

## INTERFACE STRUCTURE AND CRYSTAL GROWTH FROM THE MELT – A MODEL THEORY

N.H. FLETCHER

*Department of Physics, University of New England, Armidale. NSW 2351, Australia*

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A simplified atomic model is developed which displays the essential characteristics of a two-phase system, one of the phases being highly disordered (quasi-liquid) and the other nearly completely ordered (crystalline). This model is applied to discuss the equilibrium structure of the interface between the two phases and it is shown that this interface will either be sharp or diffuse depending on the entropy of fusion and on the coherence length for cooperative structural effects in the liquid. The interfacial free energy is typically in the range 2 to 10 times  $kT_m$  per surface atom, where  $T_m$  is the melting temperature, and is contributed largely by entropy loss in liquid layers near the interface. Finally the model is applied to the crystallization of the liquid, and the concentration of defects quenched into the crystal is calculated as a function of crystallization velocity.

### 1. Introduction

In a recent paper [1], to be referred to as I, the present author proposed a new approach to the discussion of interface structure and crystal growth based, not upon the usual treatment in terms of surface steps, dislocations and interfacial roughness, but rather upon an examination of the structure of the liquid near the interface. This new approach was seen as complementing rather than replacing the usual treatment but, as an initial exercise, the liquid viewpoint was adopted exclusively.

The treatment presented was an heuristic one and suffered from many defects, some of which arose from the fact that the formulation was couched in continuum terms, like diffusion theory, despite the fact that the characteristic lengths involved were only a little greater than the elementary stochastic steps. This shortcoming, as well as reducing the quantitative validity of the results, could actually be taken to cast doubt upon some of the basic conclusions of the treatment.

The purpose of the present paper is therefore to redevelop the whole argument using an entirely different technique to treat the liquid structure and the process of crystal growth. It is not claimed that the model adopted is necessarily a good approximation to reality for physically interesting cases, but it should

exhibit the same general behaviour. The model, it is hoped, is sufficiently simple and explicit that both its assumptions and their implications are clear.

### 2. The equilibrium phases

One of the major difficulties in formulating the crystal growth problem, for the case of a crystal growing from its melt, is that of setting up a single atomic model which can consistently represent the crystalline and liquid states, as well as the transition region across the interface, without introducing such poorly defined concepts as “liquid-like” and “solid-like” states for the interface atoms. To set up such a universal structural model in the general case is obviously very difficult, since it must exhibit the proper structural properties for simple liquids and crystalline solids as well as describing the transition between these two bulk phases. We shall therefore be content with a very simple model which achieves the same results without necessarily providing a refined structural account of the liquid state.

Consider an assembly of  $\mathcal{N}$  atoms and their relationship to  $\mathcal{N}$  lattice sites of unspecified geometry in some region of space. We postulate two possible states for the atoms – normal states in which they occupy one of the lattice sites and defect states in

which they are displaced to some sort of interstitial site, leaving a lattice site vacant. If we choose the zero of energy to be that for an atom on a lattice site then we can associate a positive energy  $\epsilon$  with each atom in a defect state, and introduce cooperative effects by assuming that  $\epsilon$  depends upon the fraction of atoms in defect states. This model then has some relation to the "hole" theory of melting discussed long ago by Frenkel [2] and subsequently extended by other workers.

Suppose that, at a given temperature  $T$ ,  $n$  of the total  $\mathcal{N}$  atoms occupy defect states, the number of accessible lattice sites and interstitial sites each being  $\mathcal{N}$ . The number of configurations possible is

$$W = [\mathcal{N}!/n!(\mathcal{N} - n)!]^2 \quad (1)$$

and the associated entropy can be evaluated as  $S = k \ln W$  which, using Stirling's approximation as usual in the factorial functions, leads to a total free energy

$$F = n\epsilon - 2kT[\mathcal{N} \ln \mathcal{N} - n \ln n - (\mathcal{N} - n) \ln(\mathcal{N} - n)]. \quad (2)$$

If we define  $f = F/\mathcal{N}$  to be the free energy per particle and  $c = n/\mathcal{N}$  to be the fraction of defects, then

