Controlling solid-liquid interfacial energy anisotropy through the isotropic liquid

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Although the anisotropy of the solid-liquid interfacial free energy for most alloy systems is very small, it plays a crucial role in the growth rate, morphology and crystallographic growth direction of dendrites. Previous work posited a dendrite orientation transition via compositional additions. In this work we examine experimentally the change in dendrite growth behaviour in the Al-Sm (Samarium) system as a function of solute concentration and study its interfacial properties using molecular dynamics simulations. We observe a dendrite growth direction which changes from ⟨100⟩ to ⟨110⟩ as Sm content increases. The observed change in dendrite orientation is consistent with the simulation results for the variation of the interfacial free energy anisotropy and thus provides definitive confirmation of a conjecture in previous works. In addition, our results provide physical insight into the atomic structural origin of the concentration dependent anisotropy, and deepen our fundamental understanding of solid-liquid interfaces in binary alloys.
Though interfaces constitute a vanishingly small volume fraction of bulk materials, they play an essential role in determining bulk properties. Among the myriad of ways that interfaces impact on properties, one of the most important is their use to control microstructures resulting from phase transitions. In solidification, it is the intrinsic properties of the solid–liquid interface that determines the morphology of the selected product phase and the composition distribution. The interfacial free energy also determines the characteristic scale and morphology of the microstructure of the solid. This connection arises directly from the tendency for pattern formation via dendritic growth owing to the solid dendrite arms wanting to grow parallel to crystallographic directions whose interfacial energy is highest. The practical significance of such dendritic growth and its consequences for the properties of bulk products are broad, from the strength of additively manufactured parts to the performance of metal-ion batteries. The significance of this has driven an enormous body of work in the past 10–15 years aimed at identifying the key structural parameters that correlate to the properties of interfaces at the atomistic scale.

According to the generally accepted microscopic solvability theory, dendritic growth velocity and tip radius are sensitively controlled by the (small) anisotropy in the solid–liquid interfacial free energy, \( \gamma \). Moreover, the anisotropy also determines the crystallographic growth direction of the dendrites. Pure metals of cubic symmetry will exhibit dendrite arms extending along the \( \langle 100 \rangle \) directions so as to minimize the content of high energy \( \langle 100 \rangle \) surfaces. Due to its importance, experimental and modelling techniques have been devised to estimate the anisotropy of \( \gamma \) in several systems, yet the atomistic origin of this anisotropy remains elusive.

With well-controlled experiments and simulations, Haxhimali et al. showed that the dendrite growth direction in Al–Zn (zinc) alloys changes with an increase in the solute content. Starting from normal \( \langle 100 \rangle \) dendrites in Al-rich alloys, a transition to hyper-branched dendrites and further to \( \langle 110 \rangle \) dendrites happens when the content of Zn is increased. The hyper-branched structure is characterized by no preferred growth direction while \( \langle 110 \rangle \) dendrites have distinctly crystallographic morphologies but with arms oriented parallel to \( \langle 110 \rangle \). The authors showed that the observed dendrite orientation transition (DOT) could be explained by assuming that the solid–liquid anisotropy changes in some fashion with Zn concentration.

Two parameters are often used to characterize the anisotropy of \( \gamma \) when the solid phase has underlying cubic symmetry. The first parameter \( \epsilon_1 \) represents a fourfold symmetric contribution, and the second \( \epsilon_2 \) a sixfold contribution. Using phase-field simulations, Haxhimali et al. found that the space spanned by various values of \( (\epsilon_1, -\epsilon_2) \) can be separated into three regions where \( \langle 100 \rangle \), hyper-branched, or \( \langle 110 \rangle \) dendrites dominate the microstructure. Compiling existing estimates of \( \epsilon_1 \) and \( \epsilon_2 \) for a variety of pure cubic metals, Haxhimali et al. found that most lie inside the \( \langle 100 \rangle \) region or near the \( \langle 100 \rangle / \text{hyper-branched} \) boundary. This is consistent with the dominance of \( \langle 100 \rangle \) dendrites observed experimentally. To explain the DOT in Al–Zn it was speculated that the anisotropy must vary with Zn concentration such that the combination of \( \epsilon_1 \) and \( \epsilon_2 \) move from the \( \langle 100 \rangle \) to \( \langle 110 \rangle \) regime. However, it must be stressed that there is no direct evidence why such an anisotropy variation exists in Al–Zn, nor is there any explanation as to why Al–Zn is unique with respect to this solid–liquid interfacial free energy behaviour.

