**Direct measurement of anisotropy of interfacial free energy from grain boundary groove
morphology in transparent organic metal analog systems**

by

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Definition of Symbols

$\Delta G, \Delta G_r, \Delta G_k$	is the Gibbs free energy
$\Delta T_b, \Delta T_r, \Delta T_k$	is the undercooling
ΔS_f	is the entropy of fusion
ϕ_k	is the kinetic parameter of interfacial behavior
μ	is the mobility parameter
D_T	is the thermal diffusivity
L	is the latent heat per unit volume
p	is the Peclet number
E_1	is an exponential integral
T_m	is the melting temperature
$\hat{n}$	is the local normal at the solid
v_n	is the normal velocity at a particular point on the interface
c_p	is the specific heat
κ	is the sum of principle curvatures κ_1, κ_2
κ_1	is a principle curvature
κ_2	is a principle curvature
$\phi_r, \tilde{\gamma}$	is the interfacial stiffness
σ_{SL}	is the solid-liquid energy
σ_{gb}	is the grain boundary energy
γ	is the interfacial free energy
γ'	is the first derivative of γ with respect to θ
γ''	is the second derivative of γ with respect to θ
n	is the unit interface normal
Γ	is the Gibbs-Thomson coefficient
y	is the y-coordinate along the groove (groove depth)
G	is the temperature gradient.
l_g	is a normalizing variable
Y	is the normalized value of y
K	is the normalized value of κ
α	is the surface tension anisotropy
ε_i	is the anisotropy of interfacial energy
θ	is the angle associated with the principle tangent directions

D	is the diffusion coefficient of the solute
c_0	is the concentration of the solute
k	is the partition coefficient
V_{cs}	is the velocity at above which dendritic growth occurs
m	is the slope of the liquidous line
$\bar{m}$	is the weighted slope of the liquidous line
f_α, f_β	are volume fractions

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Executive Summary

Both academia and industry alike have paid close attention to the mechanisms of microstructural selection during the solidification process. The forces that give rise to and the principles which rule the natural selection of particular morphologies are important to understanding and controlling new microstructures.

Interfacial properties play a very crucial role to the selection of such microstructure formation. In the solidification of a metallic alloy, the solid-liquid interface is highly mobile and responds to very minute changes in the local conditions. At this interface, the driving force must be large enough to drive solute diffusion, maintain local curvature, and overcome the kinetic barrier to move the interface.⁸ Therefore, the anisotropy of interfacial free energy with respect to crystallographic orientation is has a significant influence on the solidification of metallic systems.

Although it is generally accepted that the solid-liquid interfacial free energy and its associated anisotropy are highly important to the overall selection of morphology, the confident measurement of these particular quantities remains a challenge, and reported values are scarce. Methods for measurement of the interfacial free energy include nucleation experiments and grain boundary groove experiments. The predominant method used to determine anisotropy of interfacial energy has been equilibrium shape measurement.

There have been numerous investigations involving grain boundaries at a solid-liquid interface. These studies indicated the GBG could be used to describe various interfacial energy values, which affect solidification. Early studies allowed for an estimate of interfacial energy with respect to the GBG energy, and finally absolute interfacial energy in a constant thermal gradient. These studies however, did not account for the anisotropic nature of the material at the GBG. Since interfacial energy is normally dependent on orientation of the crystallographic plane of the solid with respect to the liquid, a better calculation of interfacial energy was needed. Herring described this

orientation dependence, which related the interfacial undercooling to the principle interfacial curvatures.

The present study pertains to the measurement of the anisotropy of interfacial energy by comparison of experimental and theoretical GBG geometries in pure succinonitrile (SCN) and pivalic acid (PVA). A quantity of SCN and PVA was distilled and zone refined using a process that is defined in the experimental procedure portion of this paper. Very thin (100 μm) slide assemblies were created and filled with these organic materials. For each system, several grooves were photographed and their shapes were compared with theoretical predictions. The correlation between experiment and theory was quantified and plotted as a function of the anisotropy for each of the GBG's examined, and a maximum correlation corresponded to the anisotropy of interfacial energy which describes that particular rotation of the GBG. The results from several rotations were statistically analyzed to ensure confidence in the measurement of the anisotropy of interfacial energy and, finally, compared to reported values obtained with other techniques.

Chapter I: Introduction

Generally, solidification growth morphologies can be divided into two primary groups: (i) single-phase primary structures, which may be globular, cellular, and/or dendritic; and (ii) polyphase morphologies, such as eutectics. These morphologies, alone or in combination, comprise most metallic solidification microstructures, and, as such, have been the concentration of numerous numerical and theoretical studies. Indeed, many excellent reviews have been published.^{8, 10, 22}

The principle challenge in solidification science is the prediction of the solidification structure at multiple length scales. Most generally this involves three primary tasks: (i) determining, for a given growth mode (or morphology), the relationship between local temperature composition, and velocity to the local microstructural parameters; and (ii) developing criteria for selection among possible solutions within a given growth mode and (iii) predicting the selection of growth mode.

Fundamental to the temperature-composition-velocity-radius (T-C-V-R) relationships for any growth mode are the intrinsic interfacial properties of the interface. This is evident in the liquid-solid phase transformation of metallic alloys, where large interfacial mobility and small interfacial stiffness influence an overall behavior that is particularly responsive to local conditions. Driving forces are required to overcome the intrinsic resistance to both local curvature (ΔG_r) and interface motion (ΔG_k):

$$\Delta G = \Delta G_r + \Delta G_k + \Delta G_{ext}, \quad (1)$$

where (ΔG_{ext}) indicates the energy required to drive all extrinsic processes such as the transport of heat and solute at the interface.²² Concerning the intrinsic response of the interface, the overall driving force can be written generally as

$$dG_r = \phi_r d\kappa, \quad (2)$$

$$dG_k = \phi_k dv, \quad (3)$$

where dG_r is the change in free energy associated with an incremental change in the curvature of an interface, $d\kappa$, and dG_k is the free energy associated with an incremental change in the velocity of the interface, dv . The equations (2) and (3) yield the definitions of the intrinsic interfacial properties known as stiffness and mobility. Interfacial stiffness is defined as ϕ_r in equation (2) and is commonly presented in terms of an undercooling:

$$\Delta T_r = \frac{\phi_r}{\Delta S_f} \kappa \equiv \Gamma \kappa, \quad (4)$$

where Γ is known as the Gibbs-Thomson coefficient. The kinetic parameter ϕ_k , is typically defined as a compliance with regard to interface motion, and the kinetic contribution to undercooling is written as

$$\Delta T_k = \frac{\phi_k}{\Delta S_f} v \equiv \frac{v}{\mu}, \quad (5)$$

where μ , is known as the interface mobility, and ΔT_k is the undercooling associated with interface motion and the associated atomic attachment. From equations (4) and (5), the total intrinsic component of interfacial undercooling, ΔT_i , can be written in terms of the two parameters describing intrinsic capillary and kinetic contributions as

$$\Delta T_i = \frac{1}{\Delta S_f} (\phi_r \kappa + \phi_k v) \quad (6)$$

or, in the more common form,

$$\Delta T_i = \Gamma \kappa + \frac{v}{\mu}. \quad (7)$$

For any solidification process, the local instantaneous behavior of the interface is governed by the partitioning of the driving free energy implied by equations (4) and (5). All driven interfaces will attempt to complete the transition in the most efficient way possible by constantly self-adjusting.²²

Both the mobility and stiffness of a solid-liquid interface are typically reliant upon the crystallographic direction of the interface normal, n , with respect to the orientation of the solid phase. Interfacial free energy can be quantified at equilibrium, and therefore, a logical approach is to determine this property separately. Interface mobility can be quantified later, since it is a dynamic property.²² Therefore, the solid-liquid interfacial free energy and its anisotropy will be the focus of the current study.

There have been investigations into experimentally measuring interfacial free energy and its associated anisotropy, and some values have been reported for transparent organic systems.^{9,10,13,14,26-30} These investigations, along with theoretical advancements, have created a new sense of understanding and raised new questions. To motivate the proposed work, the next chapter includes a review of the literature and a summary of the outstanding questions.

Chapter II: Literature Review

Solidification

After an initial nucleation event and solidification has begun, factors which will affect further growth include: atomic attachment kinetics at the interface, capillary forces, diffusion of both heat and mass, various forms of convection, other forms of heat transfer, and geometric constraints.¹ The relative contribution from each of these factors is highly dependent upon the local conditions during solidification, and the properties of the material. These factors determine the microstructural selection during solidification. Of these broad categories the most critical to the proposed study is the role of the capillary forces, and more specifically, interface stiffness.

Most commonly, solidification microstructures exhibit one of two typical growth morphologies, dendrites and eutectics. However, while the overall morphology associated with these growth modes are considerably different, the governing processes are quite similar.

