.[4] Atoms in the melt have a packing that is not too different from that of a solid and the densities of the two phases are comparable. As one moves from solid to liquid through the interface one expects a region of gradual transition from solid to liquid. Unlike the case of the dilute vapor, it will be difficult to find meaningful structural criteria for deciding whether individual atoms are in the solid or liquid phase. Most local measures of solidity, whether structural, energetic, or ones that probe proper-

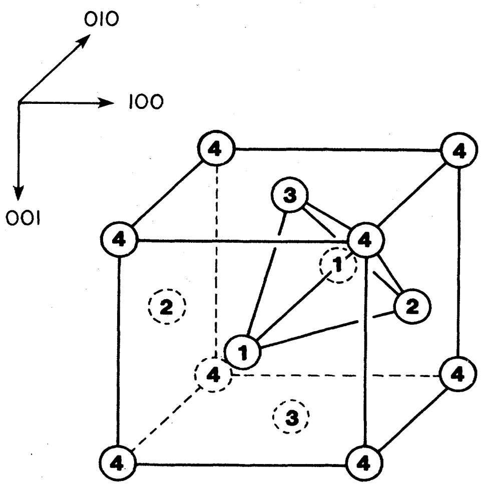

FIG. 1. Labeling of the axes and the four sublattices of the fcc lattice.

ties on the atomic level should show gradual transitions with distance as one moves from solid to liquid.

Solid interface structures and transitions will be different for different orientations. Interface structures may also change with changing temperature along equilibrium coexistence. Interface motion caused by nonequilibrium as in Landman *et al.*'s calculations also affects structure.

We report herein a calculation of the equilibrium solid-melt interface in a lattice-gas model using the cluster variation method (CVM). The calculation was done in the context of order-disorder in a binary system. Details of the procedure are published elsewhere.[6,7]

Our basic interpretation of using the lattice-gas model in treating the fluid-solid transition is the following. The system is regarded as an alloy of atoms and vacancies. When the sublattices in an ordered lattice structure are equally occupied by atoms, we identify the phase as fluid. When their occupancies are not equal, the phase is identified as solid. This interpretation is justified when we think of the limiting case of the lattice constant reducing to zero.

Based on this interpretation, we convert from the order-disorder binary alloy language to a lattice-gas language, by identifying A and B atoms with vacancies and atoms. In our model the underlying lattice is fcc and the disordered phase is an fcc lattice fluid. The ordered Cu_3Au phase can have either of two crystal structures, a simple cubic structure if we let Cu be vacancies or a complicated cubic structure if we let Au be vacancies. The CuAu tetragonal phase become a simple tetragonal crystal with a c/a ratio of $\sqrt{2}$. These changes from order-disorder to lattice-gas description are detailed in the next three sections.

In the following section we present results of our calculations of the boundary structure for two orientations (001) and (110), and for various values of the chemical potential.

Our lattice-gas calculations show the structure reported by Landman *et al.* very clearly, but only for interface parallel to the (001) which is the close-packed plane of the simple-cubic crystal. The (110) interface has a much simpler structure. Additional calculations were performed to rule out wetting arising from the triple point as an alternate explanation.

THE MODEL

We consider an fcc lattice gas with soft near-neighbor repulsion. There is no interaction between atoms beyond first neighbors. Near-neighbor pairs contribute a finite energy. In addition we introduce multiatom near-neighbor interaction terms. We vary the melting temperature (and pressure) by varying the chemical potential.

The fcc lattice can be divided into four simple-cubic sublattices which are named 1, 2, 3, and 4 as in Fig. 1. In working out the statistical mechanics of the lattice-gas model as described here, we use a tetrahedron as the basic cluster of the CVM.

Let the energy E_n of a tetrahedron containing n atoms be given by

$$\begin{aligned} &E_0=E_1=0\ ,\\ &E_2=W\ ,\\ &E_3=3W(1+A)\ ,\\ &E_4=6W(1+B)\ , \end{aligned} \tag{1}$$

where W is the near-neighbor pair interaction energy chosen to be positive when this interaction is repulsive; A and B are multiatom interaction corrections (not names of species) which can easily be introduced into the CVM if desired.

