

# THE MOLECULAR MECHANISM OF SOLIDIFICATION†

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The various theories describing molecular kinetic mechanisms for solidification are discussed with particular emphasis on the distinction between the stepwise and continuous growth mechanisms. The theory of Cahn based on the diffuse interface concept is reviewed. It predicts the former growth mode at sufficiently small undercoolings and the latter at large undercoolings. Criteria for testing the validity of the various theories are given. These consist of qualitative and quantitative observations of solidification kinetics as related to undercooling at the interface as well as the occurrence of certain topological and/or morphological features. The existing pertinent experimental data on metals, organic, and inorganic compounds are reviewed. Of the presently known theories only the diffuse interface model is consistent with all of the observations. In those cases where sufficient data were available, several independent checks have been made. The diffuseness parameter  $g$  and the molecular accommodation coefficient  $\beta$  are tabulated.

## LE MECANISME MOLECULAIRE DE LA SOLIDIFICATION

Les diverses théories décrivant le mécanisme de la cinétique moléculaire de solidification sont discutées en mettant plus particulièrement l'accent sur la distinction entre les mécanismes de croissance continue et ceux de croissance en "escalier". La théorie de CAHN basée sur le concept de l'interface diffus est revue. Elle prédit le premier des deux modes de croissance précités dans le cas de sous-refroidissements importants et le second dans le cas de sous-refroidissements suffisamment faibles. Des critères permettant de vérifier la validité des diverses théories sont présentés. Ils consistent en des observations qualitatives et quantitatives de la cinétique de solidification en relation avec la surfusion à l'interface et l'application de certaines caractéristiques topologiques et/ou morphologiques. Les données expérimentales déjà publiées et dignes de foi concernant aussi bien les métaux que les composés organiques et inorganiques, sont passées en revue. Parmi les théories connues à ce jour, seul le modèle de l'interface diffus est compatible avec toutes les observations. Dans le cas où les données suffisantes étaient disponibles, plusieurs vérifications indépendantes ont été effectuées. Le paramètre ("diffuseness")  $g$  et le coefficient d'accommodation moléculaire  $\beta$ , sont tabulés.

## DER MOLEKULARE MECHANISMUS DER ERSTARRUNG

Es werden die verschiedenen Theorien über die molekular-kinetischen Mechanismen der Erstarrung diskutiert, unter besonderer Betonung des Unterschiedes zwischen schrittweisen und kontinuierlichen Wachstumsmechanismen. Die auf der Vorstellung einer diffusen Zwischenfläche beruhende Theorie von Cahn wird zusammenfassend dargestellt. Sie sagt den ersteren Wachstumsmechanismus bei hinreichend kleiner Unterkühlung und den letzteren bei starker Unterkühlung voraus. Es werden Kriterien für die Prüfung der Gültigkeit der verschiedenen Theorien angegeben. Diese bestehen aus qualitativen und quantitativen Beobachtungen der Erstarrungskinetik in Bezug auf die Unterkühlung an der Zwischenfläche sowie auf das Auftreten gewisser topologischer und/oder morphologischer Erscheinungen. Die existierenden einschlägigen experimentellen Daten für Metall, organische und anorganische Verbindungen werden zusammengefasst. Von den z.Zt. bekannten Theorien ist nur das Modell diffuser Zwischenflächen mit allen Beobachtungen in Einklang. In Fällen, in denen genügend viele Daten zur Verfügung standen, wurden verschiedene unabhängige Prüfungen durchgeführt. Der Diffusivitätsparameter  $g$  und der molekulare Akkomodationskoeffizient  $\beta$  werden zusammengestellt.

## 1. INTRODUCTION

The interface between a crystal and its vapour is generally believed to be molecularly sharp at temperatures well below the melting point. A perfect surface grows by the spreading of layers, or equivalently, by the lateral advance of the growth steps bounding the layers. Perfect surfaces can only grow by the consecutive nucleation of new monolayers. For perceptible growth rates this condensation mechanism requires a finite supersaturation to lower the nucleation barrier sufficiently for nucleation to occur by thermal fluctuations.<sup>(1)</sup> However, in most real materials an appreciable growth rate is observed at saturations for which no growth would be expected by the nucleation mechanism. To account for this anomaly, Frank<sup>(2)</sup> proposed that crystal growth by

vapor deposition occurs in real materials by a dislocation mechanism. A dislocation intersecting a surface provides a permanent source of growth steps, if its Burgers vector does not lie in the plane of the surface.

At temperatures approaching the melting point, it was proposed<sup>(3)</sup> that the surface became molecularly rough. This was termed "surface melting." Above the critical surface melting temperature, the necessity for stepwise growth was assumed to be removed. In this temperature regime, the surface was believed to advance by the random incorporation of vapor molecules onto the surface. The layer spreading mechanism is neither necessary nor possible once continuous growth by random incorporation occurs.

On the other hand, a lateral stepwise growth mechanism was not expected to pertain to growth from the melt; for all crystals, the interface structure of a solid in contact with its melt was considered to be similar to that of the melted surface structure as far as growth mechanisms were concerned.<sup>(4-6)</sup>

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However, evidence gradually accumulated that stepwise growth did occur in solidification. The first crystal reported to grow from its own melt by the screw dislocation mechanism was lead iodide.<sup>(7)</sup> Hillig and Turnbull<sup>(8)</sup> analyzed data on the solidification rates of several substances as a function of undercooling (under conditions where heat flow might not have been the controlling factor). It was shown that the kinetics were consistent with a dislocation mechanism and not with a continuous growth mechanism. Observations<sup>(9)</sup> on the melting and freezing of *p*-toluidine offered a direct demonstration of the validity of the lateral mechanism. It was possible to superheat a perfect surface in contact with its own melt. This demonstrated that there is a barrier to melting and hence that this solid-melt interface can neither advance nor recede by a continuous growth mechanism. A review of the theory of crystal growth from the melt was presented<sup>(6)</sup> in 1958. Although the above papers<sup>(7-9)</sup> were not discussed, it was suggested that the stepwise growth mechanism might be operative for a given range of supercooling for some crystal surfaces. However, for other crystals the absence of a nucleation barrier was postulated, on the basis of the rough surface concept, to account for the growth mechanism from the melt. In brief, it was concluded that there was no single universal mechanism for growth from the melt.

Recent experimental evidence has cast doubt even on the occurrence of "surface melting" for crystals grown from the vapor near their melting point. Zinc<sup>(10)</sup> and potassium<sup>(11,12)</sup> whiskers, as well as near-perfect platelets of para-toluidine<sup>(13)</sup> can be nucleated and grown from the vapor within 2° to 4°C of their melting points. Whiskers of mercury,<sup>(14)</sup> copper,<sup>(15)</sup> and gold<sup>(15)</sup> have been grown to within 10°C of their respective melting points. If continuous growth was possible on any columnar whisker surface, the observed habit could not occur. Thus, for the only six substances for which experimental evidence exists, continuous growth and hence surface melting does not occur for growth from the vapor.

It has been shown theoretically<sup>(16)</sup> that, at small driving forces, the existence of a rough interface does not avoid the necessity for stepwise growth or the problem of step creation. If a given surface configuration corresponds to a minimum free energy, then at least locally this configuration must deviate from the lowest free energy configuration if the surface is to advance. Only at sufficiently high driving forces can a surface advance uniformly. What constitutes a sufficiently high driving force depends

primarily on how rough the interface is; the rougher it is, the lower is the necessary driving force. Crystal growth from the melt is expected to correspond to a case of a rough interface having some driving force range in which the interface must move by lateral motion of steps.

## 2. REVIEW OF THEORY

In a previous paper<sup>(16)</sup> a criterion was developed for predicting the regimes of the alternative limiting mechanisms of crystal growth. The one growth mechanism being the lateral motion of rudimentary steps (one interplanar distance  $a$ , or some integral multiple thereof in height), the growth front being stationary except during the passage of the step; the other growth mechanism being the continuous advance of the surface everywhere. This criterion is developed in terms of the magnitude of the free energy change per unit volume,  $-\Delta F_v$ , which acts as the "driving force."

It was proposed that all surfaces would advance by a lateral mechanism at sufficiently low driving forces and by continuous growth at sufficiently high driving forces. These limiting regimes are separated by a transitional regime, which encompasses a driving force range that in turn depends on the diffuseness of the liquid-solid interface. For solidification,  $\Delta F_v$  is proportional to the undercooling and is given approximately by

$$-\Delta F_v = \frac{L}{V_m T_0} \Delta T \quad (1)$$

in which  $L$  is the latent heat of fusion per mole,  $V_m$  the molar volume of solid, and  $T_0$  the melting temperature.

The diffuseness is expressible in terms of the single parameter  $g$  (called  $g_{\max}$  in Ref. 16), which depends on  $n$ , the number of atomic layers comprising the transition from solid to liquid at the melting temperature. For a sharp interface  $g$  is of order 1. For very diffuse boundaries,  $g$  is given approximately by

$$g = \pi x^3 \exp(-\pi x) \quad \text{where } x = \pi n/2. \quad (2)$$

Theoretical or experimental estimates of  $n$  could be made in principle. However, the dependence of  $g$  upon  $n$  is so sensitive that only a direct experimental evaluation of  $g$  is reliable at this stage of theoretical development. The transition from lateral to continuous growth occurs at an undercooling  $\pi \Delta T^*$  at which the driving force reaches a critical value  $\Delta F^*$  given by

$$-\Delta F_v^* = \pi \sigma g / a \quad (3a)$$

where  $\sigma$  is the interfacial free energy and  $a$  is the step

height. By comparing this with equation (1), it follows that

$$\Delta T^* = \sigma g V_m T_0 / a L \quad (3b)$$

When the driving force does not exceed  $\pi\sigma g/a$ , the lateral mechanism must operate. At very low driving forces, one expects the steps in a diffuse interface to be so far apart and to have such low curvatures that they give rise to classical lateral growth kinetics. However, as the driving force approaches  $\pi\sigma g/a$ , the nucleation barrier disappears, and the growth kinetics of both perfect and imperfect crystals must approach those of Wilson<sup>(4)</sup> and Frenkel<sup>(5)</sup> continuous growth mechanism. Thus, the growth regimes are quantitatively separable into the classical ( $-\Delta F_v < \sigma g/a$ ), the transitional ( $\sigma g/a < -\Delta F_v < \pi\sigma g/a$ ), and the continuous ( $-\Delta F_v > \pi\sigma g/a$ ) regions. The dividing mark between the classical and the transitional regimes was taken to occur at that driving force for which the estimated width of a diffuse step is approximately equal to the radius of a critical nucleus. We will now consider these regimes in greater detail.

