Abstract

Abstract goes here. Yeah. You will do this last.

Orientation-dependent Surface Energy Characterization of Rare-Earth-Free Magnetostrictive Alloys

University of Maryland, College Park

Michael N. Van Order[1]

Dr. Alison Flatau Dr. Suok-Min Na

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Copyright Statement

I declare that...

Dedication

To mom, dad, sister, Alyson, and cats.

Acknowledgments

I want to thank...

Contents

1 Introduction **9**

1.1 Background 9

1.1.1 Motivation 11

1.1.2 Preliminary investigations 16

2 Chapter 2 Title **20**

2.1 Metal Surface Energy Measurement 20

2.1.1 Phase I: Gallium Drop Method 21

3 Chapter 3 Title **32**

3.0.2 Phase II: Two-liquid-phase contact angle method 33

4 Conclusion **42**

A Derivation of Young's Equation **43**

B Derivation of Schultz's two-liquid-phase method **45**

B.0.3 Measuring dispersive solid surface energy, γ_S^D 45

B.0.4 Measuring polar solid surface energy, γ_S^P 46

List of Figures

1.1 This is an illustration of Goss and Cube textures shown with their respective axes of easy magnetization. Goss has one easy axis, and Cube has two easy axes. 12

1.2 Diagram of AGG from as-rolled sample of (Fe-19%Ga)+1.0%NbC alloy (left) to argon- (upper) and sulfur-annealed (lower) samples for annealing times of 1h (middle) and 3h (right). EBSD images scanned along the normal direction of 12x12x0.45 mm^3 sheet. Red, green and blue indicate (0 0 1), (0 1 1) and (1 1 1) grains, respectively. 13

1.3 This illustration shows a vector representation of the interfacial tensions involved in a solid-liquid-gas contact angle experiment. [Image available in public domain: wikimedia.org] 16

1.4 (a) 3D rendering of (110)/(111) grain boundary on surface of for (Fe-19%Ga)+1.0%NbC sample where the depth of groove is 8 nm. (b) A quadratic fit of a (110)/(111) grain boundary profile for a (Fe-19%Ga)+1.0%NbC sample. 18

2.1 Schematics indicating notation used and contact angles θ_i, radii of drop-solid contact area r_i, and radii of curvature for a spherical drop R_i, for two temperatures as thermal expansion induced tension P strains the substrate. 22

2.2 (a) The first design of our contact angle goniometer. The acrylic container houses the argon environment and sample. This design was modified with a more stable glass enclosure. (b) A highly deformed gallium drop next to the thermocouple on a ceramic YAG test sample at 45.5°C. 25

2.3 The second version of our gallium contact angle goniometer. The aluminum enclosure conductively transfers heat, the gas lines flow Ar gas into the chamber, top-mounted thermocouples monitor the gas and sample temperature, and the glass windows allow for backlighting of the drop profile along with high resolution image capture using a DSLR camera. 26

2.4 Pure liquid gallium obtains viscoelastic properties when trace amounts of oxygen are present via formation of oxide shell. Non-axisymmetric Ga drops form on this iron substrate. 27

2.5 This image shows the contact angle of gallium on a Galfenol sample in an argon environment before and after HCl vapor treatment. 29

2.6 The location of a gallium drop on highly Goss-textured surface. . . . 30

2.7 (a) Blue and red dots show left and right contact angle, respectively, of liquid gallium on (1 1 0) Fe-Ga. (b) Calculated surface energy values of (1 1 0) Fe-Ga grains using Equation 2.2. 31

3.1 Schematic close up of three rough 2-D surfaces. Solid is blue/gray, air is white, liquid is the cross-hatched area above the surface. Liquid–vapor and solid–liquid interfaces of drop are denoted by the black line. A smooth-topped rough surface, which (for zero penetration of liquid) has coplanar solid–liquid and liquid–vapor interface (i.e. interfaces are in line with each other). This yields $f_1 = f$ and $f_2 = (1 - f)$. Image source:[1] 35

3.2 Schemes of different wetting regimes. A – flat substrate; B – rough substrate, the Wenzel regime; C – rough substrate with air trapped under the drop, the Cassie–Baxter regime.[2] 38

3.3 The curve of Gibbs energy versus geometric contact angle for a two-dimensional drop on a heterogeneous solid surface. Each minimum represents a metastable equilibrium state. The lowest of all minima indicates the most stable state. In between every pair of equilibrium states there exists an energy barrier. Abbreviations used: PADCA, practical advancing contact angle; PRCA, practical receding contact angle; TADCA, theoretical advancing contact angle; TRCA, theoretical receding contact angle.[3] 40

List of Tables

1.1 Calculated dihedral angles and relative energies from our most symmetric grain boundary groove. 19

3.1 Hydrocarbon surface tension and water-hydrocarbon interfacial energy 34

Chapter 1

Introduction

1.1 Background

1. Magnetostriction
   (a) History and Discovery
   (b) Materials
   (c) Uses and Applications
2. Galfenol
   (a) Manufacturing
   (b) Benefits
   (c) Restrictions
3. Abnormal Grain Growth (AGG)
   (a) Theory
   (b) Proposed Mechanisms
   (c) Latest Research for AGG in Fe-based alloys

(d) Need for Orientation-dependent Surface Analysis/Surface Energy Measurements

i. Latest Research on FeGa Surface Energy

4. Methods of Surface Energy Measurement Techniques

(a) Contact Angles

i. Low Energy Surfaces

A. Owens-Wendt Method

ii. High Energy Surfaces

iii.

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4. Methods of Surface Energy Measurement Techniques

(a) Contact Angles

i. Low Energy Surfaces

A. Owens-Wendt Method

ii. High Energy Surfaces

iii. High temperature melting

A. Only averages surface energy

B. Loss of orientation dependence

1.1.1 Motivation

Magnetostrictive Fe–Ga alloys (Galfenol) have promising attributes for application to sensors, actuators and energy harvesting as Clark *et al.* first reported in 2000.[4] Galfenol has a body-centered cubic (bcc) crystal structure, and along the $\langle 1\,0\,0 \rangle$ crystal orientations, it exhibits saturation magnetostriction of $\sim$400 ppm in low applied magnetic fields of $\sim$200 Oe. It also has a mechanical strength of $\sim$500 MPa, which is high relative to more costly rare earth magnetostrictive materials. Terfenol-D alloys exhibit giant magnetostriction ($\gtrsim$1600 ppm) but are brittle and require much higher magnetic fields ($\gtrsim$1000 Oe) for saturation.[4–6] The large magnetostriction and easy magnetization in Galfenol alloys occur along the $\langle 1\,0\,0 \rangle$ orientation. It is thus desirable to obtain the $\langle 1\,0\,0 \rangle$ orientation in textured polycrystalline Galfenol, with the goal of providing enhanced mechanical properties and lower cost than single-crystal material, while preserving magnetostrictive strain.