$$f = c\epsilon - 2kT[c \ln(c^{-1} - 1) - \ln(1 - c)]. \quad (3)$$

We now introduce a further assumption by making

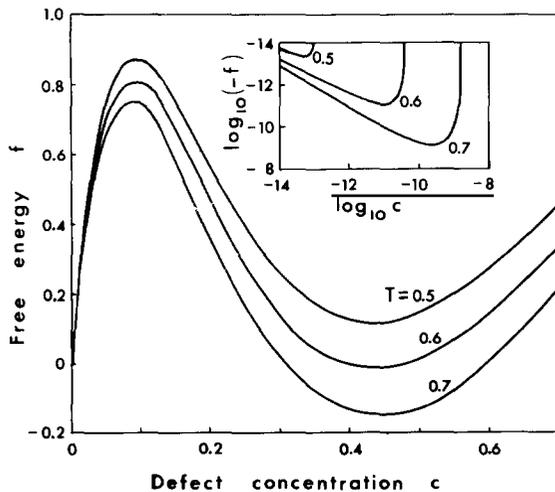


Fig. 1. The free energy per atom,  $f$ , as a function of defect pair concentration  $c$  for different values of  $kT$  shown as a parameter. The inset shows, on logarithmic scales, the behaviour near the origin. Other parameters are given in table 1.

Table 1  
Assumed values

Defect energy limit in liquid	$\epsilon_1$	= 1.5 units
Defect energy limit in crystal	$\epsilon_2$	= 30 units
Defect energy variation parameter	$\alpha$	= 10
Thermal energy at melting point	$kT_m$	$\approx 0.6$ units
Coherence length in liquid	$\lambda$	= 2
Layer separation in liquid	$d$	= $3 \times 10^{-8}$ cm
Activation energy parameter	$\gamma_0$	= 1
Fundamental frequency	$\nu_0^0$	= $10^{13} \text{ s}^{-1}$
Fundamental recombination rate	$\kappa^0$	= $10^{13} \text{ s}^{-1}$

explicit the dependence of the defect energy  $\epsilon$  upon the defect concentration  $c$ . We expect physically that  $\epsilon$  is large when  $c$  is small and that it decreases to a smaller value, which does not depend greatly upon  $c$ , when  $c$  becomes large. An appropriate form is thus

$$\epsilon = \epsilon_1 + (\epsilon_2 - \epsilon_1) \exp(-\alpha c), \quad (4)$$

where  $\epsilon_2 > \epsilon_1$  and, since  $0 \leq c \leq 1$ , we expect  $\alpha \gg 1$ .

We can now determine the equilibrium state of the system at any given temperature  $T$  by substituting (4) into (3) and then varying  $c$  to minimize  $f$ . The dependence of  $f$  on  $c$  is shown for several different temperatures in fig. 1. For high temperatures the equilibrium state is liquid-like, in the sense that it has a large entropy and a defect fraction near 0.5. For low temperatures the equilibrium state is crystalline, with a defect fraction near  $10^{-11}$  for the particular parameter values given in table 1. There also exists an equilibrium temperature  $T_m$  at which these two states can coexist, having equal free energies  $f$ . This model, though crude, thus reproduces the features of the liquid and solid states and of the transition between them which are of importance for our discussion.

### 3. The equilibrium interface

Once we leave the bulk phases and consider the interface region, we must allow for the fact that the concentration  $c$  of defects will depend on position. This position may conveniently be specified by reference to the lattice, which is assumed to extend through both crystal and liquid and, to make our analysis simpler, we shall suppose that the "interface" (soon to be defined) lies parallel to a low index plane

of this lattice. Thus, though our model is three-dimensional, its average properties are one-dimensional and are specified only for discrete values  $Nd$  of the coordinate  $z$ , normal to the interface, corresponding to the positions of the lattice planes.

The energy  $\bar{\epsilon}_N$  associated with defect states in a given plane  $N$  must now also be recognised to depend not only upon the defect concentration  $c_N$  in that plane but also, to some extent, upon the concentrations  $c_{N\pm L}$  in neighbouring planes. The weightings to be given to these neighbouring defect concentrations is a property of the liquid which depends upon its structure and upon the nature of the interatomic potential. Let us simplify matters by assuming an appropriate exponential weighting so that

$$\bar{\epsilon}_N = [\epsilon_N + \sum_{L=1}^{\infty} (\epsilon_{N+L} + \epsilon_{N-L}) e^{-L/\lambda}] / [1 + 2 \sum_{L=1}^{\infty} e^{-L/\lambda}], \quad (5)$$

where the  $\epsilon_N$  are the energies characteristic of bulk material with the defect concentration of layer  $N$ . The quantity  $\lambda d$ , where  $d$  is the interplanar spacing, has the character of a coherence length for the particular liquid involved and we might expect  $\lambda$  to lie typically in the range 0.3 to 3. As discussed in more detail in I, the coherence length normal to a plane crystalline interface is probably significantly greater than the coherence length apparent in the radial distribution function. For simplicity in our calculation we assume  $\lambda$  to be independent of  $c$  so that it has the same value for both solid and liquid phases.