#### A. The classical regime

In this range of low driving force, growth on low index surfaces should occur by the lateral mechanism and the effective step energies should be independent of undercooling. The growth rate at any place on the surface is given by

$$G = av \quad (4)$$

where  $a$  is the step height and  $v$  is the frequency with which growth steps pass over this place on the surface. If the flux of steps is such that the local density  $\rho$  of steps remains constant in time, equation (4) becomes

$$G = aV\rho \quad (5)$$

where  $V$  is the local step velocity. The classical regime is theoretically subdivided according to the source of steps, i.e. according to the state of crystal perfection.

On a crystallographically perfect surface, two-dimensional nucleation is required to create new steps. The energy barrier  $W$  for this is given by<sup>(16)</sup>

$$W = -\pi\epsilon^2/a\Delta F_v, \quad (6)$$

where  $\epsilon$  is the free energy per unit length of a step of height  $a$ . The corresponding nucleation rate<sup>(17)</sup> of new steps per unit area is approximately

$$\dot{n} = V_\infty \cdot \frac{N}{V_m} \left( \frac{L\Delta T}{RT^2} \right)^{1/2} e^{-W/RT} \quad (7)$$

where  $N$  is Avogadro's number. If  $V_\infty$  is the velocity of a straight step,  $\mathcal{L}_1$  is the largest dimension, and  $A$

the area of the crystal face, then  $\mathcal{L}_1/V_\infty$  and  $1/\dot{n}A$  are, respectively, the time for a nucleated step to spread over the whole crystal, and the average time between new nucleation events. If  $\mathcal{L}_1/V_\infty \ll 1/A\dot{n}$ , each nucleation event results in a new layer and  $v$  is equal to  $A\dot{n}$ . Thus

$$G = aA\dot{n}. \quad (8)$$

On the other hand, if  $\mathcal{L}_2/V_\infty \gg 1/A\dot{n}$ , where  $\mathcal{L}_2$  is the smallest dimension of the crystal face, many nucleation events occur on the same layer, and the steps annihilate when they impinge.  $G$  and  $v$  now become proportional to the cube root of  $\dot{n}$  and independent of  $A$ . Neglecting geometric constants of order unity the growth rate  $G$  is given<sup>(18)</sup> by

$$G = V_\infty \left( \frac{L\Delta T}{RT_0^2} \right)^{1/6} e^{-W/3KT} \quad (9)$$

Two kinds of crystallographically imperfect surfaces are known to enhance the growth rate by providing continuing sources of steps: (1) surfaces on which dislocations terminate having Burgers vectors lying out of the plane of the surface<sup>(2)</sup> (i.e. screw, as well as part screw or even edge dislocations canted to the surface); (2) surfaces on which multiple twins terminate giving re-entrant grooves.<sup>(19)</sup>

On dislocated surfaces, each such dislocation terminus is a perpetual source of growth steps. The theory of growth at dislocations outlined by Frank,<sup>(2)</sup> predicted the rotation of growth steps about the terminus and the resultant spiral ramp structure. The predicted growth rate is given by

$$G = aV_\infty/4\pi r_c \quad (10)$$

where  $r_c = -\epsilon/a\Delta F_v$  is the radius of a critical nucleus, and enters here as a measure of the spacing between steps originating from the dislocation source. Both  $V_\infty$  and  $r_c$  are functions of the interface undercooling.

No corresponding kinetic law for re-entrant twins has been developed, but there are indications that under some conditions such growth may be faster than for dislocations. This may well be because the spacing of steps originating from the dislocation cannot be less than  $r_c$ ; no reason for such a lower limit is known for the twin.

The above kinetic equations are implicitly dependent upon the diffuseness parameter through the two quantities  $\epsilon$  and  $V_\infty$ . The step free energy per unit step length is related to the surface free energy,

$$\epsilon = \sigma a \sqrt{g}. \quad (11)$$

Thus the step energy can be very small compared with

$\sigma a$ , if the surface is diffuse. Traditionally,  $\varepsilon$  has been assumed equal to  $\sigma a$ , but this assumption has not been substantiated where experimental check has been possible.

The quantity  $V_\infty$  has been estimated for solidification by Hillig and Turnbull,<sup>(8)</sup> assuming an abrupt step that advances laterally by the stepwise addition of single atoms from the liquid by a diffusion jump. In their model,

$$V_\infty = \frac{3DL\Delta T}{aRT^2} \quad (12)$$

This model assumes that the interface is sharp (i.e.  $g \sim 1$ ) and that the ordering at the growth front occurs by a monomolecular transport process. The latter can be characterized by a diffusion coefficient  $D$ , which may be approximately identified with the liquid self-diffusion coefficient. We now examine both of these assumptions and suggest appropriate modifications in equation (12).

The factor of 3 came from an estimate of how many molecules were in a position to jump into a growth site, or more specifically into a portion of a step one molecular distance in length. However, Bolling and Tiller<sup>(20)</sup> noted that, in a diffuse interface, the step width is proportional to  $g^{-1/2}$  and that the number of molecules designated as able to jump into a growth site should be increased accordingly. We propose that the factor 3 in equation (12) be replaced by  $(2 + g^{-1/2})$ , which reduces to 3 when  $g$  approaches 1 and is approximately equal to  $g^{-1/2}$  when  $g$  is small.

The factor  $D/a$  arises from the assumption that the transport process by which molecules add to the solid at the step is related to liquid diffusion. It is supposed to be equal to the quantity  $av$  where  $a$  is the amount by which a step advances when a molecule is added, and  $v$ , the attempt frequency. (As there is also a frequency of leaving a step, the factor  $L\Delta T/RT^2$  is the fraction of attempts that result in net addition.) Let us write for liquid diffusion rate

$$D = (1/6)\lambda^2 v_l$$

where  $\lambda$  is the mean jump distance in the liquid and  $v_l$  the jump frequency. Thus

$$av_i = 6 \left( \frac{a}{\lambda} \right)^2 \left( \frac{v_i}{v_l} \right) D/a = \beta D/a$$

in which the subscripts  $i$  and  $l$  indicate interface and liquid, respectively, and where we have defined

$$\beta = 6 \left( \frac{a}{\lambda} \right)^2 \left( \frac{v_i}{v_l} \right)$$

as the parameter that expresses the degree to which the simple assumption did not fit. The quantity

$a/\lambda$  is expected to be an order of magnitude larger than one, whereas the factor  $v_i/v_l$  is expected to be about 1 for symmetric molecules, and smaller than 1 for unsymmetric molecules that must rotate before they can fit into place in the solid. A temperature dependence of  $v_i/v_l$  is not precluded; however, growth kinetic measurements over temperature ranges for which the fluidity of the melt changes drastically all suggest that  $v_i/v_l$ , and hence  $\beta$ , are temperature independent. Thus a more complete expression  $V_\infty$  is given by

$$V_\infty = \frac{DL\Delta T}{aRT^2} \beta(2 + g^{-1/2}) \quad (13)$$

and the growth by a screw dislocation mechanism should be modified to read

$$G = \frac{\beta(1 + 2g^{1/2})}{g} \frac{DL^2(\Delta T)^2}{4\pi T^2 RT \sigma V_m} \quad (14a)$$

or for  $g \ll 1$

$$G = \frac{\beta DL^2 \Delta T^2}{g 4\pi T^2 RT \sigma V_m} \quad (14b)$$

### B. The continuous regime

We now turn to the regime of high driving forces ( $-\Delta F_v > \pi\sigma g/a$  or  $\Delta T > \pi\Delta T^*$ ). Crystal growth should occur by continuous advance of the surface without recourse to a lateral spreading mechanism. For this region a growth rate has been derived<sup>(4,5)</sup> using the simple assumption that identifies the transport process in liquid diffusion with that involving molecular addition to the solid as in the above discussion of equation (12). Accordingly, this growth model should also be corrected by the factor  $\beta$  and we propose

$$G = \frac{\beta DL\Delta T}{aRT^2} \quad (15)$$

### C. The transitional regime

At intermediate driving forces

$$\sigma g/a < -\Delta F_v < \pi\sigma g/a$$

growth should occur by the lateral spreading mechanism. At the "low driving force" end of this regime, all the important parameters of growth approach their "classical regime" values. At "the high driving force" end, the work  $W$  of forming a critical nucleus approaches zero, implying by equation (5) that the apparent edge energy is approaching zero also. Because of this decreasing edge energy, we expect in this region a deviation from the classical equations in the direction of faster growth.