Two viable approaches have been employed to fabricate highly textured Fe–Ga alloys.[7,8] One is a directional solidification growth process, and the other is thermo-mechanical processing involving deformation via rolling and recrystallization through grain growth and orientation mechanisms. Development of a uniform texture over

Figure 1.1: This is an illustration of Goss and Cube textures shown with their respective axes of easy magnetization. Goss has one easy axis, and Cube has two easy axes.

90% of the surface has been achieved when samples are first rolled into sheets from ingots, and then atmospherically annealed to develop large grains on the sample surface area by utilizing the abnormal grain growth (AGG) phenomenon.[9,10]

AGG is often detrimental in piezoelectric ceramics because it lowers the hardness and the larger developed grain sizes lead to degradation of the piezoelectric effect.[11] For the Aerosmart group's application goals, AGG is advantageous for targeting Goss {1 1 0} and Cube {1 0 0} textures to obtain one and two directions, respectively, of easy magnetic axes and high magnetostriction in the plane of rolled sheets. This process avoids lengthy and expensive single-crystal growth methods while still producing Galfenol with sufficient magnetostrictive properties for device application. We have been studying the development of Goss- and Cube-textured Galfenol rolled sheet as a low-cost alternative to magnetostrictive single-crystal Galfenol for several years. To optimize specific grain growth, we have incorporated pinning particles during the

Figure 1.2: Diagram of AGG from as-rolled sample of (Fe-19%Ga)+1.0%NbC alloy (left) to argon- (upper) and sulfur-annealed (lower) samples for annealing times of 1h (middle) and 3h (right). EBSD images scanned along the normal direction of 12x12x0.45 mm^3 sheet. Red, green and blue indicate (0 0 1), (0 1 1) *and* (1 1 1) *grains, respectively.*

rolling process, experimented with different annealing temperatures and times, and modified the annealing environment.[12–15]

EBSD images spatially map crystal orientations on well-polished specimen by using backscattered electron patterns from the electron beam in a scanning electron microscope (SEM). From these patterns, we can use statistical tools to measure average misorientation, grain size, and crystallographic texture. Figure 1.2 depicts electron backscatter diffraction (EBSD) images of more successful annealing conditions we have tested. As-rolled polycrystalline Galfenol (left image) exhibits a strong γ-fiber $\langle 1\,1\,1\rangle \| \mathrm{ND}$ (normal direction to the sheet surface) and weak rotated cube textures, and starts with an α-iron (B2) structure. A partly grown Goss texture developed over $\sim$39% of the sample surface area during a 3h argon-anneal (upper right image) due to grain boundary energy alone. This is because large inert argon particles do not react with the Galfenol surface, and do not modify the surface energy. We have demonstrated that small variations in surface energy have a significant impact of the development of texture.[16,17] The two lower right images show AGG with fully developed (0 0 1) and (0 1 1) grains over 90-95% of the sample surface. AGG of (011) grains

are very reproducible and insensitive to small variations in anneal conditions, while the development of (001) grains are challenging to produce/reproduce due to highly sensitive to anneal conditions. Saturation magnetostriction values equal to 90% and 84% of single-crystal (1 0 0) values for alloy of the same composition were measured in sulfur-annealed samples with (0 0 1) and (0 1 1) grain growth, respectively.

Developing protocols for making thin sheet Galfenol with Goss or Cube textures has been challenging because the mechanisms that regulate grain boundary mobility and texture development in these alloys are not well understood. Modeling techniques that examine grain boundary interactions, coincident site lattice (CSL) and high energy grain boundary (HEGB), have been investigated to understand AGG mechanisms. These techniques sufficiently describe abnormally grown Goss grains in $Fe_{100-x}Ga_x$ (x=19)+1.0 mol% NbC rolled sheets, but mechanisms for abnormally grown Cube-grains are still not understood.[16] We believe these models are insufficient because extraneous driving forces caused by the control of surface energy from atmospheric annealing conditions, as described by Kramer *et al.* , are not properly incorporated. By characterizing the surface energy of specific Galfenol grains, we can develop a more accurate thermodynamic-based framework for modeling AGG and texture development that will be used to understand why a high temperature atmospheric anneal transforms myriad crystallite grains into the highly textured, single-crystal-like polycrysalline material.

Defining Surface Energy

Thermodynamically, the physical origin of the surface free energy is the excess Gibbs free energy of matter at the interface. There is a negative free energy change when two flat surfaces, A and B, are brought into adhesive contact in a medium. Israelachvili describes this as twice the interfacial energy γ_{AB} of the A-B interface, which is positive

by convention,[18] as seen in Equation 1.1.

$$\Delta W = -2\gamma_{AB} \tag{1.1}$$

In principle, Equation 1.1 can be used to calculate the surface tension of a condensed phase held together by the long-range forces.

The interaction of a liquid with a solid is characterized by the term "wetting." Wetting can be understood as the spreading of a liquid over a solid surface. One way to quantify a liquid's surface wetting characteristics is to measure the contact angle of a drop of liquid placed on the surface of an object. The profile of contact angle formed by the solid-liquid and liquid-vapor interfaces are measured from the side of the liquid. The wetting ability of a liquid is a function of the surface energy of the solid-vapor interface, the liquid-gas interface, and the solid-liquid interface. The surface energy across an interface is a measure of the energy required to form the unit area of a new surface at the interface. The intermolecular bonds, or cohesive forces, between the molecules of a liquid cause surface tension. When the liquid encounters another substance, there is usually an attraction between the two materials. The adhesive forces between the liquid and the second substance will compete against the cohesive forces of the liquid. Liquids with strong cohesive bonds and weaker adhesive forces will tend to bead-up or form a droplet when in contact with another material. Liquids with relatively weak cohesive bonds and a strong attraction to another material will tend to spread over that material. Here, the energetically favorable outcome is the formation of adhesive bonds, such is the case with water droplets on high-surface energy metal substrates.

The solid-liquid interface plays a fundamental role in diverse fields and helps with an understanding of physical phenomena and structural knowledge of the interface at the atomic scale. Fields of interest include catalysis, lubrication, electrochemistry,

Figure 1.3: This illustration shows a vector representation of the interfacial tensions involved in a solid-liquid-gas contact angle experiment. [Image available in public domain: wikimedia.org]

colloidal systems, biological reactions, and, most relevantly, crystal growth.

