Doublon Growth in Solidification

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We present experiments on the doublon growth morphology in directional solidification. Samples used are succinonitrile with small amounts of poly(ethylene oxide), acetone, or camphor as the solute. Doublons, or symmetry-broken dendrites, are generic diffusion-limited growth structures expected at large undercooling and low anisotropy. Low anisotropy growth is achieved by selecting a grain near the {111} plane leading to either seaweed (dense branching morphology) or doublon growth depending on experimental parameters. We find selection of doublons to be strongly dependent on solute concentration and sample orientation. Doublons are selected at low concentrations (low solutal undercooling) in contrast to the prediction of doublons at large thermal undercooling in pure materials. Doublons also exhibit preferred growth directions and changing the orientation of a specific doublonic grain changes the character and stability of the doublons. We observe transitions between seaweed and doublon growth with changes in concentration and sample orientation.

I. INTRODUCTION

Over the past 20 years, surface tension anisotropy has been discovered to be fundamental in determining solidification morphology. Perhaps the greatest success was the discovery that anisotropy is required for the formation of stable cells and dendrites through a microscopic solvability condition [1]. In contrast, an isotropic surface tension leads to complicated, tip splitting growth known as dense branching morphology [2] or seaweed growth [3]. This is a generic feature of diffusion limited growth and exists in a variety of systems under isotropic or weakly anisotropic conditions, such as viscous fingering, bacterial colony growth, and electrodeposition [4].

It was predicted for the solidification of a pure material that a transition from fractal to compact seaweed occurs with increasing undercooling [5]. For a pure material, thermal undercooling increases with growth speed for both dendrites and doublons. At low speeds, perturbations at the tip lead to tip splitting while at higher speeds they convect away [6]. The basis of the compact seaweed is the doublon, or symmetry-broken dendrite, in which two asymmetric cells grow cooperatively such that there is a parabolic envelope over the pair of cells and a thin liquid gap of well-defined size separating them [7]. An example of this is shown in Fig. 1A. It is somewhat counterintuitive to observe random seaweed patterns at low driving force and oriented doublon growth at large driving force. The isotropy in surface tension is revealed in that although doublons have a clear orientation as they grow, it is expected to be randomly selected in the isotropic case [8].

The morphology diagram of Brener et al. [9] describes the expected growth as surface tension anisotropy and undercooling are changed. Although it is assumed to be a general phase diagram, the boundaries separating different types of growth are determined for the solidification of a pure material, so no explicit dependence on solute concentration is known for doublon growth in binary alloys. Solute concentration does affect the undercooling [10] and must be included for a proper analysis of solutal doublons. Solutal undercooling is proportional to sample concentration (= $mC_\infty(1-k)/k$, where $m$ is the liquidus slope, $C_\infty$ is bulk sample concentration, and $k$ is the partition coefficient). We find below that for a given grain and growth speed, doublons are preferred at low concentrations (small solutal undercooling) rather than at large undercooling as expected for thermal doublons.

Stable “parity broken cells” were first observed numerically by Brener et al. [9] and Ihle and Müller-Krumbhaar [14]. Since the early observation of an array of “doublets” by Jamgotchian et al. [15], they have attracted significant interest. The existence of doublons was noted in eutectic growth by Kassner et al. [16]. Subsequent simulations [16, 17], theories [18, 19] and experiments [14, 15, 16] have probed their stability, characteristics and formation. In particular, Losert et al. [14] imposed periodic perturbation experimentally to test doublon stability. In their work, they didn’t find doublons appearing without an imposed perturbation except as transients.

In this article, we examine the doublon morphology experimentally. In particular, we study the effects of concentration changes and sample orientation on the sta-

FIG. 1: (A) Stable doublons in 0.5% PEO-SCN at a growth rate $V = 22 \mu m/s$. (B) Seaweed growth in 0.25% PEO-SCN at the same growth rate. A transient doublon develops before breaking apart.
bility of solutal dendrites. By studying these effects in individual grains, we are able to identify the effects due specifically to either concentration or orientation. We also study the expected transition from fractal seaweed to doublon growth with increasing growth rate. We find that doublon selection depends strongly on concentration, with doublons selected at low solute concentrations (small undercooling) and seaweeds at higher concentrations (large undercooling). We also find that doublons in directional solidification have a particular orientation and that sample orientation affects the existence and character of the doublons.