For the lattice-gas model, when Z_k is the fraction of tetrahedra containing k atoms, then the energy E for a system containing N lattice sites (or $2N$ tetrahedra or $N/4$ fcc unit cells) is

$$E/NW=Z_2+3(1+A)Z_3+6(1+B)Z_4\ . \tag{2}$$

The number of atoms in the system is

$$n/N=(Z_1+2Z_2+3Z_3+4Z_4)/4\ . \tag{3}$$

In order to show that this lattice-gas model is isomorphous with the fcc ordering models, we add and subtract $6(1+B)n/N$ to Eq. (2):

$$\begin{aligned} E/NW=&-\tfrac{3}{2}(1+B)Z_1-2(1+3B/2)Z_2\\ &-\tfrac{3}{2}(1-2A+3B)Z_3+6(1+B)n/N\ . \end{aligned} \tag{4}$$

If we let $w=-W(1+3B/2)2$,

$$\begin{aligned} &1+\alpha=(1+B)/(1+3B/2)\ ,\\ &1+\beta=(1-2A+3B)/(1+3B/2)\ , \end{aligned} \tag{5}$$

we obtain

$$E/2Nw=\tfrac{3}{2}(1+\alpha)Z_1+2Z_2+\tfrac{3}{2}(1+\beta)Z_3-6(1+\alpha)n/N\ . \tag{6}$$

Except for the last term this equation is identical to Eqs. (1), (5), and (4.1)–(4.2) of Refs. 6, 7, and 8, respectively, for the binary alloy. The last term can be absorbed in the chemical potential and is not relevant to the phase diagram and boundary structure calculations.

If we instead identify atoms in the present model with species 1 (or A) in the earlier model, α and β are interchanged in Eq. (5), and we obtain a different solid phase of the lattice-gas model.

GROUND-STATE STRUCTURES AND IDENTIFICATION OF PHASES

The previous ground-state calculation demonstrated the existence of four phases whose occurrence depends on the interaction parameters and the chemical potential. These phases have one, two, three, or four atoms in the fcc unit cell and have, respectively, the following space groups and site occupancy, and Pearson symbol:

(a) $cP1$, $Pm3m$ (O_h^1)—a simple-cubic crystal with one atom at (000);

(b) $tP1$, $P4/mmm$ (D_{4h}^1)—alternate (001) layers of the fcc lattice occupied, $c/a=\sqrt{2}$;

(c) $cP3$, $Pm3m$—a complex-cubic crystal with three atoms per unit cell located only on the face centers $(\frac{1}{2}\ \frac{1}{2}\ 0)$ but no atom at the origin;

(d) $cF4$, $Fm3m$ (O_h^5)—every site equivalent. This is the ground state of lattice fluid. For large negative chemical potentials, the sites are empty (gas); for large positive chemical potentials, they are filled (liquid).

Only the lattice liquid exists in the ground state if $w<0$ and α and β are both greater than -1. For other values of the parameters, one or more of the crystalline phase exists.[9]

PHASE DIAGRAMS

Figure 2 shows the phase diagram for $\alpha=0.01$ and $\beta=-0.08$. The lettered points Q, P, and R indicate the temperatures and chemical potentials μ for which we have calculated the interfaces between coexisting phases $cP1$ and $cF4$. Q is at the triple point.

The phase diagrams show that the $Fm3m$ lattice-fluid phase spans the entire density range with no transition that might be identified as a gas-liquid change. With this range of multiatom interactions there are three crystalline phases. All along the curves of melting coexistence the lattice liquid has higher entropy than each solid. Consistent with the Konovalov rules and the equations of thermodynamics at the maximum melting point solid and liquid have equal density, and along the portions where $d\mu/dT$ is negative the liquid has higher density. The triple point Q occurs at $kT/W=0.86460$ and $\mu/W=-1.30132$. The average densities are 0.41068 for the fluid phase, 0.41072 for $cP1$, and 0.42102 for $tP1$. It is of general interest to note that the $cP1$-$tP1$-liquid triple point has recently been shown to be peritectic rather than eutectic.[10]

BOUNDARY STRUCTURE

The treatment of the homogeneous phase in the preceding section can be extended to an inhomogeneous system which includes a boundary between two phases. The details are in Ref. 7. We present the results in the context of the $cP1$ crystal-melt interface, but everything is also true for the $cP3$ complex crystal-melt interface if we exchange atoms and vacant sites.

