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Numerical Simulation of Equilibrium Liquid Configurations On and Between Rough Surfaces

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Publication Date
2011

Peer reviewed|Thesis/dissertation
Numerical Simulation of Equilibrium Liquid Configurations On and Between Rough Surfaces

By

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A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Engineering – Materials Science and Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Andreas Glaeser, Chair
Professor Ronald Gronsky
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Spring 2011
Abstract

Numerical Simulation of Equilibrium Liquid Configurations On and Between Rough Surfaces

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A numerical model of the interaction between liquids and rough solids is presented in this work. Partial-Transient-Liquid Phase (PTLP) bonding has proven an effective method of joining ceramic materials. The joining process is facilitated through the development of a thin-liquid layer between ceramic and metallic solids. Successful joining requires a liquid that will spread to fill interfacial voids, which can act as critical flaws that decrease the strength of the joined assembly. A full understanding of this method requires a model of the liquid behavior between dissimilar, rough solids. This work discusses the effect of wetting angle and surface roughness on the behavior of the liquid layer.

Numerical simulations are presented that test possible liquid configurations on rough surfaces, determining the preferred geometry based upon the total interfacial energy. Use of computational methods allows independent control of surface roughness, liquid volume, and interfacial energies. In this way, the effect of the liquid contact angle and the amplitude and wavelength of surface-roughness features on the liquid behavior is examined. Emphasis is placed upon surface-roughness parameters and the correlation with preferred liquid configurations. Models are presented and discussed for liquids in contact with one rough surface and for a liquid entrapped between two dissimilar surfaces. Comparison of the one-surface simulation to previous studies of liquid/roughness behavior is provided.

In liquid-based joining methods, the ability of the liquid layer to fill interfacial voids is strongly affected by surface roughness. Numerical simulations of a liquid flowing to fill an inter-solid gap are presented. The importance of dissimilar surface roughness, dissimilar contact angles, and inter-solid distance is discussed. It is found that increasing surface roughness can act to aid liquid-based joining in certain systems.
Dedication

This work is dedicated to my amazing wife, Kendra, who has supported me in everything for the last 11 years. I am truly grateful to have such a wonderful, caring person in my life. She is a remarkable woman, and I am continually impressed and in love with her.
# Table of Contents

1.0 Introduction 1

2.0 Background 4

## 2.1 Joining 4

- 2.1.1 Ceramic Joining Techniques 4
- 2.1.2 Solid-State Ceramic Joining 4
- 2.1.3 Traditional Liquid-State Ceramic Joining 5
- 2.1.4 Transient-Liquid-Phase (TLP) Bonding 5
- 2.1.5 Partial-Transient-Liquid-Phase (PTLP) Bonding 6
- 2.1.6 Nickel-Niobium (Ni-Nb) Binary System 7
- 2.1.7 Joining of Alumina 7
- 2.1.8 Prior Ceramic/Metal Joining 8

## 2.2 Surface Roughness 9

- 2.2.1 Historical Treatment of Surface Roughness 10
- 2.2.2 Measurement Techniques 11
- 2.2.3 Roughness Parameters 12
- 2.2.4 Surface Contact and Roughness 13
- 2.2.5 Surface Roughness and Joining 14

## 2.3 Wetting 14

- 2.3.1 Young’s Model 14
- 2.3.2 Wetting and Roughness 15

## 2.4 Background Figures 17

3.0 Description of Model 22

## 3.1 Model Assumptions 22

## 3.2 Liquid/Vapor Interfacial Curvature 22

## 3.3 Constant Curvature Geometries 23

## 3.4 Model Procedure 24

- 3.4.1 Non-Physical Geometries 24

## 3.5 Single-Surface Model 25

## 3.6 Two-Surface Model 26

- 3.6.1 Two-Surface Geometry 27
- 3.6.1 Possible Radii of Curvature 27
3.7 Description of Model Figures

4.0 Results and Discussion

4.1 Radially Symmetric Surface Features
   4.1.1 Radially Symmetric Surface – Amplitude Effects
   4.1.2 Radially Symmetric Surface – Wavelength Effects
   4.1.3 Radially Symmetric Surface – Fractal Surfaces

4.2 Continuous Surface Features
   4.2.1 Continuous Surface Features – Amplitude Effects
   4.2.2 Continuous Surface Features – Wavelength Effects
   4.2.3 Continuous Surface Features – Symmetry of Contact Points
   4.2.4 Continuous Surface Features – Fractal Features

4.3 Comparison to Previous Studies

4.4 Liquid Layers Between Two Surfaces
   4.4.1 Two-Surfaces: Continuous Surface Features
   4.4.1.1 Two Surface Amplitude Effects
   4.4.1.2 Two Surface Wavelength Effects
   4.4.1.3 Two Surface Phase-Shift Effects

4.5 Results Figures

5.0 Conclusions

6.0 References

Appendix I: Mathematica Code
Acknowledgements

There are many people who have guided me on my way to this point. I would like to thank my family (Michael Bartlow, Rebecca Blair, Lauren Streb and Alexis Bartlow) and my wife (Kendra Kirkpatrick) for always being there for me, and helping me in every way they could. To the members of the Glaeser group (Mary Trahanovsky, Melissa Santala, Josh Sugar, Joe McKeown and Mark Jhon), who made graduate school better in countless ways, and are great friends. Special thanks to The Bonding Posse (Sung Hong and Tom Reynolds), who collaborated on this work and taught me many things. I am grateful for all the help that the faculty of the Materials Science department at U.C. Berkeley has provided over the years, especially from Professor Ronald Gronsky.

Most of all, I want to acknowledge my advisor, Professor Andreas Glaeser. It would be impossible to list all the things I have learned from him in my time in graduate school. I am very lucky to have had an advisor who was so passionate about science and the importance of understanding the fundamentals of the world around you. I cannot thank him enough for making me a better scientist, teaching me about the importance of fonts, and for buying me my first beer.
1.0 Introduction

Nearly all engineered designs require joining of similar or dissimilar materials. Proper selection of the joining technique must address the materials involved and the use conditions of the assembly. Bonding methods are needed for many different length scales, from micro-electronic assemblies to bridges that span kilometers. Metallic systems are relatively simple to join: liquid-based methods such as welding, soldering or brazing are easily adapted for most metals. Additionally, solid-state methods such as friction-stir welding, diffusion bonding of metals and mechanical joining are effective joining strategies.

Extreme environments, such as high-temperature or corrosive applications often require the use of ceramic materials. While ceramics are the preferred materials for many environments, forming large ceramic pieces of complex geometry is difficult due to their brittle nature and low thermal conductivity. Ceramic applications therefore often use pieces of simple geometries, which are joined together forming large ceramic pieces of complex geometry. A quick, rapid, and relatively inexpensive joining method for ceramic and ceramic/metal assemblies is needed that will not degrade the ceramic properties.

Ceramic joining has been performed using solid-state and liquid-state methods. In diffusion bonding, a solid-state method, the entire assembly remains in a solid phase throughout the joining process. While diffusion bonding can produce high-strength joints, the process requires extensive surface preparation as well as long times at high temperatures. These detrimental aspects of solid-state joining are avoided with liquid-state methods. In brazing of ceramics, a filler material is molten at the joining temperature. In the liquid state, material redistribution occurs much more rapidly, allowing shorter joining times. Proper selection of braze materials allows strong joints that are formed at reduced temperatures. However, the melting temperature of the filler material limits the application of traditional liquid-based methods. The assembly cannot be used at temperatures approaching the joining temperature, since softening of the metal filler can be expected around half of its melting temperature. Use of filler materials with a higher melting temperature can allow higher use temperatures, but requires an increase in the joining temperature.

Transient-liquid-phase (TLP) bonding is an alternate liquid-phase joining method that allows for reduced joining temperatures, while maintaining the potential for elevated use temperatures. In TLP bonding, a melting-point depressant (MPD) is added to the filler material, producing a liquid phase at lower temperatures. During joining, chemical homogenization leads to isothermal solidification as the amount of MPD contained within the liquid is reduced. This reduction in MPD in the liquid forces solidification to maintain the liquidus concentration. Originally, TLP joining was used exclusively for metal assemblies, where the MPD could diffuse into the bulk material. However, low diffusion rates and limited solubility of metallic species in ceramics makes MPD redistribution prohibitively slow. Ceramic joining using a TLP process therefore requires a modification of the method to take advantage of the limited surface preparation and the short bonding times.

Partial-transient-liquid-phase (PTLP) bonding uses a multilayer-interlayer architecture to allow faster MPD redistribution when joining ceramics. A multilayered metallic insert is used as the filler material, composed of a relatively thick core layer sandwiched between two thin cladding layers of MPD. Proper interlayer-material selection
leads to partial dissolution of the thick core-layer at the joining temperature, increasing the liquid thickness without increasing the amount of MPD. This can improve the ultimate adhesion to the ceramic and can help reduce the amount of MPD redistribution that is required. Selecting an MPD with high diffusivity and solubility in the core layer shortens isothermal hold times. After chemical homogenization, the remelt temperature of the interlayer system can be greater than the original bonding temperature, allowing for elevated use temperatures.

Control of the liquid layer is a very important requirement for forming strong bonds quickly. The liquid layer formed must accommodate the initial surface roughness of the ceramic members. If the liquid volume is insufficient to fill the inter-ceramic/metal voids that are present due to surface roughness, the final strength of the joint can be significantly reduced. Excess liquid is also detrimental to the joining process; doubling the liquid thickness requires approximately four times longer at the annealing temperature, which can degrade the assembly properties. Successful application of the PTLP process therefore depends on proper control of the liquid-layer thickness and the interaction of the liquid and two solid surfaces.

The ability of the liquid to fill interfacial voids is dependent upon the volume of liquid present, but also upon the solid/liquid interactions and the roughness of the two solid surfaces. A liquid in contact with a solid will form a characteristic contact angle, measured through the liquid phase, which results in a minimization of total interfacial energies. If this contact angle is less than 90°, the liquid is described as “wetting” this solid surface. For angles greater than 90°, the total interfacial energy is reduced when the solid/liquid interfacial area is reduced relative to a hemispherical geometry, and the liquid is considered “non-wetting”. A wetting liquid has the potential to spread across a solid surface, and will spontaneously flow to fill certain interfacial voids.

While the above description of wetting applies to a liquid droplet on a single surface, the liquid that forms during PTLP joining forms between two dissimilar solid materials. The multilayer architecture used in PTLP bonding results in a liquid layer forming between solid ceramic and metallic materials. It is very common in PTLP applications for the liquid to form a contact angle > 90° on one surface, and < 90° on the other. The success of this joining technique can hinge upon the behavior of this liquid layer, especially in the presence of surface-roughness features. It has been shown that rough features can affect the macroscopic wetting behavior of a liquid, but an analysis of how this pertains to PTLP joining is lacking.

Surface roughness is an intuitively simple concept, but is difficult to quantitatively define. Roughness is a deviation of a surface from some ideal geometry, but this deviation can take a large number of forms. A number of instruments and methods exist to quantitatively measure a surface profile, and dozens of parameters have been defined that provide a statistical measure of the data. The correlation between a given roughness parameter and a particular surface behavior is not always straightforward or existent. A small number of roughness parameters are commonly used to report surface topography, usually statistical measurements of the height of the surface at a given position. However, the lateral spacing of roughness features or the average slope of a surface can affect the behavior of the surface. Most work on the joining of materials uses height-based parameters to quantify the roughness of the surfaces involved.

This study presents a numerical model used to examine the effect of surface roughness on the behavior of a liquid. Numerical simulation allows control of the surface roughness, the liquid position, and interfacial energies. Many liquid configurations can rapidly be sampled to
determine the resulting total interfacial energy. In this way, minimum-energy configurations can be identified. The preferred liquid configurations can be analyzed, allowing comparison to experimental results and previous models of roughness/wetting behavior. Most importantly, it allows an energetic analysis of the conditions found in a PTLP joining technique: a liquid layer between two dissimilar materials.
2.0 Background

2.1 Joining

Engineered devices usually require the assembly of multiple components to fulfill all design requirements. Many designs call for use of dissimilar materials, which present additional difficulties when joined together. A variety of joining techniques exist, allowing for customization of both joining method and materials. While several rapid, low-cost methods of creating metal-metal joints exist, the creation of metal-ceramic or ceramic-ceramic joints presents inherent difficulties. This work looks into a particular aspect of liquid-based ceramic joining, specifically the interaction of liquids on and between rough surfaces.

2.1.1 Ceramic Joining Techniques

Engineering systems often require reliable connections between materials. Limitations of material choices, design parameters, or use conditions can require specific joining techniques. A variety of techniques are available for specific material types (e.g., nails for wood, riveting and welding for metals), often providing such strong, rapid, and inexpensive joints that they become standard. Joining of ceramics is difficult due to high melting points and their chemical inertness, and no standard joining technique has been identified. A number of joining methods have been studied for ceramics and are widely used to exploit the unique properties of many ceramic materials. Unfortunately, these techniques present drawbacks that limit the commercial viability of using ceramic components. Popular ceramic-joining techniques can be broadly divided into solid-state and liquid-state methods.

2.1.2 Solid-State Ceramic Joining

Solid-state joining techniques use pressure and temperature to form a strong bond, without melting any of the components involved. Also known as diffusion bonding, solid-state ceramic joining can create high-temperature joints through diffusive processes. Successful diffusion bonds require large joining pressures to flatten surface-roughness features, maximizing interfacial area and breakdown of surface oxides. High temperatures act to increase diffusion rates, allowing faster redistribution of material near the interface. The total joining time is controlled by the time required to reduce the size and density of interfacial voids that can lead to premature failure. Stringent surface preparation can reduce the total joining time by increasing initial contact and reducing initial void volume. Pre-bonding steps, such as surface preparation, can increase the complexity and cost of diffusion bonds for industrial processes. While high bonding pressures can plastically deform the surfaces to reduce void volume, reducing the advanced preparation, asperity contact may limit the breakdown of surface oxides, limiting the success of the joint. Diffusion bonds between a ceramic and a metal benefit from the plastic deformation of the metal, which eases surface-roughness constraints.

Refractory metals are often used in joining with ceramics for two reasons. Their high-melting points allow high use temperatures, often a reason for choosing ceramic materials.
Secondly, refractory metals generally have lower coefficients of thermal expansion (CTE) mismatch with many ceramics than typical metals. Interfacial bonding first occurs at elevated temperatures in many joining techniques. Any CTE mismatch will result in differential contraction upon cooling, leaving a residual stress than can reduce joint strength. In extreme cases, these residual stresses are large enough to cause joint failure during cooling.\textsuperscript{11}

2.1.3 Traditional Liquid-State Ceramic Joining

Solid-state joining techniques are rate-limited by the diffusion rates of the solids. The time required to join can be significantly reduced if a liquid is involved. Properly selected materials will exhibit good wetting properties, the tendency of a liquid to spread to coat a solid surface. To join metallic systems, welding melts portions of the interfacial area, producing a liquid that solidifies when the heat source is removed. Other liquid-joining techniques, such as brazing and soldering, introduce a liquid whose composition may differ from the joined members. Brazing and soldering rely on the same technique, differing only in bonding temperature. Soldering is performed at temperatures $< 450^\circ$C while brazing is performed at temperatures $> 450^\circ$C. Unlike welding, CTE mismatch at the interface is possible due to chemical heterogeneity. Optimization of soldering or brazing systems requires consideration of chemical and thermal compatibility, and wetting characteristics.

The braze or solder can limit the use temperature.\textsuperscript{11} Metallic systems soften as temperatures increase, limiting the use temperature to below 50-60% of the alloys melting temperature.\textsuperscript{12} Poor selection of braze/solder materials can lead to brittle reaction layers, providing a low-energy fracture path.\textsuperscript{13} Benefits of liquid-state joining include rapid material redistribution within the interfacial region, accommodating more initial surface roughness than solid-state methods.\textsuperscript{14} Therefore what is needed is a high-use-temperature method, like diffusion bonding, which also accommodates greater surface roughness, like liquid-state joining.

2.1.4 Transient-Liquid-Phase (TLP) Bonding

Transient-liquid-phase (TLP) bonding combines high use temperatures with reduced-temperature liquid-based joining.\textsuperscript{15,16} Originally, TLP joining was developed to join high-temperature metals such as Ni-based superalloys. TLP bonding of metals, similar to brazing or soldering, involves the melting of an inserted metallic layer to form the joint region. In contrast to brazing/soldering, the inserted material in TLP joining solidifies at the bonding temperature as a result of a chemical homogenization. The insert incorporates a melting-point depressant (MPD) that leads to liquid formation at the joining temperature. As in a traditional liquid-based joining technique, this allows rapid redistribution to fill interfacial voids. TLP joining requires use of an MPD that will diffuse into the joined members. As the surfaces of the solid members incorporate MPD, small amounts of the solid members dissolve, and aid in the removal of surface oxides.\textsuperscript{17,18} With further annealing, the amount of MPD in the liquid region will decrease by diffusion, causing isothermal solidification of the joint region.\textsuperscript{16} The post-annealing joint therefore exhibits a higher melting point due to the redistribution of the MPD.
Material selection for TLP joining requires consideration of many different properties. Secondary phases are potentially created at the joining temperature with improper understanding or use of the phase diagram or due to differential diffusion of multiple MPD's. Intermetallics phases can exhibit detrimental properties such as brittleness, low melting temperatures, or CTE mismatch.

2.1.5 Partial-Transient-Liquid-Phase (PTLP) Bonding

TLP bonding of metals is made possible by the redistribution of the MPD into the adjoining metallic members. When joining ceramics, the reduced diffusion rates into the ceramic would make traditional TLP joining very time-consuming. This barrier is overcome with a slight modification of the insert structure, adding a thicker core layer that acts as an MPD acceptor. This modified process is known as partial-transient-liquid-phase (PTLP) joining since the MPD only redistributes within the insert itself, not into the entire member. A core-layer material is chosen to provide a similar CTE to, and good chemical compatibility with, the ceramic. A thin cladding layer of MPD is then deposited on both sides of the core layer. The core layer is significantly thicker than the cladding layer, allowing complete redistribution of the MPD into the core layer. Fig. 2.1a shows a simple representative phase diagram that will be used to explain the process. Before the sample is annealed, the architecture of the bond is that shown in Fig. 2.1b; the ceramic surface is in contact with the pure MPD cladding layer, which has been deposited on a much thicker metallic core layer. At the bonding temperature, a liquid forms, incorporating the entire MPD layer and dissolving some of the contacting core layer. This acts to increase the liquid thickness and quickly bring the liquid composition to that of the liquidus, $C_{\text{liq}}$, while the surface of the core layer quickly reaches $C_{\text{liq}}$ (shown in Fig. 2.1c). Upon further annealing, the MPD diffuses into the core layer, slowly decreasing amount of liquid phase in the interlayer, eventually solidifying the joint region isothermally (Fig. 2.1d). With sufficient time at elevated temperature, the entire interlayer will homogenize, with a composition of $C_{\text{final}}$, resulting in an interlayer with a remelt temperature exceeding the initial joining temperature (see Figs. 2.1a and 2.1c).