Eutectic solidification (Figure 1) involves the concurrent growth of two crystalline solid phases from a single liquid solution in a cooperative manner. This process creates an essentially periodic arrangement of the two phases, and while there are many specific morphologies that may arise with different degrees of symmetry, these morphologies are most broadly categorized as either regular or irregular. Regular eutectics exhibit a periodic structure of either lamella or rods throughout the entire microstructure. This particular microstructural growth pattern is afforded by the non-faceted (Figure 2) nature of both phases, where crystal-related interfacial anisotropy (both energetic and kinetic) are not severe enough to result in particular strongly dominant interface orientations and growth directions.

In irregular eutectics, one of the two phases is faceted, thus resulting in growth of the faceted phase along preferred crystallographic directions, often leaving behind a microstructure dominated by

particular low-energy planes. The associated high anisotropy of the faceted phase leads to a non-uniform arrangement within the microstructure.

The total undercooling can be written in the form of:

$$\Delta T = \Delta T_d + \Delta T_r + \Delta T_k \quad (8)$$

Where ΔT_d is the diffusional undercooling, ΔT_r is the capillary undercooling, and ΔT_k is the kinetic undercooling. Within eutectic growth, the concentration difference required to drive solute diffusion can be related to the undercooling leading to:

$$\Delta T_d = K_d \lambda v \quad (9)$$

Where λ is the eutectic spacing parameter, v is the growth velocity, and K_d is a constant defined in (13). Again, another portion of the total undercooling can be examined including capillary effects. Examining the only capillary effects, the undercooling can be rewritten as:

$$\Delta T_r = \Gamma \kappa = \frac{\gamma \kappa}{\Delta S_f}, \quad (10)$$

where γ is the interfacial Gibbs free energy and ΔS_f is the entropy of fusion. If equations 8, 9, and 10 are combined the relationship describing the solid-liquid interface undercooling is

$$\Delta T = K_c \lambda v + \frac{K_r}{\lambda} \quad (11)$$

where κ_d and κ_r are constants defined as:

$$K_d = \frac{\overline{m} C_0 P}{D f_\alpha f_\beta} \quad (12)$$

$$K_r = 2\overline{m} \left(\frac{\gamma_\alpha \sin \theta_\alpha}{|m_\alpha f_\alpha|} + \frac{\gamma_\beta \sin \theta_\beta}{|m_\beta f_\beta|} \right) \quad (13)$$

where $\overline{m}$ is defined as:

$$\bar{m} = \frac{|m_\alpha| m_\beta}{(|m_\alpha| + m_\beta)} \quad (14)$$

From equations 11 and 13 it is apparent that stiffness, and orientation are very important on the overall selection of eutectic morphology, and therefore, anisotropy (i.e. the orientation dependence of the interfacial free energy) plays a major role in this selection.

Dendritic morphologies (Figure 3) are particularly common in conventional shape castings and ingot castings. It is important to understand dendritic growth dynamics as dendritic growth is central to the current study. As explained, this growth morphology is dependent upon interfacial free energy along with kinetics.

During dendritic solidification under isothermal conditions, if a seed crystal is surrounded by a melt, the latent heat of melting that is released by the freezing liquid must be diffused away from the interface. It is this process which determines the growth rate, and is governed by the diffusion equation. The temperature profile must satisfy the diffusion equation.²

$$\frac{\partial T}{\partial t} = D_T \nabla^2 T \quad (15)$$

In this thermal diffusion equation, D_T is the thermal diffusivity, or the rate at which heat is conducted through the medium. Provided there is no kinetic limitation, the solid state growth rate is governed by the diffusion of heat from the interface.

$$L v_n = \llbracket c_p D_T \hat{n} \cdot \nabla T \rrbracket \quad (16)$$

The latent heat per unit volume is represented by L , c_p is the heat capacity, v_n is the normal velocity at a particular point on the interface, and $\hat{n}$ is the local normal at the solid. The final consideration during the solidification process is the melting temperature dependence on interface curvature. At thermodynamic equilibrium, the Gibbs-Thomson condition must hold, where κ is the local curvature of the interface and γ is the interfacial free energy.

$$T_m(\kappa) = T_m - \left[\frac{T_m \gamma \kappa}{L} \right] \quad (17)$$

$$T_m - T_m(\kappa) = \frac{\gamma \kappa}{\Delta S} = \Gamma \kappa \quad (18)$$

The physical foundation of such a relationship is based upon the relationship of molecules with one another in the protrusions of the interface. If the solid is protruding into the liquid phase ($\kappa > 0$), then the number of solid neighbors is reduced, thus reducing the number of molecules to possibly bind to, which in turn makes these molecules easier to displace from the interface. This process effectively lowers the melting temperature. If the opposite occurs and the liquid protrudes into the solid phase ($\kappa < 0$), the number of neighboring molecules is increased, thus allowing for more tightly bound molecules, which in turn raises the melting temperature.²

Beginning in 1947 with Ivanstov³, equations predicting dendritic growth were evaluated. It has been long understood that dendritic growth occurs in undercooled crystal melts; defined by a dendrite tip radius (r), and a growth velocity (v). Ivanstov analytically solved the problem of the diffusive growth of a needle-shaped crystal with a parabolic tip, and found a family of curves which, in the absence of surface tension, give the undercooling as a function of the Peclet number, $p \equiv \rho v / 2D_T$. The (dimensionless) undercooling, Δ , is given by:

$$\Delta = \frac{(T_m - T_\infty)c_p}{L} = p e^p E_1(p); \quad (19)$$

where E_1 is the first exponential integral, $E_1(p) = \int_1^\infty \frac{e^{-t}}{t} dt$, and T_m is the melting temperature.

While these solutions are generally accepted for the dendrite tip, the corresponding family of solutions does not specifically define the process of dendritic solidification. This gives an undercooling verses p , and thus this gives ρv ; there is still one degree of freedom. The understanding

of selection has been the subject of considerable experimentation^{9, 10, 36, 40, 50-52, 66} and theoretical investigation.^{46, 47, 48, 67-6}

Langer and Müller-Krumbhaar⁴⁶ developed the first scaling analysis of dendritic growth by hypothesizing that dendritic growth occurs at the radius of marginal stability. They suggested that the steady-state tip radius matched a critical wavelength, λ^* and by coupling Ivantsov's solution with a linear stability analysis, they showed that λ^* is proportional to the geometric mean between the thermal diffusion length, and the capillary length, d_0 , which is the ratio between surface tension and latent heat. If λ^* were equated with the operating tip radius, R , Langer and Müller-Krumbhaar found

$$\sigma^* = \frac{2Dd_0}{v\rho^2} \quad (20)$$

where σ^* , is the theoretical scaling constant, and $d_0 = \gamma_0 T_m C_p / L^2$. In the years since the suggestion of the marginal stability hypothesis, this method has been adapted to the theory of microscopic solvability and steady-state theories which specify that the anisotropy of interfacial energy is the main factor in selecting the dendritic operating state. The development of the solvability theory has led to the understanding that the anisotropy acts as a singular perturbation and sets the tip velocity uniquely.⁴⁸ The microscopic solvability theory indicates the scaling parameter, σ^* , approaches a constant at low undercooling which is only depended upon anisotropy. While the microscopic solvability theory has provided a generally accepted basis for selection, research in this area is ongoing.^{9, 10, 36, 40, 50-52, 66-68}

Interfacial Free Energy and Anisotropy

The earliest reports of interfacial free energy for metallic systems date to around 1950 with Turnbull's^{4-6, 45} study of nucleation. Applying the classical theory of homogeneous nucleation, the measured rate at which nucleation occurs within an undercooled liquid can be utilized to determine interfacial free energy. In the classical theory of homogeneous nucleation of crystals within a liquid,

the nucleation time is defined as the amount of time necessary for a crystal of a particular size to nucleate by means of thermal fluctuations. The radius of the critical size nucleus is directly proportional to the solid-liquid interfacial energy, and inversely related to the difference in free energy volume between the solid and liquid phases. From the basis of these concepts, the equation relating homogeneous nucleation rate to interfacial energy is:

$$I = Ae^{\Delta G^*/kT} \text{ where } \Delta G^* = \frac{\kappa \gamma^3}{\Delta F_v^2} \quad (21)$$

where $A = nkTe^{-\Delta F_A/kT}$, I is the number of nuclei per unit volume, n is the number of atoms per unit volume, K is a factor determined by the nucleus shape, σ_{SL} is the solid-liquid interfacial energy, ΔF_v is the change in free energy from solid to liquid for a given volume, and ΔF_A is the free energy of activation for transporting an atom across the interface. This allows for the calculation of the interfacial energy from measurement of the nucleation rate. While this is a viable method, it yields the lower limit for the interfacial free energy, as the existence of heterogeneous nucleation sites increases the nucleation rate above that expected for the homogeneous case. This technique can require the passing of the liquid through filters in order to cause homogeneous nucleation by removing catalysts. The removal of these catalysts thus affects the nucleation rate and the determination of interfacial free energy. Therefore, such values are regarded as the lower limit of the interfacial free energy. Further studies have also indicated that these values illustrate the lower limit of interfacial free energy.^{31, 44, 55}

Comparisons can be made between Turnbull's and others works in Table 2.