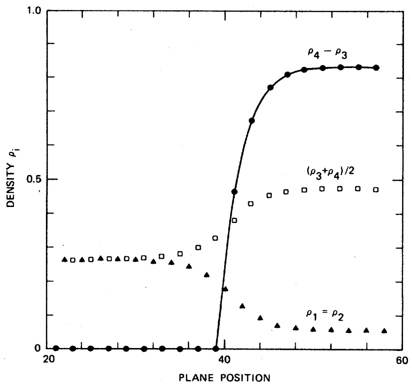

FIG. 3. Atomic density profile on each sublattice across the solid-fluid boundary. This is the (001) boundary at P of Fig. 2. Note the transition where the occupancy of 3 and 4 becomes identical.

Figure 3 shows how various order parameters vary with distance along the normal of a (001) interface. In the crystal, $\rho_1=\rho_2=\rho_3$ but ρ_4 is different. In the liquid they are all equal. The in-layer order parameter $\rho_4-\rho_3$ represents ordering within a (001) plane. Since sites 1 and 2 are on the inbetween plane, the difference between $(\rho_3+\rho_4)/2$ and $\rho_1=\rho_2$ represents the layering of atoms. Their sum represents the local overall composition. We see that for different chemical potentials the scale of these curves changes but that they all show the same qualitative behavior. Figure 3 shows that after the in-layer order parameter $\rho_4-\rho_3$ plunges to zero, the layering continues. Furthermore, the local composition varies smoothly from liquid to solid. In particular, for the profile of the interface at the triple point in Fig. 4 the local composition does not rise to that of the $tP1$ phase (0.4210), nor do the layer compositions approach, respectively, 0.1034 and 0.7387 for the ρ_1 and $(\rho_3+\rho_4)/2$ atomic layers of $tP1$.

Figure 5 shows a completely different profile for the (110) interfaces. The two order parameters $(\rho_4-\rho_3)$ and $(\rho_4+\rho_3)/2-\rho_1$ both decay with approximately the same rate. We computed profiles for various chemical poten-

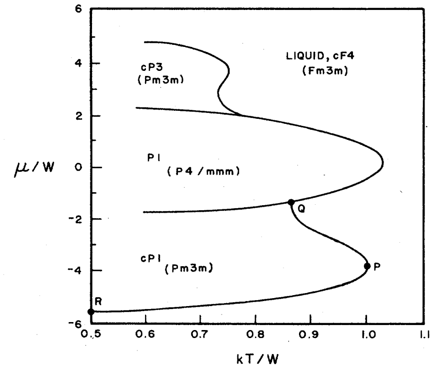

FIG. 2. The fluid-solid phase diagram for $\alpha=0.01$, $\beta=-0.08$.

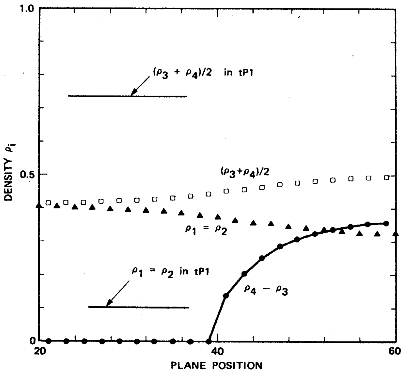

FIG. 4. Density profile for the (001) boundary at Q at the triple point of Fig. 2.

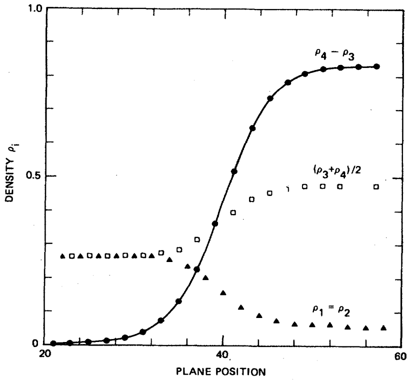

FIG. 5. Density profile for the (110) boundary at P of Fig. 2. Note the absence of a transition.

tials between Q and R on Fig. 2 and found no qualitative change in structure. The (001) continued to display the intermediate structure.

We were not successful in finding a scaling relation for these curves. In general the interfaces broadened towards the triple point.