PTLP joining of ceramics allows rapid processing and has the potential to raise use temperatures compared to brazing or soldering. As with brazing and soldering, interfacial voids are rapidly filled, but like solid-state joining diffusion controls the total bonding time. The total bonding time is controlled by the amount of time needed to redistribute the MPD. Joining can be accelerated by selecting material combinations with high MPD solubility in the core as well as a high diffusion rate at the joining temperature. Reducing the liquid thickness will help minimize the time at elevated temperature by reducing the time required to redistribute the MPD. Excess liquid can lead to the formation of secondary phases or can cause liquid to squeeze out of the joint, necessitating post-bonding processing. Insufficient liquid can leave interfacial voids. Since void volume is determined by surface topography, optimization of PTLP joining of ceramics requires a thorough understanding of roughness.
2.1.6 Nickel-Niobium (Ni-Nb) Binary System

The nickel-niobium (Ni-Nb) system has many desirable properties for PTLP joining of a ceramic. The high melting point of Nb (2469°C), combined with a relatively low CTE, suggests it would serve well as the thick core layer. PTLP joining requires the formation of a liquid at reduced temperature, ideally dissolving some of the core layer to increase the liquid thickness without increasing the amount of MPD. In the Ni-Nb phase diagram, shown in Fig. 2.2, the lowest-temperature liquid is thermodynamically stable at 1184°C, incorporating at least 53 at% Nb at a reasonable bonding temperature. For joining temperatures greater than 1280°C, no intermetallics phases are stable in the Nb-rich region of the phase diagram. The core Nb layer can accommodate several at% Ni at the temperature range considered. Ni is also an anomalously fast diffuser in Nb.  

2.1.7 Joining of Alumina

Alumina (Al₂O₃) is commonly used for studying ceramic joining and is the most widely used ceramic. Many studies have been performed with both polycrystalline and single-crystal Al₂O₃ using both liquid-state and solid-state joining methods. Al₂O₃ has also been used as a model system for previous PTLP joining studies, allowing direct comparisons of interlayer chemistry effects on joint strength. The use of Nb as a joining interlayer has been shown to be effective. Specifically Nb is chemically compatible with Al₂O₃, and the CTE mismatch between Nb and Al₂O₃ is small. The CTE for Nb, averaged over the temperature range from 27°C to 1827°C is 8.8 × 10⁻⁶ K⁻¹. The average CTE for Al₂O₃ is 8.5 × 10⁻⁶ K⁻¹. During cooling, the Al₂O₃ will therefore contract less than the Nb, leaving the Al₂O₃ interface in a slight state of compression. The CTE mismatch with Nb is smaller than with other possible refractory metals (CTE averaged from 27°C to 1927°C: V - 12.9 × 10⁻⁶ K⁻¹, Ta - 7.5 × 10⁻⁶ K⁻¹, Mo - 6.9 × 10⁻⁶ K⁻¹, W - 5.3 × 10⁻⁶ K⁻¹). While the CTE of V is greater than that of Al₂O₃ (therefore also putting the ceramic interface into compression upon cooling), the CTE mismatch is greater, leading to a higher residual stress at the interface. Work is underway to examine the possibility of alloying refractory metals to maximize chemical compatibility while minimizing CTE mismatch between the ceramic and core metallic interlayer. High-purity, oxygen-free Ni has also been shown to be chemically compatible with Al₂O₃.

Wetting of ceramic surfaces by metallic liquids presents a problem for PTLP joining. Most liquid metals form obtuse contact angles on Al₂O₃. This includes pure Ni which exhibits a contact angle of ~109° on Al₂O₃. Use of metals such as Al, Cu and Ti, can assist wetting on a number of ceramics. For a PTLP joining system, the simplest analysis requires that the average contact angle (ceramic/liquid-metal and solid-metal/liquid-metal) be < 90° to form strong joints. Significantly smaller contact angles on Al₂O₃ are formed with the use of reactive-metal additions, sometimes < 20°. Reactive metals can form reactive layers, which enhance the wetting properties, but potentially weaken the joint through the formation of a brittle layer or a low-energy fracture path. Previously published results demonstrate that addition of Nb to the Ni liquid reduces the contact angle of the liquid to < 90° without the formation of a reaction layer. As mentioned earlier, the sum of the metal/liquid-metal and the ceramic/liquid-metal contact angles must be < 180° to promote wetting. Metal/liquid-metal contact angles are generally very low (~20-30°), suggesting that the use of a Ni/Nb
liquid will allow spontaneous liquid flow to fill interfacial roughness on both the ceramic and the solid-metal surface.31

2.1.8 Prior Ceramic/Metal Joining

Prior efforts in ceramic/metal joining have explored the use of noble metals, alloyed metals, and refractory metals. Diffusion bonding of noble metals42-45 to ceramics such as Al₂O₃ has proven successful. Au bonds were performed in a variety of atmospheres, with a joining temperature of 1050°C,42 but average shear strengths were limited to 62 MPa. Diffusion bonding of Al₂O₃ to Ag showed the importance of both chemical adhesion and plastic flow to form a void free interface with increased strength.45 A study of similar Ag/Al₂O₃ joints showed that Ag could diffuse into the ceramic, altering the properties near the interlayer.46 Specifically the toughness of the ceramic was shown to decrease nearly 20% with the incorporation of the Ag from the metallic interlayer.

Extensive examination of ultrahigh-vacuum diffusion bonds between Nb and single-crystal Al₂O₃ has been performed. The effect of orientation relationship on fracture toughness for single-crystal Nb/sapphire (single-crystal Al₂O₃) bonds was studied; fracture toughness was a strong function of orientation relationship.47 Toughness was maximized for Nb orientations that maximized the density of Nb atoms at the interface. Additionally, dopants were found to affect the fracture toughness: Ti, a reactive metal, increased toughness47 while Ag48 and Sn49 decreased the toughness compared to undoped samples with the same orientation relationships. Nb has been shown to form Al₂O₃ joints with fracture energies higher than most ceramic/metal systems.50 Additionally, pre-cracks formed in the ceramic were shown to blunt in the interface. Control of interlayer thickness was shown to have a strong effect on yielding behavior, due to constraints imposed by the ceramic/metal interface.51 By decreasing the Nb thickness, cracks are formed at significantly higher stresses.52

Liquid-based joining methods of various ceramics have also been extensively studied. Active-metal brazing techniques use metallic components that react with the ceramic surface, often forming a reaction layer that can prove problematic. Reactive chemistries can enhance the strength of the joint according to the McDonald and Eberhart model.53,54 In this model, the joint strength can be correlated to the work of adhesion (W₀), a measure of the energetic change for separating two phases.55 One study confirmed the predicted relationship of tensile strength to W₀ for Al₂O₃ joints, but only for solid/solid W₀. The study did not find any link between the tensile strength of the solidified joint and the liquid-metal/ceramic W₀. For Ni alloy/Al₂O₃ joining, a correlation was also found between the oxygen-affinity of alloying metals and bond strength.
PTLP joining of ceramics has also been studied, using a variety of ceramic and metal interlayer systems. Si₃N₄ has been joined using an interlayer of Au/80Ni20Cr/Au, producing joints with an average tensile strength that matched diffusion-bonding results. By varying processing conditions, this interlayer produced joints with average strengths as high as 272 MPa, lower than the monolithic strength of Si₃N₄. Cu-Au/Ni/Cu-Au interlayers were used to join Si₃N₄ with a small amount of Ti added to the Cu-Au layers. A thin reaction layer was observed near the ceramic interface and the average strength of the joints was as high as 770 MPa. PTLP joining of Al₂O₃ has been performed using many interlayer systems: Cu/Ni/Cu, Cr/Cu/Ni/Cu/Al, Cu/80Ni20Cr/Cu, Cu/Pt/Cu, and Cu/Nb/Cu. All interlayer systems proved successful, allowing reduced joining temperatures and with some joints failing exclusively in the ceramic. The particular success of the Cu/Nb/Cu system prompted further studies of the interface evolution to identify critical parameters for success. In this system the liquid promotes formation of Nb-Al₂O₃ contact, but with time the initially continuous liquid film becomes discontinuous. Other studies examined the fracture energies for single-crystal Al₂O₃ bonded with Nb/Cu/Nb interlayers. These studies analyzed the effects of metallic grain size, bonding load, and processing time upon the bond characteristics.

2.2 Surface Roughness

Surface roughness can play an important role in many different engineering disciplines. In mechanical systems improperly controlled surface roughness can reduce efficiency or performance due to friction, or lead to wear of components that results in catastrophic failure or reduction of part lifetimes. In electrical engineering, roughness between interfaces can lead to reduced electrical contact, alterations of band-gap structures near surfaces, and destruction of hard drives due to contact with the read/write head. For materials science, surface roughness comes into play in multiple sub-disciplines. In semiconductor technology, the topography of a sample can affect charge-carrier mobility, electron scattering, and the electronic structures of semiconductors near interfaces. The mechanical interaction of solid materials is governed by their combined roughness and hardness properties. Understanding of this interaction is necessary to develop polishing systems, avoid excessive wear, or control material-removal rates. Characterizing the effectiveness of machine tools is strongly related to the surface roughness of the part and the tool. In selecting material-forming processes, it is critical to know the dimensional tolerances that are achievable, and whether they are compatible with design requirements, or if further surface conditioning is required. When attempting to join materials, the initial roughness of the materials can affect the final strength of the joint region. Additionally, some joining methods such as welding or brazing can lead to rough surfaces, requiring subsequent finishing that can affect the joint properties. All of these factors must be included in the design process and materials selection, and careful consideration of surface roughness is an important, but often overlooked, aspect of this process.
2.2.1 Historical Treatment of Surface Roughness

Engineers first systematically considered the effects of surface roughness when designing cannon barrels in the 1700’s. Large deviations in the inner-barrel surface could significantly reduce the firing distance of armaments as well as decrease the accuracy of the gunners. Early engineering attempts to control surface roughness lacked quantifiable or repeatable measurements. Experts were required to gauge the roughness, and their method of measurement generally involved rubbing the thumbnail across the surface. These measurements were inherently imprecise and lacked a means of communicating or recording results. Many measurement techniques were developed, including placing the material on a phonograph table and listening to the sounds produced when the needle was dragged across the surface. While this method produced an output that was proportional to the height of the surface, there was no method to record or analyze the data, and once again relied on the interpretation of individuals.

The first modern measurement system for surface roughness was the profilometer. Developed by Abbott in 1938, the profilometer involved a stylus head that was held in contact with the test surface. The displacement of the arm could be read and recorded using a simple electronic system, allowing the surface height as a function of position to be recorded. This method was both reproducible and quantifiable, which was a significant step towards a scientific treatment of surface roughness. Limitations of this system included the fact that it was a two-dimensional measurement and that the output was not a direct measurement of the surface. Early profilometers were fitted with an electrical circuit that would automatically output the root-mean square (RMS) deviation of the signal, providing one of the earliest surface roughness parameters. The RMS deviation of the electrical signal was divided by an algebraic factor to approximate the RMS deviation of the surface height from its mean. This method was only numerically correct for a purely sinusoidal surface, but provided a consistent methodology for measuring and comparing surfaces and their properties.

While quantifiable comparisons of surfaces were now possible, it was unclear how to correlate surface behaviors, such as wear or friction, to a statistical measurement of the surface profile. One of the first attempts to provide a useful statistical measurement was known as the Abbott-Firestone curve, shown in Fig. 2.3. The Abbott-Firestone plot shows the percentage of a surface that is lower than a given height. Fig. 2.3a shows a simulated profile, while Fig. 2.3b shows the resulting Abbott-Firestone curve. Two surfaces in contact under a given load will result in deformation of the roughness features until a critical percentage of the surface is in contact. The Abbott-Firestone curve therefore provides a direct correlation between profilometry data and the physical interaction of surfaces.

One weakness of both RMS measurements and the Abbott-Firestone curve is the lack of information about length scale. Both provide a statistical summary of profile height, but contain no information about how those heights are distributed. Awareness of this problem led to efforts in the 1940’s to separate features into different length scales. Short-scale “roughness” features were shown to be the effect of defects in tool faces whereas longer “waviness” features were the result of mechanical vibrations of the machining system. These mechanical vibrations were an unavoidable consequence of the machining process, and the waviness features were viewed as beyond the engineers’ control. Roughness features, however, were the result of tool production, and as such became the focus of engineering efforts. Electronic filters were implemented on topography measurements to divide a measured profile
and only examine the roughness of concern, i.e., short-scale features. Standard measurements of surfaces were confined to length-scales on the order of a few mm.  

2.2.2 Measurement Techniques

For nearly one hundred years, instruments have been developed to provide quantitative measurements of surface topography. The simplest methods, represented by the Abbott profilometer, are known as stylus instruments. These instruments impose physical contact between a small stylus and the sample surface, but vary in the method of measuring the stylus position. By mounting the stylus head on a flexible cantilever arm and measuring the deflection of this arm as a function of position, a two-dimensional map of the surface is produced. Many methods are used to measure the deflection of the arm, including optical interferometry, induction coils, linear-variable-differential transformers (LVDT), or piezoelectric transducers. Since the stylus instruments require continual physical contact, wear of the sample surface and of the stylus tip must be considered. Stylus tips are typically created from hard materials, reducing wear of the tip component, but increasing the likelihood of damaging the sample itself. By using materials with a low elastic constant, the cantilever arm can deflect easily, reducing the force imparted on the surface.

All surface interactions must be considered on multiple scales. Although proper material selection can minimize the total force imparted on a surface by a stylus instrument, the scale that this force acts over is critical. The ability to record a surface feature of a given size is related to the size of the stylus tip. This is shown schematically in Fig. 2.4. If the stylus tip has a larger radius of curvature than the surface features, the measured profile will be artificially smooth, as the instrument is incapable of recording features smaller than the radius tip. Modern profilometers can achieve lateral resolution < 0.1 μm. A high resolution requires a small contact area, leading to high-contact pressures, even when the force is minimized. Over time, this contact pressure can wear down the stylus tip, effectively increasing the tip radius and decreasing the machine resolution. Fig. 2.5 shows the effect of increasing tip radius on the measured profile. This flattening both decreases the sensitivity to specific features, but also decreases the amplitude differences, lowering the calculated roughness values.

Stylus-type measurements remain the most widely used, due to relatively low cost and availability, but additional instrument types have been developed to increase resolution, reduce sample damage, and measure three-dimensional topography. Scanning Tunneling Microscopy (STM) makes use of the quantum tunneling current as a precise measurement of the distance between the microscope probe and the sample surface. Due to the uncertainty principle applied at angstrom length scales, a small number of electrons can jump between surfaces that do not form a traditional electrical contact. This current is extremely sensitive to the distance between the surfaces, thereby providing a method of measuring surface topography. To measure the current, the STM tip must be metallic, and is held at a constant distance (~0.2 nm) from the surface. The positioning is maintained with a force-feedback system, which uses the changes in tunneling current to adjust the probe height.

The need for a conductive sample limits the uses of an STM. To correct this requirement, an atomic-force microscope (AFM) uses a combination of STM and profilometer techniques. As with a profilometer, an AFM physically contacts the sample with a probe made of a hard material (with a radius of ~20-50 nm). The tip is held in contact with the surface
with a force-feedback system, and the change in position of the tip is measured with an STM probe. The AFM is capable of three-dimensional scans, but is limited to reduced scan lengths compared to a traditional profilometer. Both the STM and the AFM are capable of vertical and horizontal resolution on the order of nm, but are limited to scan lengths on the order of 100 µm. The next evolutionary step from contact-stylus instruments is classified as non-contact profilometry. When characterizing samples that are easily damaged, such as magnetic media, optical methods are often used. There are several optical techniques, with measurements performed based upon changes in the angle or intensity of reflected light. Optical profilometry can be performed rapidly, allowing scans of surfaces on the assembly line without decreasing throughput. Additionally, since no physical contact is made, surface damage is not a concern and probe tips do not need to be replaced to maintain accuracy. However, if the optical properties of the sample vary by position (for example, in a composite), optical techniques can report false topographies. The rapid feedback provided by optical methods could also be used to provide real-time information for surface grinders.

2.2.3 Roughness Parameters

Over 50 roughness parameters have been identified, divided into amplitude, length, and hybrid categories. The most commonly used parameters fall within the amplitude-based category, with \( R_q \) being the most often cited. \( R_q \) is defined as the root-mean-squared deviation of the height from a calculated mean level. \( R_q \) is given by

\[
R_q = \sqrt{\frac{1}{L} \int_0^L (y(x))^2 \, dx}
\]  

(2.1)

where \( L \) is the length of the surface considered and \( y(x) \) is the difference between the height at a position, \( x \), and the mean height of the surface. For quantized data, as would be collected by modern techniques, the equation must be modified to reflect the discrete nature of the data. For \( N \) discretely recorded position-height pairs, \( R_q \) is given by

\[
R_q = \sqrt{\frac{1}{N} \sum_{i=1}^N (y_i - \bar{y})^2}
\]  

(2.2)

where \( y_i \) is the height of the surface at position \( i \), and \( \bar{y} \) is the mean height of the profile.

A similar amplitude parameter, also commonly used, is \( R_a \), the average deviation of the height from a calculated mean. Expressed for a continuous and discrete analysis of a surface, \( R_a \) is given by Equations (2.3) and (2.4) respectively.

\[
R_a = \frac{1}{L} \int_0^L |y(x)| \, dx
\]  

(2.3)
$$\text{Ra} = \frac{1}{N} \sum_{i=1}^{N} |y_i - \bar{y}|$$

While both parameters express a statistical summary of the amplitudes of a surface, the parameters are sensitive to different aspects of a surface's topography. \text{Rq} is more sensitive to extreme deviations in height than \text{Ra}. As a demonstration of this behavior, Figs. 2.6a and 2.6b show two simulated profiles that differ only by one aberrant peak, evident in Fig. 2.6b. By applying Equations (2.2) and (2.4), the \text{Rq} and \text{Ra} values are as follows: \text{Rq} = 0.707 and \text{Ra} = 0.636 for the profile in Fig. 2.6a and \text{Rq} = 0.743 and \text{Ra} = 0.666 for the profile in Fig. 2.6b. The aberrant peak therefore increased the \text{Rq} value by 5.1% while the \text{Ra} value only increased by 4.7%. While this is not a significant difference, for surfaces with many deviant features, \text{Rq} will demonstrate this aspect of the surface more clearly. Since large deviations in height often play a large role in surface interactions, \text{Rq} is the most-cited roughness parameter.