Subsequent molecular dynamics (MD) simulations revealed that the \( \gamma \) anisotropy can indeed vary with composition within the \( (\epsilon_1, -\epsilon_2) \) space. However, for systems examined so far, such as hard-spheres, Lennard-Jones, and Cu–Ni, there is no example where the system can vary sufficiently to predict a complete transition from \( \langle 100 \rangle \) to \( \langle 110 \rangle \), which is in contrast with Al–Zn experiments. This illustrates that the DOT phenomenon and the associated anisotropy variations are quite unusual. Interfacial properties are intrinsically determined by the atomic-scale structure of interfaces. For solid–liquid interfaces, a well-accepted feature is that the liquid extending a few interatomic distances from the the crystal exhibits partial ordering. This interfacial ordering has been investigated extensively (see review and references therein) and are related to different interface-control phenomena including nucleation and glass formation. But even though liquid ordering is generally observed, the DOT has only been reported in a few systems. This indicates that the DOT must rely on yet undescribed features of interfaces.

In this work, we demonstrate from laser melting experiments on the Al–samarium (Sm) system that a complete DOT takes place with increasing concentration of Sm. Through MD simulations, we verify that its anisotropy behaviour is consistent with the Haxhimali et al. conjecture of the observed dendrite morphology. We also provide evidence of an unusual atomistic structure of the solid–liquid interface that may provide insights to the origin of the DOT.

### Results

**DOT in Al–Sm alloys.** Figure 1 presents two abnormal microstructures observed in laser melted Al–Sm (samarium) alloys. Figure 1a shows a columnar seaweed microstructure obtained from a laser remelted Al–2.2 at.% Sm alloy. The key feature of a seaweed microstructure is that it exhibits no shape-preserving steady-state tip morphology. Such a seaweed microstructure is similar to the hyper-branched structure discussed by Haxhimali et al. and Dantzig et al. Figure 1b shows equiaxed dendrites obtained from a laser remelted sample of Al–5.6 at.% Sm. The equiaxed dendrites shown in Fig. 1b notably display six

![Fig. 1 Dendrite orientation transition in Al–Sm alloys.](https://example.com/dendrite.jpg)
branches in one section, implying that these cannot be (100) dendrites since a (100) dendrite can have six secondary arms but those can be only simultaneously viewed in three-dimensions (3D), for example, see Fig. 2 in ref. 12. Six branches in one plane however can be observed with (110) dendrites. As a comparison, a three-dimensional (110) dendrite calculated via phase-field simulation is shown in Fig. 1c to illustrate how six branches can lie in one section. Since dendrites grow from pure Al melts are (100) oriented, Fig. 1 provides compelling evidence of a transition with increasing Sm content in the liquid, from (100) to a hyperbranched/seaweed structure at approximately 2.2 at.% Sm, and to (110) at ~5.6 at.% Sm. To make this interpretation fully quantitative, modern high-resolution diffraction techniques could be employed in future studies. It should also be mentioned that the small size of the observed dendrites is due to the small excluded volume available. This may also limit the time/space available for the final arm-selection mechanism to operate. While morphologies can be influenced when dendrites are confined in space/time, quantitative phase-field simulations do not provide evidence of a significant change in the number or orientation of dendrite side-arms once the initial crystallographic pattern emerges.