Other methods for the experimental determination of interfacial free energy have been used. A method which uses the morphology of the grain boundary groove at a solid-liquid interface (as in the current study) has been used to experimentally determine interfacial free energy values. Recently a technique for measuring the interfacial energy directly from a solid-liquid interface at a grain boundary groove has been utilized to report values for a number of systems (Table 2).^{13-15, 20}

Gündüz and Hunt²⁰ introduced an experimental method for determining the solid-liquid interfacial energy from the shape of a GBG. The GBG is held at equilibrium in a stable temperature gradient in order to produce a macroscopically planar interface for imaging, and then detailed descriptions of the GBG must be made in order to determine the Gibbs-Thomson constant. From this, the solid-liquid interfacial energy can be calculated using a derivation described in a later section equations (38-40) lead to the definition of the Gibbs-Thomson coefficient, from which the interfacial energy can be determined

$$\frac{1}{2} G \gamma^2 = \Gamma(1 - \sin \theta) \quad (22)$$

The interface shape was preserved by quenching the material rapidly. Bayender *et al.*¹³⁻¹⁴ made measurements of the solid-liquid interfacial energy of camphene, PVA, and SCN. The method employed was that described by Gündüz and Hunt; however the images were collected under an optical microscope without rapid quenching. Reported values can be seen in Table 2.

These techniques have all been utilized to determine the interfacial free energy, however; the orientation dependence (anisotropy) of the interfacial free energy has not been defined experimentally extensively. Since interfacial energy is normally dependent on orientation of the crystallographic plane of the solid with respect to the liquid, the anisotropy is important in microstructure selection, and warrants further investigation.

Recently more studies have been able to predict the interfacial free energy of a system. Early experimentation based upon equilibrium shape of the interface was performed by Glicksman and Singh⁹ reported values for the interfacial energy anisotropy of SCN and PVA. Droplets of material were trapped within the solid, allowed to equilibrate and were then imaged. Measurements of droplet shape allows for direct determination of the degree of anisotropy of interfacial energy. A technique using equilibrium droplet shape was also employed by Napolitano, Liu and Trivedi^{6, 57} with interest in

the anisotropy of Al-Cu, Al-Sn, and Al-Si systems. In 1901, Wulff⁵⁸ described the equilibrium shape of a droplet in a secondary phase as

$$\frac{\gamma_1}{\gamma_2} = \frac{r_1}{r_2} \quad (23)$$

where the subscripts 1 and 2 indicate arbitrary crystallographic directions. From this, the equilibrium shape can be determined from a function of $\gamma(\theta)$. By reducing this to a two-dimensional problem, the Wulff plot can be written in a general form:

$$\frac{\gamma_q}{\gamma_0} = 1 + \sum_{m=2}^k \varepsilon_m^q \cos(m\theta) \quad (24)$$

where m is the degree of crystal symmetry and q is the cross-sectional normal. For cubic metals, such as those examined, $m = 4$. Thus the two-dimensional equation becomes

$$\varepsilon_4^{001} = \sec(4\theta) \left[\frac{r_4^{001}(\theta)}{r_0} \right] \quad (25)$$

This technique has been used to determine the anisotropy for transparent systems^{9, 10} and by Napolitano, Liu and Trivedi, for opaque systems. The application of the technique using equilibrium shape is more difficult in opaque systems. By examining small liquid droplets within the systems, a rapid quench can be performed, and these droplet shapes can be used to determine anisotropy of interfacial energy.

Muschol, Liu, and Cummins¹⁰ reported anisotropy of interfacial energy for SCN and for PVA, again based upon equilibrium shape of the interface, which they used to for comparison with the microscopic solvability theory which can be seen in Table 1. With respect to the calculation of σ_{theor}^* , the analysis for the microscopic solvability theory assumes a nearly parabolic shaped needle

crystal without sidebranching, boundaries, or neighboring dendrites that may, in part, lead to the discrepancies between σ^*_{theor} and σ^*_{exp} noticed within Table 1.

Research to determine the anisotropy of interfacial energy is driven by the need to describe selection of growth morphology. The microscopic solvability theory has been the subject of ongoing experimentation. Within the theory, the anisotropy of interfacial energy is described as the main factor in selecting the dendritic operating state, and makes experimentally determining anisotropy a general method in attempting to validate this theory on growth selection.

Table 1 Theoretical and experimental values of σ^* for reported materials.

Material	m	ε_m	Reference	σ^* theoretical	Reference	σ^* experimental	Reference
SCN	4	0.005	9	0.009	10	0.0195	49
		0.0055 ± 0.0015	10	0.011 ± 0.004	10	0.0195	49
PVA	4	0.05	9	0.14	10	0.022	9
		0.025	10	0.054 ± 0.004	10	0.022	9
						0.024	66
PVA + ethanol	4	0.006 ± 0.002	50	0.024 ± 0.01	10	0.05 ± 0.02	50
		0.26 ± 0.002	10	0.107 ± 0.007	10	0.05 ± 0.02	50
NH ₄ BR	4	0.016	36	0.072 ± 0.018	10	0.081 ± 0.02	36
H ₂ O	6	0.002	40	0.012	10	0.075	40
He						0.0013	51
Kr						0.017 ± 0.009	52
Xe						0.022 ± 0.012	52

Table 2 Reported anisotropy of interfacial energy values. The method used to obtain the values listed was equilibrium shape measurement.

Material	γ (mJ/m ²)	ϵ_4	Method	Reference
SCN	8.9	0.005	Equilibrium Shape	9
	28 ± 4		Grain Boundary Groove	26
	8.94 ± 0.5		Grain Boundary Groove	27
		0.0055 ± 0.0015	Equilibrium Shape	10
	8.02		Theoretical Calculation	15
	7.86 ± 0.79		Grain Boundary Groove	15
SCN - CTB	8.80 ± 0.88		Grain Boundary Groove	15
PVA	2.54		Grain Boundary Groove	14
	2.84	0.05	Equilibrium Shape	9
		0.025 ± 0.002	Equilibrium Shape	10
PVA + Ethanol		0.39		28
		0.26 ± 0.002	Equilibrium Shape	10
Camphene	5.3		Grain Boundary Groove	29
		0.03	Equilibrium Shape	30
	5.99		Grain Boundary Groove	13
	6 ± 1		Grain Boundary Groove	26
CBr ₄	10-20		Grain Boundary Groove	26
Naphthalene	61 ± 11		Grain Boundary Groove	26
Diphenyl	50 ± 10		Grain Boundary Groove	26
White Phosphorous	12 ± 2		Grain Boundary Groove	26
Ethylene dibromide	35 ± 7		Grain Boundary Groove	26
Benzene	44 ± 10		Grain Boundary Groove	26
NH ₄ Br + H ₂ O		0.016	Equilibrium Shape	36
H ₂ O	41		Grain Boundary Groove	29
	44 ± 10		Grain Boundary Groove	26
	33		Grain Boundary Groove	28
	20		Dendritic Growth	37
	16		Dendritic Growth	38
	15-32		Nucleation	28
	10-21		Theoretical Calculation	28,39
	38-50		Theoretical Calculation	5

(continued on next page)

Table 2 (continued)

Material	γ (mJ/m ²)	ϵ_4	Method	Reference
Al	115	0.015	Molecular dynamics Simulation	31
	150 ± 2	0.009 ± 0.001	Molecular dynamics Simulation	44
	92		Nucleation	5
	108		Nucleation	55
	149		Simulation	20
	93		Various Methods	33-35
		0.002 ± 0.001		40
Al-Cu		0.0097	Equilibrium Shape	7
	162		Grain Boundary Groove	21
Al-Cu-Fe	90		Nucleation	56
Al-Cu-Co	110		Nucleation	56
λ -Al ₁₃ Fe ₄	160		Nucleation	56
μ -Al ₅ Fe ₂	170		Nucleation	56
β -AlCuCo(B2)	180		Nucleation	56
Al-4 wt% Cu		0.00973	Equilibrium Shape	57
Al-2 wt% Si		0.0167	Equilibrium Shape	7
Al _(s) - AlCu _(L)	163.4 ± 21.24		Grain Boundary Groove	20
	160.01 ± 19.20		Grain Boundary Groove	43
Al _{2(s)} - AlCu _(L)	87.78 ± 11.41		Grain Boundary Groove	20
	88.363 ± 10.60		Grain Boundary Groove	43
Al _(s) - AlSi _(L)	168.95 ± 21.96		Grain Boundary Groove	20
Si _(s) - AlSi _(L)	352.41 ± 45.81		Grain Boundary Groove	20
Al _(s) - AlTi _(L)	174.623 ± 20.95		Grain Boundary Groove	43
Pb _(s) - PbSn _(L)	56.24 ± 7.31		Grain Boundary Groove	20
Sn _(s) - PbSn _(L)	132.43 ± 17.22		Grain Boundary Groove	20
NH ₄ Cl		0.012	Equilibrium Shape	59
Bi	61.3		Grain Boundary Groove	32
	54		Various Methods	33-35
Ni	325.88	0.02269	Molecular dynamics Simulation	41
	255		Various Methods	33-35
Pb	150-160		Wetting	42
	33		Various Methods	33-35
Ag	126		Various Methods	33-35
Au	132		Various Methods	33-35
Hg	24		Various Methods	33-35
Al	93		Various Methods	33-35
Ge	165		Various Methods	33-35
Sn	55		Various Methods	33-35
Fe	204		Various Methods	33-35
Li	30		Various Methods	33-35
Na	20		Various Methods	33-35
Cu	177		Various Methods	33-35
Pt	240		Various Methods	33-35