2.2.4 Surface Contact and Roughness

Contact between two surfaces is governed by the elastic/plastic behavior of the materials, the imparted forces, and the surface topography. Two surfaces in contact usually exhibit a much smaller contact area than macroscopic observation would suggest, an effect of surface roughness and asperity contact. Hertz\textsuperscript{95} provided a model of asperity contact, simplifying the problem into the contact of two elastic spheres. Studies have shown that the Hertz model is generally valid, with deviations at light loading due to surface-energy effects.\textsuperscript{94} Greenwood and Williamson\textsuperscript{95} showed that the true contact area was determined by the load, not the apparent area. The points of contact deform until an increased contact area supports the force.

Asperity deformation has been used to explain Archard's laws of friction.\textsuperscript{21,96} Noting that friction depended on load, not apparent contact area, Archard used multiple-length-scale roughness to explain true versus apparent contact area.\textsuperscript{97} Archard showed that Hertzian theory could be improved by invoking short-wavelength features on the spherical asperity contacts, further reducing the true contact area. Recent models of multi-scale roughness have shown the potential for computers to simulate contact between fractal surfaces.\textsuperscript{75,76,98}
2.2.5 Surface Roughness and Joining

Surface roughness affects many joining techniques. Studies have been performed on adhesive bonding,\textsuperscript{99,100,101} diffusion bonding,\textsuperscript{3,102,103} welding,\textsuperscript{102,103} soldering,\textsuperscript{14,104-106} and mechanical joining\textsuperscript{107} to correlate the effect of roughness on bond strength. The subject of roughness, especially pertaining to length scale and parameters, is not treated equally throughout the joining literature. Two of the above joining studies look at multiple length scales for roughness features.\textsuperscript{3,107} A common problem is citation of roughness values without describing the testing method or equipment.\textsuperscript{100,103} In rare cases, roughness is cited as the cause of premature failure, with no attempt at measuring or reporting the surface topography.\textsuperscript{105} Studies can be found that give a numerical value of “roughness”, without specifying the parameter calculated.\textsuperscript{100}

2.3 Wetting

Wetting describes the interaction of solid and liquid materials, often in a surrounding medium. Each interface has a unique energy per area based upon the phases that are interacting, and the balance of these energies determines the ultimate liquid morphology. Scientists have been studying the shape that droplets form on surfaces for over two hundred years, with many theories proposed as to the exact geometries taken. Surface roughness can have a strong effect on the wetting behavior of materials, but the exact nature of that effect is still under discussion.

For liquid-based joining methods, the wetting of the surface is a critical step towards making a strong bond. If the liquid-solid energies are high, the droplet will respond by reducing the total amount of liquid-solid area, leading to internal voids in the joined layer, which can lower the ultimate strength.

2.3.1 Young’s Model

The primary model of wetting behavior was proposed by Young in 1805.\textsuperscript{108} In one of his many influential works, Young defines the concept of surface tension. The Young equation is based upon the concept of surface tension acting as a force parallel to the interface between two different phases. The geometry of the droplet that forms is therefore ruled by a force-balance along all contact lines. Simple uses of Young’s equation treat the solid surface as non-deforming, reducing the force balance from a two-dimensional to a one-dimensional equation. As shown in Fig. 2.7, the force balance in the plane of the solid surface is given by

\[
\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos(\theta) \tag{2.5}
\]

where \( \gamma_{sv} \) is the solid-vapor interfacial energy, \( \gamma_{sl} \) is the solid-liquid interfacial energy, and \( \gamma_{lv} \) is the liquid-vapor interfacial energy. If the contact angle, \( \theta \), measured through the liquid, is less than 90\(^\circ\), this condition is known as “wetting”. Work of adhesion is defined as the work done to separate an interface into two interfaces (e.g., a solid-liquid interface separated into a solid-vapor and a liquid-vapor interface).
\[ W_{ad} = (\gamma_{sw} + \gamma_{lv}) - \gamma_{sl} \quad (2.6) \]

Combining Equations (2.5) and (2.6), we arrive at

\[ W_{ad} = \gamma_{lv} \{1 + \cos(\theta)\} \quad (2.7) \]

The mechanical strength of an interface is treated as proportional to the work of adhesion \( W_{ad} \). As \( \theta \) changes from 0° to 180°, the interfacial strength is reduced to 0. A low contact angle is formed when it is energetically favorable to replace solid-vapor interface with a solid-liquid interface. Therefore, liquids with low-contact angles can spontaneously flow to fill interfacial gaps. Joining systems that employ low-contact angle liquids can therefore reduce the number of large defects in an interface, potentially increasing the strength of the joint. Conversely, a high-contact-angle liquid can recede, preventing the liquid from filling in interfacial voids.

2.3.2 Wetting and Roughness

Young's original analysis holds for idealized, planar geometries. As discussed earlier, real surfaces inevitably contain deviations from the ideal topography. Surface roughness can affect the wetting by changing the interfacial area, as well as creating orientation effects. Liquids in contact with a rough surface often contact the surface at a local orientation that does not match the macroscopic orientation of the surface. Young's equation is still maintained locally, even in a rotated reference frame. The liquid can therefore appear to have a macroscopic contact angle that differs from that predicted on a planar surface. Additionally, a rough surface has a larger area than a flat surface, changing the energetic balance of a droplet in contact with a surface.

In 1936, Wenzel presented the first numerical treatment of the above effect, altering Young's equation to address this change in area. By defining a roughness factor that defined the ratio of real surface area to the projected area on an ideal plane, Wenzel calculated that the effective surface tension for a rough interface was effectively multiplied by this roughness factor. This has the effect of increasing the surface area with interfacial energies \( \gamma_{sl} \) and \( \gamma_{sv} \), leading to a change in the predicted angle. Wenzel's analysis predicts that surface roughness increases the wetting or non-wetting nature of a system: contact angles greater than 90° increase, while those less than 90° would decrease based upon roughening of the surface. Wenzel's analysis requires a radially symmetric surface. \(^{111,112}\) Experiments have shown that Wenzel's analysis does not hold as the magnitude of the roughness becomes large in comparison to the droplet size. \(^{113}\) More recent studies allow for more complicated systems, with varying length scales between the surface and liquid dimensions \(^{114}\) or high-energy surfaces. \(^{115}\) Cassie and Baxter showed that chemical heterogeneity or extreme surface roughness can lead to entrapped voids along a solid-liquid interface. \(^{111}\)

Wetting on many surfaces exhibits hysteresis behavior. That is, the contact angle of the liquid is observed to change depending upon whether the liquid front is advancing or receding on the solid surface. Shuttleworth and Bailey \(^{112}\) helped explain contact-angle hysteresis as an effect of micro-scale roughness that could act to pin a liquid front, thereby altering the macroscopically observed contact angle. Subsequent papers presented theoretical models that explained the ability of roughness to pin the liquid front. \(^ {116}\)
Wetting on rough surfaces has proven to be a fertile area for both theoretical and experimental work. Studies of wetting behavior on rough surfaces often focus on creating superhydrophobic surfaces (contact angle > 150°). Work has been performed to replicate the wetting observed on lotus leaves, in which water beads up to a contact angle approaching 180°. The goal of many of these studies is to increase water resistance through the use of patterned surfaces. Si is often used as the solid surface due to well-developed methods of creating controlled surface features. The transition to superhydrophobic surfaces is the subject of many papers, often modeled after Cassie and Baxter’s analysis.

Roughness also plays a role in capillary behavior between two solid surfaces. Capillary forces are altered in the region near asperity contact due to the roughness of the two surfaces. Patterned surfaces can lead to capillary forces that spontaneously lead to liquid flowing along the rough surface. Studies of liquid flow through channels have shown a pinning effect similar to that observed in static wetting studies. The liquid front must overcome the energetic barrier of a rough surface before continuing to flow, leading to liquid drag that can affect the flow patterns in a channel. It is possible to enhance capillary flow through patterned, chemically heterogeneous channels, due to a reduction in energetic barriers preventing flow.

None of these studies directly pertain to PTLP joining. Unlike in capillary flow, the liquid redistributes over a small area and has no net movement. Additionally, unlike most surface roughness/wetting studies, two surfaces, with dissimilar contact angles are involved. Previous studies have shown the power of computational models in exploring surface roughness and wetting issues. What is needed is a study of liquid entrapped between dissimilar surfaces, and the potential for void formation due to incomplete liquid redistribution as observed in PTLP joining of ceramics.
2.4 Background Figures

Fig. 2.1: a) Representative phase diagram, highlighting compositions and temperatures important in a TLP joining system. b) Original architecture of bond region. Cladding layer is unmelted and between the ceramic member and the thicker core layer. c) At the joining temperature, a liquid forms incorporating the cladding layer MPD and some of the core layer, quickly reaching the liquidus composition. The contacting surface of the core layer is at the solidus composition. d) After sufficient annealing, the MPD redistributes into the solid core, causing isothermal solidification of the joint region. e) With further time at the bonding temperature, the interlayer region homogenizes, with a new remelt temperature that exceeds the joining temperature.
Fig. 2.2: Phase diagram of the Ni-Nb binary system. Taken from Okamoto.\textsuperscript{23}

Fig. 2.3: a) A simulated profile and b) the Abbott-Firestone plot for the same surface. The plot shows the amount of the surface that is higher than a given height.
Fig. 24: The radius of the stylus tip (shown in red) affects the ability to measure small features. As this figure schematically shows, tracing the relatively large stylus tip over the rough surface results in a measured profile significantly smoother than the true surface profile.
Fig. 2.5: The above figures highlight the effect of stylus tip flattening. As the stylus is used repeatedly, wear can lead to a flattening of the tip, resulting in increasingly inaccurate measurements. With a flatter tip, not only are small features lost from the measured profile, but also the amplitude of the features is reduced.
Fig. 2.6: Two simulated profiles, differing only in the aberrant peak in b).

Fig. 2.7: Schematic of wetting condition. The contact angle, $\theta$, is determined by a balance of the surface tensions, which are proportional to $\gamma_{sl}$, $\gamma_{sv}$, and $\gamma_{lv}$.
3.0 Description of Model

The model presented in this work functions by rapidly calculating the geometry and total interfacial energies of possible liquid configurations. In this section, the assumptions behind the model are discussed, as well as the specific steps taken in calculating possible liquid configurations and the corresponding total interfacial energies. The liquid configurations are defined by the geometry of the solid/liquid, solid vapor and liquid/vapor interfaces. The intersection of these three interfaces is known as the triple line. In order to perform these calculations, a generalized description of the geometries involved, applicable to any surface, must be developed.

3.1 Model Assumptions

The liquid configurations calculated by this model, whether the liquid is on a single surface or confined between two surfaces, will be controlled by certain constraints.

1) For this model, it is assumed that the liquid volume remains fixed throughout any redistribution process. No losses due to evaporation or any other process are considered.
2) The droplet is considered to be small, relative to the capillary length, which will be defined in the next section. In this way, gravitational effects on the geometry of the droplet will not be considered.
3) The energy of all interfaces will be considered isotropic. The local orientation of the surface will not have an effect on the interfacial energy.

The above assumptions will limit the possible geometries of liquid configurations. The rest of this section will describe these geometries, and some mathematical approaches to rapidly calculating them.

3.2 Liquid/Vapor Interfacial Curvature

The geometry of a liquid droplet on a solid surface is defined by the curvature of its interface. It can be shown for a static liquid/vapor interface that a capillary pressure develops between the separated phases. The change in pressure across a curved interface is given by

\[ \Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  

(3.1)

where \( \Delta p = p_{\text{liquid}} - p_{\text{vapor}} \), \( \gamma \) is the interfacial energy, and \( R_1 \) and \( R_2 \) are the principle radii of curvature of the interface. Throughout this work, the curvature of an interface will be defined as positive when the pressure of the liquid is higher, and the center of curvature is in the liquid phase. For large droplets, the gravitational effect on fluid pressure as a function of height can
lead to changes in droplet curvature. As a fully generalized equation, gravitational effects can be accounted for as shown below

$$\Delta p = \rho gh - \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$  \hspace{1cm} (3.2)$$

where $\rho$ is the density of the fluid, $g$ is the gravitational constant, and $h$ is the height of the fluid. For a sufficiently small droplet, the surface-energy effect exceeds the gravitational change in pressure. This boundary in length scale is known as the capillary length, given by

$$L_c = \frac{\gamma}{\rho g}$$  \hspace{1cm} (3.3)$$

For most liquid metals, the capillary length is on the order of a few mm. For liquids with isotropic liquid/vapor interfacial energy, droplets smaller in diameter than the capillary length can be assumed to have constant pressure, and therefore constant curvature, across the entire interface.

### 3.3 Constant Curvature Geometries

Defining liquid configurations with constant curvature relies on the geometry of circular segments. The geometry of a circular segment is shown in Fig. 3.1, with the area of importance shown in blue. The area enclosed is a function of the distance between the two endpoints and the radius of curvature. The red, triangular segment, shown in detail in Fig. 3.2 has an area of:

$$A_{\text{triangle}} = \frac{C}{2} H$$

$$A_{\text{triangle}} = R \cos \left( \frac{\theta}{2} \right) \cdot R \sin \left( \frac{\theta}{2} \right)$$

$$A_{\text{triangle}} = R^2 \cos \left( \frac{\theta}{2} \right) \sin \left( \frac{\theta}{2} \right)$$

$$A_{\text{triangle}} = \frac{R^2 \sin(\theta)}{2}$$  \hspace{1cm} (3.4)

The total filled area (red and blue) in Fig. 3.1 is

$$A_{\text{wedge}} = \pi R^2 \frac{\theta}{2\pi}$$  \hspace{1cm} (3.5)$$

Combining Eqns. (3.4) and (3.5), we arrive at the area of the circular segment of concern.
\[
A_{\text{segment}} = A_{\text{wedge}} - A_{\text{triangle}}
\]
\[
A_{\text{segment}} = \pi R^2 \frac{\theta}{2\pi} - \frac{R^2 \sin(\theta)}{2}
\]
\[
A_{\text{segment}} = \frac{R^2}{2} (\theta - \sin(\theta))
\]  \hspace{1cm} (3.6)

Given the values of \(C\) and \(R\), the value of \(\theta\) can easily be calculated. The area of the circular segment is therefore a function of the distance between endpoints, \(C\), and the radius of curvature, \(R\).

3.4 Model Procedure

The function of the model is to examine a large number of possible configurations for a fixed volume of liquid. By using a computational approach, surface roughness, inter-solid volume, total liquid volume, and surface energies can be independently controlled. Interfacial area and total surface energy are a function of liquid configuration, making certain liquid configurations energetically preferred. As will be shown in the next chapter, when a droplet contacts a rough surface, the surface features create energetic barriers to liquid movement. For a liquid between two rough surfaces, these energetic barriers can lead to void entrapment.

All models presented will determine possible liquid configurations based upon certain constraints. For each calculation, the volume of the liquid is held constant. Many possible liquid configurations are tested by systematically varying the triple-point boundaries of the liquid. By fixing the triple-point positions, the liquid/vapor interface is forced to assume a certain radius to maintain the liquid volume. The contact angle of the liquid is never explicitly controlled in this model. As the positions of the triple lines are shifted and their separation distance is altered, the constant-volume constraint forces the contact angles at the triple points to adjust. The result of these calculations is therefore many possible configurations, with fully defined geometries and interfacial areas. Multiplying these interfacial areas by their corresponding energies allows determination of energetically preferred configurations.

3.4.1 Non-Physical Geometries

The calculation of liquid volume is performed automatically, and will return a result even if that result is not physically possible. One example of a non-physical solution is shown in Fig. 3.3. In this case, the area calculation was performed, but the solid crosses the liquid/vapor interface. The calculated liquid area erroneously includes the solid-area that extends past the interface. The model automatically checks whether the solid crosses the liquid/vapor interface, and if so removes these configurations.
3.5 Single-Surface Model

The single-surface model looks at the possible configurations of a liquid droplet on a solid surface. It is therefore assumed that the total volume of the droplet is fixed through any translation. Two types of surfaces will be examined: surfaces that are radially symmetric, and surfaces that are continuous in one direction. The model examines possible configurations through the following steps:

1) Vary triple-point locations
2) Determine interfacial curvature required to maintain liquid volume
3) Calculate interfacial areas
4) Multiply interfacial areas by surface energies

A liquid droplet with constant curvature forms a spherical cap on a solid surface. For surface topographies that are radially symmetric, it is possible to quickly calculate possible configurations by examining a two-dimensional cross section. It has been shown that surface features that are continuous in one direction, similar to the simulated surface shown in Fig. 3.4, can lead to droplets with high-aspect-ratio morphologies. These droplets can be modeled as long tubes of liquid, and in this case two-dimensional cross sections are also useful for quick calculations of surface-area effects. To determine the cross-sectional area (and therefore the volume) of a droplet, the following geometry is used. As shown in Fig. 3.5, the interfaces of a liquid in contact with a rough surface are affected by the roughness. Specifically the solid/vapor and solid/liquid interfacial areas are increased. The area of the cross section can be rapidly calculated with the following formula.

\[
\text{Area} = \frac{R^2}{2}(\theta - \sin(\theta)) + \int_{x_1}^{x_2} \text{Line}_{nm} - \text{Surface}(x)dx
\]

(3.7)

where Line\(_{nm}\) is the equation of the line that connects points \(n\) and \(m\) and Surface\((x)\) defines the profile of the rough surface. The first term is the area of a circular cap, as discussed previously. The integral corrects for changes in area due to surface roughness. As shown in Fig. 3.6, by performing this integral, it cancels the solid regions inside the circular cap and adds the liquid regions outside of the circular cap. It is possible to form a circular cap that includes more than half of the circle, in which case the area formula is altered to

\[
\text{Area} = \pi R^2 - \frac{R^2}{2}(\theta - \sin(\theta)) + \int_{x_1}^{x_2} \text{Line}_{nm} - \text{Surface}(x)dx
\]

(3.8)
For the single-surface model, there are no limitations on liquid/vapor interfacial curvature, as long as non-physical solutions are avoided. All possible liquid configurations involve positive liquid/vapor interfacial curvature.

3.6 Two-Surface Model

A liquid entrapped between dissimilar surfaces leads to significantly more complicated geometries. Again, the droplet forms a three-dimensional geometry, complicated by the interaction with many different surface features. However, surface roughness that results from machining often has a distinctive orientation relationship. In the direction of machining, roughness features develop due to tooling imperfections and mechanical vibrations. These features have amplitudes and wavelengths that are characteristic of the machine used. In rolling, grinding, and cutting procedures, this can create troughs that extend for large distances along one axis. Features that extend along one axis are observed in profilometry of both the as-ground ceramic surfaces and the rolled metal foils.\textsuperscript{127}

These characteristic troughs can lead to voids with high aspect ratios. These voids are observable in specially constructed bonds. By using single-crystal Al\textsubscript{2}O\textsubscript{3} (sapphire), which is optically transparent, the void structure can be directly observed in post-joining samples. As shown in Fig. 3.7, the void structures observed form high-aspect-ratio morphologies. These voids can therefore be modeled with two-dimensional cross sections.