We attribute the above DOT to solute-induced changes in interfacial free energy anisotropy rather than to possible solute effects on the interfacial kinetics. Although laser melting is often taken as an example of rapid solidification, the solidification conditions vary with position inside the melt pool. The local solidification velocity, \( v_s \), is related to the laser beam scanning velocity, \( v_b \), by \( v_s = v_b \cdot \mathbf{n} \) where \( \mathbf{n} \) is the normal vector to the melt pool boundary after the remelting process reached the steady state. From the bottom of the melt pool \( v_s \) increases from zero to the possible order of \( v_b \) at the top surface, depending on the specific shape\(^\text{19} \). In our case, the seaweed and (110) dendrites are observed near the bottom of melt pools. For the seaweed microstructure, we can estimate the growth velocity to be roughly the order of \( \text{mm s}^{-1} \) since \( v_b = 10 \text{ mm s}^{-1} \). For equiaxed dendrites, the controlling parameter is the undercooling which can be estimated using the columnar to equiaxed transition (CET) model\(^\text{20} \). Specifically, the equiaxed grains under constrained growth conditions form by heterogeneous nucleation driven by the constitutional undercooling ahead of the columnar grains. The undercooling of columnar fronts can be approximated as the bath undercooling of equiaxed grains. Unfortunately, the equiaxed grains near the melt pool boundary as in our case (also observed in ref. 21) cannot be explained satisfactorily by CET theory since the local solidification velocity and thus undercooling approaches zero there. We believe those equiaxed grains are due to nucleation of pre-existing inclusions with very high potency, perhaps from the first scan. Under these speculated conditions, even a negligible undercooling should be enough to trigger nucleation and growth near the melt pool bottom/boundary although it is difficult for us to put an accurate value on this undercooling based on available data.

At first sight, a direct comparison between experiments under constrained growth conditions and phase-field simulations in free growth conditions is not obvious. We emphasize that as long as kinetic effects on anisotropy are not too strong the transition is expected to happen whether the growth condition is constrained or not. That is the same strategy used by Haxhimali et al.\(^\text{12} \). The main purpose of phase-field simulations is to illustrate how dendritic growth direction changes with the anisotropy and to illustrate six side-arms in 2D is only possible for (110) dendrites. A quantitative comparison between simulations and experiments in terms of supersaturation and the operating state of dendrite is not attempted here. From previous work\(^\text{22,23} \), it is expected that at a speed of \( \sim 100 \text{ mm s}^{-1} \), kinetic effects (although present) are not expected to change the selection mechanisms of dendritic arms for atomically rough interfaces. If the growth rates become sufficiently high such that the interface deviates from local equilibrium, then one needs to consider other factors (including latent heat production and dissipation and the kinetic effect) into a discussion. For the purposes of the following, we deal only with conditions where the local equilibrium approximation is appropriate such that the anisotropy of the interfacial free energy contributes to the dendrite arm orientation primarily.

**Solute-dependent interfacial anisotropy.** To better understand the atomistic origins of the DOT in Al–Sm alloys, we have employed MD simulations. An empirical Finnis-Sinclair type potential developed by Mendeleev et al.\(^\text{24} \), obtained by fitting the ab initio calculated properties of a range of Al–Sm compounds with compositions close to Al\(_{100}\)Sm\(_{10}\) was used here. Notably this potential included fitting of the structure of liquid Al\(_{90}\)Sm\(_{10}\) in its construction. The Al-rich equilibrium phase diagram predicted by this potential for equilibrium between the liquid and Al-rich FCC phase was computed using semi-grand canonical Monte Carlo simulations (see refs. 25, 26 and the Methodology section for details of the method employed). A comparison between the CALPHAD (CALCulation of PHAse Diagrams) computed Al–Sm phase diagram and that obtained from the Mendeleev interatomic potential is shown in Fig. 2. As can be seen, the agreement between the two estimations are good, though the phase diagram obtained from the Mendeleev potential exhibits a lower melting point for pure Al and thus a lower liquidus line. Most notable for our purposes is that the Mendeleev potential reproduces the negligible solubility of Sm in FCC-Al solid solution.

From the results presented in Fig. 2 it was possible to construct equilibrium solid–liquid interfaces at various temperatures/alloy compositions in MD simulations. Equilibrated solid–liquid interfaces were obtained with (100) and (110) crystal orientations. Once equilibrated, the capillary fluctuation method (CFM)\(^\text{28,29} \) was used to obtain the interfacial stiffness, from which \( \epsilon_1 \) and \( \epsilon_2 \) can be calculated (see Methods)\(^\text{12} \). Figure 3 illustrates the results of calculated \( (\epsilon_1, -\epsilon_2) \) values made for interfaces held at temperatures between 800 and 900 K in 25 K increments. Overlaid on this plot are the expected regimes where (100),
Methods. are calculated based on propagation of stiffness uncertainty, as described in Haxhimali et al. DOT conjecture\textsuperscript{12}. As discussed above, several growth mode shifts from 8.3 at.% at 800 K. As the Sm content in the liquid increases (temperature/C\textsuperscript{24} alloys, namely \(h\) transition from \(h\) microstructures predicted in between.