II. EXPERIMENTAL TECHNIQUES

The experimental apparatus used presently has been described previously [17] and additional details will be presented elsewhere [18]. We perform experiments with a traditional directional solidification apparatus in which a quasi-two-dimensional sample \((13 \, \text{cm} \times 1.5 \, \text{cm} \times (5 - 60) \, \mu\text{m})\) is pulled through a linear temperature gradient at a constant pulling velocity. After an initial transient, the average speed of the solidification front is equal to the pulling speed, set by a linear stepping motor with 4 nm step size.

The cell consists of two glass plates glued together and filled with the sample. The glass plates are cleaned in stages using detergent, acetone, methanol, an acid solution (sulfuric acid and NoChromix), and distilled water. The glue used is the epoxy Torr-Seal. The nominal cell depth is set by a Mylar spacer.

In each set of runs, we maintain the temperature gradient \(G\) at a fixed value between 3 and 50 K/cm with a stability of \(\pm 2 \, \text{mK}\). The temperatures of the hot and cold sides are above and below the equilibrium melting temperature of \(\approx 58^\circ\text{C}\) so that the solid-liquid interface remains within the gap between the temperature controlled blocks. It is also possible to rotate the cell within the sample plane between runs. This allows for control over in-plane sample orientation.

The sample used is a model alloy of succinonitrile (SCN) and a small amount of added solute. The solutes used in this study are either 0.25% poly(ethylene oxide) (PEO) [19], 1.5% acetone (ACE), or 1.3% camphor (CAM). The diffusivities \(D\), partition coefficient \(k\), solute concentration \(C\) (weight %), and sample thickness \(d\) (\(\mu\text{m}\)) are listed in Table I. The properties of samples used in this study are summarized in Table I.

| \(D \, (\mu\text{m}^2/\text{s})\) | ACE-SCN | CAM-SCN | PEO-SCN |
|-----------------------------|---------|---------|---------|
| \(k\)                       | 0.1\(^a\) | 0.33\(^b\) | 0.01    |
| \(C\) (weight %)            | 1.5%    | 1.3%    | 0.25%   |
| \(d\) (\(\mu\text{m}\))     | 20      | 22      | 60      |

TABLE I: Properties of samples used in this study. Succinonitrile alloys with acetone, camphor and poly(ethylene oxide) as solutes. Diffusivity \(D\), partition coefficient \(k\), solute concentration \(C(\pm 0.02\%)\), and sample thickness \(d(\pm 2\mu\text{m})\) also listed. \(^a\) from [24], \(^b\) from [21], \(^c\) from [22].

and quench it, seeding a number of grains. We select one grain with the desired orientation and all others are melted off so the chosen grain can grow and fill the width of the cell. To have a nearly isotropic effective surface tension within the growth plane, the chosen grain must be near the \(\{111\}\) plane \(\mathbf{6}\). Before each run, the sample is kept stationary \((V = 0)\) for a sufficient time to equilibrate.

III. RESULTS

Our early observations of doublons confirmed the fact that they are generally unstable to tilting \(\mathbf{6}\). Doublons that appear to be growing straight will eventually begin leaning towards one side and the cell on that side will suddenly be convected away. The remaining cell then splits to form another transient doublon. The tilting instability generally repeats on the same side since a small amount of crystalline anisotropy usually breaks the symmetry. In one of our first efforts to study doublon formation, we examined the degenerate seaweed described previously [17, 23]. At higher growth velocities, we do find the expected doublonic structures, but they are often intermittent and short-lived. As a doublonic dendritic forms, there are initially two asymmetric cells with a characteristic gap of well defined thickness as in Fig. \(\mathbf{13}\). Although there is not a parabolic envelope over the tips, they are clearly asymmetric with the tips closer together than the cellular spacing and the gap appears to be well selected.

Doublons are predicted to be the basis for seaweed growth, so it is no surprise that the same description of the tilt instability could be given of seaweed tip splitting. During the tip splitting of seaweeds, the cell briefly appears as a pair of asymmetric cells as in Fig. \(\mathbf{2}\). This is the same grain as in Fig. \(\mathbf{13}\) at a lower growth speed. The gap \(b\) between the fingers is also quite regular. To show this more clearly, in Fig. \(\mathbf{3A}\), the interface near the tip region has been extracted in subsequent images and displaced upwards a distance \(V\Delta t\) where \(\Delta t\) is the time interval between pictures, i.e. this is an image in a frame where the tip grows upwards at speed \(V\). There we see that the initial gap between seaweed lobes is clearly se-
FIG. 2: Degenerate seaweed at low growth speed. The initial tip splitting appears similar to the process of doublon formation. The sample is 0.25% PEO-SCN at $V = 2.71 \, \mu m/s$ and $G = 18K/cm$.