In a PTLIP joining process, the liquid forms at the joining temperature. The presence of interfacial voids, such as those shown in Fig. 3.7, can be related to insufficient liquid volume or incomplete liquid redistribution. In terms of purely geometric definitions, there is no difference between a liquid droplet surrounded by a vapor phase and a vapor phase surrounded by a liquid. The defining feature of both systems is the geometry of the liquid/vapor interface. In order to model the formation of voids, the energetics of a liquid flowing to penetrate an inter-solid gap are calculated. This model analyzes a liquid film entrapped between two dissimilar solids of infinite extent and a vapor phase of infinite extent, separated by a single interface. As the interface is displaced, the total interfacial energy varies, resulting in possible energy barriers to liquid penetration.

The two-surface model calculates the interfacial areas of many possible liquid configurations and the resulting total interfacial energy in the following way.

1) Start with a defined liquid volume
2) For given liquid volume, systematically vary possible contact points
3) Determine interfacial curvature required to maintain liquid volume for given contact points
4) Calculate all interfacial areas
5) Determine total interfacial energies
6) Determine preferred contact points based upon total-interfacial energy
7) Increase liquid volume by incremental amount and repeat Steps 2-6

Successful modeling of this system requires a rapid method of calculating liquid volumes. In the next section, a liquid/vapor interface entrapped between two solids will be used for purposes of explaining the geometric constructions employed by the model.
3.6.1 Two-Surface Geometry

As discussed previously, the use of two-dimensional cross sections allows a complete description of these three-dimensional geometries. The geometric constructions and methods used to calculate the liquid volume are therefore based upon these two-dimensional cross sections.

The generalized procedure for calculating the volume of liquid configurations is presented below. Fig. 3.8 shows a liquid-configuration cross-section that has been divided into discrete areas. The total area of the liquid cross section is given by the sum of both areas (Area$_1$ and Area$_2$), which are functions of the topography of the surface, the intersection coordinates (x$_1$, x$_2$), and the radius of curvature of the liquid-vapor interface. Area$_1$ can be calculated with a simple system of integrals. Area$_2$ is calculated with the geometry of circular segments, as explained previously.

The geometry of Area$_1$ depends upon the relative locations of x$_1$ and x$_2$. Fig. 3.9 shows the effect of reversing the horizontal position of x$_1$ and x$_2$. While this reversal does not change the total area in this example, it does suggest a rapid, robust method of calculating this area must account for changes in horizontal position of the intersection points. The equation used is shown below:

\[
\text{Area}_1 = \int_{x_0}^{x_1} \text{Surface}_1(x) - \text{Surface}_2(x) \, dx + \int_{x_1}^{x_2} \text{Line}_{x_1x_2}(x) - \text{Surface}_2(x) \, dx
\] (3.9)

where Surface$_n$ is the equation that defines the $n^{th}$ surface and Line$_{12}$ is the equation of the line that connects points x$_1$ and x$_2$. The coordinate x$_0$ is chosen to be far from the interface (within the liquid phase), to provide a reference point for volumetric and surface-area calculations. Depending upon the horizontal position of the various points, some of these integrals can have negative values. However, no matter the relative positions of points x$_1$ and x$_2$, the sum of both integrals will always be equal to Area$_1$. When x$_1$ is to the right of x$_2$, Integral 1 includes areas that are not in the area of concern. This is accommodated by Integral 2, where the limits of integration will result in a negative value that directly counteracts the increased area of Integral 1. This is shown graphically in Fig. 3.9.

Calculation of Area$_2$ relies on the geometry of circular segments that was discussed previously. The area enclosed is a function of the distance between the two endpoints and the radius of curvature. The value of Area$_2$ can therefore be determined by the points x$_1$, x$_2$ and a radius of curvature R.

3.6.2 Possible Radii of Curvature

Not all radii of curvature are physically or geometrically possible. The value of R is a function of the contact coordinates and volume of the liquid phase. As discussed earlier, for droplets of small diameters, the radius of curvature must be constant across the entire
interface. In a two-dimensional cross section, the interface is pinned between two points on the surface. For a given pair of points, the minimum radius of curvature is half the distance between those points. An interface with a smaller radius of curvature could not intersect both triple-line points.

The curvature of the liquid/vapor interface can be positive or negative. Additionally, the contact angles can vary between 0 and 180°. Combining these geometric possibilities, there are four classifications of liquid-vapor interfaces that must be considered, and require alterations of the geometric constructions used to calculate areas. These classifications are shown graphically in Fig. 3.11. The curvature of the liquid/vapor interface can be negative, as in Fig. 3.11a and b, or positive, as in Fig. 3.11c and d. The equations involved are the same for both cases, but the sign of the curvature determines whether the circular segment adds to or decreases the liquid area.

The other classification is based upon the orientation of the circular segment. If we define $\omega$ as the angle between the interface and the line that connects the triple-points of the interface, as shown in Fig. 3.11, the value of $\omega$ alters the geometry of the circular segment. For $\omega < 90^\circ$, the area is calculated as described above. However, if $\omega > 90^\circ$, then the relevant liquid-phase area is given by

$$A = \pi R^2 - \frac{R^2}{2} (\theta - \sin(\theta))$$

(3.10)

and must be properly accounted for in the model.
3.7 Description of Model Figures

Fig. 3.1: Geometry of circular segment. Area of upper segment is dependent upon the chord length $C$ and radius $R$.

Fig. 3.2: Triangular area shown in Fig. 3.5 above. The area of the triangular segment is given by $A_{\text{triangle}} = \frac{C}{2} H$. 
Fig. 3.3: Possible non-physical geometry. In this case, the model does not account for the solid surface crossing the liquid/vapor interface and this geometry is removed from consideration.

Fig. 3.4: Schematic of simulated surface with features that are continuous along one axis. Machining methods like grinding can create surfaces of this type. Liquids in contact with surface features such as these can form high aspect-ratio morphologies.
Fig. 3.5: Schematic of a liquid droplet on a rough solid surface. The roughness affects the total interfacial areas and can therefore affect the preferred liquid configuration.

Fig. 3.6: Diagram showing the calculated areas for single-surface model. The total liquid volume can be calculated by adding the area of a circular cap (that intersects at $x_1$ and $x_2$) to an integral that accounts for the surface roughness.
Fig. 3.7: Optical microscopy of bond formed with optically transparent sapphire. The voids form high-aspect ratio morphologies.

Fig. 3.8: General liquid/vapor interfacial geometry for liquid front advancing between two surfaces. The void geometry is defined by the two contact points and the curvature of the interface.
Fig 3.9: Demonstration of area calculation for two possible positions of $x_1$ and $x_2$. Both integrals are positive for the trapezoidal shape shown in a), while the second integral shown in b) is negative. This, when added to Integral 1, results in correct calculation of the total area.
Fig. 3.10: Graphical representation of 4 possible configurations of sign of curvature and value of \( \omega \), the angle between Line_{x_1x_3} and the interface. a) Interfacial curvature is negative and \( \omega \) is less than 90°. b) Interfacial curvature is negative and \( \omega \) is greater than 90°. c) Interfacial curvature is positive and \( \omega \) is less than 90°. d) Interfacial curvature is positive and \( \omega \) is greater than 90°.
4.0 Results and Discussion

The model presented rapidly calculates many possible liquid configurations, and the corresponding total interfacial energy. Analysis of this data can demonstrate the relationship between surface roughness, liquid volume, interfacial energies, and the resulting liquid behavior. The most energetically preferred liquid configurations can be identified, and the smaller-scale energetic barriers to liquid movement can be quantified.

Descriptions of the simulated systems require length and interfacial-energy units. The model results presented below examine the effects of the amplitudes and wavelengths of roughness features, interfacial energies, and the amount of liquid present. As will be shown, many effects of a rough surface on wetting behavior scale with the height and length dimensions of the roughness features. As such, the following results are presented with dimensionless units, relative to a length scale, $L$, and an energy per area, $\gamma$. Discussion of length-scale effects is aided through the use of dimensionless terms. As discussed previously, for droplets smaller than the capillary length, it is safe to assume that gravitational effects can be neglected. Although this model is presented in terms of a dimensionless scale, it is important to consider gravity if the droplet becomes large enough. The numerical simulations presented therefore only allow comparison of the sub-capillary-length regime.

4.1 Radially Symmetric Surface Features

Wenzel's original analysis of surface roughness effects on observed contact angles was not directly applied to generically rough surfaces. The assumed geometry for the Wenzel model involved a droplet with a spherical-cap geometry, placed at the center of a radially symmetric, rough surface. As the liquid front extended or receded, the triple-line would encounter the same surface orientation along the entire circumference. This simplified the analysis considerably, allowing an analytical approach to modeling roughness effects on observed contact angles. The model presented in this work allows comparison of numerical simulations to roughness/wetting models that have been used for years, such as the Wenzel model.

As a basis for comparison, the total interfacial energy of a droplet on an ideally flat surface is presented. For a radially symmetric system, the geometric description of the system can be limited to a two-dimensional cross section. This cross section, if revolved about the vertical axis, describes the three-dimensional geometry of the system, as well as correctly accounting for surface-area and volumetric effects. All analysis for droplets on a surface will refer to surfaces that are symmetric about the point $x = 0$. The triple-line boundary of the droplet will be referred to as $(-x_c, x_c)$, but symmetry allows us to just refer to one contact coordinate, $x_c$.

One advantage of using numerical techniques to address this problem is the ability to fix the triple-line at any position. Due to the constraint that the liquid volume is conserved, the radius of the droplet is a function of the contact coordinate, as shown in Fig. 4.1. By fixing the contact point and volume, the surface area of both the solid/liquid and liquid/vapor interface is predetermined. The total interfacial energy can then be plotted as a function of...
contact point. For a perfectly smooth surface, this plot is shown in Fig. 4.2a. Three curves are shown, corresponding to the same liquid configurations, with different values of $\gamma_s$, $\gamma_w$, and $\gamma_v$. All three curves were calculated with a fixed amount of liquid, with a volume of 500 L$^3$. Young’s analysis of the interfacial energies would predict contact angles of 60°, 90° and 120° for the three systems plotted. Fig. 4.2b shows the resulting macroscopic contact angle for the liquid configuration depending upon the contact coordinate, $x_c$. By comparing the minimum total interfacial energies of the three curves in Fig. 4.2a with the macroscopic contact angles plotted in Fig. 4.2b, it is observed that Young’s analysis holds for a liquid in contact with a perfectly smooth solid.

As the surface roughness increases, the areas of the solid/liquid and liquid/vapor interface are affected. Wenzel’s analysis predicts that the macroscopic contact angle will change according to the equation

$$\cos(\theta_{\text{Wenzel}}) = r \times \cos(\theta_{\text{Young}}) \quad (4.1)$$

where $r$, the Wenzel roughness parameter, is the ratio of the true surface area covered by the liquid to the surface area of a perfectly smooth surface. In the case of a non-wetting liquid, $\theta_{\text{Young}} > 90^\circ$, and the value of $\cos(\theta_{\text{Young}}) < 0$. A value of $r > 1$ is therefore expected to increase the macroscopic contact angle, leading to a more non-wetting configuration. Conversely, if $\theta_{\text{Young}} < 90^\circ$, and the value of $\cos(\theta_{\text{Young}}) > 0$, increases in roughness are expected to decrease the macroscopic contact angle, enhancing the wetting of the liquid. Fig. 4.3 shows a simulated, radially symmetric surface that is the basis of the next two sections. The height of the surface is a sinusoidal function of the radial distance from the origin.

### 4.1.1 Radially Symmetric Surface – Amplitude Effects

Using numerical simulations, it is possible to examine the effect of the roughness feature’s amplitude on the liquid-droplet behavior. Two-dimensional cross sections of the liquid/solid system allow for easier visualization of the configurations described. Fig. 4.4 shows a two-dimensional cross section of a generic, radially symmetric, sinusoidal surface feature. The amplitude, $\alpha$, can be varied independently. The results presented in Section 4.1 are effectively for a surface with $\alpha = 0$. By varying $\alpha$, and systematically testing many values of the contact coordinate, $x_c$, we can begin to examine the effects of roughness on liquid behavior.

Initial results presented are for a system with a liquid droplet with a volume of 500 L$^3$, $\lambda = L$, interfacial energies of $(\gamma_s = 1 \gamma, \gamma_w = 1 \gamma, \gamma_v = 1 \gamma)$, and with $\alpha$ between 0.02 L and 0.4 L. Fig. 4.5 shows the effect of $\alpha$ on the total interfacial energy versus contact-coordinate profile. As seen in the plot, for low-$\alpha$ surface features, the curve is similar to that shown in Fig. 4.2a. With increasing $\alpha$, the roughness features create larger peaks and troughs in the energy/position curve. The plot shows portions that are blank. These areas are filled with contact points that cannot physically be obtained on the specified surface with the liquid volume used. Fig. 4.6 shows one such non-physical liquid configuration. For the given contact coordinate and liquid volume, a specific liquid/vapor interfacial curvature is required to fulfill the geometric requirements. In the case shown in Fig. 4.6, these requirements necessitate a
liquid/vapor interface that passes through the solid surface, resulting in a non-physical configuration. For a real system, the system could respond by separating into two droplets, but this can be energetically costly. For this radially-symmetric surface, the system could overcome some of these non-physical solutions by shifting to a non-radially symmetric configuration. In order to compare these results to roughness/wetting models presented previously, these non-physical configurations are removed from consideration.

By examining the morphology of these blank regions, one of the effects of surface roughness is observed. As $\alpha$ of the features increases, a larger range of configurations becomes inaccessible to the liquid droplet. Specifically, contact-coordinate regions where the liquid would contact the solid at high or low contact angles are the first to become inaccessible. In these regions, only the peaks of the surface features result in possible configurations.

The plot shown in Fig. 4.5 corresponds to total interfacial energies where the Young's contact angle is equal to 90°. As such, the general shape of the plot is similar to that shown in Fig. 4.2a for $\theta_\text{Young} = 90°$. The sinusoidal roughness topography creates local sinusoidal features in the energy profile that are overlaid upon the large-scale curvature. To demonstrate the effect of this change in the energy profile, Fig. 4.7 shows the total interfacial energy versus contact coordinate for the surface with $\alpha = 0.02 \text{ L}$. The energy profile shown in Fig. 4.7a shows slight perturbations that are the result of the surface roughness. In Fig. 4.7b, the macroscopically observed and local contact angles of the liquid surface are plotted as a function of contact coordinate. Due to the surface roughness, the local orientation of the surface is a function of position, and the local contact angle therefore diverges from the macroscopically observed contact angle. Fig. 4.8 shows a close-up view of the minimum total-interfacial-energy region, for both the energy profile and the contact-angle plot. Here it is clearly shown that the minimum-energy configuration occurs not when the macroscopically observed contact angle is equal to Young's predicted contact angle, but when the local contact angle equals 90°.

The results for this numerically simulated system are in conflict with the prediction of Wenzel's analysis. According to Eqn. (4.1), a system with $\theta_\text{Young} = 90°$ should not be affected by increasing roughness. In this case, Wenzel's roughness factor, $r$, is only equal to 1.0039. But Wenzel's model predicts no change in the macroscopically observed contact angle, while the numerical simulation shows an increase in the macroscopically measured contact angle of over 2°. Wenzel's analysis is based upon the change in solid/liquid interfacial area due to surface roughness. However, for a liquid that forms a Young's angle of 90°, the change in total interfacial energy only comes from changes in the liquid/vapor interfacial area. The model presented by Wenzel did not address the changes in liquid/vapor interfacial area due to the shifting of the liquid contact points. Therefore, the model predicts no change due to roughness for liquids with $\theta_\text{Young} = 90°$.

Using the same analysis for the roughest profile plotted in Fig. 4.5, we arrive at the energy profiles and contact-angle curves shown in Figs. 4.9 and 4.10. Both the energy profile and the macroscopic and local-angle curves show gaps corresponding to non-physical configurations, as discussed previously. The surface used for this analysis has $\alpha = 0.4 \text{ L}$ and $\lambda = 1 \text{ L}$. Again, the liquid volume used is 500 $\text{L}$. In this case, with much greater $\alpha$ but the same $\lambda$, the energy profile shows large energetic barriers for the liquid to spread over the rough features. Comparison of the energy profile to the angle curves (Fig. 4.10) shows that, again, the minimum total interfacial energy occurs when the local contact angle is equal to the Young's contact angle. In this case, Wenzel's analysis also holds true, as the macroscopic contact
angle equals 90° at the minimum-energy configuration. However, energetic minima do not occur with all liquid configurations that have a macroscopic contact angle of 90°.

Shuttleworth and Bailey\textsuperscript{112} presented an analytical model that showed that a liquid spreading over a liquid could be pinned at locations where the local contact angle equaled the Young's contact angle. Careful examination of Figs. 4.9 and 4.10 confirm the premise of their model. The energy profile shown in Figs. 4.9a and 4.10a passes through several local minima. At each of these configurations, the local contact angle is equal to the Young's contact angle. It is important to note that local energetic maxima also occur when the contact angle is equal to Young's angle.

For each simulated surface, it is possible to determine the lowest-energy liquid configuration and the resulting contact angles. Fig. 4.11 plots the macroscopic and local contact angles of the minimum-energy configurations for every energy profile shown in Fig. 4.5. The horizontal axis of the plot is $\alpha$ of the surface features. At small $\alpha$, there is no direct correlation between the macroscopic and local contact angles. This is most likely because the large-scale effect of droplet radius has a larger effect than the local deviation of the surface. As $\alpha$ becomes sufficiently large, both angles converge to the same value. In this region, the liquid is making contact near the bottom of a sinusoidal trough, making the macroscopic and local contact angles equal. Comparing these results to Wenzel's predicted analysis, we see that Eqn. (4.1) does not hold in this case. For a system with $\theta_{\text{Young}} = 90°$, Wenzel's model predicts no shift in observed contact angle for a rough surface. Examining Fig. 4.12, it is shown that even in this simple case, this does not hold. Wenzel's analysis was based solely upon the change in surface area, and did not consider the influence of the geometric form of the surface roughness.

The model allows variation of the interfacial energies as well as control of the surface features. For the same group of rough surfaces, Fig. 4.13 shows the energy profile as a function of contact coordinate and $\alpha$ of the surface feature for a liquid that forms a Young's contact angle of 60°. As in Fig. 4.5, the “blank” regions of the plot reflect non-physical liquid geometries. For high-$\alpha$ surface features, the minimum total interfacial energy shifts to higher contact coordinates, which corresponds to increased solid/liquid interfacial area. If the system involves a non-wetting liquid, with Young’s angle of 120°, the energy profile is shown in Fig. 4.14. In the case of a non-wetting liquid, the low-energy configurations are shifted towards lower contact coordinates. Increasing $\alpha$ leads to a decrease in contact coordinate for the minimum-energy configuration, an increase in the non-wetting behavior. This general trend agrees with Wenzel’s analysis for the effect of roughness, in which increases in surface roughness enhance the wetting or non-wetting character of the liquid.