In the case of the emergent dislocation model, this temperature dependence of effective edge energy

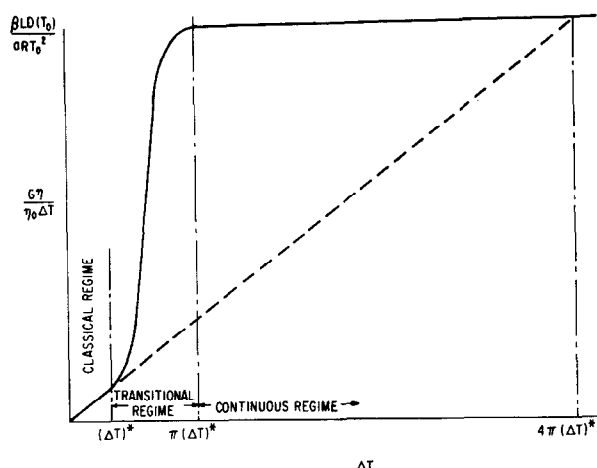


FIG. 1. Theoretically predicted growth rate curve for surfaces with emergent dislocations. The curve in the transitional regime is shown schematically. The ordinate is the growth rate adjusted for the temperature dependence of the melt viscosity and divided by the interface undercooling. A linear growth law is displayed as a horizontal straight line, and a parabolic law is shown as a straight line which intersects the origin.

results in a spiral step density that increases faster than linearly with undercooling. A similar conclusion can be reached by examining Fig. 1. Here shown schematically is the growth rate divided by the undercooling and corrected for the temperature dependence of the diffusivity (or viscosity). The continuous mechanism should give a constant value (horizontal straight line) independent of undercooling, provided that  $\beta$  is temperature independent. The classical dislocation mechanism should give a linear plot through the origin. The  $(\Delta T)^*$  is the undercooling for which  $-\Delta F_v = \sigma g/a$ . The extrapolated rates for the dislocation mechanism and for continuous growth (equations (14) and (15)) intersect at an undercooling equal to  $4\pi(\Delta T)^*$  so that these two growth laws appear to join at approximately four times the expected undercooling (see equation (3)). Since we should reach continuous growth at a much smaller undercooling  $\pi(\Delta T)^*$ , we could expect that the growth rate should deviate in the transitional regime from the classical equations in the direction of faster growth. This is shown schematically in the figure.

We have shown that the single parameter  $g$  enters into the undercooling criterion separating the two major mechanisms of growth. It also enters into the edge energy that can be measured in growth by two-dimensional nucleation. In addition, it enters into the growth rate that can be obtained from measurement on growth by a screw dislocation mechanism. The second parameter  $\beta$  enters into the

magnitude of the growth rate and can be obtained from measurements thereon.

Finally, we examine the absolute range of undercooling over which the lateral growth mechanism is expected to operate in order to ascertain whether the various regimes are experimentally observable.<sup>†</sup> At the transition temperature defined by equation (3b) the growth rate given by equation (15) is

$$G^* = \frac{\pi\beta D\sigma g V_m}{a^2 R T} \text{ at } \Delta T = \pi(\Delta T)^*. \quad (16a)$$

From Turnbull's empirical expression<sup>(21)</sup> for  $\sigma$  in simple substances,  $V_m\sigma/a = BL$ ,  $B$  being a constant that lies between 0.2 and 0.5 for nonpolymeric materials, the above equation yields

$$G^* = \pi\beta g BDL/aRT \text{ at } \Delta T = \pi(\Delta T)^* \quad (16b)$$

and the transition undercooling

$$\Delta T^* = BgT. \quad (17)$$

Hence, whether these transitions are experimentally attainable depends on the magnitude of  $g$ . For very small  $g$  only the continuous regime may be observed; for large  $g$  it may be difficult to attain the continuous regime.

#### D. Nonisothermal surfaces

In many growth situations, e.g. the advance of a planar crystal face, the solidification front will not be isothermal. In the continuous growth regime the only temperature of concern in producing the local growth rate is the local temperature. On the other hand, in the lateral growth regime the local growth rate depends on step sources, which not only may be remote but also may be at another temperature. The growth rate of a crystal face is usually determined by the most active step source, e.g. the coldest dislocation terminus. It is possible for a nonisothermal planar crystal surface to have the same growth rate over all its surface, if it is everywhere below the melting point. The step velocity  $V$  will be less and the density of steps higher in the warmer portions keeping the product  $\rho V$  and hence growth constant. Naturally, should a portion of the surface reach the melting point, no further growth is possible there.

### 3. INTERPRETABILITY OF EXPERIMENTAL EVIDENCE

The verification of the foregoing ideas requires an experimental determination of whether lateral

<sup>†</sup> A criterion based on two-dimensional nucleation energy ( $\pi\sigma a < 50 kT$ ) given earlier is not valid for very small  $g$  since it only considered whether  $W$  could reach a reasonable magnitude and ignored the kinetics of step motion. For very small  $g$ , the transitional undercooling is so small that growth is slow because the step velocity ( $V_\infty$ ) is small, even though the nucleation rate is appreciable.

or continuous growth is occurring in a variety of conditions and checking certain quantitative predictions. Therefore, this section is concerned with a discussion of the types of experiments that permit one to reach a conclusion about the growth mechanism and ways to determine experimentally the theoretically significant parameters. The mechanisms differ on an atomic level, but the experiments are usually macroscopic and, therefore, indirect. We will attempt to state exactly what the experiments do prove or what they imply.

On the basis of their definitions a distinction can be made on an atomic scale between the mechanisms. If we could detect growth of less than an atomic layer, then in the case of lateral growth, we would find, on the average, no growth except along steps: there will be constant fluctuations in the local position of the interface, but we expect these to average to zero except during the passage of a step.

On the other hand, with continuous growth, the interface should advance more or less uniformly everywhere. The variations in rate of advance should, of course, correlate to certain geometrical features of the surface, such as curvature and orientation. The variation of growth rate with surface orientation deserves special examination. Situations are conceivable in which a surface growing continuously could exhibit some features characteristic of the lateral growth mechanism. For example, consider growth in the direction of minimum growth rate of a material having a high growth rate anisotropy. Small deviations in orientation from the growth plane normal to this direction can be analyzed in many cases in terms of a terraced surface, the steps being one or more unit cells high. By virtue of the postulated growth-rate anisotropy, the terrace steps will advance sideways much faster than the terrace surface can advance normally. This continuous growth mechanism then resembles the lateral, and we shall term it the mock-lateral.

Although so far we have no experimental evidence for the existence of the mock-lateral mechanism, we must keep it in mind when interpreting experimental evidence. Because the mock-lateral mechanism requires a high degree of growth anisotropy, we would expect it only in crystals of low symmetry. Ultimately, we must distinguish between lateral and mock-lateral on the basis of whether or not the average growth rate is zero on the terraces.

When the mock-lateral mechanism is suspected for a system, one might measure growth rate vs. orientation and compare it both with the apparent step velocities observed on a stepped surface and with

the rate of advance of the terraces. If the mock-lateral terrace structure is not to grow out of existence, a continuing step source is required. This implies localized catalysis in the slow growth direction or a continuous ramp source as, for example, a dislocation.

The basic distinction is thus whether or not there is *any* growth except by passage of steps; a more convenient distinction is made on whether most growth occurs by passage of steps, bearing in mind the possibility of the mock-lateral mechanism. This is shown schematically in Fig. 2. We will now discuss in more detail the individual kinds of experimental evidence.

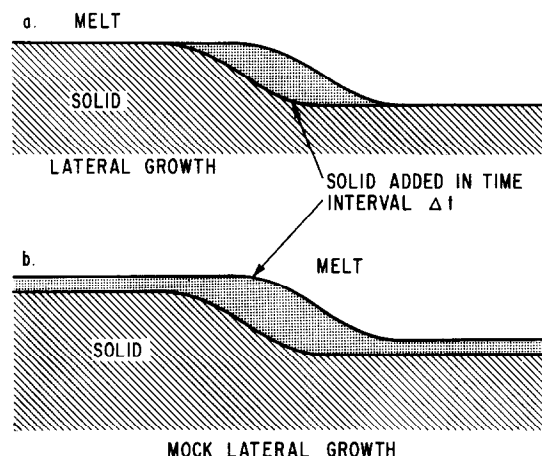


FIG. 2. Schematic representation of difference between lateral growth (a) and mock-lateral growth (b).

#### A. Lateral growth

Basically, there are three classes of observation that indicate that a lateral growth mechanism is operative in solidifications: (1) kinetics, (2) topology, and (3) morphology. The subdivisions within each class are listed in Table 1 and are briefly reviewed here.

TABLE 1. Types of observation that indicate a lateral growth mechanism is operable

i. Kinetics
(a) Change in kinetic law with introduction of defects
(1) By mechanical damage
(2) By twist component of boundary
(3) By multiple re-entrant twins
(b) Measurement of kinetic laws
(1) Two-dimensional nucleation
-a- Quantitative functionality
-b- Go/no-go aspect—qualitative functionality
(2) Screw dislocation kinetics
ii. Topology (growth terraces)
(a) Viewed in action
(b) Fossilized
iii. Morphology

(i) *Kinetics*. The kinetic argument for the existence of a stepwise growth mechanism consist of the following types:

(a) Perhaps the strongest qualitative evidence for

the operation of a layer spreading mechanism occurs if the introduction of step sources (such as a screw dislocation or re-entrant twin) into an otherwise perfect crystal results in a radical change in the growth kinetics. This behavior absolutely eliminates the usual continuous growth mechanism, but not the mock-lateral.

(b) Since the various growth mechanisms predict different kinetic laws, quantitative observations of the growth kinetics provide powerful evidence regarding the growth mechanism. For example, the continuous growth law predicts a growth rate for small surface undercooling  $\Delta T$  that is linear in undercooling (equation (15)); the dislocation law predicts a growth rate that is approximately proportional to  $(\Delta T)^2$  (equations (14a) and (14b)); the growth of a perfect surface is expected to follow an exponential law in  $(\Delta T)^{-1}$  [equations (6)–(9)]. The mock-lateral being a continuous growth mechanisms should have a term linear in  $\Delta T$  from the terraces plus contributions from the “steps” between the terraces. For example, if the “step” originates at a “dislocation” ramp, this additional contribution should be proportional to  $(\Delta T)^2$  and, therefore, relatively unimportant at low undercoolings. To interpret the kinetics, it is essential that the interface temperature be known or estimated. Often only the temperature of the thermal reservoir is known. This can lead to confusions in interpretations that are discussed under Section 3.C, headed “Heat Flow.”