Figure 1 Schematics and micrographs of (a) regular (Al-Cu alloy) and (b) irregular (Al-Si alloy) eutectic solidification.⁵³

Figure 2 The forms of faceted (a) and non-faceted (b) interfaces are illustrated above. A faceted interface (a) is jagged and faceted at the microscopic scale (upper diagram), but smooth at the atomic scale (lower diagram). A non-faceted interface (b) appears microscopically flat (upper diagram), while being jagged on the atomic scale (lower diagram).¹

Figure 3 Cellular growth (a). Dendritic cell formation (b). Dendritic growth morphology (c). Because of the anisotropy of solid-liquid interfacial energy and growth kinetics, dendrites will grow in preferred orientations which are closest to the heat flow direction.¹

Chapter III: Objectives and Impact

Interest in materials properties and the microstructures which control them have driven the study of solidification microstructures. Factors such as the forces responsible for driving diffusion, maintaining local curvature, and kinetic factors such as mobility, lead to the selection of structural pathways during solidification. Moreover, a lack of fundamental knowledge with regard to the basic principles determining dynamics, limits our ability to control the solidification process and accurately predict microstructure. While the concept of anisotropy is understood, many of its implications upon the selection of growth planes, side-branching, and overall growth morphology are not well understood, making this very important in the large picture of understanding microstructure selection.

Research Scope and Objectives

The study proposed here focuses upon determining the anisotropy of interfacial energy with high confidence. This determination will be made directly from the GBG morphology at a solid-liquid interface at equilibrium. A series of images will be gathered from both SCN and PVA in order to extract a high confidence measurement of anisotropy of interfacial energy directly from GBG morphology. This will be done through the placement of ultra pure (>99.9%) samples upon a thermal gradient stage upon a light microscope for imaging. Each image will be recorded, and then analyzed to determine the anisotropy of interfacial energy.

The objectives of the proposed work are:

- to determine high confidence measurement of the solid-liquid interfacial energy, the Gibbs-Thomson coefficient, and the anisotropy of interfacial energy
- to obtain stable GBG's of pure SCN and PVA in a thermal gradient
- to obtain high resolution images of GBG's at solid-liquid interface at equilibrium in transparent organic systems

- to determine the crystallographic orientations of the included grains
- use digital image analysis to obtain a quantitative measurement of groove shape
- obtain a measurement of the thermal gradient, G
- using appropriate theoretical approach, determine anisotropy of interfacial energy for the given systems

Scientific Significance and Technological Impact

The current research is intended to provide high confidence experimental determination of the anisotropy of interfacial energy. From this, increased understanding of the dynamics of solidification can be further achieved with further experimentation. The high confidence anisotropy of interfacial energy that results from this work will be of great value in the further examination of side-branching, growth selection, and overall growth morphology for various materials. Reliable measurements of critical thermodynamic properties, such as $\gamma(\hat{n})$, are essential for meaningful qualitative validation of theoretical treatments leading to fundamental understanding of morphology selection in solidification. Also, prior experimental measurements of interfacial free energy and its associated anisotropy are limited. The coupled-groove method which is employed in the present work is a new approach to measuring such interfacial properties directly from the GBG morphology. This new method may indeed lead to more sophisticated approaches and strategies for measuring such properties.

Chapter IV: Theoretical Approach

The theoretical approach for this proposed study is based upon the orientation dependence of interfacial energy. We address the specific case of a GBG in a constant thermal gradient. There are two constraints for this analysis: the interface is planar in the far-field limit, and thermal equilibrium is held. Generally the relation of the Gibbs free energy with the principal curvatures is:

$$\Delta G_r = \tilde{\gamma} \bullet \kappa \text{ (where } \kappa = \kappa_1 + \kappa_2 \text{);} \quad (26)$$

Herring¹⁷ described the orientation dependence of interfacial energy, which related the interfacial (Gibbs-Thomson) undercooling to the principle interfacial curvatures, κ_1 and κ_2 . (Figure 4)

Considering a homogeneous system with m intersecting interfaces in two dimensions the total energy of the system is

$$e(s, \gamma) = e_v + e_p + \int \gamma ds \quad (27)$$

where e_p is the energy contribution from the junction itself, and e_v is the total volume free energy for all phases present. Excluding all regions but those very close to the intersections, the interfaces are considered planar, and

$$e(s, \gamma) = e_v + e_p + \sum_{n=1}^m \gamma(\theta_i) s_i \quad (28)$$

Assuming that e_p and e_v are constant, an arbitrary protrusion of the interface results in a change in the free energy of the system.

$$\delta e = \sum_m \left[\left(\frac{de}{ds} \right) \delta s + \left(\frac{de}{d\theta} \right) \delta \theta \right] = \sum_m \left[\gamma \delta s + \left(\frac{d\gamma}{d\theta} \right) \delta \theta \right]_m \quad (29)$$

Herring, by considering the geometry of an interface, noted

$$s \delta \theta = \delta r (r \bullet n) \quad (30)$$

$$\delta s = \delta r (r \bullet t)$$

where t and r are the unit tangent and normal vectors for each interface, and δr is the magnitude of the variation of the interface position in the direction r . Finally by substituting (30) into (29),

$$\nabla e = F_j = \sum_{i=1}^m \left(\gamma_i t_i + \frac{\partial \gamma}{\partial \theta} n_i \right) = 0 \quad (31)$$

where F_j is the net force acting on the interface. This is Herring's well known equation which can be then written in form of,

$$\Delta G_r = \left[\kappa_1(n) \left(\gamma(n) + \frac{\partial^2 \gamma(n)}{\partial n_i^2} \right) \right] \quad (32)$$

This can be written in terms of undercooling; the most common form of the Herring equation.

$$\Delta T_r = \frac{1}{\Delta S_f} \left[\kappa_1(n) \left(\gamma(n) + \frac{\partial^2 \gamma}{\partial n_i^2} \right) \right] \quad (33)$$

where comparison with equations (2) or (4) reveals that the stiffness,

$$\phi_r = \gamma + \gamma_{\theta\theta} \quad (34)$$

for this two-dimensional case.

In 1985 Gündüz and Hunt²⁰ developed a technique to measure solid-liquid interfacial energy based upon GBG after annealing eutectics in a temperature gradient. Using the relationship for the 2D case

$$\Delta T_r = \Gamma \kappa = \frac{\Gamma}{r} \quad (35)$$

where r is the local radius, and then integrating this equation with respect to the y -axis from the flat surface to a point on the groove (Figure 5)

$$\int \Delta T_r dy = \Gamma \int \frac{1}{r} dy \quad (36)$$

The right hand side of this equation can be evaluated for any shape by defining $rd\theta = ds$ so

$$r = \frac{ds}{d\theta} = \frac{ds}{dy} \frac{dy}{d\theta} = \frac{1}{\cos \theta} \frac{dy}{d\theta} \quad (37)$$

Thus giving

$$\int \frac{1}{r} dy = (1 - \sin \theta) \quad (38)$$

The left hand side of (30) can be evaluated if the thermal gradient, G , is known as a function of y .