The equilibrium structure of the interface, as measured by the variation of  $c_N$  with  $N$ , can now be determined by minimizing the total free energy function for the interfacial region at the melting temperature  $T_m$ ,

$$F_i = \sum_{N=-M}^M f_N = \sum_{N=-M}^M \quad (6)$$

$$\times [c_N \bar{\epsilon}(c_N) - kT_m [c_N \ln(c_N^{-1} - 1) - \ln(1 - c_N)]].$$

The interface is nominally located near  $N = 0$  and the summation is taken over  $M$  planes on each side of this position,  $M$  being sufficiently large that the last planes are effectively in bulk crystal and bulk

liquid respectively. The minimum value of  $F_i$ , multiplied by the number of atoms per unit area in the plane of the interface, gives the interfacial free energy  $\sigma_i$ .

The minimization of  $F_i$  is most easily accomplished numerically, assuming particular values of the parameters in  $\epsilon$  and performing a relaxation calculation over the  $2M + 1$  layers with  $c_{-M}$  held at the crystalline and  $c_M$  at the liquid equilibrium defect concentrations. The results of such calculations are shown in fig. 2, both for the case of a sharp interface ( $\lambda = 0.5$ ) and that of a diffuse interface ( $\lambda = 2$ ). Other parameters are as in table 1.

It is interesting to pursue the distinction between sharp and diffuse interfaces in a little more detail. We can state an appropriate criterion for diffuseness to be that the defect concentration  $c$  across the interface changes from plane to plane by an amount which is always less than a small fraction of the defect concentration  $c_q$  in bulk liquid. This in turn means that the energy  $\bar{\epsilon}$  changes from layer to layer by an amount which is less than about  $kT_m$  and, by (5), this leads to an approximate criterion for diffuseness as

$$(\epsilon_2 - \epsilon_1)/2\lambda < kT_m. \quad (7)$$

The quantity  $(\epsilon_2 - \epsilon_1)$  is essentially  $c_q^{-1}$  times the enthalpy of fusion and  $\lambda$  typically lies in the range 0.3 to 3, so that this criterion is very closely related to that of Jackson [3], derived from an entirely different starting point. It is also very similar to the results of the multi-layer treatment of Temkin [4] and to the less explicit criterion derived in I. Because of the averaging (which we interpret as ensemble averaging) over all configurations in the  $x, y$  plane in our simplified treatment of our model, we make no distinction between diffuseness and roughness, and one generally implies the other.

In fig. 3 we show the local free energy function  $f$  for each layer near the interface, and again we find a distinction between sharp and diffuse cases. For a sharp interface there is a high free-energy barrier separating the crystalline and liquid states, and a nucleation process is involved for each layer to crystallize. For the diffuse interface several layers near the interface have configurations distributed across the free energy hump. While the free energy barrier to crystal growth may not be strictly zero in this case, it is quite small, and layers can make the transi-

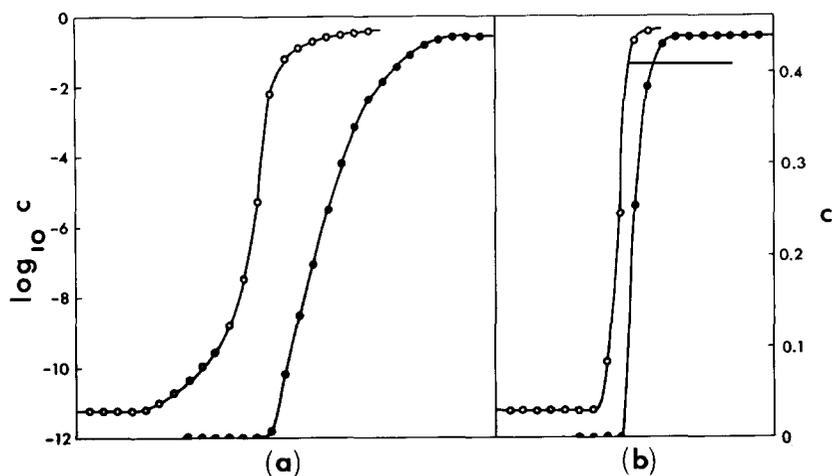


Fig. 2. Variation of defect concentration  $c$  across (a) a diffuse (rough) interface ( $\lambda = 2$ ), and (b) a sharp (smooth) interface ( $\lambda = 0.5$ ). Other parameters are given in table 1. In each case the open circles refer to the logarithmic scale on the left and the filled circles to the linear scale on the right.