For small undercooling, the temperature dependence of the factors, in equations (8), (9), (14), and (15), is negligible, and we shall simply use their value at the melting temperature. However, over wider ranges of undercooling, especially for the more viscous materials, it is worth while to correct  $G$  for temperature dependence of these other factors. As indicated in 2.C, this is done adequately by multiplying  $G$  at each temperature by the ratio of  $D$  (or the fluidity  $1/\eta$ ) at the melting temperature to its value at the growth temperature. The corrected  $G$  should then reveal the mechanistic aspects of its dependence on undercooling over a much larger temperature range. It is to be emphasized that the kinetic laws are based on theoretical inference about how rapidly steps move and what the density of the steps will be. Thus, adherence to a particular kinetic law can only rule out other models, but it cannot definitely prove the validity of the model with which it is consistent.

Because of the mathematical form of equations (6) and (7), two-dimensional nucleation theory predicts that a small but finite undercooling is required before perceptible growth can occur on a perfect surface.

This go/no-go aspect of nucleation theory leads to a convenient qualitative test of interface perfection and of the lateral mechanism.

(ii) *Topological*. Topological evidence consists of observing growth terraces moving during the growth of a crystal, or finding them on crystal surfaces after decanting the melt under circumstances in which the production of these features for irrelevant reasons (such as surface ripples from adhering melt or continued crystal growth by vapor deposition) can be eliminated. We will take topological evidence as strong indication that lateral or mock-lateral mechanisms are operative.

(iii) *Morphological*. The development of well-defined crystallographic surfaces during growth implies that the ordinary continuous growth mechanism could not be operative. In other words, growth must have proceeded by a layer-spreading mechanism. A near perfect whisker is bounded by low index lateral faces. Since it maintains a constant cross section while growing axially, there is a barrier to growth of the lateral faces. Similar conclusions can be drawn from other morphologies, such as near perfect platelets.

It is important not to confuse the morphology produced during active growth with the morphology of an equilibrated crystal. The shape of the latter is controlled by the surface free energies of the various faces and is independent of the growth mechanism.

## B. Continuous Growth

Critical evidence for continuous growth is much more difficult to obtain. Absence of proof for a lateral mechanism is not proof of the continuous. Corresponding to the categories of proof for lateral growth, we have for continuous growth the following types of evidence.

(i) *Kinetics*. The absence of a growth rate difference between perfect and imperfect surfaces would constitute proof of a continuous growth mechanism. There appears to be the necessity of caution here in that, at higher undercoolings, the material grown onto a perfect surface can be imperfect.<sup>(22)</sup> Therefore, the perfection of the surface must be checked again after the growth rate experiment.

The observation of a kinetic law, linear in undercooling after a correction for viscosity has been made, constitutes strong evidence for continuous growth, although there are lateral mechanisms that might lead to the same law. While the kinetic law has not been derived theoretically for the growth of a re-entrant twin from the melt, this rate may also be linear in undercooling, since there is no obvious linear relation

between step density and supercooling as there is in dislocation growth. Growth from the vapor by a dislocation mechanism can also lead to a linear growth rate, but since there exists no corresponding diffusion problem in growth from the pure melt, it does seem unlikely that the dislocation mechanism can lead to a linear law, provided the crystal width,  $\mathcal{L}_2$ , exceeds  $r_c$ . For crystals less than  $r_c$  in width a linear law would result from the dislocation mechanism.

(ii) *Topological*. The failure to observe growth steps can only be used as evidence for continuous growth if steps one atom layer high could be detected on the growing surface.

(iii) *Morphological*. Absence of all morphological evidence for lateral growth should be evidence for a continuous growth mechanism. However, here again we must offer a word of caution. Regardless of the interface growth mechanism, a crystal will be rounded under conditions where the growth rate is limited by heat flow considerations. Thus the search for morphological evidence must be limited to situations where heat flow is not controlling. As before, it is important not to confuse the morphology produced during active growth with that of an equilibrated crystal.

### C. Heat flow

Many theoretical treatments of solidification rates are based entirely upon heat flow. In this paper, we are concerned primarily with the relation between growth velocity and actual undercooling at the interface. The interface temperature is almost never under direct experimental control and is determined by many factors of which heat flow is an important one. For the purposes of this paper, it is sufficient to know what the interface temperature actually is. There have been several attempts to measure the interface temperature directly, but this is a very difficult problem.<sup>(22-25)</sup> A very promising technique for determining the relation between undercooling and growth rate has recently been described by Kramer and Tiller<sup>(23)</sup> who measure the attenuation of a thermal pulse by the liquid-solid interface.

The temperature away from the interface has no direct influence on the instantaneous interface velocity; it has only the indirect, but very important, effect of determining how much of the latent heat generated at the interface can be conducted away and thereby determines whether the interface temperature will rise or fall.

In many situations, the interface velocity is said

to be controlled by heat flow. The interface temperature is very close to the equilibrium temperature and the interface advances only as rapidly as the latent heat can be conducted away. Here one can estimate the interface velocity from the heat flow by assuming that the interface temperature is at the melting point. The actual interface undercooling will only be a small correction to the boundary conditions of the heat flow problem since it is a fraction of the temperature differences in the system. Nevertheless, if one were to measure the actual interface undercooling in such situations, it would be related to the growth velocity of the interface. Kramer and Tiller's technique offers a method of measuring the actual interface temperature in this type of experiment.

Many solidification experiments are conducted under almost isothermal conditions. With proper experimental design, the latent heat can be conducted away by temperature differences that are small fractions of the applied undercooling. One way this can be achieved is by solidifying in thin capillaries at very small undercoolings. If the observed growth rates are insensitive to heat flow parameters, such as thermal conductivity or thickness of capillary walls, one can conclude that the interface temperature is nearly equal to that reported for the melt or wall.

In many other experiments, interface undercooling is not reported and can only be estimated with varying precision from the geometry and the solution to the heat flow equations. For the case of the growth rate of dendrites and dendritic needles, the solution<sup>(26)</sup> to the heat flow equations predicts a growth velocity that has a similar dependence on *applied* undercooling ( $\Delta T^{2.1}$  to  $\Delta T^{3.0}$ ) as the screw dislocation mechanism has on interface undercooling ( $\Delta T^2$ ). This has led to an additional complication or confusion in interpreting these types of kinetic laws; however, in principle at least, this can be resolved by detailed analysis of the heat flow contributions, aimed at estimating the actual interface undercooling.

In the case of certain morphological evidence, quite strong arguments regarding mechanism can be made from qualitative heat flow considerations. For instance, the development of well-defined crystallographic surfaces during growth shows that one has the same growth rate all over a surface that cannot be isothermal. This rules out continuous growth. Similarly, a thin plate or whisker morphology shows that the most rapid growth has occurred at the edges or ends that are also the warmest portions of the bounding surface.

To summarize, for the purposes of this paper we are only interested in the actual interface temperature.



Unfortunately, we only rarely have reliable information about it.

#### 4. EXPERIMENTAL EVIDENCE

We now examine the critical evidence that characterizes the solidification mechanism for various substances. Our intent is to summarize in each investigation the salient features. For convenience, the substances have been grouped and will be considered as follows: (A) metals; (B) inorganic compounds and nonmetallic elements; (C) organic compounds.

##### A. Metals

Solidification of metals is of great practical and scientific interest. Because molten metals are frequently monatomic melts, orientation and transport processes are thought to be particularly simple. Unfortunately, metals are opaque,<sup>†</sup> ruling out direct observation of the solidification interface. The solidification rates are usually high, and the fluidities of the melts are temperature insensitive. For these reasons, measurements of solidification rates at very large undercoolings are unavailable.

(i) *Aluminium*.<sup>‡</sup> In some commercial continuous castings, highly twinned aluminium crystals win out in competitive growth over the usual columnar  $\langle 100 \rangle$  crystals. These twinned crystals have been variously described as basaltic<sup>(27,28)</sup> or feather (fieder)<sup>(29)</sup> crystals.

Basaltic crystals are twinned on  $\langle 111 \rangle$  planes with rapid growth occurring in one of the  $\langle 112 \rangle$  directions in the twinning plane. Such growth is in contrast to the usual observation of most rapid growth in  $\langle 100 \rangle$  directions. The twins are spaced quite regularly at about  $100 \mu$  intervals; hundreds of such twin lamellae form a single large grain, which often extends across the entire casting.

It appears that ordinarily the  $\langle 112 \rangle$  direction grows more slowly than the  $\langle 100 \rangle$  direction. Twinning, therefore, alters the growth kinetics in the  $\langle 112 \rangle$  direction; i.e., this growth is structure sensitive and rules out the continuous mechanism in the  $\langle 112 \rangle$  direction.

(ii) *Tin*. Recently, Kramer and Tiller<sup>(23)</sup> have devised an elegant technique for determining the dependence of  $G$  upon the interface undercooling  $\Delta T_i$ . The technique consists of measuring the modulation of a thermal pulse as it passes through a solid-melt interface. Their results for tin<sup>(30)</sup> freezing in the

close-packed direction are given by

$$G = 50(\Delta T_i)^2 \text{ cm/sec.}$$

These kinetics are evidence of a lateral spreading mechanism.

The earlier work of Rosenberg and Winegard<sup>(31)</sup> as well as of Orrek<sup>(32)</sup> gives similar results, but Orrek's analysis of heat flow gave strong indication that in these experiments the interface temperature is not well approximated by the melt temperature.