Contact angle measurements, as described by Thomas Young in 1805, remain the most accurate method for determining the interaction energy between a liquid (L) and a solid (S). A contact angle is defined geometrically as the angle formed by a liquid at the three-phase boundary, where vapor, liquid, and solid intersect. The magnitude of a contact angle can be directly correlated to the magnitude of liquid cohesion energy, γ_L, and the energy of adhesion between a liquid and solid. Young described the equilibrium contact angle at the three-phase boundary in terms of the vectorial sum, as shown in Figure 1.3, resulting in an equilibrium force balance. The famous Young's equation (Equation 1.2) is derived in Appendix A from the Gibbs free energy at equilibrium.

$$\boxed{\gamma_{SV} = \gamma_{SL} - \gamma_{LV} \cos\theta} \tag{1.2}$$

1.1.2 Preliminary investigations

There are currently no experimental methods available to measure surface energies associated with different crystallographic orientations of metals. High temperature methods involving cylindrical metal samples and destructive methods involving drop shape samples of a targeted liquid metal near the melting point are available for measuring surface energy of amorphous and isotropic solid metals.[19–21] For glass

and polymeric solids with relatively low surface energies, the water-drop method has been shown to be effective for the determination of surface energy at room temperature.[22–24] A previous group member, Hyunsuk Chun, attempted to use the water drop method for contact angle measurements on (0 0 1), (0 1 1) and (1 1 1) facets of 17.9%Ga Galfenol single-crystal samples using facilities at NIST.[25] Averaging water contact angles in air on (0 0 1), (0 1 1) and (1 1 1) facets from 20-30 measurements resulted in 72.±5.3°, 87.01±5.4°, and 63.11°, respectively. These measurements were used to estimate surface energy using the Girifalco–Good–Fowkes–Young (GGFY) equation, $\gamma_{LV}(1 + \cos\theta) = 2\sqrt{\gamma_{LV}\gamma_{SV}}$. Determined values of γ_{SV} for each facet (γ_{001}= 0.0277 J/m^2, γ_{011} = 0.0199 J/m^2, γ_{111} = 0.0380 J/m^2) are too small to be correct. The values are about two orders of magnitude smaller than expected when compared to values of α-iron DFT calculations (γ_{100} = 2.6660 J/m^2, γ_{110} = 2.0535 J/m^2, γ_{111} = 2.5271 J/m^2).[26] A water contact angle in air works well for estimating surface energy of solids with magnitudes less than water surface tension ($\gamma_W \sim 72$ mJ/m^2), and fails for metallic solids, where the drop surface tension is several orders of magnitude lower than that of metals.

Thermal Grooving

The thermal grooving technique was considered as a possible approach to understanding the interactions between adjacent grains in Galfenol that we target for AGG. Annealed samples were polished and re-annealed to develop thermal grooves. EBSD identified where (1 0 0), (1 1 0), and (1 1 1) orientations met on each sample. By measuring the dihedral angle formed at these grain boundaries, the ratio of grain boundary energy and surface energy was calculated according to the following equation:

$$\frac{\gamma_{GB}}{\gamma_S} = 2\cos\left(\frac{\Psi_S}{2}\right) \tag{1.3}$$

where γ_{GB} is the grain boundary energy, γ_S is the surface energy, and Ψ_S is the dihedral angle, as described in Rohrer *et al.*[27] The most symmetric thermal groove came from a (1 1 0)/(1 1 1) grain boundary on a rolled and annealed (Fe-19%Ga)+1.0%NbC sample made by Suok-Min Na, as seen in the Figure 1.4. The grain boundary profiles

Figure 1.4: (a) 3D rendering of (110)/(111) grain boundary on surface of for (Fe-19%Ga)+1.0%NbC sample where the depth of groove is 8 nm. (b) A quadratic fit of a (110)/(111) grain boundary profile for a (Fe-19%Ga)+1.0%NbC sample.

were measured using atomic force microscopy (AFM), and the dihedral angles were extrapolated from the profiles using both AFM software by Bruker and a quadratic fit. The results are shown in Table 1.1. This groove in particular had a depth of ∼8 nm which is significantly smaller in depth compared to grooves of other metal alloys.[28] Relative energies between 1/4 and 1/2 are expected for metals, but this unusually small groove might explain why we see high variation in dihedral angles. To properly analyze the thermal grooving technique, an extensive grain boundary study of the effect annealing temperatures and times have on Galfenol would need to be investigated. While this may be an interesting avenue of research in the future, the resultant calculations of relative grain energies do not contribute to the ultimate goal of achieving a comprehensive AGG model for Galfenol. Realization of this project's goal lies in the measurement of orientation-dependent surface energy using contact angle measurements.

Table 1.1: Calculated dihedral angles and relative energies from our most symmetric grain boundary groove.

fe-ga-s12-006 profile analysis - GB (110)/(111)				
	Bruker Software		Quadratic Fit	
Profile	Dihedral Angle (°)	Relative Energy	Dihedral Angle (°)	Relative Energy
1	156.957	0.399471	151.253	0.496475
2	156.244	0.411657	157.093	0.397144
3	154.402	0.443063	155.554	0.423432
4	157.221	0.394955	152.785	0.470541
5	154.732	0.437445	154.966	0.433458
6	158.386	0.375003	154.482	0.441706
Avg	156.324 ±1.529	0.410266 ±0.0261178	154.356 ±2.069	0.443793 ±0.0351932

Chapter 2

Chapter 2 Title

2.1 Metal Surface Energy Measurement

1. See MRS Advances paper

The interactions of water with a low-energy and high-energy solid surface differ significantly. The relative energy of a solid compared to a liquid has to do with the bulk nature of the solid. Solids with weak molecular crystals (e.g., fluorocarbons, hydrocarbons, etc.) where the molecules are held together by weak physical forces (e.g., van der Waals and hydrogen bonds) are termed low-energy solids. A very low input of energy is required to break these solids, thus they typically have surface energy <72 mJ/m^2. Metals, glasses, and ceramics are known as "hard solids" because the chemical bonds that hold them together (e.g., covalent, ionic, or metallic) are very strong. Thus, these surfaces are high-energy because of the high amount of energy needed to break these solids to make two new surfaces, (e.g. see Equation 1.1 in Section 1.1.1). High energy solids typically have surfaces energies >72 mJ/m^2. The threshold between these two types of surfaces lies in their surface energy values relative to the surface tension of water, ∼72 mJ/m^2. Water tends to partially wet a low energy surface and completely wet a high energy surface based on how much

lesser or greater the surface energy of the solid is compared to water, respectively.

I will investigate two approaches to overcome the challenges involved in measuring the surface energy of metals using contact angle measurements. The first will study temperature variations of Galfenol surface energy using a droplet of gallium as the probe liquid. Gallium is a liquid with a surface tension at room temperature that is roughly one order of magnitude higher than that of water: γ_{Ga} ~715.3 mJ/m^2. It is expected that a measurable contact angle will form between Galfenol and liquid gallium, and this information will be incorporated into an analytical model to extract the solid surface energy. The second will build on the two-liquid-phase technique to form a measurable water contact angle on the surface of Galfenol. To supplement this measurement, Galfenol samples will be patterned with a planned roughness to increase the water contact angle and properly determine the Young's contact angle to be used in surface energy calculations. Both experiments will use highly Goss textured Galfenol as well as single-crystal Galfenol samples to assure isotropic crystal orientation for contact angle measurements.