Figs. 4.15 and 4.16 show the effect of increasing $\alpha$ on the macroscopic and local contact angles for wetting and non-wetting liquids. In both figures, the contact angles of the minimum total-interfacial-energy configurations are presented as a function of $\alpha$. The macroscopic contact angle for a wetting liquid (Fig. 4.15) continually decreases as $\alpha$ of the surface increases. The steps in the curve occur when the liquid spreads past a surface feature and moves to the next trough. The local contact angle does not continually decrease, but oscillates about the Young's contact angle. For a non-wetting liquid (Fig. 4.16), the macroscopic contact angle increases as $\alpha$ of the surface feature increases, and the local contact angle oscillates around the expected Young’s contact angle. Wenzel’s model predicts a continuous change in the wetting behavior, whereas the simulated data shows step-like behavior.

Research into wetting behavior often cites the most commonly used roughness parameter, Rq. Figs. 4.17 and 4.18 compare the macroscopic and local angles for three distinct
liquids with the $Rq$ value of the solid surface. These $Rq$ values are computed along a line that passes through the origin and exceeds the length scale of both the surface features and the liquid diameter. Measurements over lengths that are shorter than those of the surface features in question can lead to mischaracterization of the surface. Fig. 4.17 shows no direct correlation between the measured roughness parameter and the macroscopic contact angle for the wetting or non-wetting liquid. For the $\theta_{\text{Young}} = 90^\circ$ liquid, the macroscopic contact angle does not vary significantly from $90^\circ$. The general trend of increasing roughness enhancing the wetting or non-wetting character of the liquid is followed. A plot of the local contact angle of the minimum-energy configuration versus the roughness parameter $Rq$ (Fig. 4.18) again shows the local contact angle oscillating around the Young’s angle. There is no correlation between the local contact angle and the value of $Rq$.

4.1.2 Radially Symmetric Surface – Wavelength Effects

When $\alpha$ is fixed, the horizontal spacing of surface features ($\lambda$) can affect the wetting behavior of liquids due to the local change in surface slope. Fig. 4.19 shows the energy profile versus contact coordinate and $\lambda$ of a radially symmetric surface. All surfaces simulated for this plot have $\alpha = 0.2$ L and $\lambda$ varies between 0.5 and 5 L. The surface features are evident in the energy profile, as was observed with changes in $\alpha$. The surface roughness creates localized energy minima and maxima, with length scales that depend on $\lambda$. Each simulated surface has a liquid configuration with a minimum total interfacial energy. Figs. 4.20 - 4.22 plot the macroscopic and local contact angle for these minimum-energy configurations as a function of the $\lambda$ of the surface-feature for liquids with Young’s angles of 60, 90 and 120°. Again, the minimum-energy configuration generally has a local contact angle that is close to the Young’s angle. For the liquids with $\theta_{\text{Young}}$ equal to 60° and 120°, surfaces with small $\lambda$ result in macroscopic contact angles that deviate significantly from the Young’s angle. However, even with $\theta_{\text{Young}} = 90^\circ$, the macroscopic angle oscillates by as much as $40^\circ$.

Since $\alpha$ is constant for these surface profiles, and $Rq$ is a purely amplitude-dependent parameter, the results shown are also for a fixed value of $Rq$. As $\lambda$ is varied, the local contact angle changes slightly while the macroscopic angle changes dramatically. Therefore any characterization of the surface that relies solely on amplitude-based parameters cannot predict these contact-angle variations.

Wenzel’s roughness factor does change with $\lambda$; it is therefore possible to evaluate the accuracy of Wenzel’s model. Fig. 4.23 shows the macroscopic contact angle as a function of the Wenzel factor, $\tau$. For this simulation, decreasing $\lambda$ increases the surface area, and thus $\tau$. The general trend predicted by Wenzel’s model holds: greater roughness leads to enhancement of the wetting/non-wetting character of the liquid. Fig. 4.24 plots the simulated macroscopic contact angle versus $\tau$ and compares it to the actual predictions of Wenzel’s model. While the trend holds, the simulated contact angles differ by as much as $18^\circ$ from the predicted values. A similar relationship holds for the $\theta_{\text{Young}} = 120^\circ$ data. Wenzel’s model does not predict the local contact angle. As Fig. 4.25 shows, the increasing roughness factor has little effect on the local contact angle.
4.1.3 Radially Symmetric Surface – Fractal Surfaces

Real surfaces generally exhibit multiple roughness features with different amplitudes and wavelengths. To model such realistic surfaces, simulations were performed on fractal surfaces with ten distinct surface features. These surfaces are still treated as being radially symmetric; this geometry could result from a sample that was machined by a lathe. For this section, forty separate fractal surfaces were simulated, each with randomly selected values of $\alpha$ and $\lambda$.

4.2 Continuous Surface Features

As stated previously, a common result of certain machining processes is a surface-roughness features that are continuous along one axis. An example of this is shown in Fig. 3.9. For a surface topography of this type, a two-dimensional cross-section of the surface can fully define the surface features. It has been shown that liquid in contact with surfaces of this type can form microstructural features, notably pores, of high aspect ratio. To model this system, all analysis will be performed based upon tube-like configurations. By calculating the total interfacial energies for a two-dimensional cross section with unit depth, the results can be generalized approximate those of a liquid or pore channel with very high aspect ratios. The ends of the liquid tube will affect the total interfacial energy of the liquid configuration, but this correction is small for very high aspect ratios. All volumetric and surface measurements will be discussed in terms of a unit depth.

This system has features that are continuous along one axis, and therefore does not have radial symmetry as discussed in the previous section. As such, it is possible for contact points $x_1$ and $x_2$ to move independently. In this model, the liquid volume per unit depth, and thus cross sectional area is held constant, while the contact points are shifted. For each contact-point pair, the volume requirement is met by adjusting the droplet radius. This is similar to the radially symmetric configurations described previously, but the variation in two contact points means the contact angle is not necessarily equal along both contact lines, which can result in more complicated geometries and associated energy profiles. Fig. 4.29 shows two possible liquid configurations that have the same volume per unit depth and the same contact point $x_1$. By varying the contact point $x_2$, the solid/liquid and liquid/vapor interfacial areas change, and with them the total interfacial energy. For the two configurations shown, the change in $x_2$ alters the contact angle at $x_1$, but can also lead to significant changes in the local contact angle at $x_2$ due to differences in the surface topography.

4.2.1 Continuous Surface Features – Amplitude Effects

The first effect discussed for surface features that are continuous along one axis will be demonstrated using a simple sinusoidal curve with varying $\alpha$. As a reference, we can examine the effect of varying the contact points on a flat surface. This is effectively a sinusoidal surface with $\alpha = 0$. For this analysis, we will calculate possible liquid configurations for a liquid with volume $10 \, \text{L}^3$ per unit depth. The total-interfacial-energy profile that results from fixing $x_1$ at
0 and varying the other is shown in Fig. 4.30. This profile corresponds to a liquid with $\theta_{\text{Young}} = 90^\circ$. The total interfacial energy goes through a minimum that corresponds to the configuration with contact angles equal to the Young’s angle. Since this analysis is performed on a perfectly flat surface, the minimum total interfacial energy occurs when $x_3$ is a specific distance from $x_1$, which can be calculated based upon the interfacial energies and liquid volume used. For a flat surface, an equal displacement of both contact points, that keeps $x_2 - x_1$ constant, results in a rigid displacement of the minimum-energy configuration.

This effect is clearly demonstrated by varying both contact points. Fig. 4.31 shows the effect of allowing both $x_1$ and $x_2$, and thus $x_2 - x_1$, to vary. The contact points are defined such that $x_1 < x_2$. This limits the possible configurations to those shown in the triangular region of Fig. 4.31. The front boundary of the three-dimensional surface corresponds to the energy profile shown in Fig. 4.30 where $x_j = 0$ L. As $x_j$ is varied, the energy profile is effectively shifted by a corresponding amount. The resulting energy profile is what is plotted in Fig. 4.31. The line along which the energy is at a (constant) minimum value is associated with the rigid shifts described previously in which $x_3 - x_1$ is held constant. This translation thus generates a family of liquid drops of identical geometry but distinct positions along the surface. These configurations are all related by a rigid displacement of the equilibrium configuration.

Introducing a single sinusoidal perturbation to produce a “rough” surface changes both the energy profile and the contact angles. Figs. 4.32 – 4.34 show the energy profile versus contact points for three distinct surfaces with distinct values of $\alpha$. All three surfaces have a sinusoidal feature with $\lambda = 1$ L, extending along one axis. The amplitudes corresponding to the energy profiles shown in Figs. 4.32 – 4.34 are $\alpha = 0.02$ L, 0.06 L, and 0.12 L, respectively. The volume and Young’s contact angle are held fixed at the same values of 10 L$^3$ and 90$^\circ$, to allow a direct comparison to the results in Fig. 4.31. Several effects of increasing roughness are evident. While the general form of the plots is unchanged, there are many local deviations in the energy profile that are the result of the sinusoidal feature. Global energy minima are no longer continuous across the surface. That is, while it is possible to move from one minima to another through a translation of the contact points, there is now an energetic barrier to this translation. Additionally, the minimum-energy configuration is not defined completely by the distance between contact points, as it was with the flat surface. The local deviations in the surface have the potential to alter both the solid/liquid and the liquid/vapor interfacial areas for a given pair of contact points.

Another important feature of these energy profiles, especially observed in Figs. 4.33 and 4.34, are the large gaps that represent non-physical solutions. As seen in Fig. 4.31, increasing $\alpha$ leads to regions where the system cannot fulfill all of the restrictions imposed by this model. These regions are largely confined to the upper-left region of the plot, where the two contact points are in close proximity. In these regions, the radii of curvature required to fulfill the volume requirement prevent the liquid droplet from fully penetrating into the troughs of the surface. As $\alpha$ increases, these regions become larger, until only the peaks of the sinusoidal features are accessible to the liquid. In this region, the development of Cassie spaces is one option for the liquid droplet.\textsuperscript{111}

The results of this simulation provide useful insight into the importance of both the macroscopic and local contact angle. As $\alpha$ increases, the horizontal position of the minimum-energy configuration does not shift. Fig. 4.35 shows four separate minimum-energy configurations on surfaces with different $\alpha$. The triple lines remain at the same positions on
the sinusoidal curve as \( \alpha \) increases. Additionally, the radius of curvature varies insignificantly as \( \alpha \) of the surface feature increases. Fig. 4.36 shows the macroscopic and local contact angles of the minimum-energy configuration as a function of \( \alpha \). The macroscopic contact angle remains constant as \( \alpha \) increases. The local contact angle increases significantly as \( \alpha \) increases. While the contact point does not shift dramatically, the slope of the surface is a function of \( \alpha \), leading to a greater local contact angle. For a liquid with a Young's angle of 90°, the liquid configuration is not affected greatly by \( \alpha \).

Liquids with wetting or non-wetting contact angles are also considered. Fig. 4.37 shows the total interfacial energy versus contact coordinate for a liquid with Young's angle of 60°. Comparing this energy profile to that shown in Fig. 4.33, the same regions of non-physical configurations are evident. These are a function of geometry, not interfacial energy. The change in value of the solid/liquid interfacial energy results in decreased total interfacial energy when the solid/liquid area is large (contact points far apart), and a decrease in total interfacial energy when the solid/liquid area is small (contact points close together). This is evident in the energy profile shown in Fig. 4.37, shifting the location of the low-energy configurations. These low-energy configurations have different geometries, and therefore different contact angles than those for a liquid with a Young's angle of 90°.

As with the 90° liquid, the preferred contact points for the 60° and 120° liquids remained near the peaks of the sinusoidal features. Figs. 4.38 and 4.39 show the macroscopic and local contact angle of liquids with Young's angles of 60° and 120° respectively as a function of \( \alpha \) of the surface features. Starting with Fig. 4.38, several important features of the plot can be connected to physical changes in the liquid. The macroscopic contact angle remains close to the expected Young's angle until \( \alpha \) reaches a critical value. For \( \alpha \) greater than \( \sim 0.16 \) L, the increase in solid/liquid interfacial area due to roughness makes it energetically favorable for the contact points to move farther apart by \( \lambda \); the liquid still contacts at the peaks of the surface features, but covers one more wavelength of the surface. At the same critical \( \alpha \), the local contact angle also decreases due to this shift in contact position. In general, as \( \alpha \) increases, the local contact angle increases, due to the changes in the surface orientation. This increase in interfacial area occurs several times as \( \alpha \) increases, creating the saw-tooth pattern seen. The local contact angle remains within \( \sim 15° \) of the expected Young's angle, while the macroscopic contact angle continuously decreases with increasing roughness.

Examining Fig. 4.39, a similar behavior is seen for the liquid with Young's angle of 120°. For this liquid, the initial solid/liquid interfacial area starts off smaller, as expected for a non-wetting liquid. As \( \alpha \) increases, the macroscopic angle remains fairly constant until a critical value of \( \alpha \) is reached. Again, there is a jump in contact angle, in this case due to a reduction of the liquid-droplet footprint. This decrease in interfacial area is achieved by the contact points moving closer by \( \lambda \); the liquid still contacts at the peaks of the surface features, but covers one less wavelength of the surface.

The macroscopic and local contact angles can be compared to the \( R_q \) roughness parameter and the Wenzel roughness factor. Fig. 4.40 shows the macroscopic contact angle for all three liquids as a function of \( R_q \). The increasing roughness has little effect on the 90° liquid, but the 60° liquid becomes more wetting and the 120° liquid becomes less wetting as \( R_q \) increases. The general trend that increasing roughness enhances the wetting or non/wetting nature of the liquid is followed.
Examining the change in local contact angle versus roughness value (shown in Fig. 4.41), it is much harder to describe any general trend. As Rq increases, the 60° liquid oscillates around the expected Young's angle. The 90° and 120° liquids are not as well behaved. The local contact angle of the 120° liquid decreases significantly, largely due to the change in slope of the surface features. At the same time, the local contact angle of the 90° liquid increases until it exceeds 120°. Again, these changes are strongly influenced by the local orientation of the surface, making a universal prediction of this angle unlikely. The macroscopic contact angle is plotted against the Wenzel roughness factor in Fig. 4.42, allowing comparison of these results to Wenzel's model. Here, the Wenzel model predicts the general trend of the macroscopic contact angle, but errs by a larger margin at high roughness values.

4.2.2 Continuous Surface Features – Wavelength Effects

Numerical simulations on the effect of surface-feature wavelength were also performed. For this simulation, all surfaces topographies were defined as sinusoidal profiles with \( \alpha = 0.1 \) L and varying \( \lambda \). Wavelengths were varied between 0.5 L and 5 L. The liquid volume was fixed at 10 L³ and the total interfacial energy of three liquids were examined, corresponding to liquids with Young’s contact angles of 60°, 90° and 120°.

Figs. 4.43 through 4.45 plot the total interfacial energy versus contact coordinate for three surfaces, with \( \lambda = 0.5 \) L, 1.5 L and 2.5 L, respectively. All three surface features have the same \( \alpha \), but the difference in \( \lambda \) leads to changes in the local orientation of the surface. Additionally, small \( \lambda \) reduces the inter-peak separation distance, leading to a large number of non-physical configurations for proximate contact points. Comparing the upper-left regions of Figs. 4.43 through 4.45, the increase in possible configurations with wavelength is evident. Looking at the depression of each energy profile, the effect of \( \lambda \) is also demonstrated by the spacing between energetic minima. As \( \alpha \) is unchanged between these simulations, the energetic barrier does not vary significantly, but the number and location of energetic minima is a function of \( \lambda \).

Comparing the minimum-energy configurations to amplitude-based roughness parameters is not useful. The value of Rq for all surfaces used in this section is equal, since all simulated-surface profiles have a sinusoidal form and the same \( \alpha \). The Wenzel roughness parameter, however, is a hybrid parameter that depends upon both \( \alpha \) and \( \lambda \) of the surface features. Fig. 4.46 plots the macroscopic contact angle of minimum-energy configurations versus \( \lambda \) of the profile for a liquid with Young’s angle of 90°. Both contact angles oscillate as \( \lambda \) increases. These oscillations occur when it becomes energetically favorable for a discontinuous shift in the triple-line positions. The macroscopic contact angle oscillates about the expected Young’s angle, with an average of 88.7° and a standard deviation of 5.6°. The local contact angle varies much more significantly, with an average of 86.6° and a standard deviation of 12.7°.

Repeating this exercise for liquids with Young’s angles of 60° and 120°, a similar trend is observed. Figs. 4.47 and 4.48 plot the contact angles of the minimum-energy configurations versus \( \lambda \) of the surface-feature for liquids with Young’s angles of 60° and 120°, respectively. In both cases, the macroscopic contact angle varies about the expected Young’s angle, while the local contact angle varies more significantly. The summary of the average and standard deviation of the contact angles for all three liquids is contained in Table 4.2. For all three
liquids, the deviation of the local contact angle is ~2× greater than the deviation of the macroscopic contact angle.

As was stated previously, the Wenzel roughness parameter does change with λ. Fig. 4.49 plots the macroscopic contact angle versus the roughness parameter, r. Wenzel's model predicts the trend of this data very well. Again, the macroscopic contact angle oscillates around the Wenzel prediction, with the largest discrepancies at low values of r.

### 4.2.3 Continuous Surface Features – Symmetry of Contact Points

The previous two sections discussed highly symmetric surfaces. Both α and λ effects were discussed in terms of sinusoidal profiles. All results presented above had additional symmetries in the minimum-energy configurations. While it is possible for the liquid to contact the surface, for example, at a surface-height maximum on one side and a surface-height minimum on the other side, these configurations always resulted in higher total interfacial energy. All minimum-energy configurations had symmetrical contact points. This does not necessarily hold true for surfaces that are not as symmetric.

### 4.2.4 Continuous Surface Features - Fractal Features

Fractal surfaces were simulated, with surface profiles defined by ten distinct surface features, with varying α and λ. The surface profile is assumed to extend indefinitely in one direction. For this section, forty distinct fractal surfaces were simulated, each with randomly selected α and λ.

For surfaces with profiles that are continuous along one axis, the analysis can be performed based upon the orthogonal cross section and assuming a unit depth. The contact points were varied between 0 L and 10 L, for a liquid with a volume of 10 L^3 per unit depth. The interfacial energies were then varied to model three liquids, with \( \theta_{\text{Young}} = 60^\circ, 90^\circ, \) or \( 120^\circ \). For each surface, the minimum total interfacial energy was calculated, and the resulting macroscopically observed and local contact angles were recorded.