(iii) *Zinc*. When a globule of molten zinc contained in a clean fused silica vessel is cooled in a HCl gas atmosphere,<sup>(33)</sup> or in a very clean vacuum,<sup>(34)</sup> an unusual faceted morphology results: when freezing commences, thin platelets of zinc skate on the surface and repel one another. They grow predominantly edgewise until they impinge. The platelets attain diameters up to 3 mm and remain thinner than 0.1 mm. Heat flow can be ruled out as a factor in producing such a geometry. This large growth anisotropy ( $>30:1$ ) in a metal system is indicative of a lateral growth mechanism on the basal plane.

(iv) *Germanium*. The formation of lath-like crystals of germanium grown by pulling a seed crystal from the undercooled melt has been the subject of detailed study.<sup>(35-39)</sup> The lateral  $\langle 111 \rangle$  lath faces do not advance at sufficiently small undercoolings. Growth only occurs in a  $\langle 211 \rangle$  direction in the presence of twinning and then only if the specific  $\langle 211 \rangle$  direction corresponds to a re-entrant groove. Multiple twinning is required so that the active grooves are not grown out of existence. The go/no-go aspects and the structure sensitivity of the growth kinetics point to a lateral growth mechanism.

(v) *Bismuth*. Recently, topological studies of bismuth telluride crystals drawn from a stoichiometric melt have been reported by O'Connor.<sup>(40)</sup> The crystal, drawn from the melt in a  $\langle 2130 \rangle$  direction, assumed a ribbon form. The  $\langle 0001 \rangle$  ribbon faces were flat and mirror-like and were occasionally crossed by  $25 \mu$  steps normal to the  $\langle 2130 \rangle$  direction. At small undercoolings the width of a ribbon was observed to change, while the thickness remained constant. The cessation of  $\langle 0001 \rangle$  growth at low supercoolings demonstrates a two-dimensional nucleation mechanism. It was corroborated by etching a portion of the ribbon that no screw dislocations emerged on the  $\langle 0001 \rangle$  surfaces. No evidence was presented bearing on rapid growth in the  $\langle 2130 \rangle$  direction.

(vi) *Bismuth*. High-purity bismuth<sup>(41)</sup> freezes at undercoolings less than about  $10^\circ\text{C}$  to form well-defined faceted rhombohedral structures. If certain favourable twin planes are introduced into a seed

<sup>†</sup> Alkali metals are transparent in the ultraviolet.

<sup>‡</sup> We are indebted to Dr. Bruce Chalmers for bringing these observations to our attention.

crystal, the growth rate is much enhanced and a prism results. Such prismatic crystals all have a growth direction of  $[00\bar{1}]$ , the prism faces being (100),  $(\bar{1}00)$ , (010) and  $(0\bar{1}0)$ . Twinning occurs on the (110) plane, and the re-entrant angle of  $173^\circ 8'$  appears on the growing face. The prism faces are usually very flat but frequently growth terraces are visible. The morphological evidence and structural dependence of kinetics indicate a lateral growth mechanism.

(vii) *Antimony*. Crystals of high-purity antimony grown from the melt contain one or more twin planes.<sup>(41)</sup> Observations, similar to those made on bismuth, were also made for antimony, but details are not given. Apparently, growth occurs by the lateral mechanism in this case as well.

### B. Inorganic compounds and nonmetallic elements

Although not many substances in this class have been studied, the work in this area includes some of the earliest and most powerful evidence regarding the mechanism of solidification. For lead iodide, water and phosphorus, the dependence of mobility on temperature is relatively weak. Potassium disilicate is characteristic of the very interesting glass-forming compounds that have a very large temperature coefficient of mobility. As a result, the growth rate goes through a maximum and decreases again at large undercoolings. If a viscosity correction is made for the growth rate, the maximum disappears and the growth rate curves assume a more familiar shape. Unfortunately, considerable attention<sup>(42)</sup> is often focused on the temperature and velocity at this maximum in the opinion that this is the most significant fundamental parameter for characterizing growth kinetics. Consequently, there is little data at very small undercoolings for such systems.

(i) *Lead iodide*. The existence of a layer spreading mechanism from the melt was first deduced<sup>(7)</sup> from topological observations on lead iodide. Spiral growth markings were found on habit planes of crystal after rapidly decanting the melt. An analysis of requisite mass transfer showed that vapor transport after decantation would have been 10,000 times too slow to account for the observed spiral topology. Since molten  $PbI_2$  could be undercooled no more than  $2^\circ C$ , the growth occurred, at small undercoolings.

(ii) *Ice*. The solidification of water has been studied extensively. Quantitative growth velocity data are available over three decades in undercooling for growth parallel to the basal plane, and over two decades in undercooling for growth perpendicular to the basal plane. In many cases these data refer to

situations in which corrections can be made for heat flow effects or in which such effects can be shown to be insignificant. The kinetics of growth normal to the basal plane have been determined<sup>(22)</sup> for perfect surfaces. When these surfaces are rendered imperfect, a significant and spectacular increase in growth rate is observed. If these surfaces are allowed to remain perfect, lath-like ice crystals can be grown that exhibit a growth rate anisotropy in excess of 50,000 at about  $0.02^\circ C$  undercooling.

The growth rate for solidification onto a perfect basal plane surface (c-direction growth) is given by

$$G = 0.03 \exp [-(0.35/\Delta T)] \text{ cm/sec}$$

for undercoolings up to about  $0.65^\circ$ . At larger undercoolings the crystal becomes imperfect spontaneously, and the following growth law is then observed

$$G = 0.01 \Delta T^{1.23} \text{ cm/sec.}$$

Once such a crystal surface has been rendered imperfect, this latter growth law persists down to  $0.02^\circ$ , the smallest undercooling measured.

The latter is similar to the more commonly observed maximum growth rate kinetics observed in the direction parallel to the basal plane. Ice grows in thin-walled glass capillaries according to the law.<sup>(8)</sup>

$$G = 0.16 \Delta T^{1.7} \text{ cm/sec}$$

or

$$G\eta/\eta_0 = 0.16 \Delta T^{1.8} \text{ cm/sec.}$$

Other measurements<sup>(24,43,44)</sup> have been carried out under a variety of heat flow conditions. In one case, a measurement<sup>(24)</sup> of the interface temperature was made and related to the growth rate. The various results are summarized in Table 2. In most cases the growth kinetics differ little at small undercoolings. It is apparent that, in the case of free growth, heat flow<sup>(44)</sup> complications occur.

Comparison of the kinetics observed for growth on perfect ice basal planes with equations (8) or (9) shows accord with the expectations of two-dimensional nucleation. The dependence of the growth kinetics upon crystal perfection, the form of the kinetic law for the imperfect surface, and the lath-like morphology are proof that growth on the basal plane occurs by the lateral spreading mechanism. The parabolic kinetic law for growth parallel to the basal plane is indicative of the same mechanism in this direction as well.

(iii) *Phosphorus*. The earliest quantitative solidification rate data, known to us, is that on the freezing of phosphorus reported by Gernez in 1882.<sup>(45)</sup> His investigation covered the range of undercoolings  $0.4^\circ$  to  $19.3^\circ$  over which the rates increased by three

TABLE 2. Solidification kinetics of ice in maximum growth rate direction

Conditions	Tube dimensions (mm)		Law observed (cm/sec)	Range of undercool (C°)	Ref.
	ID	OD			
In Nonex tube	0.97	0.26	0.130 $\Delta T^{1.59}$	0.07–15	43
In Nonex tube	0.58	0.18	0.150 $\Delta T^{1.73}$	0.14–10	43
In Nonex tube	0.55	0.18	0.168 $\Delta T^{1.73}$	0.01–1.2	43
In Pyrex tube	0.23	0.04	0.180 $\Delta T^{1.64}$	0.03–3	43
In silver tube	0.38	0.30	0.250 $\Delta T^{1.54}$	0.07–5	43
In glass tube	2 to 4.7	1	0.160 $\Delta T^{1.75}$	0.2–5	24
On glass rod			0.13 $\Delta T^{2.0}$	1.8–4	44
On brass plate			0.17 $\Delta T^{2.5}$	1.1–3	44
Free growth			0.028 $\Delta T^{2.3}$	2.3–5.2	44
Outward growth on refrigerated surface			0.1 $\Delta T^{1.5}$	0.02–0.1	24

orders of magnitude. At the largest undercooling a spectacularly fast rate exceeding 1 m/sec was noted. These data referred to growth in thin-walled (0.2 mm) glass capillaries. The effect of heat flow was studied by varying the capillary diameter. Below 2.7 mm no effect of size on the kinetics was found. More recently, another investigation was made by Powell, Gilman and Hildebrand<sup>(46)</sup> and covered undercoolings from 1.6° to 19°. In this case, the phosphorus was contained in a 4-mm-diameter tube. The results were in excellent accord with the earlier ones except at undercoolings in excess of 11°. These investigators were the first to propose a parabolic growth rate law in  $\Delta T$ . The rates† obey

$$G = 0.6 \times \Delta T^{1.95} \text{ cm/sec}$$

or

$$G\eta/\eta_0 = 0.6 \times \Delta T^2 \text{ cm/sec.}$$

Because of the parabolic law and the lack of dependence of growth rates on parameters related to heat flow, a lateral dislocation mechanism is indicated.

(iv) *Potassium disilicate*. Growth kinetics for  $K_2O \cdot 2SiO_2$  have been observed<sup>(47)</sup> over a 300° undercooling range. Unfortunately, data were not gathered at a temperature greater than 1008°C. The liquidus temperature is stated to be 1030°C, as compared with the value 1045°C listed by National Bureau of Standards Bulletin 500. At sufficiently large undercoolings (ca. 160°) the corrected growth velocity is linear in undercooling as is indicative of continuous growth and is given by

$$\frac{G\eta}{\eta_0} = 2.7 \times 10^{-5} \Delta T \text{ cm/sec.}$$

The shape of the  $G\eta/\Delta T\eta_0$  plot vs.  $\Delta T$ , using the liquidus temperature given by the investigator,

† This law covers the entire range of observed undercoolings for both investigations and differs slightly from that reported by Hillig and Turnbull<sup>(8)</sup> who gave somewhat greater confidence to the data obtained at undercoolings in excess of 3°.

suggests that the latter temperature is in error and that at small undercoolings the stepwise growth mechanism operates. This will be considered later in the Discussion section.