Once experimental results are validated with published values, DFT predictions of the surface energy associated with different crystallographic orientations in Fe-Ga and Fe-Al will be tested and verified. This task and the resultant capability should have broad applicability beyond the needs of this proposal for extension to polycrystalline textured metals and thin films.

2.1.1 Phase I: Gallium Drop Method

The first technique employs measurement of contact angles and drop size of a liquid metal, gallium, resting on a metal surface as the metal is heated. Changes in surface tension will be introduced by controlled thermal expansion of the substrate at temperatures ranging from ~30-100°C to give mobility to the molten gallium drop. A video system will be used to precisely quantify dimension changes in substrate and

Figure 2.1: Schematics indicating notation used and contact angles θ_i, radii of drop-solid contact area r_i, and radii of curvature for a spherical drop R_i, for two temperatures as thermal expansion induced tension P strains the substrate.

liquid metal drop during thermal expansion will be used. The surface energy of the free surface of the substrate as a function of temperature, $\gamma_{SV}(T)$, can be related to thermal-expansion-induced changes in the liquid gallium drop contact angle θ, the radius r of the liquid gallium drop in contact with the metal surface, and the height h of the hemisphere of liquid gallium.

These can be modeled as a tensile load $+P(T)$ caused by substrate thermal expansion (Figure 2.1), which effectively appears as a uniform radial expansion of the planar solid surface as temperature increases. By letting the system equilibrate at different temperatures before measuring liquid drop geometry, terms due to variation in thermal energy and variation of the total Gibbs free energy vanish. Then, the interface energy between the substrate solid and the liquid gallium drop, γ_{SL}, is given as $\gamma_{SL} = P(T)/2\pi r$. The uniform tension introduced by thermal expansion of substrate can be expressed as:

$$P(T) = E_{sub}\alpha_{sub}(T - T_{mp}) \tag{2.1}$$

where T_{mp} is the melting temperature of gallium, E is the substrate Young's modulus, and α is the linear thermal expansion coefficient. A linear function can be used to write the gallium-air interfacial tension a function of temperature, $\gamma_{LV} = a - b(T - T_{mp})$, where a and b are positive constants found experimentally.[29,30] Putting the

terms for γ_{SL} and γ_{SV} into Young's equation:[31,32]

$$\gamma_{SV} = \frac{E_{sub}\alpha_{sub}(T - T_{mp})}{2\pi r} + [a - b(T - T_{mp})]\cos\theta$$

A relationship between the variable radius $r(T)$ associated with the area of the circular region of solid-liquid contact $A_{SL}(T)$, the contact angle $\theta(T)$ and the volume V of the spherical cap formed by the drop is derived next. To determine the radius $r(T)$, the geometric relationships based on the radius of curvature $R(T)$ of a sphere is mapped onto the hemispherical liquid cap. The drop is modeled as being part of a sphere whose radius is $R(T)$. It is assumed that he volume V of the drop is the volume of the spherical cap, and remains constant. The radius $R(T)$ can then be expressed in terms of the volume and the angle:

$$R(T) = V^{1/3}\left[\frac{\pi}{3}\left(2 - 3\cos\theta(T) + \cos^3\theta(T)\right)\right]^{-1/3}$$

Using the relation $r(T) = R(T)\sin\theta(T)$ (i.e. θ =0°corresponds to complete wetting of the surface and at $\theta = 90°$, $r = R$) the following formula for surface energy as a function of temperature T and contact angle $\theta(T)$ (shown as θ_T) is:

$$\gamma_{SV} = \underbrace{\frac{E_{sub}\alpha_{sub}(T - T_{mp})}{2\pi}\left[\frac{\pi\left(2 - 3\cos\theta_T + \cos^3\theta_T\right)}{3V\sin^3\theta_T}\right]^{1/3}}_{\gamma_{SL}\ (\mathrm{T})} + \underbrace{[a - b(T - T_{mp})]}_{\gamma_{LV}\ (\mathrm{T})}\cos\theta_T \tag{2.2}$$

This gives the surface energy γ_{SV} of specific grains as a function of temperature by measuring T and θ at thermal equilibrium.

One of the challenges in developing this new surface energy measurement capability is the need to expose the surface of the metal substrate that is shielded by surface oxides. The following strategies for removing the oxide layer and preventing natural oxidation, thereby increasing the accuracy of measurement, will be employed

independently and in combination:

- A flux used in high-temperature metal joining processes plays roles of dissolving of the oxides on the metal surface and preventing of re-oxidation as a chemical agent.
- Colloidal silica polishing with nano-sized particles, such as is used for precise surface observations, like EBSD scans, which require clean surfaces to accurately detect patterns.
- Electro-polishing is effective for passivation of clean surfaces after chemical and mechanical polishing for removal of surface oxides.

It should be noted that all of these techniques will not prevent oxides from forming for an extended period of time. Therefore, the cleaning would have to be followed by isolation in high vacuum, an inert environment, or another liquid environment that prevents oxidation.

Contact Angle Goniometer (Verison 1)

Preliminary designs of my contact angle goniometer implement a radiative temperature control box which encloses an argon gas filled container where the sample resides, as seen in Figure 2.2a. The presence of argon is meant to prevent any further oxidation of the Galfenol sample as well as the gallium droplet. The container was initially made of a clear acrylic plastic, but prolonged exposure to temperatures above 80°C caused thermal deformation of the plastic making longer experiments impossible to perform without environment contamination. A clear pyrex container replaced the acrylic box to fix this issue. Application of the liquid gallium drop to our surfaces was done via a mounted plastic syringe with disposable stainless steel hypodermic needles that were available at the time. Liquid gallium tends to adhere strongly to the stainless steel needle tips which makes wetting to the sample very difficult. The stainless

steel tip tends to deform the highly viscous gallium drop resulting in non-uniform hemispheric drop shapes, as shown in Figure 2.2b.

(a) *(b)*

Figure 2.2: (a) The first design of our contact angle goniometer. The acrylic container houses the argon environment and sample. This design was modified with a more stable glass enclosure. (b) A highly deformed gallium drop next to the thermocouple on a ceramic YAG test sample at 45.5°C.

For this experiment to succeed, a number of challenges were overcome. The simplest task involved polishing Galfenol samples using incrementally higher grit SiC paper and subsequent 0.1 μm colloidal silica particles to decrease the roughness to below 40 nm, as proven using AFM measurements. The radiative box that housed this experiment had a high variability in temperature according to thermocouple readings, so a smaller apparatus with a top-side syringe opening is made to properly perform gallium drop tests at specific temperatures and prevent interaction with the experiment environment. There must also be bright white backlighting to obtain a high contrast drop profile. In this radiative box configuration, the high-reflecting liquid metal surface prevents a high contrast drop profile image, as seen in Figure 2.2b. Proper contact angle measurements also require the gallium droplets to carefully wet the surface while forming an axisymmetric and spherical-like shape on the solid surface. A height adjustment system must be used to move the gallium pendant drop close enough to the sample surface for solid adhesive forces to overcome the adhesion to the needle. Lastly, the argon gas environment could be more well contained, instead of just filling up the glass sample enclosure from the bottom and spilling out

Figure 2.3: The second version of our gallium contact angle goniometer. The aluminum enclosure conductively transfers heat, the gas lines flow Ar gas into the chamber, top-mounted thermocouples monitor the gas and sample temperature, and the glass windows allow for backlighting of the drop profile along with high resolution image capture using a DSLR camera.

the top due to higher density argon displacing the surrounding air environment.