When the thermal conductivities of the solid and liquid are equal, then temperature is dependent on G and the distance giving

$$\Delta T_r = Gy = \Gamma \kappa \quad (39)$$

To normalize the values of x , y , the term l_g is dependent on stiffness, $\tilde{\gamma}$ and thermal gradient, G as shown:

$$l_g = \sqrt{\frac{\gamma}{G}} \quad (40)$$

Rearranging (39) and combining with (40) gives (41).

$$\frac{y}{l_g} = l_g \kappa \quad (41)$$

The normalized value of y , is Y :

$$Y = \frac{y}{\sqrt{\gamma_0/G}} = \frac{y}{l_g} \quad (42)$$

K is the normalized value of κ :

$$K = \kappa \sqrt{\gamma_0/G} = \kappa l_g \quad (43)$$

The relationship between normalized and non-normalized data is shown:

$$\frac{Y}{K} = \frac{y/l_g}{\kappa l_g} = \frac{y}{\kappa l_g^2} \quad (44)$$

The orientation depended energy term

$$\gamma = \gamma(\vec{n}) \quad (45)$$

and assuming a two-dimensional case, γ is a function of θ . We define ε_4 as the anisotropy of interfacial energy from:

$$\gamma = \gamma_0(1 + \varepsilon_4 \cos 4\theta) \quad (46)$$

Substituting into (29):

$$\phi_r = \gamma_0[(1 - 15\varepsilon_4 \cos 4\theta)] \quad (47)$$

and thus the undercooling is:

$$\Delta T_r = \frac{\phi_r}{\Delta S_f} \kappa = \frac{\gamma_0[(1 - 15\varepsilon_4 \cos 4\theta)]}{\Delta S_f} \kappa \quad (48)$$

From (39) and (48) the relationship between stiffness, curvature, temperature, and groove depth is evident.

$$\Gamma = \Gamma_0[(1 - 15\varepsilon_4 \cos 4\theta)] \quad (49)$$

Simplifying with (44) yields:

$$\frac{\Gamma}{\Gamma_0} = \frac{Y}{K} = 1 - 15\varepsilon_4 \cos 4\theta \quad (50)$$

From (50) it is apparent that in order to solve for ε_4 three other values must be known. For this particular study, Y , K , and θ are all quantities needed for such a solution. Further examination will indicate that K is a function of X , Y , and θ , and θ varies with X , and Y . Thus K becomes a function of

X , and Y which are measurable quantities that vary critically with anisotropy of interfacial energy. Thus, given equation (50) and confident experimental results, it is theoretically possible to determine the anisotropy of interfacial energy from the geometry with high confidence.

With measured values of x , y , and initial angles of orientation for each grain, Y , K , and θ are all easily calculated. X and Y are easily computed by normalizing x and y . K is found by first solving for theta:

$$\theta = \tan\left(\frac{\partial Y}{\partial X}\right) \quad (51)$$

From this, a change in θ can be determined. In addition the change in arc length is defined as:

$$dS = \sqrt{Y^2 + X^2} \quad (52)$$

Finally K can be determined using the change in θ and (50) to give:

$$K = \frac{d\theta}{dS} \quad (53)$$

From (50-53) it is evident if confident measurement of the x - y coordinates for a GBG can be made, these can be used to determine the anisotropy of interfacial energy. Figure 5 illustrates the measurable quantities x and y and can be used to illustrate the relationship between the GBG morphology, stiffness, and anisotropy outlined here from just those two parameters.

Figure 4 Illustration of physical protrusion examined by Herring.¹⁷

Figure 5 Illustrating the definitions of θ , $d\theta$, ds , x , and y .

Chapter V: Experimental Program

Sample Materials and Specimen Preparation

The current study pertains to the equilibrium morphology of a GBG of a pure material in a thermal gradient. The transparent organic materials, specifically succinonitrile (SCN) and pivalic acid (PVA) are explored (see Figures 6-7). These are cubic transparent organic metal-analogs which are often used as model experimental materials for the study of solidification in metals. Crystallographically, SCN is body-centered cubic, while PVA is face-centered cubic (Figure 8).⁹ Metals, and many of the transparent organic systems, solidify with macroscopically smooth solid-liquid interfaces.

High interfacial mobility, low stiffness, and low anisotropy of interfacial properties similar to metals results in the appearance of dendritic growth along crystallographically determined directions. Thus, these transparent organic systems are very analogous to metallic systems in regards to solidification. In addition to the similarities in solidification behavior, the low melting temperatures and transparent nature of these materials make them well suited for the current study.

The presence of even relatively few impurities causes significant changes in crystallization processes. For this reason, distillation and zone-refining of commercial purity succinonitrile and pivalic acid was performed prior to experimentation. The samples were distilled and torch sealed within glass tubes. These glass tubes were then put through a rigorous zone-refining process. The tubes were passed through the zone-refining apparatus approximately 30-50 times, depending on the material. The zone-refining process requires a motor which slowly advances the glass tube through a series of ring heaters. This repeated solidification and remelting relocates impurities to the extreme end of the sample, leaving behind an ultra-pure (>99.9%) sample. Purity was confirmed by melting point testing of the materials after distillation and zone-refining. With the melting point of SCN found to be 58.2°C and PVA was found to be 36.1°C.

Ultra-pure pivalic acid (PVA) physical properties include:

- a melting temperature of 35.90°C,¹²
- and a solid-liquid interfacial energy, σ_{SL} , of $2.8 \times 10^{-3} \text{ J/m}^2$.¹³⁻¹⁵

The physical properties of ultra-pure succinonitrile include:

- a melting temperature of 58.08°C,¹⁶
- and a solid-liquid interfacial energy, σ_{SL} , of $8.95 \times 10^{-3} \text{ J/m}^2$.¹³⁻¹⁵

Further information regarding the physical properties of succinonitrile and pivalic acid is given in Table 3.

The preparation of transparent material test specimens involved three primary procedures:

- the purification of test materials by distillation and zone refining,
- the design and assembly of the specimen cell slides,
- and the filling of the specimen cell slides with the appropriate purified test material.

The relevant details regarding these processes are explained further here.

The experimental technique requires the preparation of thin slides containing the high-purity test material and the necessary thermocouple assemblies. The specimen cells were created such that the test material was contained between two glass cover-slips, with dimensions of 34 mm in length, 24 mm in width, and 0.15 mm in thickness. Silicone adhesive was used to attach and seal the cover-slips on three sides with four type-K thermocouples (0.050 mm in diameter) affixed within the cell, and distributed along the length direction with spacing of 2-3 mm. Before filling the cell with SCN or PVA, the silicone sealant was allowed to cure for at least 24 hours at room temperature to avoid any reaction between the test material and the adhesive silicone. The slides were oriented such that the largest surface was in the x - y plane, and the z -direction was minimized to reduce curvature, κ , and heat flow in the z -direction. This z -direction distance was on approximately 100 μm .

In order to reduce the complexity of analysis, the current study must be reduced to a two-dimensional case, and SCN must be directionally grown into a slide. However, growing a pure material in a directional solidification furnace results in planar growth and this in turn limits the ability to determine grain orientation. Dendritic growth occurs in the presence of both thermal and solute instabilities; however, a directional solidification furnace has a controlled thermal setting. And using a pure material, there is no solute field, thus resulting in planar rather than dendritic growth. To alleviate this, solute is allowed to diffuse into a portion of the slide. This allows for dendritic growth for the portion of the slide containing the solute. After the solute is consumed, a switch to planar growth occurs with the pure material holding the orientation of the previous dendritic growth. For the case of SCN, water was used as a solute. The SCN-water system has reported diffusion coefficients⁷⁰, as well as a well established phase diagram (Figure 9).⁷¹

Diffusion profiles were created for various times to indicate the distance the solute would travel within the pure slide for each associated time. Using this data, a timeframe for diffusion of water in SCN was determined (Figure 10). From the constitutional supercooling criterion, V_{cs} is the velocity at which instabilities cause dendritic growth.

$$V_{cs} = -\frac{DGk}{mc_0(l-k)} \quad (54)$$

where G is the thermal gradient, D is the diffusion coefficient of the solute, c_0 is the concentration of the solute, m is the liquidous slope, and k is the partition coefficient.

A slide is filled with pure SCN in a technique described in the experimental process section. After filling, this slide was exposed to solute and then sealed and placed in a directional solidification furnace for growth under a constant thermal gradient. From the calculation of V_{cs} and the diffusion profile, the expected distance and concentration of solute are shown for various times. From the calculations shown in Figure 10, the velocity above which dendritic growth occurs, and the time of exposure to deionized water for diffusion lead to an estimation of the distance at which the transition

from dendritic to planar growth would occur. From these calculations, the water was allowed to diffuse into the pure slide for one hour, and then this slide was sealed and placed in a directional solidification furnace and solidified at a speed of $10 \mu\text{m/s}$ under the same constant thermal gradient as the prior pure same. The solute field allows dendritic growth within the slide until the solute is consumed and only pure material remains. At this point the interface becomes planar while holding the orientation which was present, and measurable, in the dendritic growth region (Figure 11).

These initial experiments lead to the application used to grow SCN directionally into the aforementioned slide assembly. This sample slide was inserted into a secondary glass slide apparatus (Figure 12)

The test specimens were prepared by the remelting of purified SCN/PVA material under vacuum, followed by the introduction of the material into the prepared cover-slip specimen cells. During this procedure, the material is kept within a specialized filling chamber (Figure 13) designed to minimize contamination from ambient air and maintain vacuum pressure.