Fig. 3 Composition-dependent anisotropy parameters \(\epsilon_1\) and \(\epsilon_2\). The boundaries (dashed lines) separating different dendritic growth regimes are reproduced from ref. \textsuperscript{12}. The coloured points indicate the specific temperatures at which equilibrium MD simulations were performed. As the temperature drops, the Sm composition in the liquid phase increases along the liquidus line while the solid phase remains pure Al as shown by the phase diagram in Fig. 2. The liquid composition increases from \(\sim 1.7\) at.% at 900 K to \(\sim 3.9\) at.% (875 K) to \(\sim 6.1\) at.% (850 K) to \(\sim 7.4\) at.% (825 K) to \(\sim 8.3\) at.% at 800 K. As the Sm content in the liquid increases (temperature drops), the interfacial anisotropy changes such that the expected dendritic growth mode shifts from \(\langle 100\rangle\) to hyper-branched to \(\langle 110\rangle\). The error bars are calculated based on propagation of stiffness uncertainty, as described in Methods.

Within the uncertainty of the calculated values of \(\epsilon_1\) and \(\epsilon_2\) one can see a clear variation in anisotropy predicted for the Al–Sm alloys, namely \(\langle 100\rangle\) oriented dendrites predicted for low Sm contents (<4 at.% Sm, \(T > 875\) K), \(\langle 110\rangle\) oriented dendrites for high Sm contents (>8 at.% Sm, \(T < 800\) K) and hyper-branched microstructures predicted in between.

Both our experiments and atomistic simulations show the full transition from \(\langle 100\rangle\) to \(\langle 110\rangle\) in Al–Sm alloys. Therefore, the above results represent the definitive confirmation of the Haxhimali et al. DOT conjecture\textsuperscript{12}. As discussed above, several MD simulations on various binary alloy systems have shown a variation in anisotropy within the \((\epsilon_1, -\epsilon_2)\) space, but no previous case has explicitly demonstrated a change from \(\langle 100\rangle\) oriented dendrites to the \(\langle 110\rangle\) oriented dendrites. Ideally, one would like to compare with experimentally measured anisotropy parameters. In principle, \((\epsilon_1, -\epsilon_2)\) can be derived from the Wulff shape by measuring the shape of a liquid droplet embedded in a solid matrix. As the anisotropies of solid–liquid interfaces are extremely weak, experimental attempts have been only very limited\textsuperscript{30,31}. In addition, the results either suffer from experimental uncertainty or are not consistent with the observed dendrite growth directions.

Atomic structures of interfaces. While the above results give clear evidence that changing the Sm content of the liquid can change the anisotropy of the interfacial free energy, the mechanistic origins of this change remain unclear. Another way to view the data shown in Fig. 3 is directly in terms of the difference in interfacial free energy between the \(\langle 100\rangle\) and \(\langle 110\rangle\) directions (Fig. 4). As can be seen, the anisotropy strength (left axis) decreases while the average interfacial energy (right ordinate) increases with Sm content in the liquid. Both of these trends are unusual in alloy systems and the increase of \(Y_0\) with decreasing temperature runs counter to the well known result of Spaepen valid for pure metals\textsuperscript{10}. However, it is worth mentioning that in a recent MD study by Hoyt et al\textsuperscript{32}, the results shown in Fig. 4 are also observed in Cu–Zr alloys. It is also noteworthy that both Al–Sm and Cu–Zr exhibit a very small solid solubility and a large size mismatch. Although it is unclear how these factors directly affect the interfacial energy and its anisotropy, we discuss below how the presence of Sm in Al–Sm alloys creates an unusual solid–liquid interfacial structure, which may provide a possible atomistic origin of the DOT.