Version 2

The new experimental apparatus can be seen in Figure 2.3. The main structure is made of aluminum with two round glass windows on the front and back. The aluminum is meant to conductively transfer heat to the substrate by means of a heating cable wrapped around the outside of the structure. The high thermal conductivity of aluminum allows for a quick transfer of heat, thus an increased control of sample temperature. The time percentage dial controller attached to the heating tape is calibrated with the sample temperature using a thermocouple placed on the sample surface. Sample temperature can be consistently controlled with $\pm 0.5°C$ accuracy. Backlighting greatly improved the drop profile contrast by having only one white light source coming from one side of the droplet, as seen in Figure 2.4. The Ar environment is also far more contained and controlled. The silicone sealant creates a

(a) (b)

Figure 2.4: Pure liquid gallium obtains viscoelastic properties when trace amounts of oxygen are present via formation of oxide shell. Non-axisymmetric Ga drops form on this iron substrate.

nearly air-tight system where the argon will displace all gas contaminants that could oxidize the sample or gallium droplet. Once the sample is inserted and sealed in the environmental chamber, the Ar prevents oxidation throughout the experiment.

While extensive steps have been taken to inhibit oxidation on the metal surfaces, preventing oxidation on the surface of liquid gallium was a greater challenge. Pure gallium and Gallium-based alloy surfaces instantly oxidize in ambient environments, turning into a thin layer of gallium oxide (Ga_2O_3 and Ga_2O).[33–35] This oxide layer is solid and remains elastic until it experiences a yield stress. Therefore, that an oxidized gallium droplet does not behave as a simple liquid, but as a viscoelastic material. In addition, the oxide layer of gallium is known to adhere to almost any solid surface, causing a severe stiction problem that interferes with interfacial energy measurements.[35] This shows how dramatically the gallium surface tension decreases when the oxide forms. Khan *et al.* showed that gallium oxide forms hydroxyl groups on their exterior surface, making the drops lyophilic as opposed to the expected lyophobic behavior of pure gallium, a high surface tension liquid.[29,30]

Figure 2.4 shows our direct observation of this phenomenon with teardrop shaped droplets formed by adhering to the iron surface while still being pulled upwards by

the deposition needles. The general shape of these drops were unchanged for many hours even at temperatures approaching ∼100°C, thus exhibiting the stability of viscoelastic properties caused by the solid oxide layer. Removing the oxide layer from liquid gallium will return normal liquid properties to gallium and allow the use of axisymmetric drop analysis calculations: Young-Laplace equation,

Oxide removal permits liquid gallium to directly interact with metal surfaces instead of gallium oxide; the derived terms for γ_{SL} and γ_{LV} in Equation 2.2 become more robust. A number of techniques have been developed to remove and recover gallium oxide on liquid gallium: ultra-high vacuum (UHV) techniques,[33,34] chemical vapor etching,[36,37] and electrohydrodynamic phenomena.[38] A chemical vapor etch is the best option for this experiment because it has a minimal effect on the surface of metals and the experimental apparatus does not need to be changed. To execute the vapor etch, a pendant drop of gallium was formed and a pipette of 37wt% HCl was brought in close proximity to etch away the oxide layer. The same procedure was performed on the sessile drop of gallium on the desired surface to etch away any oxide left on top of the droplet, as seen in Figure 2.5. The contact angles of gallium on bare glass before and after HCl vapor treatment are similar to respective contact angle values in Kim *et al.*[36]

With the HCl vapor treatment added to the procedure, temperature-varying gallium contact angle measurements in an argon environment were executed in the aluminum chamber on multiple metal substrates. Polycrystalline samples of high purity (>99.99%) tin, copper, and iron were polished and had liquid gallium deposited on their surfaces. The temperature in the chamber was slowly (<10°C/min) increased from 30°C to just below 100°C. Beyond 100°C, the heating tape becomes inconsistent with the intervals of heat applied to the chamber. Photographs of gallium drop profiles are taken at 10°C intervals to observe progression of the drop shape as temperature increases. The same procedure is done as the temperature is decreased

Figure 2.5: This image shows the contact angle of gallium on a Galfenol sample in an argon environment before and after HCl vapor treatment.

to 30°C to observe reversibility of this process, since we assume that the thermal expansion of the substrate drives the change in γ_{SL} from Equation 2.2.

It is known that liquid gallium tends to corrode most metal surfaces.[39–41] Since experiments lasted for less than one hour, corrosion between the two metals should not be significant enough to effect the measurement. For the polycrystalline tin and copper samples, gallium began to visibly corrode through the surface between 60°C and 70°C, as evident by a rapid contact angle decrease on only side of the drop profile. Polycrystalline iron samples did not experience corrosion problems throughout the experiments. It is expected that as the temperature increases, the thermal expansion of the solid will isotropically expand the drop thus decreasing the contact angle. Some gallium contact angles decrease on iron, but it is often that the decrease occurs on one side of the drop profile as the temperature increases. This is most likely due to the polycrystalline grains having different thermal expansions, hence the drop spreading is anisotropic. This suggests that a single-crystal grain or highly-textured surface grain is needed to properly observe an isotropic drop expansion.

Since the iron sample did not corrode in the presence of gallium, we proceeded to a Galfenol sample with an abnormally grown (1 1 0) grain. Figure 2.6 shows the loca-

Figure 2.6: The location of a gallium drop on highly Goss-textured surface.

tion of a gallium droplet in contact with the highly Goss-textured surface. Using the same temperature intervals, the right and left contact angles were measured and the surface energy was calculated using Equation 2.2. The contact angle measurements and surface energy calculations are shown in Figure 2.7. The contact angle measurements show anisotropic spreading behavior since the left contact angle recedes as temperature increases while the right contact angle advances. At 60.7°C, the contact angles reached close to the same value which may indicate an equilibrium point of combating thermal expansions caused by nearby island grains.