### C. Organic compounds

Detailed solidification data are available for this class of compounds and many of the data are very significant from the point of view of interpretation. Low crystal symmetries and pronounced growth anisotropies are typical. These are the circumstances under which the mock-lateral mechanism, if it occurs, is possible. Rotation of growth spirals has been observed during solidification. Topological and morphological evidence for lateral growth is particularly rich. Some of the most extensive growth data with respect to the range of undercoolings are available for these substances.

(i) *Benzene*. The solidification kinetics of benzene<sup>(48)</sup> have been measured at undercoolings of 0.01° to 1.5° in thin-walled glass capillaries. The benzene was zone refined and was exceptionally pure. It had a triple point of 5.527°C, which was 0.002° higher than the highest literature value. Heat transfer effects were shown to be negligible.

At small undercoolings <0.10°, the initial growth rate at a given undercooling decreased to a steady-state value. This was demonstrated to be caused by impurity rejection at the solid-liquid interface. However, the form and constants of the kinetic law were unaffected by the small amounts of impurity present, when the  $\Delta T$  was corrected for the true melting point of the individual samples.

The growth law was given by

$$G = (0.108 \pm 0.008)(\Delta T)^{1.64} \text{ cm/sec.}$$

Some measurement in silver capillaries gave

$$G = 0.191 (\Delta T)^{1.64} \text{ cm/sec.}$$

The form of the growth law is consistent with the dislocation mechanism.

(ii) *p-Toluidine*. Both morphological and qualitative kinetic observations have been reported<sup>(9)</sup> for the growth of *p*-toluidine crystals. At small undercoolings, platelets grow at nearly constant thickness, to give lateral diameter/thickness ratios of 1000:1. The thickening rate is a sensitive function of the applied undercooling. The estimated undercooling for which the two-dimensional nucleation rate becomes appreciable is about 1°. In addition, the introduction of defects when a platelet rapidly grows into a wall causes an abrupt change in the growth behavior and thickening rate. These observations are consistent with a lateral mode of growth.

(iii) *Durene*. Various morphological and kinetic observations have been made<sup>(49)</sup> during the solidification of durene on completely immersed crystals. Near perfect platelets were grown from the melt: at an applied undercooling of 0.25°, brightly interference colored platelets existed at constant color for several minutes; at 0.50°, the colors faded in a few minutes; at 3.0° undercooling the thickening was essentially instantaneous. When a platelet at an applied undercooling of 0.50° was touched and stuck to a second crystal, it thickened almost instantly.

Whiskers were grown to lengths of about 1 cm with constant widths of about 50  $\mu$  and thicknesses of about 1  $\mu$ . This demonstrates that both sets of bounding side surfaces required a finite undercooling to grow at an appreciable rate. On the other hand, sidewise growth of platelets occurred at even the smallest applied undercoolings.

The thickening rate of a durene habit face increased drastically when it was mechanically damaged. For example, when a durene ribbon slowly grew into a wall, it bent to conform to the wall until its strain limit was exceeded. At this instant, plastic deformation and the onset of rapid thickening occurred.

The lateral spreading mechanism of growth on the habit faces is supported by the go/no-go growth behavior and by the effect of mechanical damage to perfect habit faces. The lateral mechanism occurs on the prism faces as well, as is evidenced by whisker growth in the melt.

(iv)  *$\beta$ -Methylnaphthalene*. Kozlovskii<sup>(50)</sup> has microscopically observed the growth of thin platelets of  $\beta$ -methylnaphthalene from the melt. He observed the formation of screw dislocations of large Burgers vectors during lateral platelet growth around tiny graphite particles. The rate of platelet thickening increased sharply with the introduction of the dislocation. The spiral layer spreading was observed

directly. Either a lateral or mock-lateral mechanism is involved.

(v) *Salol*. Next to the freezing of water, the solidification of salol (phenyl salicylate) has yielded the most critical data. These have been used to test various heat flow and kinetic models. Of particular interest to this report is the fact that two distinctly different growth laws have been observed at small undercoolings. Danilov and Malkin<sup>(51,52)</sup> report

$$G = K_1 \exp(-K_2/T) \times \exp(-K_3/T\Delta T) \text{ cm/sec}$$

for the growth rate of isolated well-developed polyhedral crystals in which

$$K_1 \exp(-K_2/T_0) = 5.2 \times 10^{-2} \text{ cm/sec}$$

and

$$K_3 = 7020(\text{C}^\circ)^2.$$

These kinetics conform to the two-dimensional nucleation law.

On the other hand, Pollatschek's<sup>(53)</sup> data at small undercoolings for salol contained in a glass tube can be given by

$$G = 4 \times 10^{-5} \Delta T^{1.7} \text{ cm/sec}$$

or

$$G\eta/\eta_0 = 3 \times 10^{-5} \Delta T^2 \text{ cm/sec}$$

Those two papers report growth velocities differing by  $3\frac{1}{2}$  orders of magnitude at 1.5° undercooling. Although we do not know to which crystal directions these two sets of data correspond, both pertain to the fastest growth directions for the respective crystals. Danilov and Malkin report data obtained on the fastest growing edge face, while Pollatschek reports data on what is presumed to be a crystal face that has won out in a competition with the slower growing crystals in the direction of the capillary axis. The more recent work of Neumann and Micus,<sup>(25)</sup> performed under more favorable heat flow conditions (smaller tubes), was in good agreement with that of Pollatschek. Unfortunately, it was not carried out to as small undercoolings.

For convenience in comparing these experimental results with the theoretical expected behavior, the data of the latter two investigations are plotted in curve A of Fig. 3 in terms of  $G\eta/\eta_0\Delta T$  vs.  $\Delta T$ , using the viscosities reported by Jäntschi<sup>(54)</sup> to correct the growth rates. It is to be noted that the departure from the  $\Delta T^2$  law occurs at undercoolings greater than about 6° and that a linear growth law is observed at undercoolings in excess of 15°. In the latter range

$$G\eta/\eta_0 = 8.8 \times 10^{-4} \Delta T \text{ cm/sec},$$

which is in accord with the transition to a continuous

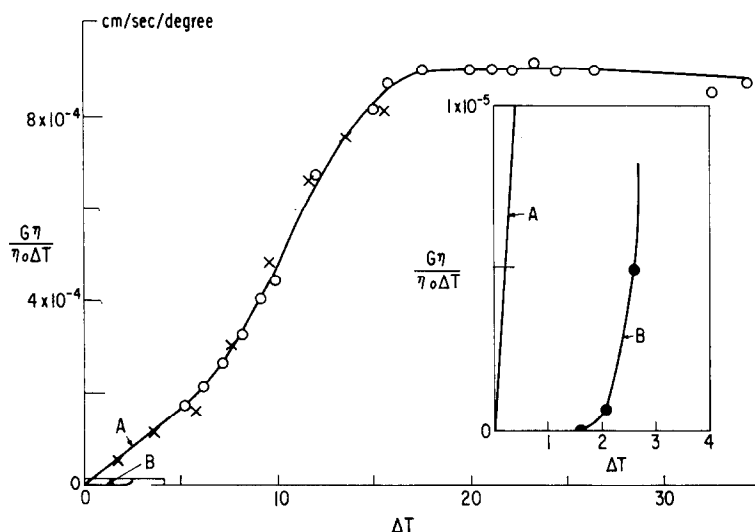


FIG. 3. Growth rate curves for Salol. Curve A, the data of Pollatschek,<sup>(51)</sup> is represented by X and that of Newmann and Micus<sup>(52)</sup> by O. Curve B is based on the observations<sup>(50)</sup> of Danilov and Malkin and presumably pertains to growth on a perfect crystal surface.

mechanism at high driving forces. For the presumably perfect crystals, curve B shows the expected go/no-go behavior characteristic of two-dimensional nucleation.

The growth kinetics characteristic of two-dimensional nucleation as well as the observance of a parabolic limiting growth law under conditions in which heat flow is negligible is strong demonstration of the lateral growth mechanism. In addition, the well-developed morphology during freezing supports this conclusion.

Furthermore, the linear growth law at larger undercoolings is in accord with the expectation that the growth ultimately occurs by the continuous mechanism.

(vi) *Glycerine*. Solidification kinetics and the viscosity of glycerine have been measured by Volmer and Marder<sup>(55)</sup> to  $57^\circ$  below its freezing point. Growth is so slow that the experiment is almost isothermal. At small undercoolings, the limiting growth law is given by

$$G = 1 \times 10^{-6} \Delta T^{1.7} \text{ cm/sec}$$

or

$$G\eta/\eta_0 = 1.05 \times 10^{-6} \Delta T^2 \text{ cm/sec.}$$

These data were obtained by microscopic observation on small, well-deformed crystals. As in the case of salol these data are plotted in terms of  $G\eta/\eta_0 \Delta T$  vs.  $\Delta T$  in Fig. 4. It is seen that the quadratic law is observed down to about  $11^\circ$  undercooling. If a linear law finally is obeyed, its regime is apparently beyond  $50^\circ$  undercooling.

The quadratic growth law at small undercoolings and the well-defined morphology are taken as evidence of the lateral growth mechanism.

## 5. DISCUSSION

### A. Qualitative aspects

The theories of solidification kinetics distinguish between two main mechanisms: the lateral and continuous. It may be that the emphasis on lateral growth in this paper is attributable to the relative ease of obtaining evidence for this mechanism. In any case, most of the pertinent interpretable experiments indicate the operation of this mechanism at low driving forces.