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Figure 5a shows the fine grained number density as a function of distance perpendicular to the liquid–solid interface for both the \(\langle 100\rangle\) and \(\langle 110\rangle\) interfaces at the highest (900 K) and lowest (800 K) temperatures studied. Both Al atomic density and the atomic density of the Sm (orange) are shown in the plots. The density profile of Sm is multiplied by a factor of 10 to more clearly compare with the Al density. Focusing on the Al density we see the expected behaviour, with partial ordering extending 3–4 layers into the liquid with a characteristic spacing between peaks similar to that of the solid (see e.g. ref. \textsuperscript{13}). However, a striking feature of the density profiles in Fig. 5a is the peaks of the Sm profile do not align with the Al density peaks. To the best of our knowledge this misalignment differs from any previous MD study of the structure of solid–liquid interfaces in other systems, see e.g., Cu–Ni\textsuperscript{15} and Lennard-Jones\textsuperscript{14}. A solute density profile that is displaced from the total density (dominated by Al) will result in excess number of solute atoms and excess interfacial energy contributions that are not found in the more commonly observed aligned structure and these additional excess quantities will affect the interfacial free energy\textsuperscript{32}. From the point of view of the DOT, however, a more significant observation is the fact that the displacement between profiles appears to be greater for the \(\langle 110\rangle\) orientation than for the \(\langle 100\rangle\) interface for all temperatures studied. Therefore, this unique atomistic structure of the Al–Sm solid–liquid interface provides an additional source of anisotropy, which may play a crucial role in identifying those alloys likely to undergo a DOT.

A possible source of the temperature dependence of the interfacial energy and anisotropy is provided in Fig. 5b. These panels show the total in-plane ordering obtained by time averaging the atomic density in a layer \(\sim 3\) Å wide (grey shaded
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results of this study offer other insights into the DOT and hence

efforts aimed at quantitative prediction of this effect would be desirable. Even without a fully quantitative model, however, this correlation suggests a route to identify alloying elements that would be suitable for inducing a DOT. This in turn would pave the way for additional alloy design possibilities. That is, solute additions whose main role is to alter the dendrite morphology and produce more desirable properties in the solidified material. More broadly, these results also point to the role that solute could play in modifying the partial ordering of the liquid at the liquid–solid interface can have a strong effect on both the absolute magnitude and anisotropy of the interfacial free energy, it then suggests that efforts aimed at quantitative prediction of this effect would be desirable. Even without a fully quantitative model, however, this correlation suggests a route to identify alloying elements that would be suitable for inducing a DOT. This in turn would pave the way for additional alloy design possibilities. That is, solute additions whose main role is to alter the dendrite morphology and produce more desirable properties in the solidified material. More broadly, these results also point to the role that solute could play in modifying the partial ordering of the liquid at the liquid–solid interface.

Aside from changing interfacial free energy anisotropy, this ordering has been cited as an important ingredient for promoting or suppressing crystallization, being an important consideration both for grain refinement in commercial alloys and in the production of bulk metallic glasses.

Discussion

The above observations suggest that in alloys which exhibit an interface structure with misaligned total density (dominated by the solvent density) and the solute density peaks may be candidates for identifying a DOT. It is of course difficult to assess whether the same structure observed in Fig. 5 is also present in the Al–Zn system studied by Haxhimali et al., but it is worth noting that in Al–Zn the equilibrium crystal structure of Zn is HCP and not FCC. Therefore, one can imagine that at high enough Zn content an out-of-phase density structure may be possible, at least in some crystallographic directions. In addition to the structural properties of the solid–liquid interface, the results of this study offer other insights into the DOT and hence the variation in interface anisotropy. Because the crystal induces local ordering in the liquid at the interface, it is tempting to conclude that any variation in anisotropy arises from changes in the crystalline structure with composition (e.g. lattice parameter). But in the case of Al–Sm there is no solubility in the solid and the origin of the anisotropy is necessarily more complicated. Also, while the DOTs in Al–Sm and Al–Zn alloys appear superficially similar, it must be recalled that Zn, unlike Sm, can be dissolved significantly (up to 67 at.%) into solid Al. This suggests that the solution thermodynamics of the bulk liquid and solid phases do not play a significant role in the explanation of the DOT

behaviour.