FIG. 3: The evolution of the tip region over time is shown on the left. The regularity of the gaps suggests doublon formation. The gap thickness $h$ is plotted versus pulling speed for ($\triangle$) PEO-SCN and ($\bigcirc$) ACE-SCN. The solid line shows $h \propto V^{-0.5}$. Fitting the exponent gives ($\triangle$) $-0.45 \pm 0.05$ and ($\bigcirc$) $-0.52 \pm 0.05$. This compares to Brener et al.’s predicted exponent for doublons ($h \propto V^{-7/9}$, dashed line).

Selected, as with doublons. In Fig. 3B, the gap thickness is measured for seaweeds at different pulling speeds. The gap thickness scales approximately as $h \propto V^{-0.5}$. The scaling for the seaweed gap thickness is consistent with the $\lambda \propto V^{-0.5}$ scaling found for fingering wavelengths in solidification and inconsistent with the prediction of $h \propto V^{-7/9}$ for doublons. The discrepancy could indicate that the seaweed tip is not strictly a transient doublon and that doublons are not the fundamental building blocks of seaweed growth. However, we are not able to verify the $7/9$ exponent for the solutal doublons we observe, since the resolution of our images is not sufficient to resolve the doublon gap thickness.

We find the stability of doublons to be strongly concentration dependent. In a seaweed grain showing unstable doublons, we allowed a flat interface to grow at small pulling speeds, effectively zone-refining a section of the cell. After backing up and growing through the zone refined area and into a region of higher concentration, we observe stable doublons which break apart into unstable seaweed structures as the solute concentration increases, as in Fig. 4. This is repeatable for the different mixtures used in this study. In one case, we then rotated the cell $180^\circ$ and forced the grain to grow from a region of high concentration to low concentration and saw the opposite transition from unstable seaweeds to stable doublons. The latter transition is shown in Fig. 5. Note that since the average interface position is at a higher melting temperature for lower solute concentration, the camera is moved along the growth direction and the relative thermal undercooling cannot be determined directly from these images.

FIG. 4: Doublon to seaweed transition with an increase in concentration. The same grain is grown from a (A) zone refined (low concentration) into a (B) bulk (high concentration) region of the same cell. The sample is CAM-SCN at $V = 86.4 \, \mu m/s$ and $G = 40 \, K/cm$.

FIG. 5: (A) Seaweed to (C) doublon transition with a decrease in concentration. During this transition, the interface rapidly advances, forming (B) transient superdendrites before forming doublons. The sample is CAM-SCN at $V \approx 150 \mu m/s$ and $G = 18 \, K/cm$. 

FIG. 6: (A) Seaweed to (C) doublon transition with a decrease in concentration. During this transition, the interface rapidly advances, forming (B) transient superdendrites before forming doublons. The sample is CAM-SCN at $V \approx 150 \mu m/s$ and $G = 18 \, K/cm$. 
FIG. 6: seaweed to doublon transition with a decrease in concentration. The sample is CAM-SCN at \( V \approx 150 \mu m/s \), and \( G = 18 \text{ K/cm} \).

In the seaweed to doublon transition, since the interface must advance quickly towards a new equilibrium interface location as the concentration decreases, we see transient superdendrites, shown in Fig. 6B. These are triangular growths that commonly form at large growth velocities \([22]\). The progression is counter to what might be expected from Brener et al.'s morphology diagram. At lower concentration, the interface advances to lower undercooling, so we might expect a transition from doublon to seaweed growth, contrary to our observations. However, as mentioned earlier, the morphology diagram is discussed in the context of a pure sample and may not be applicable with concentration changes. We show a second example of the seaweed to doublon transition in Fig. 6.

It is interesting to note that the unstable seaweed growth in each case still maintains a coarse spacing that is similar to that for the doublons. The doublons we observe though are not alternating shallow and deep grooves as in \([14]\). Particularly in Fig. 6A, we see dendritic doublons with much more strongly developed side-branches than most previous observations \([6]\).

At low concentrations, doublons appear to be stable and rarely undergo the tilting instability described above. Doublons appear to be strongly selected without an imposed modulation (e.g. Fig. 4) unlike what is reported by Losert et al. \([14]\).