The increasing surface energy trend as the temperature increased was not an expected result. As the temperature of a metal surface increases, the cohesive force binding atoms will decrease because the atoms will vibrate more rapidly. Since surface energy depends on the net inward cohesive force, a decrease in surface energy with increasing temperature was expected. Moreover, such a high difference in surface energy as the temperature increased was not expected. The $\gamma_{SL}(T)$ term is extremely dominant compared to the $\gamma_{LV}(T)$ term. This is due to the high Young's modulus value associated with Galfenol. The values of surface energy for the (1 1 0) Galfenol

grain are two orders of magnitude greater than predicted values of α-iron, γ_{SV} = 2.0535 J/m^2.[26] After presenting these preliminary findings at the XXIV International

(a) *(b)*

Figure 2.7: (a) Blue and red dots show left and right contact angle, respectively, of liquid gallium on (1 1 0) *Fe-Ga. (b) Calculated surface energy values of* (1 1 0) *Fe-Ga grains using Equation 2.2.*

Materials Research Congress and 2015 MRS Fall Meeting,[42,43] I discussed possible avenues of improvement for the gallium contact angle experiment with colleagues and potential collaborators. A more concrete measurement of γ_{SL} between liquid gallium and solid would need to be examined, a very non-trivial task. Ultimately, we decided to suspend the gallium drop experiment and re-evaluate the measurement strategy.

Overall, this was an exploration of well-proposed and innovative research. Assumptions were made about how the system would interact and efforts to achieve good results in the lab were made. It was determined that these assumptions were too great and the experiment failed to meet expectations. Much was learned about the complexity of surface energy research from both a theoretical and experimental perspective. This failure persuaded me to find a more robust and promising method for accomplishing project goals within the constraints of orientation-dependent surface energy characterization.

Chapter 3

Chapter 3 Title

1. Schultz Method (Two-liquid-phase method)
    (a) Experimental Apparatus
2. Nearly-flat surface results
    (a) Polishing procedure to remove oxide layer
        i. Polishing and cleaning options at UMD
            A. XPS results + quantitative analysis
        ii. Polishing at NSWC Carderock
    (b) Results for Carderock polished single crystal samples
        i. Retained presence of iron oxide
    (c) Dry polish results (Week of Jan 2nd)
    (d) Plasma sputtered result (Week of Jan 9)
        i. Using sputterer in Phaneuf glovebox
3. Patterned surface results
    (a) Learn to use sputterer in Phaneuf glovebox?

(b) Learn to do spin-coating from FabLab

   i. Thick photoresist using A2 4620 (suggested by FabLab), which can get a 14 μm thick layer

(c) Perform dry etch and spin coating in Phaneuf glovebox

(d) Do UV processing somewhere

   i. FabLab?

(e) Use Ion mill for etching by scheduling with Xiaohang on Google Calendar

   i. Ask for one more demo with him supervising.

4. Force curve measurement

3.0.2 Phase II: Two-liquid-phase contact angle method

The next method returns to the idea of water contact angles on metal surfaces. As described previously, water will spread completely on a nearly-flat metal surface surrounded by a gaseous environment. Instead of a gaseous environment, the water-metal system can be surrounded by another liquid. It has been observed that instead of wetting completely, a water droplet will only partially wet a metal when the surrounding environment is an immiscible liquid. This is called the two-liquid-phase contact angle method developed by Jacques Schultz.[44–46]

A full derivation of this method can be found in Appendix B. In order to calculate the dispersive component of γ_{SV} for a solid surface, the water contact angle must be measured on a solid immersed in n-alkanes. By interpreting Equation B.5 as a classic linear function, $y = mx + b$:

$$\underbrace{\gamma_W - \gamma_H + \gamma_{WH}\cos\theta_W}_{y} = \underbrace{2(\gamma_S^D)^{1/2}}_{m}\underbrace{[(\gamma_W^D)^{1/2} - (\gamma_H^D)^{1/2}]}_{x} + \underbrace{I_{SW}^P}_{b}$$

γ_W, γ_H, and γ_{WH} are known from consistently confirmed literature values,[47–50] and are listed in Table 3.1. A data set of xy-coordinates will be made by dropping water in an n-alkane environment to determine γ_S^D and I_{SW}^P. γ_S^D will be calculated from the slope of the measured dataset.

Table 3.1: Hydrocarbon surface tension and water-hydrocarbon interfacial energy

n-alkanes	γ_H (mJ/m^2)	γ_{WH} (mJ/m^2)
hexane	18.4	50.1
octane	21.7	49.8
decane	23.8	51.0
hexadecane	27.5	51.3

The polar component of the solid surface energy is determined using the same method described above,[44] but the bulk liquids now have both dispersive and polar components. This is also derived in Appendix B. These bulk liquids of chloroalkanes, nitroalkanes, aromatics, or alcohols are expected to establish a linear relationship between I_{SW}^P and the square root of the polar component of surface tension from the bulk liquids. Schultz *et al.* suggests that this result allows all nondispersive interactions to be grouped together as a polar interaction, and they may be represented by the geometric mean of the polar component of the surface free energy of liquid and solid, as proposed by Owens and Wendt in Equation 3.1. This expression is verified experimentally, but there are no theoretical reasons why all nondispersive interactions should be represented by a geometric-mean expression.[51]

$$\begin{aligned} I_{SW}^P &= 2(\gamma_S^P \gamma_L^P)^{1/2} \\ \rightarrow \ \gamma_S^P &= \frac{(I_{SW}^P)^2}{4\gamma_L^P} \end{aligned} \tag{3.1}$$

The solid surface energy can then be determined from Equation 3.2:

$$\gamma_S = \gamma_S^D + \gamma_S^P \tag{3.2}$$

Figure 3.1: Schematic close up of three rough 2-D surfaces. Solid is blue/gray, air is white, liquid is the cross-hatched area above the surface. Liquid–vapor and solid–liquid interfaces of drop are denoted by the black line. A smooth-topped rough surface, which (for zero penetration of liquid) has coplanar solid–liquid and liquid–vapor interface (i.e. interfaces are in line with each other). This yields $f_1 = f$ and $f_2 = (1 - f)$. Image source:[1]

Preliminary two-liquid-phase method experiments on muscovite mica showed quick and complete wetting of water on pristine mica surfaces cleaved in decane and hexadecane, contradictory to published results.[46] Clearly, more iterations of this experiment must be done to recreate this seminal paper's data, but this made me consider how a water droplet on a mirror-finished material of even greater surface energy (e.g. Fe and Fe alloys) would spread even faster than it had on a pristine mica surface. A contact angle may not stabilize on a well-polished Galfenol sample even using this two-liquid-phase method, thus we must consider more options to create a measurable contact angle that can extract Young's contact angle.

When mica samples were removed from the decane environment, they were wiped clean with lint-free wipes and further cleaned with acetone. When the samples were returned to the decane environment, a droplet wet the surface with an observable contact angle. When this process was repeated in hexadecane, the observed contact angle increased as observed in Schultz *et al.* This shows that even a rough surface can be measured for surface energy using the two-liquid-phase method. If this roughness is controlled by patterning the surface to a specific geometry, the same trend can be observed with the added benefit of a robust calculation of Young's contact angle by way of Equation 3.4.