As discussed in the previous section, the possibility exists for different contact angles at \( x_1 \) and \( x_2 \). Fig. 4.50 plots the macroscopic contact angle at \( x_1 \) versus the macroscopic contact angle at \( x_2 \). The dashed line represents when the macroscopic contact angles on both sides are equal. For all three liquids simulated, most minimum-energy configurations are close to this dashed line. It is worth noting that the 90° and 120° data show some overlap. These configurations do not occur on the same fractal surface, but demonstrate an interesting finding. Wetting experiments that were conducted on different surfaces can measure similar macroscopic contact angles for liquids with significantly different Young's angles, depending upon the topography of the solids used.

The comparison of the local contact angles of the minimum-energy configuration is provided in Fig. 4.51. This data shows no correlation between local contact angles for the minimum-energy configurations. The local contact angle is strongly affected by the local surface orientation. For these fractal surfaces, the minimum-energy configurations contact the surfaces
in two locations with different surface orientations, leading to the large variation in local contact angles.

Fig. 4.52 plots the macroscopic contact angle at contact point \( x_1 \) versus the roughness parameter \( R_q \), for each fractal surface. The best linear-fit curve is shown for each set of data. For the 90° liquid, the average macroscopic contact angle remains close to the Young's angle, but still shows a range of over 20°. Increasing roughness appears to lower the macroscopic contact angle of the wetting, 60° liquid. The same effect is seen in the 120°-liquid data, with a decrease of the observed angle as the roughness parameter increases. However, based upon the large variation in data points, this trend is not significant. Both the 60° and 120° data sets show considerably more spread than the 90° data. Fig. 4.53 plots the same relationship for the macroscopic contact angles at the second contact point, \( x_2 \). This plot is very similar to Fig. 4.52, as would be expected by examining Fig. 4.50, although the slope of the best-fit line for the 120° data is not as negative.

The relationship between the roughness parameter \( R_q \) and the local contact angles is shown in Fig. 4.54. Here, the 60° and 90° best-fit lines follow a similar trend to that shown with the macroscopic contact angles. However, the best-fit line of the 120° data has a positive slope, meaning a general increase in the local contact angle with increasing roughness, most likely due to the sensitivity to the local orientation of the solid surface. The data itself shows large variations for all three liquids. The data for all three liquids overlap, presenting no clear relationship between local contact angle and the roughness parameter \( R_q \). Table 4.3 summarizes the data plotted in Figs. 4.52 through 4.54. These statistics combine the contact angles for both contact coordinates. While the averages of the local and macroscopic contact angles are quite close for all three liquids, the standard deviation of the local contact angles are between \( \sim 3 \times \) and \( 6 \times \) greater than for the macroscopic contact angle. This implies a much stronger relationship between macroscopic contact angle and the roughness parameter \( R_q \).

Examining the general trend of the energy profiles in Figs. 4.31 through 4.34, the energetic effect of contact-point separation is significantly larger than the effect of local surface orientation. The macroscopic contact angle is a product of this triple-line separation, while the local contact angle is affected strongly by the local surface orientation.

The comparison between this numerical simulation and Wenzel’s model is shown in Figs. 4.55 and 4.56. These plots show the macroscopic contact angle versus Wenzel's roughness parameter, \( r \), for the contact points \( x_1 \) and \( x_2 \) respectively. For both data sets, the 60° and 90° data is clustered about the line showing Wenzel's prediction. As the roughness parameter increases, the 90° contact angles remain near 90°. With increasing roughness, the 60° liquid macroscopically appears to decrease in contact angle. As expected, the 120° liquid contact angle does increase with increasing roughness, but the Wenzel model consistently predicts a larger contact angle.

For each fractal surface, possible liquid configurations with contact coordinates between \( L \) and \( 10L \) were simulated, for a liquid with a volume of \( 500 \) \( L^3 \). The interfacial energies were then varied to model three conditions: \( \theta_{\text{Young}} = 60°, 90°, \) or \( 120° \). For each surface, the minimum total interfacial energy was calculated, and the resulting macroscopically observed and local contact angles were recorded. Fig. 4.26 plots the macroscopic contact angle versus the roughness parameter \( R_q \), for each fractal surface. The best linear-fit curve is shown for each set of data. Using these lines as a guide, increasing roughness leads to very modest enhancement of the apparent wetting/non-wetting nature of the liquids. However, the individual data points vary
considerably from these best-fit curves. Similarly, the local contact angles are clustered about the Young’s angle, as shown in Fig. 4.27. Again, the best linear-fit curve is shown as a solid line, which remains near the expected Young’s angle for all three data sets. Table 4.1 lists the averages and the standard deviations of the contact angles for each liquid. As was shown before, the local contact angle of the minimum-energy configuration is closer to the Young’s contact angle, but shows more variation in the data. Fig. 4.28 plots the macroscopic contact angle of the minimum-energy configuration versus Wenzel’s roughness factor, r. The macroscopic contact angle predicted by the Wenzel model is shown as a solid curve. For the fractal surfaces simulated, the general trend of the Wenzel model does hold, but individual surfaces show significant deviations from the model.

4.3 Comparison to Previous Studies

The behavior of liquids in contact with rough solids has been the focus of scientific study for nearly a century. A significant number of papers have focused on replicating hydrophobic behavior observed on plant leaves and developing superhydrophobic surface through the use of micro-scale roughness. Associated models focus on the enhanced hydrophobicity due to an increase in solid/liquid interfacial area. The results agree with the model presented here, in that increased roughness increases the contact angle for non-wetting liquids.

A computer simulation of liquid configurations was performed specifically for geometrically-anisotropic surfaces. This work focused on surface geometries that were similar to the continuous surfaces presented here, but the surface features were modeled as square-wave features instead of sinusoidal features. The model pinned the liquid droplet to the edges of these pillars and calculated the low-energy liquid geometry that corresponded to this state. The simulations found that the droplet will form non-spherical geometries, leading to high-aspect ratios.

Experimental studies of enhancing wetting as a result of roughened surfaces have been performed. One study of polymer surfaces found that the contact angle of diiodomethane on various polymers could be decreased from 59° to 46° when increasing Ra from ~0.2 µm to 4 µm. Wetting measurements of initial contact angles of molten Si on graphite showed that increasing the Ra roughness from 0.11 µm to 0.56 µm lowered the macroscopic contact angle from ~25° to 0°, but the formation of a reaction layer occurs rapidly with this system. A study of water contact angles on polycrystalline TiO₂ found that the Wenzel model predicted a larger shift in the macroscopic contact angle than observed. Increasing roughness was also found to enhance film-stability, preventing rupture by enhancing the wetting of a liquid, due to increases in favorable solid/liquid interfacial area. A study of different types of roughness features, including radially symmetric and continuous surface features showed that Wenzel’s model was useful in predicting the contact angles. It also showed that spreading over a continuous surface occurred by irreversible jumps over energetic barriers.

Numerical simulations have also been applied to wetting/roughness studies. Most studies have found that hydrophilic liquids exhibit enhanced wetting with increasing roughness. However, a computational model of liquids and roughness on the molecular scale predicts that at that scale, a hydrophilic liquid would see an increase in contact angle with
roughness. Several studies have confirmed that Wenzel’s model breaks down at nano length scales.\textsuperscript{139,140} A theoretical work treating a surface as fully fractal found no change in wetting angle with roughness for liquids in a static configuration.\textsuperscript{141} This analysis was performed for a two-dimensional liquid front. A continuation of the work found that when dynamic processes were considered, increasing the roughness of the surface was found to increase the contact angle, independent of the Young’s contact angle.\textsuperscript{142} This work included the force of gravity in the theory and subsequent numerical simulations. Other theoretical works have correlated increasing roughness to increased contact angles in hydrophobic systems and reduced contact angles in hydrophilic systems.\textsuperscript{143,144} All of these works have focused on liquids in contact with a single substrate. To fully understand the importance of roughness in liquid-state joining, it is necessary to consider a liquid that forms between two solid substrates.

### 4.4 Liquid Layers Between Two Surfaces

In PTLJ joining of ceramics, the liquid layer develops between two dissimilar solid surfaces. The metallic liquid forms between a ceramic solid and a metallic solid, each with some level of surface roughness. The redistribution of a liquid between two surfaces also depends upon the relative values of the interfacial energies involved. For a liquid front, moving between two surfaces, the roughness will affect the total-interfacial energies in two ways. The distance between surfaces is a function of position, changing the liquid/vapor interfacial area. Additionally, the roughness changes the local orientation of the surfaces, altering the energetic barrier for movement of the liquid front.

For a liquid/vapor interface between two dissimilar solids, there exist two distinct contact angles: one that defines the boundary between the solid/liquid/vapor phases for each solid surface. As stated previously, the Young’s angle for a non-reactive liquid metal in contact with a solid ceramic is often $\sim 120^\circ$, while a metallic liquid in contact with a metallic solid usually forms a contact angle $<< 90^\circ$. The behavior of this liquid, and its ability to fill the inter-solid volume, can strongly affect the strength of the joined assembly.

The numerical simulations presented in this section discuss a liquid that is filling the space between two dissimilar solid surfaces. The liquid/vapor interface is assumed to separate a liquid film of infinite extent and a vapor of infinite extent parallel to the interface. The focus is thus on the energetics of displacing the interface. This model differs from the one-surface simulations discussed earlier in that the liquid volume in the calculation changes. This would treat situations where an excess of liquid is available to fill voids, and thus focuses attention on whether this “filling” is energetically favorable. In this simulation, the triple-line positions are not fixed. Instead, a simulation is performed for a specific region of the system, and the volume of liquid in this region changes. For each liquid volume, many possible triple-line positions are tested. This is shown schematically in Fig. 4.57. In this diagram, two possible liquid/vapor interfaces are shown. For each of these geometries, the volume of the liquid is conserved through changes in the liquid/vapor interfacial curvature. The total solid/liquid and liquid/vapor interfacial areas differ between these geometries. The preferred liquid/vapor interfacial geometry will depend upon the values of $\gamma_{sl}$ and $\gamma_{sv}$ for both solid surfaces and the value of $\gamma_{lv}$. 

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47
To simulate the change in total-interfacial energy as the liquid/vapor interface translates horizontally, the volume of liquid is systematically increased. The resulting change in total-interfacial energy determines whether the liquid will spontaneously advance through the inter-solid channel, or will be locally pinned in place. In a real system, this pinning action can be significantly more complicated than is possible to model in this simulation. Changes in the surface geometry with position could act to pin the liquid front locally, while allowing advancement in different areas. These simulations can be performed for different values of Young's angle on each surface to determine the relationship between surface roughness, contact angles, and the ability of a liquid to fill interfacial voids in a PTLP process.

4.4.1 Two-Surfaces: Continuous Surface Features

As stated previously, a common result of some machining processes is a surface roughness that is continuous along one axis, as shown in Fig. 3.4. This section will deal with a liquid entrapped between two such surfaces. With surfaces of this type, high-aspect-ratio voids form, as seen in Figs. 3.7. To model these liquid configurations, analysis will be performed for two-dimensional cross sections, assuming unit depth. The inter-solid volume will vary in some simulations. As such, plotting results as a function of liquid volume will not always be intuitively obvious. Additionally, since the triple-line positions will vary non-linearly with the amount of liquid in the system, this does not provide a good basis for comparison. Instead, energy profiles will be presented in terms of the horizontal "position" of the liquid/vapor interface. For each liquid volume, one possible liquid configuration corresponds to a completely flat liquid/vapor interface that is also vertical. Results will be plotted as a function of this theoretical vertical interface, even when the preferred liquid configuration has a different interface. The total-interfacial energy is plotted relative to the same region with no liquid present, and the relative values thus provide a measure of whether the liquid phase infiltration is favorable.

4.4.1.1 Two Surface Amplitude Effects

Previously, a liquid in contact with a single surface with a sinusoidal profile was considered. Here with two solids that normally have distinct contact angles, the energetics of a liquid constrained between two rough surfaces will be more complicated. The amplitude of the sinusoidal profile of each surface can affect the behavior of the liquid in multiple ways: the amplitude of the surface features affects the local orientations of the surfaces, as well as controlling the inter-solid distances. Numerical simulation allows independent variation of the roughness of each surface, providing a comparison of the relative importance of these two effects. The first amplitude-based simulation involves the bottom surface being ideally flat, while the top surface has a sinusoidal surface profile with controlled amplitude $\alpha$ and wavelength $\lambda = 1$ $L$, where $L$ is the relative measurement of length used throughout this work. As $\alpha$ is varied, the volume between the solids does not change, but the local orientation and distance between the surfaces does vary. A schematic of this system is shown in Fig. 4.58.

For systems with two dissimilar surfaces, the preferred configuration is affected by the Young's angle of the liquid on both the top and bottom surfaces. As a basis of comparison, the
energy of a liquid entrapped between two ideally flat surfaces is presented. Young's angle reflects the energetic change of advancing a liquid front along a flat surface. For liquids that exhibit a Young's contact angle of 90°, there is no change in interfacial energy when an area of solid/vapor interface is changed to a solid/liquid interface. A wetting contact angle \( \theta_{\text{Young}} < 90° \) means it is energetically favorable when a liquid covers a solid/vapor interface. For a non-wetting contact angle \( \theta_{\text{Young}} > 90° \), it is energetically unfavorable when a solid/liquid interface replaces a solid/vapor interface.

When a liquid is entrapped between two flat surfaces, the sum of contact angles can be related to the energetic change when the liquid advances. For contact-angle sums equal to 180°, there is no change in total-interfacial energy when the liquid advances, and the liquid/vapor interface that forms will be flat. This holds true for any combination of contact angles that add to 180° (60°-120°, 90°-90°, 120°-60°, etc.). Liquids with contact-angle sums < 180° will reduce the total-interfacial energy by advancing between two flat surfaces, and will form a liquid/vapor interface with negative curvature. For contact-angle sums > 180°, it is energetically unfavorable for the liquid to advance, and the liquid/vapor interface will have positive curvature. Research into liquid-state joining often considers the contact-angle sum < 180° as the required condition for favorable wetting.\(^{21}\) One effect of surface roughness is to change the local orientation of the surface, resulting in a more stringent contact-angle requirement.

To begin this discussion, the results of a system are presented where the Young's angle on both surfaces is 90°. As a basis for comparison, when \( \alpha = 0 \), the preferred liquid configurations form vertical liquid/vapor interfaces, with macroscopic- and local-contact angles equal to 90°. A Young's contact angle of 90° occurs when \( \gamma_s = \gamma_w \). Therefore there is no associated change in total-interfacial energy when the liquid/vapor interface is shifted in this system. As \( \alpha \) increases, the total-interfacial energy does change as a function of liquid/vapor interface position. For this numerical simulation, as the volume of liquid is increased, the preferred liquid configuration is determined by varying the triple-line positions, and determining the minimum-total-interfacial-energy configuration. These results are shown in Fig. 4.59. The increase of \( \alpha \) leads to energetic barriers to liquid penetration. Graphically, an energetic barrier to liquid penetration can be identified by the slope of the energy profile shown in Fig. 4.59. The liquid can become locally pinned whenever an increase in the liquid front position raises the total-interfacial energy. Therefore, any point on the surface with positive slope along the liquid front axis is a point where the liquid will become pinned. Due to the variable distance between the solid surfaces, the liquid/vapor interface area is minimized when the two surfaces are close. For the liquid to move past these points, the liquid/vapor interface has to extend, increasing the total-interfacial energy.

As with the 90°-90° system just discussed, a system with Young's contact angles of 60°-120° or 120°-60° in a smooth channel (\( \alpha = 0 \)) shows no change in total-interfacial energy with a translation of the liquid/vapor interface. As \( \alpha \) increases, it is not energetically neutral for the liquid to advance. Fig. 4.60 shows the total-interfacial energy as a function of \( \alpha \) and the liquid/solid-interfacial position for a system with Young's contact angle of 60° on the rough surface, and 120° on the smooth surface. Note the difference in scale on the total-interfacial energy axis. The general change in the energy profile with increasing \( \alpha \) is a decrease in the total-interfacial energy. This effect becomes more pronounced with large \( \alpha \) due to the increase of solid surface area due to the rough profile. Similar to Wenzel's analysis of a single-surface system, the increase in surface area is beneficial when the Young's angle on the rough surface is
< 90°, in that it decreases the total-interfacial energy when the liquid advances between these two surfaces. Again, there are local deviations in the energy profile that correspond to increases in the liquid/vapor interfacial area, but these barriers are significantly reduced compared to the 90°-90° system. While it is possible that the liquid would be pinned by these local effects, the total-interfacial energy is significantly decreased by the advancement of the liquid/vapor interface, especially at large $\alpha$.

In contrast, a system with Young’s contact angles of 120° on the rough surface and 60° on the smooth surface increases the total-interfacial energy by advancing the liquid/vapor interface. Similar to Wenzel’s analysis of a non-wetting liquid in contact with a single rough solid, the increased surface area inhibits liquid spreading. The energy profile for this system is shown in Fig. 4.61. Again, when $\alpha = 0$, there is no energetic change with the position of the liquid/vapor interface, because the sum of the Young’s contact angles is 180°. In this case, the increasing surface area on the rough solid makes it energetically unfavorable for the liquid/vapor interface to proceed. In fact, the system simulated would lead to a minimization of the solid/liquid interfacial area on the rough surface, increasing the void population in a PTLP joining process.

These trends are observed in the results for other Young’s contact angle pairs. For systems with a wetting contact angle on the rough surface, it is energetically favorable for the liquid to penetrate, with small energy barriers encountered whenever the inter-solid distance is minimum. When the Young’s contact angle on the rough surface is 120°, it is energetically unfavorable for the liquid to advance. These effects are altered by the Young’s contact angle on the flat surface, but the overall trend holds. As an example, the energy profile for 60°-60° and 120°-120° systems are shown in Figs. 4.62 and 4.63. As expected, the 60°-60° system has a large driving force for liquid penetration at all values of $\alpha$. The effect of increasing $\alpha$ is not as important compared to the 60°-120° energy profile. In the 60°-60° case, the increased surface area with increasing $\alpha$ decreases the total-interfacial energy when the liquid front proceeds, i.e., no energetic barriers exist. However, in the 60°-120° system, where there was no driving force for liquid advancement when $\alpha = 0$, the increase of surface area plays a larger role in making it energetically favorable for the liquid front advance. Similarly, the 120°-120° system shown in Fig. 4.63 shows an energetic barrier to advancing the liquid/vapor interface even when $\alpha = 0$. The increase of surface area due to increasing $\alpha$ provides an additional energetic barrier, but this effect is small compared to the behavior of the system when $\alpha = 0$.