The results presented above open new challenges and opportunities for furthering our understanding of the role of the liquid–solid interface structure and composition on interfacial free energy and consequently solidification microstructure evolution. If the above interpretation is correct, and alloying elements that disrupt the partial ordering in the liquid at the liquid–solid interface can have a strong effect on both the absolute magnitude and anisotropy of the interfacial free energy, it then suggests that efforts aimed at quantitative prediction of this effect would be desirable. Even without a fully quantitative model, however, this correlation suggests a route to identify alloying elements that would be suitable for inducing a DOT. This in turn would pave the way for additional alloy design possibilities. That is, solute additions whose main role is to alter the dendrite morphology and produce more desirable properties in the solidified material. More broadly, these results also point to the role that solute could play in modifying the partial ordering of the liquid at the liquid–solid interface. Aside from changing interfacial free energy anisotropy, this ordering has been cited as an important ingredient for promoting or suppressing crystallization, being an important consideration both for grain refinement in commercial alloys and in the production of bulk metallic glasses.

Methods

Experiments. The laser remelting experiments presented in Fig. 1 were performed on material prepared from master alloys prepared as part of a previous study. These alloys were prepared by chill casting 99.999 wt% pure Al and 99.99 wt% Sm in a cylindrical mould water cooled from the bottom. The cast ingots were then cut into plates of thickness of 3 mm. The laser remelting experiments were conducted with a laser operated at 1280 W using a scanning speed of 10 mm s⁻¹ for the Al–2.2 at.% Sm (11 wt% Sm) alloys. Due to the formation of large primary intermetallic compounds during chill casting in the Al–5.6 at.% Sm (25 wt% Sm)
Phased field simulations. The quantitative phase-field model presented in Fig. 1 was used to simulate equiaxed dendritic growth. This model has been implemented in a 3D Adaptive mesh refinement Message Passing Interface C++ code as described by Greenwood et al. The simulations were performed using dimensionless parameters, i.e., $W_a = 1$, where $W_a$ and $r$ are the characteristic interface width and the kinetic attachment time, respectively. The interfacial free energy anisotropy to produce the results shown was taken as $\epsilon_2 = 0$, $\epsilon_3 = -0.02$. In addition the supersaturation was taken to be $\omega = 0.55$, solute distribution coefficient $k = 0.1$ and dimensionless diffusion coefficient $D = 3$.

Atomatic simulations. All atomistic simulations (MD and Monte Carlo simulations) were performed using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software. All calculations were performed using the semi-empirical potential developed by Mendelev et al. for the properties of Al–Sm alloys. The liquidus and solidus boundaries shown in Fig. 2 were obtained using the thermodynamic integration technique described by Ramalingam et al., which computes the relative free energy between solid and liquid phases. The melting point of pure Al which serves as the reference for all free energies is determined in a 3D Adaptive mesh refinement Message Passing Interface C++ code as described by Greenwood et al. The simulations were performed using dimensionless parameters, i.e., $W_a = 1$, where $W_a$ and $r$ are the characteristic interface width and the kinetic attachment time, respectively. The interfacial free energy anisotropy to produce the results shown was taken as $\epsilon_2 = 0$, $\epsilon_3 = -0.02$. In addition the supersaturation was taken to be $\omega = 0.55$, solute distribution coefficient $k = 0.1$ and dimensionless diffusion coefficient $D = 3$.

Data availability

The data that support the findings of this study are available from the corresponding author upon request.

Code availability

The codes that support the findings of this study are available from the corresponding author upon request.

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Author contributions
The first idea started from discussions about the seaweed formation between L.W. and N.P. at McGill University. L.W. observed the abnormal dendritic morphologies in Al-Sm alloys and initiated the collaboration with the other authors. L.W. and J.J.H calculated the interface energy anisotropy. N.W. did the laser remelting experiments. L.W. and N.P. conducted the phase-field simulations. C.S. contributed his expertise in atomic-scale simulations and interfacial thermodynamics. All authors co-edited the manuscript.

Competing interests
The authors declare no competing interests.

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