Before remelting, the chamber atmosphere is established through three cycles of evacuation to a pressure of 33 Pa ($3 \times 10^{-4} \text{ atm}$), along with a nitrogen backfill to ambient pressure after each successive evacuation. After the final evacuation the filling chamber at a pressure is approximately 33 Pa , and the test material is remelted and let stand for 30 minutes. Following the 30 minute period, the directional solidification apparatus and cover-slip test cell are immersed into the liquid SCN/PVA, and a nitrogen pressure of approximately 130 kPa (1.3 atm) is applied to quickly force-fill the cover-slip specimen cell. After filling, the specimen cell is permitted to cool until the material is fully solidified. Finally, the specimen is removed from the chamber. The ends of the thin tubes are immersed in a bath of deionized water, permitting water to diffuse into the solid SCN. After a prescribed diffusion time of one hour, the slide was reheated and allowed to solidify directionally from the open (water-rich) end of the tubes toward and into the slide, yielding a bicrystalline

specimen. The slide is removed from the directional growth apparatus and affixed to the rotating turret on the microscope stage using aluminum tape as described in the next section.

Experimental Design

The objective of the experimental approach is to obtain high resolution images of a GBG of a particular transparent organic metal analog system at equilibrium at a solid-liquid interface. To achieve this objective, a temperature gradient stage was affixed to an optical microscope to record images of GBG geometry in transparent organic systems. In the current work, the apparatus was designed to enable rotation of the specimen within the thermal gradient. The rotation of the sample slide allows variation of the orientation of the solid-liquid interface while maintaining a fixed grain boundary misorientation. The experimental equipment consists of a circular, disc-shaped rotating turret, positioned between a hot stage and a cold stage, as part of the larger gradient stage illustrated in Figure 14

The hot stage is comprised of two copper plates which are heated resistively by Kanthal wires. These wires are insulated in alumina tubes and integrally threaded within the plates of the hot stage. A transformer was positioned in the supply circuit, stepping the maximum current down in order to maximize the thermal stability of the hot stage. A fully proportional thermistor-based control system was incorporated, allowing hot stage temperature control to within 0.1°C .

The cold-stage design is very similar to that of the hot stage. However, cooling is achieved by circulating an aqueous ethylene glycol solution through the two plates again allowing for control within 0.1°C . The gradient-stage consists of the disc-shaped specimen turret that is press-fitted between two copper plates on either side of the microscope stage. These plates are connected thermally to both the hot-and cold-stages. The specimen cell fits inside a recess machined into the turret. The specimen turret has a machined cut-out to provide a viewing area of 220 mm x 500 mm through the specimen.

Along the two opposite short edges of the specimen cell, the copper assembly is made to have good thermal contact with both glass plates of the cell through the use of aluminum tape. With this configuration, the thermal gradient across the specimen is dependent on the hot stage temperature, the cold stage temperature, the separation distance between the stages, as well as the angular position of the rotating specimen turret.

This entire gradient-stage system described above was mounted to the stage of an optical microscope, which is designed for transmitted-light operation. A CCD camera was placed above the light microscope apparatus to record digital images of a crystal-melt interface at a GBG. The images were 8 bit grayscale and had a resolution of 4080 x 3072 pixels, which translated to roughly 0.068 micron per pixel using a 40x optical lens.

Grain Boundary Groove Measurement

The thermocouple wires are then accordingly wired to a reference ice bath, and then a thermometer (Figure 14). The ice bath was used to allow a reference point of 0°C. Using the thermocouple spacing measured from digital images, and temperature measurements, the thermal gradient could be measured. Once the sample is loaded and the thermocouples attached for data acquisition, the cold stage power supply is turned on and the temperature set. For SCN the cold stage temperature is set to 18.0°C. For PVA, the cold stage temperature is set to 10.0°C. The hot stage is then turned on, slowly increasing the temperature until melting occurs in the desired location. The final temperature setting should place the solid-liquid interface between the middle two thermocouples. The grain boundary is then allowed to equilibrate for approximately 1 to 2 hours until equilibrium is reached at the interface. After equilibration, the grain boundary groove shape is described using the digital camera. Then an undercooling is applied and dendrites are photographed for each rotation.

The turret is rotated. The interface is then allowed to re-equilibrate, and the groove shape is recorded again. This is repeated several times with the turret being rotated in approximately 5 degree increments. The thermocouples are used as an angular reference to measure the rotation angles. Also, the sample is undercooled by passing air across the slide at low magnification to allow dendritic growth. This allows for the measurement of rotational orientation of each individual grain. This is done for each GBG examined at the crystal-melt interface. These images are recorded digitally from atop the optical microscope and are then prepared for analysis.

Groove Shape Analysis

Once images have been acquired as described in the previous chapter, the grayscale images are processed to extract a numerical description of the groove shape. This process involves several steps and the use of imaging software designed for such analysis, along with specialized programs created to aid in the conversion to a two-dimensional coordinate system.

The interface was located midway between the overall transition from the light to dark portion of the interface seen in the grayscale images as seen in the inlay in Figure 15. This midpoint is achieved by scanning the image by pixel intensity. The profile of the intensity verses distance creates a data set from which this point can be determined. Over the range examined, there will be an intensity maximum which crosses past the baseline to an intensity minimum. Calculating the derivative of this profile, the local maxima and minima can be identified, and the inflection point will become the minimum point between these zero values which can be used to determine the GBG shape quantitatively.

While this method removes some "background noise" associated with image acquisition, some perturbations still exist within the data set. While resolution of the digital images is high, it is apparent that the exact boundary cannot be perfectly defined by the approximation of the interface by use of pixels. Even with one pixel being roughly 0.068 microns, the image is acceptable; however, an

exact representation of the interface is not possible. Another possible limitation exists within the ability of the imaging software. While the method used is designed to designate one color (or gray shades) from another, the number of recognizable shades must be limited. If a pixel, or set of pixels, is incorrectly assigned due to these limitations, the end result is affected. This gives rise to small perturbations in the data set. While small, these perturbations can have a dramatic affect upon results. Very slight changes in defining the interface can result in dramatic changes to the solid-liquid boundary, and overall, cause changes when calculating interfacial energy and its anisotropy. To reduce the impact of such fluctuations, a Loess (locally weighted scatter-plot) technique is used to “smooth” the data set. Loess smoothing is accomplished by fitting a linear regression for many small parts of the x-axis and piecing together the line segments. The loess regression weights the close (local) data points more than more distant data points, and is similar to a moving average. The weights are given by the function shown below:

$$w_i = \left(1 - \left| \frac{x - x_i}{d(x)} \right|^3 \right)^3 \quad (55)$$

where x is the predictor value associated with the response value to be smoothed, x_i are the nearest neighbors of x as defined by the span, and $d(x)$ is the distance along the x-axis from x to the most distant predictor value within the span. Then a weighted linear least squares regression is performed and a second degree polynomial is used. The smoothed value is given by the weighted regression at the predictor value of interest.

As discussed previously, the anisotropy of interfacial energy can be calculated directly, under given conditions, from the measured grain boundary groove geometry. The relationship between the normalized (by l_g which is defined in equation (36)) values of groove depth, y , curvature, k , and the angle θ allow for calculation of the anisotropy of interfacial energy through the orientation dependence of stiffness. These values are either measured, or calculated from measurements taken

from the GBG images. By using the x and y-coordinates, X , Y , k , K , and θ can all be determined. This allows for the measurement of interfacial anisotropy parameter directly from the GBG geometry.

Plotting Y/K verses θ (Figure 17) illustrates the interfacial anisotropy as shown in (43). This plot varies with anisotropy and can be used to extract the closest fit with respect to ε_4 . These results have shown a very intense sensitivity of K to minute variances in θ , X , and Y . A slight variation, due to even one misplaced pixel, has detrimental effects upon the values of K , the stiffness (Y/K), and thus on ε_4 .

To compensate for this high sensitivity associated with the numerical approach, the generation of a series of theoretical curves using varying parameters for the anisotropy of interfacial energy was employed. An alternate approach is to simply compare the experimentally measured groove shapes with a series of theoretical curves computed for a range of anisotropy values.

Comparison with Theory

Once numerous theoretical curves are generated, they are compared to the experimental results by interpolating the data (Figure 18) for direct comparison, and then calculating the correlation coefficient between these two curves. The correlation is determined from

$$R_{x,y} = \frac{\frac{1}{n} \sum_{j=i}^n (x_j - \mu_x)(y_j - \mu_y)}{\sigma_x \sigma_y} \quad (55)$$

Plotting ε_4 verses the correlation coefficient (Figure 19) illustrates the local maxima, and thus the anisotropy parameter with the highest correlation to the experimental data for the given GBG.