As stated previously, there can be two energetic effects of increasing $\alpha$ on the total-interfacial energy: the separation between surfaces and the local orientation of the surfaces. To try to provide a comparison of these effects, the geometry of the system is modified slightly. For these simulations, both surfaces are rough, with sinusoidal profiles with equal $\alpha$. Again, $\lambda = 1$ L. The bottom surface has been shifted so that the peaks of both surfaces are aligned. A schematic of this geometry is shown in Fig. 4.64. Using this geometry, the inter-solid distance is equal to that in the previous simulation when $\alpha$ is reduced by half (shown schematically in Fig. 4.58), while the local orientations of both surfaces are affected. The results of these numerical simulations are presented in the same format used for the previous geometry. For this system, it does not matter which surface has a specific Young’s contact angle. That is, the results of the simulation for a 60°-120° system are identical to those of a 120°-60° system.

To begin this analysis, the energy profile of the 90°-90° system is presented in Fig. 4.65. Again, increasing $\alpha$ leads to increases in the energetic barriers. There is no driving force for continued liquid penetration. The effect of the roughness is to make certain liquid/vapor
interfaces energetically preferred, based upon the interfacial area required. Comparing this plot to that shown in Fig. 4.59, the major difference is the development of a secondary minimum of the energy profile, especially at large $\alpha$. The largest total-interfacial energies for this system occur when the liquid/vapor interfacial area is maximum. Generally speaking, this occurs when the inter-solid distance is largest. In the one-rough surface/one-flat surface system, forming a vertical interface minimized the liquid/vapor interfacial area. In the two-rough surfaces system, the interfacial area can be reduced slightly by forming a flat, but tilted interface. While the vertical spacing between the two solids is the same between the one-rough surface system and the two-rough surface system, this only holds true looking at a single horizontal position. When both surfaces are rough, the distance between the surfaces at different horizontal positions is altered. This leads to the development of new energetic minimums, with corresponding energy barriers, as seen in Fig. 4.65. As discussed previously, these secondary energy minimums are the result of decreased inter-solid dimensions when the triple-line positions are not vertically aligned.

The importance of this altered geometry is seen in Fig. 4.66. This energy profile corresponds to a 60°-120° (or 120°-60°) system. For this system, increasing $\alpha$ does not lead to an energetic driving force as seen in Fig. 4.60 (or an energetic barrier as seen in Fig. 4.61). Since increasing $\alpha$ increases the surface area of both solids, there is no advantage to having a low Young's contact angle on the rough surface. Additionally, multiple energetic barriers are seen as the liquid/vapor interface advances. While the energy barriers in Figs. 4.60 and 4.61 are present, they evolve into two-peaked barriers in Fig. 4.66. As with the flattening of the energetic barrier in Fig. 4.65, this change in the energy barrier is the result of decreased distance between the surfaces, at different horizontal positions.

### 4.4.1.2 Two Surface Wavelength Effects

Varying the wavelength of the surface features can also affect the total-interfacial energy as the liquid/vapor interface moves across the surface. For these simulations, one surface is rough with $\alpha = 0.2 \text{ L}$ while $\lambda$ is varied between 0.5 L and 2.5 L. These features are assumed to extend indefinitely along one axis. The other surface is flat. This is shown schematically in Fig. 4.67, where two rough surfaces, with different values of $\lambda$ are plotted. Since all surfaces simulated in this section have the same $\alpha$, all amplitude-based roughness parameters, such as $R_q$, will be equal for all surfaces simulated and could not be used to differentiate the systems. With changes in $\lambda$, the surface area is altered, and it can be shown that there is an effect from this change.

To begin this analysis, a 90°-90° system is presented in Fig. 4.68. At small $\lambda$, the surface area is at its maximum. The energy profile presented is significantly more complicated than that shown for changes in $\alpha$. At small $\lambda$, the distance between peaks is reduced. This can lead to discontinuous behavior of the liquid/vapor interface. That is, as the liquid-front advances, the triple-line boundaries of the preferred liquid configurations vary quickly with liquid volume. The total-interfacial energy is minimized if the liquid/vapor interface makes contact with the asperities that are closest to the flat surface. For small $\lambda$, this holds true even as the liquid/vapor interface proceeds, until it becomes energetically favorable for the triple-line position to jump to the next asperity. The mechanism of this jump cannot be simulated with this model. Only the identification of the minimum-energy configurations is performed.
These discontinuous changes in triple-line positions lead to the complicated appearance of the lower region of Fig. 4.68, as well as the reduced barrier heights. As $\lambda$ increases, this behavior is no longer possible, resulting in an energy profile similar to those seen previously.

The effect of dissimilar contact angles was also considered for the two rough surfaces system. Fig. 4.69 shows the energy profile as a function of $\lambda$ and the liquid/vapor-interfacial position for a system with Young's contact angles of 60° on the rough surface and 120° on the flat surface. The increased surface area with small $\lambda$ decreases the total-interfacial energy when the Young's contact angle is < 90° on that surface. As $\lambda$ increases, this effect is diminished, resulting in a decreased driving force for liquid penetration. Similarly to Fig. 4.69, at small $\lambda$ the energy barriers due to the surface roughness are diminished. The opposite behavior is again observed with Young's contact angles of 120° on the rough surface and 60° on the flat surface. The energy profile for this system is shown in Fig. 4.70. The orientation of the plot has been altered to allow easier visualization of the data. The increased surface area at small $\lambda$ dramatically increases the total-interfacial energy as the liquid fills the inter-solid volume. The effect is diminished as $\lambda$ increases.

For the analysis of $\alpha$ effects earlier, the importance of surface area was reduced when the Young's contact angles were identical. That behavior is also observed when varying $\lambda$. Fig. 4.71 plots the total-interfacial energy versus $\lambda$ and liquid/vapor-interfacial position for a system with Young's contact angles of 60° on both surfaces. Again, the orientation of the plot has been changed to allow visualization of the data. While the increased surface area associated with small $\lambda$ does increase the driving force for liquid penetration, the effect is smaller compared to the overall trend of the energy profile. This system has a driving force for liquid penetration even without increased surface areas, so the importance of roughness is diminished. Similarly, when an energy barrier for liquid penetration exists, the effect of increasing surface area is reduced. This is shown in Fig. 4.72 for a system with Young's contact angles of 120° on both surfaces. The overall change in total-interfacial energy is large compared to the effect of increased surface area with small $\lambda$.

### 4.4.1.3 Two Surface Phase-Shift Effects

In order to determine how sensitive these results are to the exact position of the surfaces, simulations of a system were performed where the lateral position of one surface was varied. For these systems, both surfaces were modeled as sinusoidal profiles, that were continuous along one axis, with $\alpha = 0.2$ L and $\lambda = 0$ L. Changing the lateral position of a surface is equivalent to a phase shift of the sinusoidal profile. This is shown schematically in Fig. 4.73. The phase shift, $\phi$, is defined as 0 when the asperities of both surfaces are aligned.

As will be shown, the effect $\phi$ is much smaller than the effect of $\alpha$, $\lambda$, or the Young's contact angles of the system. As such, only three examples will be provided: a 60°-60° system, a 60°-120° system, and a 120°-120° system. Since both surfaces are rough, there is no need to define which surface shows which Young's contact angle. Fig. 4.74 plots the total-interfacial energy as a function of the liquid front position and $\phi$ for the 60°-60° system. The overall trend of the data is as expected: there is an energetic driving force for liquid penetration. The effect of $\phi$ is seen as the slight rippling of the energy-profile surface. While the specific liquid configurations and energy barriers calculated do depend upon $\phi$, the effect is very small.
compared to other aspects of the system. This pattern is repeated in the 60°-120° system (Fig. 4.75) and the 120°-120° system (Fig. 4.76). In the 60°-120° case, there is no overall driving force for liquid penetration, as the sum of contact angles is 180°. The effect of $\phi$ is again evident, but does not significantly alter the size of the energy barriers. For the 120°-120° system, again, the total-interfacial energy increases dramatically if the liquid/vapor interface moves forward. This effect dwarfs the small changes seen as a function of the specific alignment of the surfaces.
Fig. 4.1: Schematic showing three droplet boundaries on a flat surface. Systematically varying the contact points and fixing the total droplet volume allows analysis of many possible droplet configurations. While all three droplets shown above have the same total volume, the area of the solid/liquid and liquid/vapor interfaces change. Therefore, the total interfacial energy changes as a function of contact point.
Fig. 4.2: a) Total interfacial energy versus horizontal contact coordinate, $x_c$, for a liquid droplet on an ideally flat surface. Energy curve is shown for three combinations of $\gamma_d$, $\gamma_{sv}$, and $\gamma_v$, resulting in Young’s contact angles of 60°, 90°, and 120°. b) Macroscopically observed contact angle versus horizontal contact coordinate, $x_c$, for the same system. By comparing the two plots, it is determined that Young’s analysis matches the numerical analysis for a non-rough system. The minimum total interfacial energy occurs when the macroscopic contact angle matches Young’s angle.
Fig. 4.3: Simulated profile of radially symmetric surface. The height of the surface is a sinusoidal function of the radial distance from the origin.

Fig. 4.4: Two-dimensional cross-section of radially symmetric, rough surface. All dimensions are relative to length scale $L$. For simple sinusoidal surface, the important parameters are the wavelength, $\lambda$, and the amplitude, $\alpha$. 
Fig. 4.5: Total interfacial energy for a liquid droplet on a rough surface as a function of contact coordinate, $x_c$, and $\alpha$ of roughness feature. The effect of roughness is to create local energetic barriers, making certain liquid configurations less favorable as $\alpha$ of the roughness increases. The blank portions of the plot are the result of non-physical liquid configurations, as shown below in Fig. 4.6.
Fig. 4.6: Close up of contact for a specific liquid configuration. By fixing the contact coordinate at $x_c = 9.5$ and the liquid volume at 500 $L^3$, the system is forced into a non-physical configuration. It is not possible (with that liquid volume, constant interfacial curvature, and radially symmetric surface roughness and liquid configuration) for the liquid to intersect the surface at $x_c = 9.5$. 
Fig. 4.7: a) Total interfacial energy versus contact coordinate for a liquid, with volume 500 L$^3$, on a rough surface. The surface has a radially symmetric, sinusoidal profile with $\alpha = 0.02$ L and $\lambda = 1$ L. With the interfacial energies selected, Young’s analysis would predict a contact angle of 90°. The presence of the surface feature creates small perturbations in the energy profile, leading to a shift in the preferred liquid configuration. b) Plot showing the macroscopically observed contact angle and the local contact angle as a function of contact coordinate. In this case, the roughness makes the local contact angle diverge from the macroscopic contact angle.
Fig. 4.8: a) Close up of Fig. 4.7a. Minimum total interfacial energy occurs at a smaller solid/liquid footprint, due to the effect of the small surface roughness. b) Close up of Fig. 4.7b. The minimum total interfacial energy observed in a) corresponds to a liquid configuration that forms a 90° local contact angle.
Fig. 4.9: a) Total interfacial energy versus contact coordinate for a liquid, with volume 500 L$^3$, on a rough surface. The surface has a radially symmetric, sinusoidal profile with $\alpha = 0.4$ L and $\lambda = 1$ L. With the interfacial energies selected, Young’s analysis would predict a contact angle of 90°. The gaps in the data are due to non-physical configurations. b) Plot showing the macroscopically observed contact angle and the local contact angle as a function of contact coordinate. In this case, the macroscopic angle and local contact angle are equal at the minimum-energy configuration.
Fig. 4.10: a) Close up of Fig. 4.9a. Higher-α features create larger energetic barriers to liquid moving over rough surface. b) Close up of Fig. 4.9b. The minimum total interfacial energy observed in a) corresponds to a liquid configuration that forms a 90° local contact angle and 90° macroscopically observed contact angle. It is worth noting that the peak of the local energy barrier shown in a) occurs at a local contact angle of 90°. The black dashed line around $x_c = 6.4$ corresponds to a liquid configuration in which the macroscopically observed contact angle nears 90°, but no energetic maximum or minimum occurs.
Fig. 4.11: Macroscopic and local contact angle of the minimum total-interfacial-energy configuration, plotted as a function of $\alpha$ of the surface feature. For high $\alpha$ features, the local and macroscopic angles coincide.

Fig. 4.12: Macroscopic and local contact angle of the minimum total-interfacial-energy configuration, plotted as a function of the Wenzel factor, $r$. Wenzel’s analysis would predict no change in the contact angle for this system, but that is not consistent with the numerical simulation results.
Fig. 4.13: Total interfacial energy of liquid configurations as a function of contact coordinate and \( \alpha \) of surface features for a system with \( \theta_{\text{Young}} = 60^\circ \). Again, the low \( \alpha \) surface is similar to the energy profile shown in Fig. 4.2a, but high \( \alpha \) surfaces lead to non-physical configurations. At high \( \alpha \), the lowest-energy configuration occurs at a larger contact coordinate, meaning that the roughness of the surface will tend to increase the solid/liquid interfacial area.
Fig. 4.14: Total interfacial energy of liquid configurations as a function of contact coordinate and $\alpha$ of surface features for a system with $\theta_{\text{Young}} = 120^\circ$. Again, the low $\alpha$ surface is similar to the energy profile shown in Fig. 4.2a, but high $\alpha$ surfaces lead to non-physical configurations. At high $\alpha$, the lowest energy configuration occurs at a smaller contact coordinate, meaning that the roughness of the surface will result in a decreased radius of contact relative to a flat surface.
Fig. 4.15: Macroscopic and local contact angle of the minimum total-interfacial-energy configuration, plotted as a function of $\alpha$ of the surface feature, for liquid with $\theta_{\text{Young}} = 60^\circ$. The large jumps in angles occur when the liquid droplet crosses over a feature, and spreads to the next trough in the surface. While the macroscopically observed angle continually decreases with $\alpha$, the local contact angle oscillates around the Young’s angle of $60^\circ$.

Fig. 4.16: Macroscopic and local contact angle of the minimum total-interfacial-energy configuration, plotted as a function of $\alpha$ of the surface feature, for liquid with $\theta_{\text{Young}} = 120^\circ$. The large jumps in angles occur when the liquid droplet crosses over a feature, and recedes to the next trough in the surface. While the macroscopically observed angle continually increases with $\alpha$ of the surface features, the local contact angle oscillates around the Young’s angle of $120^\circ$. 
Fig. 4.17: Macroscopic contact angle of the minimum total-interfacial-energy configuration, plotted as a function of the surface roughness, as measured by $R_q$. Three curves are plotted, corresponding to liquids with Young’s angles of 60°, 90°, and 120°. No direct correlation is observed between roughness parameter and macroscopic angle.

Fig. 4.18: Local contact angle of the minimum total-interfacial-configuration, plotted as a function of the surface roughness, as measured by $R_q$. Three curves are plotted, corresponding to liquids with Young’s angles of 60°, 90°, and 120°. No direct correlation is observed between roughness parameter and local angle. Again, the local contact angle oscillates around the expected Young’s angle.
Fig. 4.19: Total interfacial energy versus contact coordinate and $\lambda$ for simulated surfaces. All simulations are for surface with $\alpha = 0.2 \text{ L}$, a liquid volume of $500 \text{ L}^3$, and a Young’s contact angle of $90^\circ$. Non-physical configurations are more common with small $\lambda$, due to the increased slope of the surface profile. The surface roughness creates local minimums in the energy profile, and the spacing of these minima depends upon the wavelength of the surface.
Fig. 4.20: Macroscopic and local contact angles for minimum-energy configurations for liquid with Young’s angle of 60°. For surfaces with small λ features, the deviation of the macroscopic contact angle from the local contact angle is large. This is due to the larger slopes encountered with small λ features.

Fig. 4.21: Macroscopic and local contact angles for minimum-energy configurations for liquid with Young’s angle of 90°. While local contact angle remains close to 90°, the macroscopically measured angle oscillates by as much as 40°.
Fig. 4.22: Macroscopic and local contact angles for minimum energy configurations for liquid with Young’s angle of 120°. Again, large surface slopes present for features with smaller $\lambda$ leads to a greater divergence between the macroscopically measured and local contact angles.

Fig. 4.23: Macroscopic contact angle of minimum energy configurations versus Wenzel roughness factor, $r$. Small $\lambda$ features result in greater surface area and therefore are on the right side of the plot. The general trend of Wenzel’s model holds: increasing $r$ corresponds to enhancement of the wetting/non-wetting character of the liquid.
Fig. 4.24: Simulated macroscopic contact angle versus Wenzel factor, $r$, compared to Wenzel’s model prediction. The general trend predicted by Wenzel holds, but deviations as large as $18^\circ$ do occur, especially at low values of $r$.

Fig. 4.25: Local contact angle of minimum-energy configurations versus Wenzel roughness factor, $r$. Small $\lambda$ features result in greater surface area and therefore are on the right side of the plot. Increased surface area has little effect on the local contact angle of the minimum-energy configuration.
Fig. 4.26: Macroscopic contact angle of minimum energy configurations versus roughness parameter, Rq. Plot contains data for three liquids, with Young’s angles of 60°, 90° and 120°. Lines show the best linear-fit curve for each data set. With increasing Rq values, some trends are visible: the increasing roughness seems to enhance the wetting/non-wetting nature of the liquids. However, the individual data varies considerably from the best-fit curves.

Fig. 4.27: Local contact angle of minimum energy configurations versus roughness parameter, Rq. Plot contains data for three liquids, with Young’s angles of 60°, 90° and 120°. The lines represent best linear-fit curves to each data set. With increasing roughness, the local contact angle linear fits remain close to their predicted Young’s angles. However, the individual data points vary considerably with no apparent pattern.
Table 4.1: Averages and standard deviations of macroscopic and local contact angles for data shown in Figs. 4.26 and 4.27.

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Fig. 4.28: Macroscopic contact angle versus Wenzel roughness factor, $r$. The macroscopic angle predicted by Wenzel’s model is shown as a solid line. The data does follow the trend of these curves, but individual data points show large variance.
Fig. 4.29: Schematic showing a pair of droplet boundaries on a surface that is continuous along one axis. Figure shows two-dimensional cross section of a liquid configuration that extends indefinitely in the perpendicular axis. Systematically varying the contact points and fixing the total droplet volume allows analysis of many possible droplet configurations. Both droplets shown have the same total volume per unit depth, but the area of the solid/liquid and liquid/vapor interfaces change. Therefore, the total interfacial energy changes as a function of contact point. The ability to vary both contact points independently leads to configurations where the contact angle is not equal at all points.