Experimentally, it is much easier to disprove theories about mechanisms than it is to prove them. At best, one can show that a theory is consistent with all the experimental evidence, whereas even one carefully established inconsistency is usually sufficient to invalidate a theory. Thus, we shall begin by ruling out certain theories. For this it will be convenient to note the conditions for which a given theory requires a continuous mechanism and to look there for evidence of lateral growth.

It is clear from the experimental evidence presented that any theory predicting that solidification *never* requires a lateral mechanism can be ruled out immediately. Thus, surface roughening or surface "melting" either does not occur, or if (as we believe) it does occur, the requirement for a lateral growth mechanism remains.

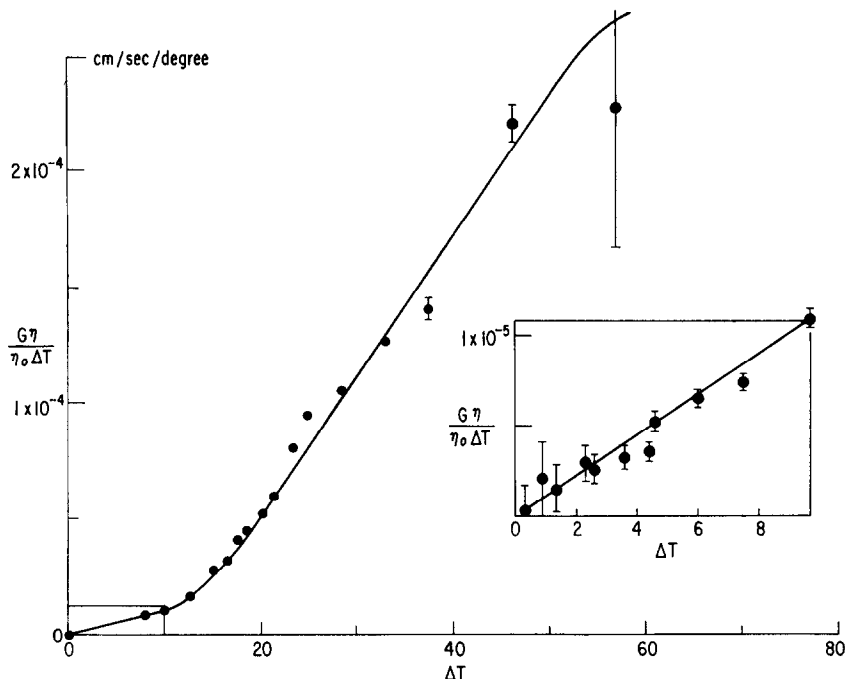


FIG. 4. Growth rate curve for glycerine derived from data<sup>(54)</sup> of Volmer and Marder.

Consider next Jackson's theory<sup>(56)</sup> based on the assumption that systems that have a rough surface grow by a continuous mechanism at all undercoolings. He attempts to predict the roughness from a numerical coefficient  $\alpha$  defined by

$$\alpha = \xi L/RT$$

where  $\xi < 1$  is a geometric coefficient equal to the ratio of the nearest neighbor coordination number in the surface to that in the bulk. Hence, it reflects the crystal structure and the surface orientation. The model predicts that the surface is rough if  $\alpha$  is less than 2. Ignoring  $\xi$ , the value of  $L/RT$  is 1.65, 1.37, and 1.13 for tin, aluminium, and zinc, respectively. Since these substances show evidence for lateral growth, this theoretical model is inconsistent with experiment. This implies either that the basic assumption relating roughness to growth mechanism is untenable, or that the roughness cannot be correlated sufficiently precisely with the parameter  $\alpha$ .

Finally, let us test our contention that solidification from pure melts occurs by a lateral mechanism at sufficiently small undercooling and undergoes a transition to a continuous growth mechanism at greater undercoolings. For all systems examined there appears to be positive evidence for the lateral mechanism at small undercoolings. In a few systems (ice, potassium disilicate, durene, salol and glycerine) we have some evidence for the predicted transition from the lateral to the continuous mechanism.

#### B. Quantitative aspects

In the presently proposed theory the temperature of the transition and the quantitative kinetic laws depend on the parameters  $g$  and  $\beta$ , which can be independently estimated from a variety of observations.

1. From the undercooling  $(\Delta T)^*$  that marks the limit of the parabolic law, i.e. the onset of the transition region, we estimate

$$g = \frac{aL(\Delta T)^*}{V_m \sigma T_0} \quad (18)$$

In this equation and all the following, Turnbull's relation may be used to eliminate  $\sigma$ :

$$g = \frac{(\Delta T)^*}{BT_0} \quad (18a)$$

2. The departure from the classical two-dimensional nucleation law to a transition law should occur at the same undercooling. Thus this transition in the case of growth of perfect crystals also provides an estimate of  $g$ .

3. The transition to the linear law should occur at an undercooling  $(\Delta T)^{**}$ , which should equal  $\pi(\Delta T)^*$ . This also provides an estimate of  $g$ , similar to the previous case in that

$$g = \frac{(\Delta T)^{**}}{\pi BT_0} \quad (19)$$

4. The two-dimensional nucleation law for large crystals can be rearranged to give an estimate of  $g$ .

$$g = \frac{3kL}{\pi\sigma^2aV_m} \frac{d \ln [G/(\Delta T)^{7/6}]}{d(1/\Delta T)}. \quad (20)$$

4'. Often only the go/no-go aspects of two-dimensional nucleation are reported. The two-dimensional nucleation law predicts a change of five orders of magnitude in growth rate in going from an undercooling where  $W = 60kT$  to one where  $W = 40kT$ . When  $W = 40kT$ , growth is of the order of microns per second and easily detectable. Taking the undercooling,  $(\Delta T)_{go}$ , which marks the onset of detectable growth, as occurring at an undercooling for which  $W$  equals about  $50 kT$ , we obtain from equations (1), (6) and (11)

$$g = \frac{50 kL(\Delta T)_{go}}{\pi\sigma^2aV_m}. \quad (21)$$

5. The kinetics of the dislocation mechanism give us the ratio of  $g/\beta$

$$g/\beta = \frac{L^2D(\Delta T)^2}{4\pi RT^3\sigma V_m G}. \quad (22)$$

6. The pre-exponential of the law for growth by the two-dimensional nucleation mechanism provides the product

$$\beta g^{-1/2} = \left(\frac{a}{D}\right) \left(\frac{RT_0}{L}\right)^{7/6} \lim_{1/\Delta T \rightarrow 0} G(T_0/\Delta T)^{7/6}. \quad (23)$$

7. We have at present only one direct method of determining  $\beta$  and that is from the linear law,

$$\beta = \frac{aRT^2G}{LD\Delta T}. \quad (24)$$

Because the two parameters  $\beta$  and  $g$  are sufficient to specify so many independent kinetic characteristics, consistency among these constitutes very stringent test of the theory. For example, in the generalized plot (Fig. 1)  $\beta$  enters only as a scaling factor in the vertical scale and  $g$  enters only as a scaling factor in the horizontal scale. Conformity to the shape of the plot means two tests for self-consistency have been satisfied (four independent quantities with two parameters). Furthermore, if data are available for growth by the two-dimensional nucleation mechanism, the number of checks for self-consistency increases. For example, consider salol, one of the best studied substances. Although information on surface free energies and step heights is unavailable, we can use Turnbull's relation for the former and the cube root of the molecular volume for the latter and obtain from Fig. 2 the following estimates:  $\beta = 0.003$ ,  $g = 0.06$ . These

two numbers would be theoretically sufficient to specify correctly these four experimental quantities the dislocation law, the continuous law, and the two transition temperatures. We can also predict both the pre-exponential and the exponential terms of the two-dimensional nucleation law from these values. This self-consistency test, implied by the theory, is in good quantitative agreement with the observations on salol.

For almost all the substances discussed we have some quantitative information, from which we can estimate  $g$  or  $\beta$ . For instance, the mere fact that lateral growth is observed at all means that  $g$  cannot be too small. If we have some knowledge of the growth rate for which lateral growth was shown to exist, as in the case of tin, we can make use of the fact that the observed growth rate  $G$  must be less than  $G^*$ . By rearranging equation (16) we obtain

$$g\beta = \frac{G^*a^2RT}{\pi D\sigma V_m} > \frac{Ga^2RT}{\pi D\sigma V_m}, \quad (25)$$

so that

$$g > \frac{Ga^2RT}{\beta\pi D\sigma V_m} \text{ if } G < G^*.$$

Similarly, a lower limit to the quantity  $\beta$  can also be obtained by examining the ratio of the actual growth rate to that predicted by the Wilson-Frenkel law

$$\beta \geq \frac{GaRT^2}{DL\Delta T}. \quad (26)$$

For example, even though phosphorus, growing at 1 m/sec, is still not in the continuous regime, it is already growing 15 times faster than predicted by the Wilson-Frenkel law. Thus  $\beta$  must be at least 15. These two are examples of a variety of limits that can be set upon  $\beta$  and  $g$ .

In Table 3 we have collected our best estimates for  $g$  and  $\beta$ . Some are based on much data, others on an almost parenthetical quantitative statement by the investigator. We feel that in most cases at present only the approximate magnitude of these numbers has significance.

It may be worth while to note that the parameter  $g$  correlates quite well with Jackson's parameter  $\alpha$ . If  $\alpha$  is large,  $g$  approaches unity. If  $\alpha$  is small,  $g$  becomes quite small compared to one. Thus it may well be that both  $\alpha$  and  $g$  are related to interface diffuseness.