Since Schultz published his seminal paper, his method has been used to measure very high surface energy materials ranging from 50 mJ/m^2 to 487 mJ/m^2.[50] However,

many of these studies fail to consider the wetting modes of water on their solid surfaces in a bulk n-alkane environment. Giljean *et al.* examines the dependence of contact angles on the roughness of high surface energy titanium surfaces using the two-liquid-phase method. They show that, depending on the cleaning technique used to remove surface contaminations, the contact angle will change more with a decrease in roughness. Sound arguments are made for the type of wetting regime (Wenzel, Cassie-Baxter, or somewhere in-between) encountered at each step of wetting. An issue occurs when the authors attempt to use the Cassie-Baxter equation to calculate the Young contact angle. The Cassie-Baxter equation (Equation 3.3), as defined in the original publication,[52] is designed for a general surface, where f_1 is the *total* area of solid under the drop per unit projected area under the drop and $\theta_Y, 1$ is the contact angle on a smooth surface of material 1. f_2 is defined similarly to f_2 where material 2 is air or some other medium. Many papers, as pointed out by Milne *et al.* ,[1] falsely use Equation 3.4 for randomly rough surfaces when this equation is for the special case of a coplanar liquid-vapor and solid-liquid interface, as illustrated in Figure 3.1. To use this simple equation, a surface would have to be patterned with rectangular pillars with a small enough spacing to prevent capillary forces from causing the liquid to penetrate the roughness. Keeping this in mind, I moved to the two-liquid-phase experiment originally performed on cleaved mica sheets.

$$\cos\theta_{CB} = f_1 \cos\theta_Y - f_2 \tag{3.3}$$

$$\cos\theta_{CB} = f \cos\theta_Y - (1 - f) \tag{3.4}$$

Considering all these factors, I postulate that by combining the two-liquid-phase method with a patterned surface of single-crystal Galfenol, the probe water droplet will not spread and a Young's contact angle can be calculated for use in measuring

the orientation-dependent surface energy of Galfenol. Single-crystal Galfenol samples were prepared at the DOE Ames Laboratory by the modified Bridgman technique at compositions of $Fe_{100-x}Ga_x$ where $x = 19, 25$. These samples can be cut to obtain target orientations (1 0 0), (1 1 0), and (1 1 1) using electro-discharge machining. The isotropic surface created by single-crystal samples ensure that the triple-phase-line will maintain exactly the same $L_1 - S$ interaction about the entire droplet perimeter. The patterned surfaces will be etched to have large enough pillars which retain as much surface orientation dependence on the contact angle as possible, as well as small enough gaps to allow for a Cassie-Baxter state in the $L_1 - L_2 - S$ system. A Cassie-Baxter wetting mode would offer the greatest contact angle of the three main wetting modes illustrated in Figure 3.2, and if a well patterned surface can be achieved similar to Figure 3.1, the Young contact angle can be easily calculated from Equation 3.4.

Possible errors with this method will arise from non-atomically flat surfaces and pillars, imperfect Cassie-Baxter states caused by gravity or capillary forces drawing the probe liquid into the gaps between pillars, and oxide formation at the sample surface. However, such errors should be neglible given extensive polishing protocol, the immiscibility of water with n-alkanes, a controlled surface patterning, and a known cleaning procedure for rough metal surfaces. Therefore, I propose the assumption that our $L_1 - L_2 - S$ system can be treated as the coplanar state depicted in Figure 3.1 is reasonable. Concerning the displacement of n-alkanes by water during the droplet depositing step, the wetting criteria has been proven by Schultz *et al.*[46,53]

Experimental plan

1) For measuring the dispersive solid surface energy component, four different acrylic glass (Poly(methyl methacrylate), PMMA) boxes for hexane, octane, decane, and hexadecane environments will be used to contain the experiment. Acrylic has a high chemical compatibility with n-alkanes, and the transparent optical properties will

Figure 3.2: Schemes of different wetting regimes. A – flat substrate; B – rough substrate, the Wenzel regime; C – rough substrate with air trapped under the drop, the Cassie–Baxter regime.[2]

not affect the contact angle pictures taken.[54] Since most adhesives are stored in n-alkanes (also commonly used as industrial strength degreasers), PMMA boxes must be chemically welded together by a solvent at room temperature to keep the liquid environment contained. The same boxes will be created for the other liquid mediums used to measure the polar solid surface energy component.

2) Single-crystal samples ($Fe_{100-x}Ga_x$ where $x = 19, 25$) will be polished using SiC paper followed by 0.1 μm particle colloidal silica gel to achieve a mirror finish. EBSD or single-crystal XRD is used to find surface orientation. After the main sample surface orientation is discovered, the sample can be cut using wire cut electric discharge machining to obtain (0 0 1), (1 1 0), and (1 1 1) facets. Each sample is then polished again for EBSD measurement and surface energy measurement. As soon as polished samples have reached a mirror-finish, they will be immersed in the n-alkane environment.

3) Samples will be mounted with the surface perpendicular to the dispensing needle and the two-liquid-phase method will be administered. This first experiment will attempt to measure a contact angle on the polished Galfenol samples, but the probe water will likely spread over the surface very quickly to achieve complete wetting. Advancing and receding contact angles will be measured to find the contact angle hysteresis (CAH), as well as the drop volume of respective angles. A group from the Max Planck Institute for Polymer Research has recently observed microscopic

videos of water CAH on pillared polymer surfaces using laser scanning confocal microscopy.[55,56] The UMD Department of Cell Biology and Molecular Genetics has two confocal microscopes that will be utilized to accurately measure the CAH of every Galfenol sample. By comparing this result to the CAH measured using the telescopic goniometer, we determine the necessity of confocal microscopy in future measurements. Another option for recording CAH is a high speed camera that to capture the wetting line spreading and receding. Coupled with the telescopic lens on the Kruss goniometer provided by UMD's Civil & Environmental Engineering we can use a high speed CCD camera to capture such images. From the advancing and receding contact angles, a proper averaging can be used to estimate the most stable contact angle, as seen in Equation 3.5.[57] The most stable contact angle has also been measured by simply vibrating the system for 15 s.[58] An averaging of advancing and receding contact angles is reasonable considering the practical advancing and receding contact angles are metastable states on opposite sides of a Gibbs energy vs. contact angle plot, seen in Figure 3.3.

$$\cos\theta_{ms} = (\cos\theta_a + \cos\theta_r)/2 \tag{3.5}$$

The drop volumes of advancing and receding contact angles will give us a range of volumes for static contact angle measurements on the same surfaces, which are also expected to totally wet our flat surfaces, but will be measured to validate that assumption.