Table 3 Properties of SCN, PVA

material	chemical formula	molecular weight	melting temperature (°C)	boiling temperature (°C)	$\sigma_{SL} \times 10^{-3}$ (J/m ²)	$\sigma_{gb} \times 10^{-3}$ (J/m ²)	$\Gamma \times 10^{-8}$ (Km)
SCN	C ₄ H ₄ N ₂	80.09	58.08	265-267	8.94	15.95	6.17
PVA	(H ₃ C) ₃ CCOOH	102.13	35.9	163.7-163.8	2.54	5.03	3.64

references 13-15

Figure 6 The chemical formula of and molecular structure of Succinonitrile.

Figure 7 The chemical formula and molecular structure of Pivalic Acid.

Figure 8 Illustration of SCN's BCC structure and PVA's FCC structure.

Figure 9 Phase diagram for SCN-water system.⁷¹

Figure 10 Diffusion profile of water in SCN at 25°C for various times. The critical velocity, V_{cs} , is also plotted indicating various concentrations of water needed to drive the dendritic growth of the SCN-water system.

Figure 11 Directional solidification furnace showing slide setup and growth morphologies observed with solute (deionized water) added to ultra pure SCN.

Figure 12 The above diagram represents the slide filling apparatus used to directionally grow the SCN. It is constructed from glass slide material, glass tubing, and same silicone adhesive used in slide preparation. The upper diagram is a top view, while the lower diagram is a side section view.

Figure 13 The specialized filling apparatus to prevent contamination of the sample slides is presented above. The material is melted under vacuum in order to minimize contamination from ambient air. This helps insure the purity of the material after the distillation and zone refining processes have been completed.

Figure 14 The microscope stage design and overall experimental setup is shown above. The upper diagram illustrates the overall setup, while the lower diagram details the heating and cooling systems that are affixed upon the microscope stage to induce a thermal gradient.

Figure 15 Digital photographs were taken of the GBG at a solid-liquid interface at equilibrium. Above is a typical image which was recorded along with a micron scale bar indicating the scale. The inlay shows the interface as it changes from light to dark.

Figure 16 The above figure represents a typical numerical representation of the GBG shape after data preparation techniques.

Figure 17 The polar plot of Y/K verses θ can visually give representation to equation 51. By plotting these values (stiffness verses orientation), the anisotropy can theoretically be found based on the curve amplitude which is generated. This graph plots the theoretical value of the curve for various anisotropy values.

Figure 18 For direct comparison between the theoretical and experimental data, an interpolation was performed to interpolate a Y-value in the experimental data for every X-value in the theoretical data. Above is the visual representation of the resulting curves for SCN2a.

Figure 19 Once theoretical curves were generated for the various anisotropy values, the correlation coefficient was calculated between the theoretical data and the interpolated experimental data for each anisotropy value. For each groove, a plot of the anisotropy versus correlation indicates local maximum which can be assumed to be the anisotropy for the range evaluated. Results shown above are in SCN1.

Chapter VI: Results and Discussion

Results

It is proposed that the anisotropy of interfacial free energy can be determined directly from the GBG morphology at a solid-liquid interface at equilibrium. The results with regard to such calculation in SCN and PVA will be described in detail in this section.

Results for SCN

For SCN two different grain boundary grooves (SCN1 SCN2) were examined and a total of eleven groove shapes were measured. The six groove shapes for SCN1 and five for SCN2 are shown in Figure 20.

The relevant measurement data for each groove measurements are listed in Table 4. Also shown are the associated values of G , l_g , Γ_0 , ε_t , and θ . In Figure 22, the corresponding theoretical groove shapes are superimposed on the groove images for direct comparison.

Γ_0 was found to be $6.41 \pm 0.10 \times 10^{-5}$ K mm which is in reasonable agreement with a previously reported value by Maraşlı *et al.*¹⁵ of 6.17×10^{-5} K mm. The orientation of the grains was gathered after an undercooling was applied, and dendritic growth was allowed to occur. An example image of such growth occurring can be seen in Figure 21. The orientation of the grains can be measured by measuring the angle made by the dendrites with respect to the interface accompanied by a measurement of normal direction. The orientation is adjusted by an inward rotation from the dendrite orientation to the normal axes.

Examining the theoretically generated curves and comparing them to the experimental curve that was imaged and converted to data, the curves appear to be in reasonable agreement, however; there is an amount of variation between the theoretical and experimental curves. Despite this variation, over the range of anisotropy values generated for the given orientation of the individual grains, the

curves overlaid upon the image in Figure 22 represent the closest correlation between the experimentally measured curves, and the curves generated with the conditions achieved in experimentation over the range of anisotropy examined.

Examining the anisotropies calculated for each rotation of the same GBG shows the variation in calculation of the anisotropy of interfacial energy using this method. Figure 23 illustrates the results from Table 4 for just the GBG SCN1. The average value of anisotropy for the rotations of this single GBG was determined to be 0.0048 and is represented by the solid line in Figure 23. The dashed lines indicate plus and minus two standard deviations. Again, this value is in reasonable agreement with the previously reported by Glicksman and Singh⁹ and the value 0.0055 reported by Muschol, Liu and Cummins¹⁰.

Examining the anisotropies calculated for each rotation of the same GBG shows the variation in calculation of the anisotropy of interfacial energy using this method. Figure 24 illustrates the results from Table 45 for just the GBG SCN2. The average value of anisotropy for the rotations of this single GBG was determined to be 0.0054 and is represented by the solid line in Figure 24. The dashed lines indicate plus and minus two standard deviations. Again, this value is in reasonable agreement with the previously reported.

The resultant anisotropy of interfacial energy for the both GBG's examined can again be seen in Table 4, and Figure 25 indicates anisotropies recorded for each of the two GBG's with the overall average. The values reported vary slightly over an interval of $\epsilon_4=0.004$ to $\epsilon_4=0.006$ with an average value (0.0051) that is of reasonable agreement to a value of 0.005 that was previously reported.

Results for PVA

For PVA two different grain boundary grooves (PVA1, PVA2) were examined and a total of nine groove shapes were measured. The five groove shapes for PVA1 and four for PVA2 are shown in Figure 26.

The relevant measurement data for each groove measurements are listed in Table 5. Also shown are the associated values of G , I_g , Γ_0 , ε_d , and θ . In Figure 28, the corresponding theoretical groove shapes are superimposed on the groove images for direct comparison.

Γ_0 was found to be $3.99 \pm 0.20 \times 10^{-5}$ K mm which is in reasonable agreement with a previously reported value by Bayender *et al.*¹⁴ of 3.64×10^{-5} K mm. The orientation of the grains was gathered after an undercooling was applied, and dendritic growth was allowed to occur. An example image can be seen in Figure 27. Again the orientation of the grains can be measured by measuring the angle made by the dendrites with respect to the interface accompanied by a measurement of normal direction. The orientation is adjusted by an inward rotation from the dendrite orientation to the normal axes.

Examining the theoretically generated curves and comparing them to the experimental curve that was imaged and converted to data, the curves appear to be in reasonable agreement, however; there is an amount of variation between the theoretical and experimental curves. Despite this variation, over the range of anisotropy values generated for the given orientation of the individual grains, the curves overlaid upon the image in Figure 28 represent the closest correlation between the experimentally measured curves, and the curves generated with the conditions achieved in experimentation over the range of anisotropy examined. With regard to GBG PVA1, the variation is more pronounced on the right hand side grain. However, when calculating the expected GBG angle for the various orientations, the observed values are in close agreement with those measured.

Examining the anisotropies calculated for each rotation of the same GBG shows the variation in calculation of the anisotropy of interfacial energy using this method. Figure 29 illustrates the results from Table 6 for just the GBG PVA1. The average value of anisotropy for the rotations of this single GBG was determined to be 0.023 and is represented by the solid line in Figure 29. The dashed lines indicate plus and minus two standard deviations. Again, this value is in reasonable agreement with the value 0.025 ± 0.002 which was previously reported by Muschol, Liu and Cummins¹⁰.

Examining the anisotropies calculated for each rotation of the same GBG shows the variation in calculation of the anisotropy of interfacial energy using this method. Figure 30 illustrates the results from Table 6 for just the GBG PVA2. The average value of anisotropy for the rotations of this single GBG was determined to be 0.026 and is represented by the solid line in Figure 30. The dashed lines indicate plus and minus two standard deviations. Again, this value is in reasonable agreement with the previously reported.

The resultant anisotropy of interfacial energy for the both GBG's examined can again be seen in Table 6, and Figure 31 indicates anisotropies recorded for each of the two GBG's with the overall average. The values reported vary slightly over an interval of $\varepsilon_4=0.015$ to $\varepsilon_4=0.035$ with an average value (0.023) that is of reasonable agreement to a value of 0.025 that was previously reported.