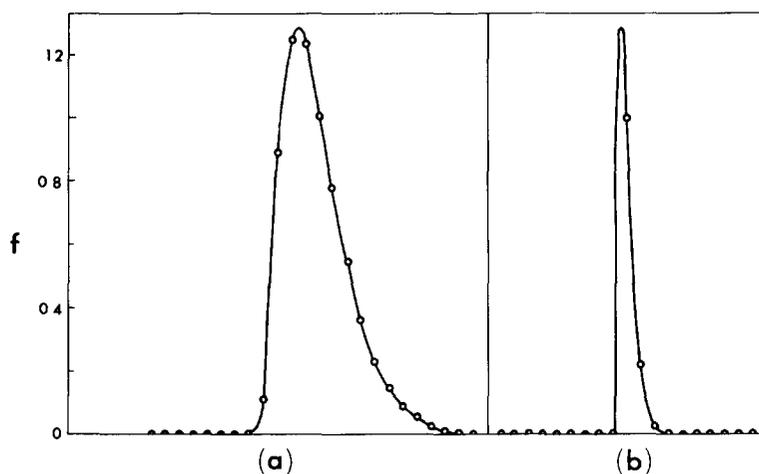


Fig. 3. The local free energy  $f$  as a function of position across (a) a diffuse interface ( $\lambda = 2$ ), and (b) a sharp interface ( $\lambda = 0.5$ ). An appropriate interpolation is given in each case.

tion from liquid to crystal continuously without greatly raising the free energy of the total system. The distinctions between rough and smooth interfaces and between nucleation and direct growth that are familiar in conventional treatments of the interface problem thus have almost exact counterparts in our present approach.

Finally we note the absolute values of the interfacial free energies for the two cases calculated. These amount to  $2.2 kT_m$  and  $11.3 kT_m$  respectively for the sharp and diffuse interfaces. If we assume

about  $10^{15}$  atoms per unit area in the surface and  $T_m \approx 300$  K, then these figures are equivalent to about 100 and 500 erg  $\text{cm}^{-2}$  respectively, which are reasonable values.

Because we have not assumed any volume change associated with the defects, there is no surface excess for any position of the Gibbs dividing surface and the interfacial free energy is a uniquely defined quantity. Both the energy and the entropy of the interface depend, however, upon the location of this dividing plane, and the most reasonable place to locate it is

at the position where the gradient  $|\partial c/\partial z|$  is a maximum. If we maintain an atomic viewpoint, then the location is only significant to the extent that it is to the right or left of a particular atomic plane. Adopting this convention we then find that the major contribution to the interfacial free energy comes from the entropy loss in the liquid phase near the interface, the energy term being relatively insignificant. Again this conclusion agrees with that reached in I.

#### 4. Kinetic considerations

Our discussion of the equilibrium interface has made no mention of time as a parameter but the equilibrium is, in fact, maintained by a balance between competing dynamic processes. Crystal growth or melting occurs when this balance is upset by a change in temperature. Before going on to consider the crystal growth process, let us look briefly at processes near an interface in equilibrium.

In layer  $N$  the defect concentration is maintained at its equilibrium value  $c_N$  by two mechanisms: diffusive interchange with neighbouring layers  $N + 1$  and  $N - 1$ , and direct generation and destruction of defects in layer  $N$  by thermal fluctuations. It is this second term which distinguishes the present problem from that of segregation near an interface in an alloy system.

The frequency  $\nu$  of diffusive jumps depends upon the local environment in the usual manner so that

$$\nu = \nu^0 \exp(-\epsilon_D/kT), \quad (8)$$

where  $\nu^0$  is an infrared frequency and the activation energy  $\epsilon_D$  is a structure-sensitive quantity. As a general rule in our present problem we expect  $\epsilon_D$  to be large for a jump between two states A and B if

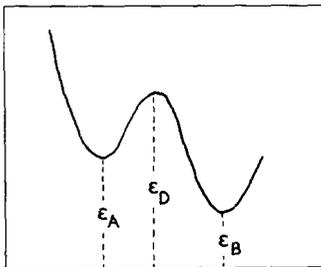


Fig. 4. Energy relations for diffusion.

the energies of the defects at A and B are large, as in the solid state, and small if the energies A and B are small, as in the liquid. This behaviour can be approximated by assuming, with reference to fig. 4, an energy barrier  $\epsilon_C$  between states A and B of

$$\epsilon_C = \gamma(\epsilon_A + \epsilon_B), \quad (9)$$

with  $\gamma \approx 1$ . This gives, for the activation energies for diffusive jumps in the two directions,

$$\epsilon_D^{A \rightarrow B} = \epsilon_C - \epsilon_A = (\gamma - 1)\epsilon_A + \gamma\epsilon_B, \quad (10)$$

$$\epsilon_D^{B \rightarrow A} = \epsilon_C - \epsilon_B = \gamma\epsilon_A + (\gamma - 1)\epsilon_B, \quad (11)$$

where  $\epsilon_A$  and  $\epsilon_B$  are given in terms of local defect concentration by (5). For our purposes here we shall assume  $\gamma = 1$  for simplicity and neglect the differences in behaviour of the two component defect types. Half the formation energy  $\epsilon$  of (4) is then ascribed to each defect.