The magnitudes of the parameter  $\beta$  also fit well into a qualitative pattern. It appears to be of order 10 for all symmetrical molecules and much smaller for the unsymmetrical ones, as expected from a steric

TABLE 3. Summary of the "best values" for the diffuseness parameter  $g$  and the kinetic correction factor  $\beta$  as derived from the various experiments

Substance	"Best values"		Observed parameters						
			$g$		$\beta$		$g/\beta$	$\beta g^{-1/2}$	$g\beta$
	$g$	$\beta$	Eqn.	Value	Eqn.	Value	Eqn.(22)	Eqn.(23)	Eqn.(25)
Sn	$>0.002$	$>8$					0.002		$>0.012$
P <sub>4</sub>	$<0.022$	$>15$			26	$>15$	0.0014		
K <sub>2</sub> O·2SiO <sub>2</sub>	0.14	5	19	0.14	24	5			
Benzene	$>0.0025$	$>0.07$			26	$>0.03$	0.038		$>0.00018$
Durene	0.07		21	0.07					
Glycerine	0.2	0.3	18a	0.14	24	0.3	0.9		
			19	0.21					
Salol	0.07	0.005	18a	0.06	24	0.003	11	0.08	
			19	0.06					
			20	0.091					
Water (C-direction)	0.003	0.006	20	0.0027			0.41	0.071	
Water (A-direction)	$>0.01$	$>0.5$			26	$>0.2$	0.024		$>0.013$

factor. It is noteworthy that the assumption that  $\beta$  is independent of temperature seems to be well substantiated by the linear law found over wide temperature ranges in glycerine, salol and K<sub>2</sub>O·2SiO<sub>2</sub>. The large dependence of  $\beta$  on the growth direction in ice may reflect the difference in the surface structure in the different growth directions.

### C. Guidelines for future experiments

In analyzing the evidences for the molecular mechanism of solidification it was disappointing that so much of the considerable body of experimental experience was inappropriate. Frequently, if mentioned at all, only casual reference was made to interpretable morphological or topological observations. Even the growth kinetic information was often incomplete in various vital respects. As pointed out previously, the molecular kinetics are controlled by the interface temperature (for a given surface perfection and growth direction). Therefore, only those data could be used for which the interface undercooling could be given with confidence. It would be advantageous to design future experiments so that quantitative heat flow corrections can be made. It would be best of all to measure the interface temperature directly. In any case, by altering the heat conduction variables, one can verify whether heat flow effects are significant.

Available measurements were frequently not carried out over a wide enough temperature range. Both very small and very large undercoolings should be employed to obtain the growth kinetics in the various regimes and to compute the various growth parameters. Even when measurements have been available over a broad temperature range, the corresponding diffusion or fluidity measurements were not made on

the same lot of material or even by the same investigators in most cases. The correction factors for the temperature dependence of the melt fluidity are frequently very large. Hence, errors may arise in the value of  $\beta$  calculated from the data in the continuous growth regime if these corrections are not known sufficiently precisely.

Certain critical thermodynamic data, needed to calculate  $\beta$ ,  $g$ , etc., have occasionally been unavailable. These include the latent heat of fusion, and even the equilibrium melting point. Most frequently, surface free energies  $\sigma$  have been lacking. These can be derived from measurements<sup>(57,58)</sup> of freezing point dependence on size, or of critical undercoolings for homogeneous nucleation.<sup>(59,60)</sup> Reasonable estimates can be made using the empirical Turnbull correlation of  $\sigma$  with  $L$  and  $V_m$ . For K<sub>2</sub>O·2SiO<sub>2</sub>, for example, the reported melting point has varied from 1015°<sup>(61)</sup> to 1045°C.<sup>(62)</sup> Solidification rate measurements are reported to 1008°C. As Fig. 5 shows, if the melting point were 1045°C, we would have a parabolic law joining a linear law at 130° undercooling without a transitional regime. If the melting point were 1060°C the expected growth curve would be obtained, and one would predict a growth rate of approximately  $8 \times 10^{-6}$  cm/sec at 1045°C. From these same data, Leontjewa<sup>(47)</sup> surmised a melting point of 1030°C, presumably on a linear extrapolation to zero growth.

Growth kinetics depend upon orientation and surface perfection. In many cases, the crystallography of the solid phase had not been sufficiently determined. Consequently, step advance heights are not known. In these cases, it is expedient to set  $a = (V_m/N)^{1/3}$ . In cases where the crystal parameters are known, the growth directions should be reported.

The perfection of the growth surface is another



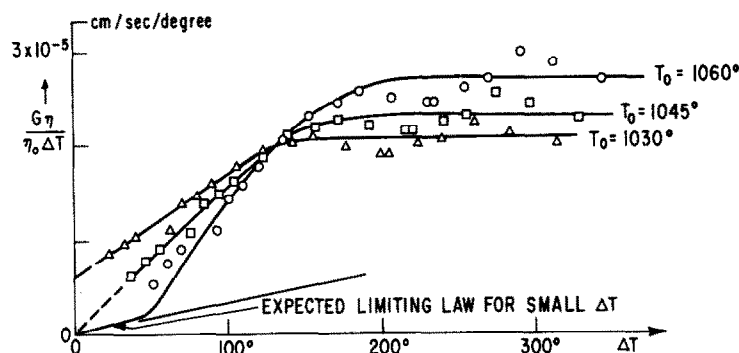


FIG. 5. The dependence of the growth rate curve for  $K_2O \cdot 2SiO_2$  upon the assumed melting point based on data of Leontjewa.

important variable. In particular, where growth by two dimensional nucleation on a perfect crystal surface is suspected, imperfections should have a marked effect on the growth kinetics. The most convincing case for continuous growth would be, if a perfect crystal surface propagated by the linear growth law, and if introducing imperfections had no effect on the kinetics. Of course, the initial perfection of the crystal would have to be demonstrated by some independent means such as an etching technique. A perfect crystal is an unusually rare event. All too often, two-dimensional nucleation theory has been applied quite generally to systems where one has no right to expect it to hold, and thereby to "explain" deviations from a linear law. The abruptness of the transition from the parabolic law to linear law is such that it can be fitted to a two-dimensional nucleation law if one ignores the parabolic law at low undercoolings. This probably accounts for the continued application of two-dimensional nucleation theory for interpreting such data.

Finally, there is some suggestion that re-entrant twins lead to growth kinetics intermediate between continuous growth and dislocation growth kinetics. It would be desirable to know when this or similar imperfections are present.

Purity of the melt can have a number of effects other than the lowering of the melting point. The edge free energy can be lowered, with a corresponding decrease in the work of forming a two-dimensional nucleus. The density of steps in the case of lateral growth on an imperfect surface will be expected to increase, but the step velocity may be significantly diminished. In the case of the growth of ice on the perfect basal plane surface, the growth rates were suppressed<sup>(22)</sup> by trace amounts of impurities. The impurity effects can be expected to be anisotropic

and may affect the resultant morphology. In general, for these reasons it is desirable to carry out studies regarding the growth mechanism on pure systems.

In many solidification studies in order to minimize heat flow effects the growth occurs in contact with a container wall. This opens the question regarding the possible effect of the wall *per se* on the growth kinetics. The effectiveness of the wall as a heterogeneous nucleation (three-dimensional) catalyst can be used to estimate the effectiveness of the wall as a growth catalyst in the case of two-dimensional nucleation. In other cases, the hypothesis of a wall effect can be tested by varying the container material. There is some evidence<sup>(63)</sup> that the roughness of the wall has a noticeable effect on the kinetics. For the most part heat transfer through the wall (or substrate) appears to be the main material variable. Ideally, those experiments are preferable in which growth kinetics can be obtained on a solidification front in contact only with the melt.

Finally, since so many of the characteristics of solidification kinetics as outlined in the theoretical section, depend upon a diffuseness parameter  $g$ , and since the experimental observations appear to be in good qualitative and quantitative accord with this model, it would be most desirable and interesting to measure such an interface diffuseness directly. The values of  $g$  derived from examination of the available literature data range from 0.2 to 0.003. According to equation (2) the thicknesses of the diffuse boundaries range from one to three molecular spacings. Measurements of elliptical polarization of light offer a possible means of measuring this thickness.

## 6. SUMMARY AND CONCLUSIONS

1. The various theories describing molecular kinetic mechanisms for solidification have been discussed.

Particular emphasis has been placed on the distinction between the stepwise and continuous growth mechanisms.

2. The theory of Cahn based on the theory of diffuse interfaces has been reviewed with special emphasis on solidification. New expressions are defined for the various kinetic laws. A transition is predicted from a stepwise growth mechanism at low undercoolings to a continuous mechanism at high undercooling. The expected growth behavior covering both regimes and the transition between them is mapped out. The transition is more abrupt than one might expect on the basis of smoothly joining the limiting laws characteristic of large and small undercoolings.

Two phenomenological parameters are defined:  $g$ , which describes the diffuseness of the interface, and  $\beta$ , which relates liquid self-diffusion to interface transport. These two parameters occur in various combinations in the many expressions for the growth rates in the various regimes for both perfect and imperfect materials. Thus, many independent checks on  $\beta$  and  $g$  are possible where sufficient data exist for a given material.

3. The meaning of various experimental observables are discussed. Many easily made observations can be used to detect the lateral growth mechanism. Surprisingly, few clear-cut criteria are known for proving the operation of a continuous mechanism.

4. The existing pertinent experimental data on metals, organic and inorganic compounds have been examined for evidence pertaining to interface mechanism. We conclude that the lateral mechanism operates in all cases where adequate information is available. In a few cases evidence for the expected transition to a continuous mechanism was found.

5. In some cases it has been possible to estimate numerical values for  $\beta$  and  $g$ . For the three substances, for which more data were available, the theory has been shown to be quantitatively self-consistent with reasonable precision. The magnitudes of  $g$  indicate a two- or three-layer solid-liquid interface; the value of  $\beta$  correlates quite well with the shape of the molecule.

6. Suggestions are offered for future work.

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