DISCUSSION

Our calculations clearly show that the boundary structure differs with orientation. The boundary parallel to (001) has a two-stage structure similar to that reported by Landman *et al.* In the first stage close to the solid, successive atomic layers parallel to the (001) plane of the crystal become increasingly disordered. Beyond a certain plane (in Fig. 3, for planes less than position no. 40), the second stage sets in, where the individual layers are fully disordered, but the atoms are still layered on alternative planes of the underlying lattice of our model. The layering gradually disappears with increasing distance. On the other hand, the (110) boundary disorders smoothly without the onset of the second stage; in this boundary, reduction in layering and reduction in order occur with similar length scales.

In comparing our results with those of Landman *et al.*, two problems are to be pointed out. The underlying lattice of our model restricts the positions that atoms can take, and so atoms are always layered even in the lattice liquid. Thus the confirmation of the layered structure is done by looking at the alternating density variation from layer to layer. Similarly, the loss of order within each atomic layer is more limited. Instead of Landman *et al.*'s orientation order parameter O_4 we have a much clearer indication of an abrupt loss of two-dimensional long-range order. However, the quantity ($\rho_4 - \rho_3$) in our model has many of the characteristics of O_4. In the $cP1$ crystal with sublattice 4 occupied and sublattice 3 empty the atoms on (001) are arrayed on a square lattice. There is thus a high degree of O_4 orientational ordering with right angles. In the liquid where $\rho_3 = \rho_4$ the (110) pairs of atoms on different sublattice introduce 45° angles. This plus the occurrence of randomly empty sites reduces O_4 to nearly its random value.

The second problem is the possibility of wetting by the $tP1$ phase.[11] In Landman *et al.*'s case the intermediate structure can be considered as a thin smectic layer that has intruded itself between solid and liquid. Since in his model there is no triple point where a smectic crystal coexists with crystal and liquid, the possibility of wetting is remote. There is always the possibility that a triple point is close but physically inaccessible. The smectic phase might be a low-lying metastable phase requiring imposition of special fields such as ones existing at interfaces. For the lattice-gas model triple points exist and the structure of disordered layers of alternating density bears a strong resemblance to a wetting layer of the $tP1$ phase.

At the triple point, wetting occurs whenever the free energy of an interface between two phases, say α and γ, exceeds the sum of the energies of interfaces between α and β and between β and γ. At the α-β-γ triple point the α-γ interface is wet by a bulk layer of β and the interfacial free energy of the α-γ interface is reduced to the sum of that of the α-β and β-γ interfaces. Away from the triple point along the α-γ coexistence curve, β becomes increasingly unstable and the intruding β layer becomes increasingly thinner and changes its character. Sufficiently from the triple point the α-γ interface may cease to be wet by β.

Our calculation exactly at the triple point, Fig. 4, shows that the layered structure differed significantly from that of bulk $tP1$ phase. In addition the thickness of the layered portion of the interface did not diverge as the triple point was approached. Its thickness increased to what appeared to be a finite limit. We therefore conclude that in the two-stage structure observed in Figs. 3 and 4 we are not seeing wetting.

Our lattice-gas model confirms the existence of a two-stage interface for the (001). We find a simple interface for (110). The fact that the in-layer order $\rho_4 - \rho_3$ vanishes before propagating into the liquid state in the (001) boundary of Fig. 3, while $\rho_4 - \rho_3$ decreases but extends into the liquid in the (110) boundary of Fig. 4 can be understood as follows. We note that the distance between (001) planes is larger than that between (110) planes. For the (110) boundary, one 3-4 plane directly interacts with adjacent 3-4 planes through the 3-4 bond, and therefore the preferential occupancy of the sublattice 4 can propagate and is kept into the liquid. On the other hand, a 3-4 plane of the (001) boundary does not interact directly with adjacent 3-4 planes and thus the difference between the 3 and 4 sublattices cannot propagate.

Based on the above interpretation, if molecular-dynamics calculations are done for the liquid-crystal boundary parallel to a dense plane of the crystal they should show the boundary's behavior similar as Fig. 5 rather than Fig. 3. This property has been recently confirmed by Landman,[12] and supports our interpretation of the behavior of the in-layer order.

Finding two such different interface structures for two different orientations suggests the possibility of an interfacial phase transition with changing orientations. Our calculations give interfacial free energies for these two orientations that differ only by a few percent.[7] With so little anisotropy it seemed unlikely that an equilibrium shaped solid particle would be faceted, but if there is a phase transition a singularity in its shape is expected.[13–15]

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