The rate of recombination of defects within a given layer  $N$  depends upon their concentration  $c_N$  and the local equilibrium concentration  $c_N^0$ . It also depends upon some of the assumptions made about the nature of the defects. For simplicity let us assume at this stage that the defects can disappear only by recombination with each other. The recombination rate is then

$$[\partial c_N/\partial t]_{\text{recomb.}} = -\kappa(c_N c_N - c_N^0 c_N^0), \quad (12)$$

where  $\kappa$  is a kinetic coefficient. The activation energy associated with  $\kappa$  is most appropriately taken equal to the activation energy for diffusion in layer  $N$ , so that

$$\kappa = \kappa^0 \exp(-\epsilon_D^N/kT), \quad (13)$$

where  $\kappa^0$  is of the order of  $\nu^0$ , and for our present discussion will be taken equal to it. It is interesting to note that the recombination rate in (12) is effectively monomolecular if  $c_N - c_N^0 \ll c_N^0$  and bimolecular if  $c_N - c_N^0 \gg c_N^0$ . The effective adjustment rate for small disturbances of  $c_N$  in the liquid (for which  $c_N^0 \sim 0.5$ ,  $\epsilon_D \sim kT_m$ ) is of the order of microwave frequencies, while in the crystalline state ( $c_N^0 \sim 10^{-11}$ ,  $\epsilon_D \sim 25kT_m$ ) times of the order of days or longer are involved, even at the melting temperature.

The fundamental differential equation governing

the concentration  $c_N$  of defects in plane  $N$  can now be written as

$$\begin{aligned} \partial c_N / \partial t = & -\kappa_N (c_N c_N - c_N^0 c_N^0) \\ & - c_N (\nu_{N \rightarrow N-1} + \nu_{N \rightarrow N+1}) \\ & + c_{N-1} \nu_{N-1 \rightarrow N} + c_{N+1} \nu_{N+1 \rightarrow N}. \end{aligned} \quad (14)$$

If the frequencies  $\nu_{A \rightarrow B}$  have been appropriately calculated (which would not be closely true of our crude model) then solution of the set of equations  $\partial c_N / \partial t = 0$  with appropriate solid-like and liquid-like boundary conditions at  $N = \pm M$  should yield the equilibrium interface configuration calculated in the previous section.

## 5. Crystal growth

To examine the crystal growth problem we should first impose a temperature gradient  $\partial T / \partial z$  or  $\partial T / \partial N$  normal to the interface. This will locate the interface position unambiguously but will otherwise make little structural difference in the region near  $T_m$ . We then cause this temperature profile to sweep through the system with velocity  $v$  by imposing the additional requirement

$$\partial T / \partial t = -v \partial T / \partial z. \quad (15)$$

When a steady state has been achieved the interface will also sweep through the system with velocity  $v$  but will be located, not at the plane  $T = T_m$ , but rather at  $T = T_m - \Delta T$ . The extent of the interface supercooling  $\Delta T$  will be proportional to the growth rate  $v$  and will depend also on the magnitudes of the kinetic coefficients  $\nu_{A \rightarrow B}$  at  $T = T_m$ .

Almost the same result can be obtained by simply lowering the temperature of the whole system by an amount  $\Delta T$ , which will then determine the growth velocity. This near-equivalence comes about because the temperature differences between adjacent layers are, in any case, small and because the free energy of the interface between two areas of differing defect concentration imposes a nucleation barrier which allows the liquid to be maintained in a supercooled state, except for the steady crystal growth.

We have already pointed out the distinction between sharp (smooth) and diffuse (rough) interfaces

in terms of the necessity for a nucleation step in the crystal growth process in the former case. This necessitates a three-dimensional treatment of the problem which we shall not pursue here. In what follows we therefore explicitly limit ourselves to the discussion of crystal growth in cases where the interface is diffuse so that quasi-continuous growth processes operate.

If we possessed an adequate model for the diffusion process involved, we might now proceed to solve the set of equations (14) over a set of planes spanning the interface and at a temperature  $T = T_m - \Delta T$ . We do not possess such an accurate model, but fortunately a simple approximation technique can be made to serve the same purpose.

From fig. 2a, for the case of a diffuse interface, we see that the calculated equilibrium defect concentrations  $c_N^0$  can be interpolated unambiguously by a continuous function  $c^0(z)$ , the coordinate  $z$  being related to  $N$  by

$$z = Nd, \quad (16)$$

where  $d$  is the interlayer spacing. We can use this same technique, along with eq. (5), to define a continuous approximation  $\bar{\epsilon}(z)$  to the defect energy in layers at various positions relative to the interface. This in turn allows  $\kappa(z)$  and the various jump frequencies  $\nu_{A \rightarrow B}$  to be approximated for planes in any position. Strictly speaking these are all equilibrium values but, since we shall deal primarily with small departures from equilibrium, the small changes which these make can be neglected without invalidating the argument to follow or significantly altering its quantitative conclusions.