Estimates of Error

Some possible sources of error arise from both the analytical and experimental procedures. Given the sensitivity of anisotropy to the various intrinsic interfacial properties, which in this study are measured from the GBG morphology and thus dependent on normalized depth, Y , and curvature, K , the interpretation of each pixel by the imaging software has an effect upon the final outcome. However, the resolution achieved allows for a very slight variation in distance per pixel (0.068 $\mu\text{m}/\text{pixel}$). Close attention must be paid to the smoothing of the data using the loess curve. The smoothing of the data, while removing irregularities generated by the experimental process can again influence the final calculation of anisotropy. The application of the loess smoothing must be consistent to remove slight anomalies caused by the random noise associated with imaging.

Experimental error could arise from multiple sources as well. If the GBG is not at reasonably equilibrium conditions or the thermal gradient is inconsistent, the values calculated for anisotropy would be affected. Kinetic properties would be associated, altering the groove depth and overall morphology and thus affecting the calculation of anisotropy of isotropy of interfacial energy.

Table 4 Measured values of G , Γ_0 , orientation, and the value of l_g calculated from these values using (32) for SCN.

GBG	G (K/mm)	l_g (μm)	$\Gamma_0 \times 10^{-5}$ (K mm)	θ_{lhs} ($^\circ$)	θ_{rhs} ($^\circ$)	θ_{gb} observed ($^\circ$)	ε_4
scn1a	1.81	5.88	6.27	88	6	12.0	0.005
scn1b	1.79	6.02	6.48	83.5	10.5	1.0	0.0045
scn1c	1.78	5.97	6.35	78.7	15.3	2.5	0.0045
scn1d	1.79	5.98	6.41	73.6	20.4	2.0	0.0055
scn1e	1.81	5.98	6.47	3	1	1.0	0.005
scn1f	1.78	6.07	6.57	7.7	86.3	0.0	0.004
scn2a	1.68	6.14	6.33	15	10.5	1.0	0.005
scn2b	1.70	6.08	6.29	10.2	15.3	2.0	0.0055
scn2c	1.69	6.23	6.55	5.9	19.6	1.5	0.005
scn2d	1.71	6.08	6.33	1.6	24.8	2.0	0.006
scn2e	1.70	6.14	6.41	19.7	5.8	1.5	0.0055

Table 5 Measured values of G , Γ_0 , the orientations, and the value of l_g calculated from these values using (32) for PVA.

GBG	G (K/mm)	l_g (μm)	$\Gamma_0 \times 10^5$ (K mm)	$\theta_{\text{LHS}}(^{\circ})$	$\theta_{\text{RHS}}(^{\circ})$	θ_{gb} observed ($^{\circ}$)	ε_4
pva1a	0.73	7.26	3.85	10.1	87.8	19.5	0.025
pva1b	0.73	7.49	4.10	14.4	83.5	20.5	0.02
pva1c	0.68	7.46	3.78	19.2	78.7	16.5	0.015
pva1d	0.70	7.72	4.17	23.7	74.2	15.0	0.025
pva1e	0.73	7.11	3.69	5.9	2	4.5	0.02
pva2a	0.72	7.67	4.25	83.5	5.5	9.0	0.02
pva2b	0.72	7.61	4.19	77	12	6.5	0.035
pva2c	0.71	7.61	4.10	71.6	17.4	2.5	0.025
pva2d	0.73	7.18	3.78	67.9	21.1	3.0	0.025

Figure 20 Typical images of GBG's in succinonitrile. Grains are photographed at a solid-liquid interface at equilibrium at a grain boundary groove. Then dendrites are grown to obtain the orientation for each grain prior to a rotation of the turret on the gradient stage and subsequent imaging.

Figure 21 Typical image of dendritic growth in SCN after an undercooling is applied to the equilibrium solid-liquid interface at a grain boundary groove. The orientation of both grains can be obtained from the direction of growth with respect to the interface and a normal axis.

Figure 22 Graphical representation of the theoretically calculated GBG shape for the anisotropy found in Table 5 in comparison to the recorded images for SCN.

Figure 23 The values of the anisotropy were plotted for GBG SCN1 and an average value of anisotropy was also calculated. The average value (solid line = 0.0048) is comparable to previously reported values of anisotropy. The literature values are indicated along with the proper reference. The dashed black lines indicate plus and minus two standard deviations.

Figure 24 The values of the anisotropy were plotted for GBG SCN2 and an average value of anisotropy was also calculated. The average value (solid line = 0.0054) is comparable to previously reported values of anisotropy. The literature values are indicated along with the proper reference. The dashed black lines indicate plus and minus two standard deviations.

Figure 25 The values of the anisotropy were plotted for GBG's SCN1 and SCN2 and an average value of anisotropy was also calculated. The average value (dashed line = 0.0051) is comparable to previously reported values of anisotropy. The literature values are indicated along with the proper reference. The dashes above the data points indicate plus and minus two standard deviations.

Figure 26 Typical images of GBG's in pivalic acid. Grains are photographed at a solid-liquid interface at equilibrium at a grain boundary groove. Then dendrites are grown to obtain the orientation for each grain prior to a rotation of the turret on the gradient stage and subsequent imaging.

Figure 27 Typical image of dendritic growth in PVA after an undercooling is applied to the equilibrium solid-liquid interface at a grain boundary groove. The orientation of both grains can be obtained from the direction of growth with respect to the interface and a normal axis.

Figure 28 Graphical representation of the theoretically calculated GBG shape for the anisotropy found in Table 7 in comparison to the recorded images for PVA.

Figure 29 The values of the anisotropy were plotted for GBG PVA1 and an average value of anisotropy was also calculated. The average value (solid line = 0.021) is comparable to previously reported values of anisotropy. The literature values are indicated along with the proper reference. The dashed black lines indicate plus and minus two standard deviations.

Figure 30 The values of the anisotropy were plotted for GBG PVA2 and an average value of anisotropy was also calculated. The average value (solid line = 0.026) is comparable to previously reported values of anisotropy. The literature values are indicated along with the proper reference. The dashed black lines indicate plus and minus two standard deviations.

Figure 31 The values of the anisotropy were plotted for GBG's PVA1 and PVA2 and an average value of anisotropy was also calculated. The average value (solid line = 0.023) is comparable to previously reported values of anisotropy. The literature values are indicated along with the proper reference. The dashes above the data points indicate plus and minus two standard deviations.

Chapter VII: Summary, Conclusions, and Suggestions for Further Investigation

Summary

A quantity of SCN and PVA has been distilled, and zone refined. Then and slide assemblies were created, and these materials filled into them. Experimental data was collected for a number of GBG's for both SCN and PVA and these were photographed and these images were then analyzed using imaging software to establish a set of data corresponding to the solid-liquid interface at a grain boundary at equilibrium. This data was then smoothed using loess fitting, to further reduce noise associated with transferring the data from the digital images. Theoretical curves were then generated over a range of anisotropy values for comparison to the experimentally measured value. The smoothed experimental data was then compared to the theoretically generated curves and a best fit over the range examined was determined. The anisotropy value which corresponded to the best fit to the experimental curve was then recorded as the anisotropy of interfacial energy. The results were recorded for all of the GBG rotations examined, averaged, and then statistically analyzed to ensure confidence in the measurement of the anisotropy of interfacial energy. Finally the average value of the anisotropy of interfacial energy was compared to literature values which have been previously reported.

Conclusions

With regard to the SCN samples examined within the current study, interfacial energy measurements were determined to be $\varepsilon_s = 0.051 \pm 0.001$, $\gamma_0 = 9.28 \pm 0.06 \times 10^{-3} \text{ J/m}^2$, and $\Gamma_0 = 6.41 \pm 0.10 \times 10^{-5} \text{ K mm}$.

When compared to previously reported values, the results are of reasonable agreement. With regard to the PVA samples examined within the current study, interfacial energy measurements were determined to be $\varepsilon_s = 0.023 \pm 0.012$, $\gamma_0 = 2.78 \pm 0.05 \times 10^{-3} \text{ J/m}^2$, and $\Gamma_0 = 3.99 \pm 0.10 \times 10^{-5} \text{ K mm}$.

When compared to previously reported values, the results are of reasonable agreement.

Areas for Future Study

One area of possible future research includes adapting this technique to obtain experimental values of anisotropy of interfacial energy in opaque metallic systems after a GBG is established and rapidly quenched. Images analysis methods used here would readily apply to such as system if orientation of both grains could be achieved. The limitations on such an application include the determination of the orientation of the grains and measurement of the thermal gradient. Also central to such a study would be the ability to rapidly quench the GBG without altering the equilibrium state needed for such an analysis. Any deviation from equilibrium due to thermal inconsistencies would affect the interface in terms of the thermal gradient, and thus the groove depth and overall morphology.

Another area for future research includes the use of the groove depth to determine anisotropy of interfacial energy directly. Currently, the process uses the entire groove depth for analysis as the limitations due to imaging and image analysis do not allow for exact determination of the groove depth. However, the anisotropy can theoretically be determined directly measurement of the groove depth verses θ (for a fixed $\Delta\theta$) in a known thermal gradient.

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