In numerical simulations, higher noise deters doublon growth \([14]\). The relevant noise in our system is most likely concentration fluctuations rather than the thermal noise relevant in growth of pure materials. In this case, higher concentrations would then correspond to larger fluctuations and larger noise. It is also possible that the surface tension changes with concentration \([20]\) which could lead to a change in morphology. This seems plausible because higher concentrations (and thinner samples) lead to seaweed growth more readily than dendritic growth, particularly when using PEO as solute.

We also observe an orientational dependence of doublon growth. It is believed that for completely isotropic systems, doublons will spontaneously select a growth direction since none is preferred \([8]\). However, Losert et al. report that no stable doublons are found for zero anisotropy in simulations \([14]\). In our experiments, anisotropies are clearly present and lead to a preferred doublon orientation. Fig. 7 shows the results of an experiment in which the cell can be rotated within the sample plane in order to further probe the effect of crystal orientation on growth. The arbitrary angle \( \alpha_0 \) reflects the fact that we know relative angles as the sample is rotated rather than absolute crystallographic orientations. We see that doublons are oriented along particular directions and their stability depends on orientation. In particular, doublons are more stable when oriented along a favored growth direction. One explanation for this is that the tilt instability described above is more prevalent for tilted doublons. We also note that the crystalline anisotropy need not be fourfold symmetric as is often assumed \([17]\).

The long-time behavior of doublon growth can be seen in Fig. 8 which shows a space-time plot for doublons shown in Fig. 1A. This is essentially a chart recording of the growth and is created by extracting lines at a fixed distance behind the interface for sequential pictures (see Fig. 2, for example). The central gap of the doublon is identified by the dark line. Although we observe a doublon tip growing for over 48 seconds (in a run of several minutes), it meanders over time. This is different from...
FIG. 8: Space-time plot of doublon growth in 0.5% PEO-SCN at V = 22 µm/s. This run corresponds to the sample shown in Fig. 1. The dark central line indicates the inner groove of a doublon as it meanders in the field of view. The image width is 243 microns and the time of 48 seconds increases upwards.

The oriented growth of dendrites which typically grow along fixed, preferred directions at steady-state. Doubons in this regime are also eliminated through the tilt instability, but their lifetime is significantly longer. The gap between fingers is observed to be very uniform over time. The positions of the tips of the asymmetric pair along the growth direction is also equal within the resolution of our data. Therefore, we are not able to test Müller-Krumbhaar et al.’s suggestion for the mechanism of doublon stability [27] in which if one finger grows ahead, it has more room and widens, leading to a lower growth velocity.

Fig. 9 shows doublonic dendrites with sidebranches perpendicular to the sample plane. In this case, the sample thickness is large enough to support the transverse sidebranching mode. In three dimensions, the triplon is predicted to be the basic building block of isotropic growth [28], although transient doublons have been observed in 3D growth of xenon dendrites [29]. If we were able to increase the thickness of the sample, we would expect a transition from the three-dimensional doublons in Fig. 9 to triplons, although the nature of the transition is unknown. In two dimensions, multiblons have been shown in numerical simulations and were argued to be generically unstable [11]. In our observations, multiblons can be seen as transients but are not found to be stable.

IV. CONCLUSIONS

In conclusion, we observe doublons in low anisotropy growth but they are often unstable to a tilting instability. We find doublon formation to be strongly dependent on solute concentration and sample orientation. Doubons are selected at low concentrations (small solutal undercooling) in contrast to the fact that doublons exist at large thermal undercoolings in pure materials. Perhaps the dominant factor is that larger concentrations lead to larger fluctuations which destabilize the tip. Doubons also exhibit a preferred growth direction and changing the orientation of a specific doublonic grain demonstrates that the character and stability of doublons depend on crystalline orientation. Even when stable, doubons tend to meander, unlike in dendrite growth. At higher concentrations and when the preferred growth direction is substantially different from the imposed growth direction, we observe the seaweed morphology. We observe seaweed-doublon transitions with changes in these parameters. In seaweed growth, the tip splitting process appears similar to the formation of transient doublons. However, the gap thickness h scales with the velocity V as $h \propto V^{-0.5+0.05}$ rather than $V^{-7/9}$ as predicted for doublons. This might indicate that seaweed growth should not strictly be viewed as composed of transient doublons. However, with the resolution of our images, we are not able to verify or reject the 7/9 exponent for the narrow gap thickness of solutal doublons.

It remains unclear what determines the stability of solutal doublons, particularly with changes in solute concentration. Doubons should also be observable in other systems if the assumed morphology diagram is generic. The effects of anisotropies or concentration in these systems are open questions.

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