Now instead of concerning ourselves with the subtle adjustments which lead to crystal growth, we simply assume that the interface advances at a uniform rate  $v$  so that

$$z \rightarrow z - vt. \quad (17)$$

This coordinate change is immediately reflected in an explicit time variation of the equilibrium defect concentrations  $c_N^0(t)$ . The problem is now reduced to solving the set of equations (14), given the explicit functions  $c_N^0(t)$  and, deduced from them, the explicit approximations  $\kappa_N(t)$  and  $\nu_{A \rightarrow B}(t)$ . As a first step we note, however, that if the concentrations  $c_N$  have their equilibrium values and the interface is

stationary, then  $\partial c_N / \partial t = 0$  at all equilibrium positions of the interface and also, by our interpolation approximation, at all interface positions. From (14) this gives

$$-c_N^0(\nu_{N \rightarrow N-1} + \nu_{N \rightarrow N+1}) + c_{N-1}^0 \nu_{N-1 \rightarrow N} + c_{N+1}^0 \nu_{N+1 \rightarrow N} = 0, \quad (18)$$

which can be combined with (14) to give

$$\begin{aligned} \partial c_N / \partial t = & -\kappa_N(c_N c_N - c_N^0 c_N^0) - (c_N - c_N^0) \\ & \times (\nu_{N \rightarrow N-1} + \nu_{N \rightarrow N+1}) \\ & + (c_{N-1} - c_{N-1}^0) \nu_{N-1 \rightarrow N} + (c_{N+1} - c_{N+1}^0) \nu_{N+1 \rightarrow N}. \end{aligned} \quad (19)$$

This form of the equations eliminates the possible effects of inaccuracy in our values of the  $\nu_{A \rightarrow B}$ .

Solution of the system of eqs. (19) is now a straightforward numerical procedure, given the explicit variation of the  $c_N^0$  with time. As an initial condition we choose  $c_N = c_N^0$  everywhere and then follow the time evolution until the  $c_N(t)$  behaviour has become cyclic.

Before carrying out such an explicit solution, however, we can see the general nature of the behaviour from (19). A plane  $N$  initially deep in the liquid has  $c_N = c_N^0$  until it enters the diffuse interface region.  $c_N^0$  then begins to fall towards the very small equilibrium value which it has in the solid, and  $c_N$  follows through the combined relaxation mechanisms of defect recombination and defect exchange with neighbouring layers. Because  $\nu_{A \rightarrow B}$  decreases rapidly as we go through the interface region towards the solid, the major interchange is with the layer  $N+1$  on the liquid side of  $N$ . The defect concentration  $c_N$  is, however, always larger than  $c_N^0$  to an extent depending upon the growth velocity  $v$ . In the nearly-liquid high-defect region of the interface the relaxation time is short but in the nearly solid region it becomes very long, so that an excess concentration of defects remains trapped nearly permanently in the growing crystal. Even more importantly, as we shall see when we come to the final discussion, we should not expect the concentrations of the two components of a defect (e.g. vacancy and interstitial atom) to be exactly equal in number or to have identical jump probabilities. It is therefore likely that

one defect type will be included preferentially in the growing crystal so that there is no possibility of complete annealing-out of the defects.

## 6. Numerical solution

The specific interface for which the calculations were performed is that discussed above for which the equilibrium properties are displayed in figs. 1, 2a and 3a. The assumed values of the basic parameters are given in table 1. This interface satisfies our assumptions by being adequately diffuse so that the transition region extends over about 10 atomic layers.

To carry out the calculation, a region containing 50 atomic layers was considered, with the interface lying initially near the left-hand end,  $N = 0$ . By fitting the data in fig. 2a the following interpolation function for the defect concentration across the interface was developed.

$$c^0(z) = c_\ell + (c'_s - c_\ell) \exp(-\beta z/d), \quad z > 0, \quad (20)$$

$$\ln c^0(z) = \ln c_s + \ln (c'_s/c_s) \exp(\beta' z/d), \quad z < 0. \quad (21)$$

With the parameter values given in table 2, this fits the calculated values for  $z = Nd$  to adequate accuracy. The interface was then allowed to sweep through the system with velocity  $v$ , as discussed in section 5, and the defect concentration in each layer followed as a function of time. For the velocities considered, a steady state is achieved after a relatively small amount of motion, and the configuration is clearly periodic in time with period  $d/v$ . Fig. 5 shows typical interpolation curves  $c(z)$  across a growing interface.