4) I will work with UMD's FabLab to determine the best protocol for creating a patterned surface on Fe-Ga samples. Patterning will occur on the mirror-finish samples made in Step 2 to ensure the flattest possible pillars. With well patterned surfaces, I will execute the same two-liquid-phase method procedure described in Step 3. I expect much greater contact angles for every surface based on the controlled roughness,

Figure 3.3: The curve of Gibbs energy versus geometric contact angle for a two-dimensional drop on a heterogeneous solid surface. Each minimum represents a metastable equilibrium state. The lowest of all minima indicates the most stable state. In between every pair of equilibrium states there exists an energy barrier. Abbreviations used: PADCA, practical advancing contact angle; PRCA, practical receding contact angle; TADCA, theoretical advancing contact angle; TRCA, theoretical receding contact angle.[3]

and I also expect dramatic differences in the calculated solid surface energies for the (1 0 0), (1 1 0), and (1 1 1) Fe-Ga surfaces using Equation 3.2.

5) These surface energy values should be similar to the α-iron DFT calculations of $\gamma_{100} = 2.6660$ J/m^2, $\gamma_{110} = 2.0535$ J/m^2, and $\gamma_{111} = 2.5271$ J/m^2.[26] While testing single-crystal samples of two different compositions ($Fe_{100-x}Ga_x$ where $x = 19, 25$), it is unclear how the surface energy of Fe-Ga will change with composition. I have asked our collaborator, Dr. Ruqian Wu, to use computer simulations to try and find such a change in surface energy with composition, which I will compare with upon experimentally determining these values.

Pending the success of this proposed research, our group will incorporate these experimentally determined orientation-dependent surface energies into to our AGG model to elucidate the driving forces of grain growth methods in Galfenol. We would like to expand this experiment to single-crystal Alfenol samples as well as many other pure and alloyed metals. Metal surface energies are extremely elusive values due to their complexities and lack of consistent experimental confirmation. My goal is that this work will contribute to the vast body of work on experimental wetting dynamics and surface energy determination for the benefit research in the near future and push the boundaries of understanding.

Chapter 4

Conclusion

In conclusion...

Appendix A

Derivation of Young's Equation

Assuming an ideally flat surface

$$V_{drop} = \frac{\pi R^3}{3}(1 - \cos\theta)^2(2 + \cos\theta) \tag{A.1}$$

$$S_{LV} = 2\pi R^2(1 - \cos\theta) \tag{A.2}$$

Where S_{LV} is the surface area of the droplet liquid-vapor interface. The Gibbs free energy of a droplet is depicted in Equation A.3.

$$G = \gamma_{LV} S_{LV} + \pi(R\sin\theta)^2 \underbrace{(\gamma_{SL} - \gamma_{SV})}_{a} \tag{A.3}$$

where γ_{LV}, γ_{SL}, and γ_{SV} are the liquid-vapor, solid-liquid, and solid-vapor interaction energies, respectively. Let $a = \gamma_{SL} - \gamma_{SV}$.

Assuming the the volume of the droplet remains constant:

$$G = \left[\frac{9\pi V^2}{(1-\cos\theta)(2+\cos\theta)^2}\right]^{2/3} [2\gamma_{LV} - a(1+\cos\theta)]$$

$$\frac{dG}{d\theta} = \left[\frac{9\pi V^2}{(1-\cos\theta)^4(2+\cos\theta)^5}\right]^{1/3} 2\left[a - \gamma_{LV}\cos\theta)\right]\sin\theta$$

$$\left[\frac{dG}{d\theta}\right]_{\theta=\theta_{eq}} = 0 = a - \gamma_{LV}\cos\theta$$

$$\therefore a = \gamma_{LV}\cos\theta$$

Appendix B

Derivation of Schultz's two-liquid-phase method

B.0.3 Measuring dispersive solid surface energy, γ_S^D

Assuming Young's equation (Equation 1.2) can be applied to a liquid-liquid(bulk phase)-solid ($L_1 - L_2 - S$) system, and the relationship follows:

$$\gamma_{SL_2} = \gamma_{L_1L_2} \cos\theta_{SL_1} + \gamma_{SL_1} \tag{B.1}$$

In this way, γ_{SV}, which is the driving force of spreading the one-liquid-phase method that causes complete wetting on high-surface energy metal surfaces, is replaced by γ_{SL_2}, where $\gamma_{SL_2} < \gamma_{SV}$. Hence, the contact angle in this system is measurable. According to Fowkes,[51] γ_{SL_1} and γ_{SL_2} are given by:

$$\gamma_{SL_1} = \gamma_S + \gamma_{L_1} - 2(\gamma_S^D \gamma_{L_1}^D) - I_{SL_1}^P \tag{B.2}$$

$$\gamma_{SL_2} = \gamma_S + \gamma_{L_2} - 2(\gamma_S^D \gamma_{L_2}^D) - I_{SL_2}^P \tag{B.3}$$

where γ and γ^D are the surface energy and its dispersive component, respectively, and $I^P_{SL_1}$ is a specific (nondispersive) interaction term that encompasses all interactions between the solid and the liquid (dipole-dipole, dipole-induced dipole, hydrogen bonds, π bonds, etc.) except London dispersion interactions.

Substituting Equations B.2 and B.3 into B.1:

$$\gamma_{SL_1} - \gamma_{SL_2} + \gamma_{L_1L_2}\cos\theta_{SL_1} = 2(\gamma^D_S)^{1/2}[(\gamma^D_{L_1})^{1/2} - (\gamma^D_{L_2})^{1/2}] + I^P_{SL_1} - I^P_{SL_2} \tag{B.4}$$

L_1 will signify water, L_2 as n-alkanes, and $I^P_{SL_2}$ may be considered equal to zero because the surface free energy of n-alkanes only consists of the London dispersion term. This is because n-alkanes only contain C-C and C-H atoms connected by σ-bonds, with a generic formula of C_nH_{2n+2}. C and H have very similar electronegativities of $\chi_C = 2.55$ and $\chi_H = 2.20$, respectively. This shows that all bonds in n-alkanes are non-polar, hence there are no polar interactions in n-alkanes. Our final equation is now:

$$\gamma_W - \gamma_H + \gamma_{WH}\cos\theta_W = 2(\gamma^D_S)^{1/2}[(\gamma^D_W)^{1/2} - (\gamma^D_H)^{1/2}] + I^P_{SW} \tag{B.5}$$

B.0.4 Measuring polar solid surface energy, γ^P_S

Beginning with Equation B.4 in the previous section and solving for $I^P_{SL_2}$, with liquid L_1 as water (subscript W):

$$I^P_{SL_2} = \gamma_{SL_2} - \gamma_{WL_2}\cos\theta_{SW} - 2(\gamma^D_S\gamma^D_{L_2})^{1/2} + C \tag{B.6}$$

$$C = I^P_{SW} + 2(\gamma^D_S\gamma^D_W)^{1/2} - \gamma_W \tag{B.7}$$

In the above two equations, the values of γ_W, γ_W^D, γ_S^D, and I_{SW}^P are available experimentally from the previous section. Therefore, measurements of γ_{L_2}, $\gamma_{L_2}^D$, θ_{SW}, and $\gamma_{L_2}^D$ lead to a calculation of the polar interaction I_{SW}^P.

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