Suppose  $c_1$  is the defect concentration at a distance of several times  $\lambda d$  behind the interface, where the kinetic coefficient  $\kappa$  has essentially its solid state value  $\kappa_s$ . Then if the crystal is annealed at its melting temperature, the defect concentration will fall according to (12). Since  $c_1$  is initially much greater than the equilibrium defect concentration  $c^0$ , solution of (12) shows that  $c$  remains nearly constant at  $c_1$  for a time about  $(c_1 \kappa_s)^{-1}$ , which is of the order of hours, after which it decreases as  $t^{-1}$ . After a time  $(c^0 \kappa_s)^{-1}$ , which may be of the order of days or years, the defect concentration begins to approach  $c^0$  and does so exponentially with a time constant  $(2c^0 \kappa_s)^{-1}$ .

Table 2  
Interpolation parameters

Defect concentration in bulk liquid	$c_l = 0.44$
Defect concentration in bulk solid	$c_s = 7.6 \times 10^{-12}$
Intermediate defect concentration	$c_s^* = 0.010$
Exponential parameter in liquid	$\beta = 0.2$
Exponential parameter in solid	$\beta' = 0.5$

In ordinary crystal growth, the crystal is held near the melting point for a time only of the order of minutes or hours, so that we may expect the concentration of quenched-in defects to be within about an order of magnitude of its initial value  $c_1$ . We can therefore take  $c_1$  as a convenient measure of this quantity, subject to the qualifications to be made later in the discussion.

When  $c_1$  is calculated for several different growth velocities  $v$ , the values shown in table 3 are found. We see that, to a reasonable approximation,  $c_1$  is proportional to growth velocity over the range  $10^{-5}$  to  $10^{-3}$  cm s<sup>-1</sup>. This is exactly the conclusion to

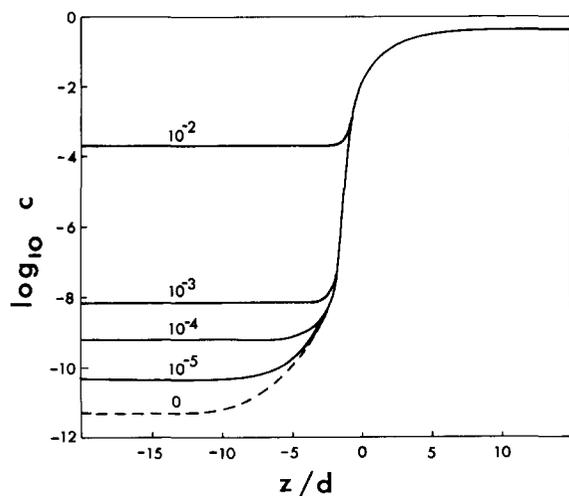


Fig. 5. Steady-state interpolation curves  $c(z)$  across an interface moving with velocity  $10^{-5}$ ,  $10^{-4}$ ,  $10^{-3}$  and  $10^{-2}$  cm s<sup>-1</sup>. The interpolation curve  $c^0(z)$  for the equilibrium interface is shown for comparison as a broken curve.

Table 3  
Quenched-in defect concentrations

Growth velocity $v$ (cm s <sup>-1</sup> )	0	$10^{-5}$	$10^{-4}$	$10^{-3}$	$10^{-2}$
Defect concentration $c_1$	$8 \times 10^{-12}$	$8 \times 10^{-11}$	$8 \times 10^{-10}$	$9 \times 10^{-9}$	$3 \times 10^{-4}$
Defect number density $n$ (cm <sup>-3</sup> )	$3 \times 10^{11}$	$3 \times 10^{12}$	$3 \times 10^{13}$	$3 \times 10^{14}$	$10^{19}$

which we were led in I. The constant of proportionality will clearly depend quite strongly on the parameters listed in table 1 but, for the reasonable values assumed there, we find

$$c_1 \sim 10^{-5} v, \quad (22)$$

if  $v$  is in centimeters per second. In terms of number densities

$$n \sim 3 \times 10^{17} v \text{ cm}^{-3}. \quad (23)$$

These results are within about an order of magnitude of those found in I.

The approximate relationships (22) and (23) apply only while the concentration of defects in the growing crystal remains small. For velocities approaching those that would appear to quench all the liquid disorder into the growing crystal, the relaxation time in the solid remains very short unless it is rapidly quenched to a low temperature. We shall not consider this possibility further here.

All this discussion has assumed that the defects with which we are concerned occur in pairs (vacancies and interstitial atoms) so that the concentrations of each type are the same. It is clear, however, that this restriction could be relaxed with very little initial physical effect. Suppose, for example, that vacancies are more common than interstitial atoms in our model of the liquid phase, so that its density is slightly lower than that of the crystalline phase. All our equations are virtually unchanged except that they must now differentiate between concentrations of the two defect types. For example, the appropriately generalized form of the recombination eq. (12) prevents a large accumulation of defects of one type in front of the advancing interface, this being an appropriate description because the liquid can readily adjust its configuration to maintain the balance between the two defect types.

In the crystal material behind the interface the situation is, however, rather different. The generalization of (12) still applies while ever the atoms can

interchange by diffusion between solid and liquid phases but, once the crystal lattice has become unambiguously established and the defects are deeply embedded in it, we must impose the additional condition that defects can only disappear by pairwise recombination so that

$$dc_+ = dc_- , \quad (24)$$

when  $c_+$  and  $c_-$  refer to the two defect types. This condition applied automatically in our previous discussion but here it leads to an equilibrium result like

$$c_+ - c_- = \text{constant}, \quad c_+c_- = c_s^2 . \quad (25)$$

If initially, just behind the interface,  $c_- > c_+$  because this reflects conditions in the liquid, then the final state in the solid will have  $c_-$  finite and  $c_+$  very nearly equal to zero, corresponding to a finite concentration of vacancies built into the crystal. If the crystal is annealed near its melting temperature, these vacancies will aggregate to form discs, then collapse to dislocation loops and ultimately to more complex dislocation structures, as discussed in I. If we assume a 10% disparity between the concentrations of the two types of defects in the liquid, which seems a reasonable figure, then, because of their assumed similarity in behaviour, a comparable disparity will occur in the crystal. From (25) the final equilibrium defect concentration will then be about 10% of that suggested by (22) and (23).

## 7. Discussion

The assumptions and predictions of our model are quite explicit and it is clear that, while modifications to the details of the mechanisms or to the numerical values used in the illustrative calculations will make an appreciable difference to the results, they will not change the basic conclusions. The main question is, therefore, whether or not the model is a reasonable idealization of the physical situation of interest: the equilibrium and growth of a crystal in contact with its melt.

There is no argument that our model is other than a poor approximation to a real liquid in a physical sense, largely because it imposes a long-range order on the liquid through its use of a reference lattice. This lattice is, of course, completely unreal for bulk

liquid but it does assume first mathematical and then physical reality as we approach the interface and enter the region of influence of the exponentially damped periodic potential produced by the array of atoms in the crystal [5]. A lattice-based description of the liquid is thus, in a limited sense, appropriate and our main idealization is in replacing the continuum of possible displacements from this lattice by two simple defects.

Again, once we are close to the crystal interface, this simplification is seen to be appropriate. Any disorder which can be removed essentially by small displacements of one or two atoms is unimportant for it will be removed very rapidly and, in fact, with a time constant of order  $(\nu^0)^{-1} \sim 10^{-13}$  s. Those disorders, however, which involve movement of one atom past others to remove an interstitial atom or a vacancy or, in the case of associated liquids, to correct a bonding defect, have relaxation times  $\nu^{-1} \sim 10^{-11}$  s and are therefore important in interfacial processes. Our idealization of such defects to two complementary species is a reasonable approximation for simple liquids, while the more complex possibilities available in associated liquids do not invalidate the general argument.

The only other major point for consideration is the fact that our model is essentially one-dimensional, with all properties being converted to ensemble averages over the other two coordinates. Such a procedure is justified for the case of a diffuse interface where the variation of quantities of interest from one atomic layer to another is small. Difficulties arise, however, if we try to apply such a procedure to a sharp interface.

Actually such a treatment, if carried out rigorously rather than by the method we adopted for the diffuse case, would show up its own deficiencies. The free energy barrier to crystal growth shown clearly in fig. 3b would inhibit any growth and lead to the classical dilemma which was resolved firstly by the Volmer–Weber nucleation theory for perfect crystals and then by Frank’s screw dislocation mechanism for real crystals. Both these theories are essentially three-dimensional, since structures in the plane of the crystal interface are involved. Our model could be expanded to include such refinements but, since they are unnecessary for the diffuse case which is our main concern, we will not pursue this further here.

We conclude therefore that our model provides a reasonable first approximation to a description of the crystal/melt interface and of the growth of crystals from the melt. In doing so it supports the conclusions reached on a more intuitive basis in our earlier paper.

Our original intention in I was to develop the view that the detailed structure of the liquid near an interface is comparable in importance to the topography of the crystal in determining the details of crystal growth. Deeper understanding now depends on developing both these viewpoints on an equal footing using more sophisticated models for the structure of the liquid and for the relaxation processes involved.

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