Fig. 4.30: Total interfacial energy versus second contact point, $x_2$, for a liquid on a flat surface. The first contact point, $x_1$, is held constant at 0 L. The total interfacial energy has a minimum value that is characteristic of the volume of the liquid, the interfacial energies, and the distance between contact points.
Fig. 4.31: Total interfacial energy versus contact-point coordinates, $x_1$ and $x_2$, for a flat surface. Many liquid configurations can result in a minimum total interfacial energy. These configurations are identical except for a translational shift. For this model, the contact points are defined such that $x_1 < x_2$. This results in the possible configurations being limited to the triangular region shown.
Fig. 4.32: Total interfacial energy versus contact-point coordinates, $x_1$ and $x_2$ for surface with a sinusoidal profile with $\alpha = 0.02 \text{ L}$. The surface roughness results in local perturbations of the energy profile, resulting in discrete energetic minima. The blank portions of the plot correspond to non-physical configurations.
Fig. 4.33: Total interfacial energy versus contact-point coordinates, $x_1$ and $x_2$, for surface with a sinusoidal profile with $\alpha = 0.06 \text{ L}$. The surface roughness results in local perturbations of the energy profile, resulting in discrete energetic minima. Comparing this profile to that shown in Fig. 4.32, the increased $\alpha$ results in larger energetic perturbation, as well as more non-physical configurations. The upper-left portion of the plot corresponds to contact points that are near each other, corresponding to a configuration with a small solid/liquid interfacial area. As $\alpha$ increases, these configurations are only possible when the liquid contacts the peaks of the surface.
Fig. 4.34: Total interfacial energy versus contact-point coordinates, $x_1$ and $x_2$ for surface with a sinusoidal profile with $\alpha = 0.12 \, \text{L}$. The surface roughness results in local perturbations of the energy profile, resulting in discrete energetic minima. Comparing this profile to that shown in Figs. 4.32 and 4.33, the increased $\alpha$ results in larger energetic perturbation, as well as more non-physical configurations. Here, $\alpha$ is great enough to prohibit most configurations with contact points separated by less than $\lambda$. 

\[ \gamma_a = 1 \, \gamma \]
\[ \gamma_w = 1 \, \gamma \]
\[ \gamma_v = 1 \, \gamma \]
\[ \theta_{\text{Young}} = 90^\circ \]
Fig. 4.35: Four minimum-energy configurations on four different surfaces. As $\alpha$ increases, the contact points do not shift significantly. The macroscopic angle does not change dramatically between these configurations, but the local contact angles do.

Fig. 4.36: Macroscopic and local contact angle of minimum-energy configuration versus $\alpha$ of surface feature with translational symmetry for a liquid with Young's angle of 90°. The macroscopic contact angle shows small variations with $\alpha$, while the local contact angle increases significantly. This is an effect of the local slope of the surface.
Fig. 4.37: Total interfacial energy versus contact-point coordinates, $x_1$ and $x_2$, for a liquid with Young’s angle of 60° on a surface with a sinusoidal profile with $\alpha = 0.06$ L. The surface roughness results in local perturbations of the energy profile, resulting in discrete energetic minima. The change in interfacial energies (specifically, the solid/liquid interfacial energy) results in low-energy configurations when the contact points are spread farther apart.
Fig. 4.38: Macroscopic and local contact angle of minimum-energy configuration versus $\alpha$ of surface feature that are continuous along one axis with Young's angle $60^\circ$. The macroscopic contact angle decreases with increasing $\alpha$. The jumps in contact angle occur when it becomes energetically favorable for the triple-line separation to increase by $\lambda$. The local contact angle oscillates as an effect of this droplet spreading.

Fig. 4.39: Macroscopic and local contact angle of minimum-energy configuration versus $\alpha$ of surface feature that is continuous along one axis for a liquid with Young's angle $120^\circ$. The large jump in macroscopic contact angle occurs when it is energetically favorable for the droplet to recede by $\lambda$. The local angle generally declines due to changes in the surface slope.
Fig. 4.40: Macroscopic contact angle of minimum-energy configuration versus $R_q$ value for liquids with Young's angles of 60°, 90° and 120°. The 60° and 120° data points show discontinuities when increasing $\alpha$ results in large changes in the minimum-energy configuration.

Fig. 4.41: Local contact angle of minimum-energy configuration versus $R_q$ value for liquids with Young's angles of 60°, 90° and 120°. The 60° and 120° data points show discontinuities when increasing $\alpha$ results in large changes in the minimum-energy configuration.
Fig. 4.42: Macroscopic contact angle of minimum-energy configuration versus Wenzel roughness factor, $r$, for liquids with Young's angles of 60°, 90° and 120°. The general trend of the Wenzel model is followed, but the Wenzel model does not account for discontinuous behavior due to the particular surface features simulated.

Fig. 4.43: Total interfacial energy versus contact points, $x_1$ and $x_2$ for surface with a sinusoidal profile with $\alpha = 0.10 \text{ L}$ and $\lambda = 0.50 \text{ L}$. The surface roughness results in local perturbations of the energy profile, resulting in many energetic minima. With this small $\lambda$, many non-physical configurations exist, with both far-apart (far-right of plot) and close-together contact points (upper-left of plot).
Fig. 4.44: Total interfacial energy versus contact points, $x_1$ and $x_2$ for surface with a sinusoidal profile with $\alpha = 0.10 \, \text{L}$ and $\lambda = 1.50 \, \text{L}$. The surface roughness results in local perturbations of the energy profile, resulting in many energetic minima. With a larger $\lambda$, many more configurations become physically possible. The larger $\lambda$ is also evident in the spacing between energetic minima.
Fig. 4.45: Total interfacial energy versus contact points, $x_1$ and $x_2$ for surface with a sinusoidal profile with $\alpha = 0.10 \, \text{L}$ and $\lambda = 2.50 \, \text{L}$. The surface roughness results in local perturbations of the energy profile, resulting in multiple energetic minima. With a larger $\lambda$, many more configurations become physically possible. The larger $\lambda$ is also evident in the spacing between energetic minima.
Fig. 4.46: Macroscopic and local contact angle of minimum-energy configuration versus \( \alpha \) of a surface feature that is continuous along one axis for a liquid with Young's angle 90°. Both contact angles oscillate as \( \lambda \) increases, with much larger deviations in the local contact angle.

Fig. 4.47: Macroscopic and local contact angle of minimum-energy configuration versus \( \lambda \) of surface feature that is continuous along one axis for a liquid with Young's angle 60°. Both contact angles oscillate as \( \lambda \) increases, with much larger deviations in the local contact angle.
Fig. 4.48: Macroscopic and local contact angle of minimum-energy configuration versus $\lambda$ of surface feature that is continuous along one axis for a liquid with Young's angle 120°. Both contact angles oscillate as the $\lambda$ increases, with much larger deviations in the local contact angle.
Table 4.2: Averages and standard deviations of macroscopic and local-contact-angles for data shown in Figs. 4.46 through 4.48.

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![Graph](image)

Fig. 4.49: Macroscopic contact angle of minimum-energy configuration versus Wenzel roughness factor, \( r \), for liquids with Young’s angles of 60°, 90° and 120°. The general trend of the Wenzel model is followed, but the Wenzel model does not account for discontinuous behavior due to the particular surface features simulated.
Fig. 4.50: Macroscopic contact angle of minimum-energy configuration at contact-point $x_2$ versus macroscopic contact angle at contact-point $x_1$, for liquids with Young’s angles of 60°, 90° and 120°. As with the more symmetrical surfaces presented earlier, the macroscopic contact angles are nearly equal for all minimum-energy configurations.
Fig. 4.51: Local contact angle of minimum-energy configuration at contact-point $x_2$ versus local contact angle at contact-point $x_1$, for liquids with Young’s angles of 60°, 90° and 120°. The local contact angles show large variations for the same minimum-energy configuration.

Fig. 4.52: Macroscopic contact angle of minimum-energy configuration versus Rq value for liquids with Young’s angles of 60°, 90° and 120°. The plot shows contact angles for the contact point $x_1$ for forty fractal surfaces. The contact angles of the 90° liquids show less spread than the data for 60° or 120°.
Macroscopic Contact Angle (°) vs. Rq (L⁻¹)

- $\theta_{\text{Young}} = 120°$
- $\theta_{\text{Young}} = 90°$
- $\theta_{\text{Young}} = 60°$

**Fig. 4.53:** Macroscopic contact angle of minimum-energy configuration versus Rq value for liquids with Young's angles of 60°, 90° and 120°. The plot shows contact angles for the contact point $x_2$ for forty fractal surfaces. The contact angles of the 90° liquids show less spread than the data for 60° or 120°. This plot is similar to that shown in Fig. 4.52, due to the similarities in macroscopic contact angle discussed with Fig. 4.51.

Local Contact Angle (°) vs. Rq (L⁻¹)

- $\theta_{\text{Young}} = 120°$
- $\theta_{\text{Young}} = 90°$
- $\theta_{\text{Young}} = 60°$

**Fig. 4.54:** Local contact angle of minimum-energy configuration versus Rq value for liquids with Young's angles of 60°, 90° and 120°. The plot shows contact angles for the contact point $x_1$ for forty fractal surfaces. The best-fit lines for each data set show the general effect of Young's contact angle, but individual data points vary widely.
Table 4.3: Averages and standard deviations of macroscopic and local contact angles for data shown in Figs. 4.50 and 4.51. For this table, the macroscopic and local contact angle statistics include the contact angles at both $x_1$ and $x_2$.

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Fig. 4.55: Macroscopic contact angle of minimum-energy configuration versus Wenzel roughness factor, $r$, for liquids with Young’s angles of 60°, 90° and 120°. The plot shows contact angles for the contact point $x_1$ for forty fractal surfaces. The general trend of the Wenzel model is followed for the 60° and 90° data. For the non-wetting, 120° liquid, Wenzel’s model almost universally overestimates the macroscopic contact angle.
Fig. 4.56: Macroscopic contact angle of minimum-energy configuration versus Wenzel roughness factor, $r$, for liquids with Young's angles of 60°, 90° and 120°. The plot shows contact angles for the contact point $x_2$ for forty fractal surfaces. As with the data shown in Fig. 4.55, the 60° and 90° data clusters around the Wenzel prediction. Again, the Wenzel prediction exceeds nearly all data points for the non-wetting liquid.

Fig. 4.57: Schematic of possible liquid/vapor interfaces for an assumed volume of liquid. **Interface 1** shows negative interfacial curvature, while **Interface 2** shows positive curvature. Both liquid configurations are possible, but the energetically preferred liquid/vapor interface is determined by the relative values of $\gamma_s$ and $\gamma_v$, for both solid surfaces and the value of $\gamma_{lv}$. 

93
Fig. 4.58: Schematic of surface used to test the effect of surface-feature amplitude. For these simulations, the top surface is a sinusoidal profile with variable amplitude while the bottom solid is an ideally flat surface. The total volume between surfaces is held constant for these simulations. The schematic shows three examples of top surfaces with different values of $\alpha$. 


Fig. 4.59: Total-interfacial energy of preferred liquid configuration as a function of $\alpha$ and liquid front position. Energy profile shown is for system with Young's contact angle of 90° on the rough surface and 90° on the smooth surface. As $\alpha$ increases, the energetic barriers to liquid penetration increase in magnitude.
Fig. 4.60: Total-interfacial energy of preferred liquid configuration as a function of $\alpha$ and liquid front position. Energy profile shown is for system with Young’s contact angle of $60^\circ$ on the rough surface and $120^\circ$ on the smooth surface. As $\alpha$ increases, the energetic driving force for liquid penetration increases.
Fig. 4.61: Total-interfacial energy of preferred liquid configuration as a function of $\alpha$ and liquid front position. Energy profile shown is for system with Young’s contact angle of 120° on the rough surface and 60° on the smooth surface. As $\alpha$ increases, the energetic barriers to liquid penetration increase dramatically.
Fig. 4.62: Total-interfacial energy of preferred liquid configuration as a function of $\alpha$ and liquid front position. Energy profile shown is for system with Young's contact angle of $60^\circ$ on the rough surface and $60^\circ$ on the smooth surface. As $\alpha$ increases, the energetic driving force for liquid penetration remains relatively constant.
Fig. 4.63: Total-interfacial energy of preferred liquid configuration as a function of $\alpha$ and liquid front position. Energy profile shown is for system with Young’s contact angle of 120° on the rough surface and 60° on the smooth surface. As $\alpha$ increases, the energetic barriers to liquid penetration remain relatively constant.

Fig. 4.64: Schematic of surface used to test the effect of surface-feature $\alpha$. For these simulations, both surfaces have sinusoidal profiles with variable amplitude. The distance between solids is identical to that shown in Fig. 4.58. The schematic shows three examples of top and bottom surfaces with different values of $\alpha$. 
Fig. 4.65: Total-interfacial energy of preferred liquid configuration as a function of $\alpha$ and liquid front position for system with two rough surfaces. Energy profile shown is for system with Young's contact angles of 90° and 90°. As $\alpha$ increases, the energetic barriers to liquid penetration increase in magnitude.
Fig. 4.66: Total-interfacial energy of preferred liquid configuration as a function of $\alpha$ and liquid front position for system with two rough surfaces. Energy profile shown is for system with Young’s contact angles of 60° and 120°. As $\alpha$ increases, the energetic barriers to liquid penetration increase in magnitude.

Fig. 4.67: Schematic of surface used to test the effect of surface-feature $\lambda$. For these simulations, both surfaces have sinusoidal profiles with variable amplitude. The total volume between surfaces is held constant for these simulations. The schematic shows two examples of top surfaces with different values of $\lambda$. 
Fig. 4.68: Total-interfacial energy of preferred liquid configuration as a function of \( \lambda \) and liquid front position. Energy profile shown is for system with Young's contact angle of 90° on the rough surface and 90° on the smooth surface. As \( \lambda \) increases, the energetic barriers to liquid penetration increase in magnitude.
Fig. 4.69: Total-interfacial energy of preferred liquid configuration as a function of $\lambda$ and liquid front position. Energy profile shown is for system with Young's contact angle of $60^\circ$ on the rough surface and $120^\circ$ on the smooth surface.
Total Interfacial Energy ($\gamma$)

Young's Contact Angles:
Rough: 120°
Flat: 60°

Wavelength ($\lambda/L$)
Liquid Front Position ($x/L$)

Fig. 4.70: Total-interfacial energy of preferred liquid configuration as a function of $\lambda$ and liquid front position. Energy profile shown is for system with Young’s contact angle of 120° on the rough surface and 60° on the smooth surface. As $\lambda$ increases, the energetic barriers to liquid penetration increase in magnitude.
Fig. 4.71: Total-interfacial energy of preferred liquid configuration as a function of $\lambda$ and liquid front position. Energy profile shown is for system with Young's contact angle of 60° on the rough surface and 60° on the smooth surface.
Fig. 4.72: Total-interfacial energy of preferred liquid configuration as a function of $\lambda$ and liquid front position. Energy profile shown is for system with Young’s contact angle of $120^\circ$ on the rough surface and $120^\circ$ on the smooth surface.
Fig. 4.73: Schematic of surface used to test the effect of phase shift $\phi$. For these simulations, both surfaces have sinusoidal profiles with the same $\alpha$ and $\lambda$. The total volume between surfaces is held constant for these simulations. The schematic shows two examples of top surfaces with different values of $\phi$. 
Fig. 4.74: Total-interfacial energy of preferred liquid configuration as a function of $\phi$ and liquid front position. Energy profile shown is for system with Young’s contact angles of $60^\circ$ and $60^\circ$. 
Fig. 4.75: Total-interfacial energy of preferred liquid configuration as a function of $\phi$ and liquid front position. Energy profile shown is for system with Young’s contact angles of 60° and 120°.
Fig. 4.76: Total-interfacial energy of preferred liquid configuration as a function of $\phi$ and liquid front position. Energy profile shown is for system with Young’s contact angles of 120° and 120°.
5.0 Conclusions

The behavior of liquids in contact with solids is important in many fields, but particularly so in liquid-based joining. The joining of ceramics to metals is a difficult process, but is assisted through the development of a liquid layer in PTLP bonding. This liquid layer must remain thin to reduce joining times but must be thick enough to fully fill interfacial voids. The presence of interfacial voids in the joined assembly has been shown to reduce the strength of the assembly. The ability of the liquid to redistribute and fill voids is therefore of critical importance to PTLP joining.

Surface roughness can affect the preferred liquid configurations due to the change in interfacial areas. In the case of a liquid droplet on a rough surface, any roughness features present increase the solid/liquid and solid/vapor interfacial areas. Liquid behavior is largely driven by the minimization of total-interfacial energy, which is a product of the interfacial areas and associated specific surface and interfacial energies. A full understanding of the wetting behavior of fluids therefore relies on an accurate model of the interaction of wetting liquids and rough solids.

In PTLP joining, this roughness of the solid members is even more critical. The rough features will define the inter-solid volume. Additionally, in ceramic/metal joining the contact angle of the liquid may be different for each solid material. This can lead to very complicated interactions between roughness and the liquid layer that is developed.

This work presented a numerical model of the energetics of liquids on rough solids and entrapped between two rough, dissimilar materials. The model operates by systematically testing many possible liquid configurations and calculating the resulting total-interfacial energy. Non-physical liquid configurations are removed from consideration, and the resulting data can be used to determine the preferred liquid configurations. Numerical simulations allow control of every aspect of the system: the roughness profile of the surfaces, the various interfacial energies, and the liquid volume.

Using these techniques, it was shown how increasing roughness could affect the contact angle of a liquid in contact with a rough solid. For a liquid with Young’s contact angle < 90°, increasing roughness, as measured by Wenzel’s roughness parameter and by amplitude-based roughness parameters, can lead to a decrease in the macroscopically observed contact angle. Similarly, for liquids with Young’s contact angle > 90°, an increase in the roughness can increase the macroscopically observed contact angle. The exact nature of this increase is difficult to predict exactly. While models such as Wenzel’s predict the correct trend of this change in contact angle, the magnitude of change is highly dependent upon the surface geometry.

All measurements of roughness attempt to provide a statistical summary of the height-position data that defines a surface. These parameters can have limitations, as discussed previously, such as a lack of any information about the lateral spacing of surface-roughness features. When determining a minimum-total-interfacial energy, the local orientation of the surface (a function of both the amplitude and lateral spacing of surface features) can affect the liquid in multiple ways. The change in surface area due to roughness can change the balance of interfacial energies. Additionally, the slope of the surface can act to make certain liquid configurations impossible.

The ability of a liquid to redistribute during a PTLP joining process and fill voids is determined in part by the roughness of the solid surfaces involved. A model of an advancing
liquid/vapor interface is presented, and the importance of amplitude, wavelength, and local-surface orientation were discussed for liquid redistribution. It is found that larger surface-feature amplitudes could aid in liquid penetration of the inter-solid gap, when the Young’s contact angles are beneficial. For systems where the liquid formed contact angles of 60° and 120° on the two surfaces, there is no interfacial-energy driving force for liquid penetration when the surfaces are both flat. It is found that increasing the surface area of the low-contact-angle solid provides an energetic driving force for liquid penetration. By examining amplitude, wavelength, and local-orientation effects, it is shown that the increase in surface area has a large effect on the ability of a liquid to infiltrate and fill the void space between to solid surfaces. This understanding of the energetics involved is critical for successful application of the PTLP process.
6.0 References


40) C. Wan, P. Kritsalis, B. Drevet and N. Eustathopoulos, "Optimization of wettability and adhesion in reactive nickel-based alloys/alumina systems by a thermodynamic..."


Appendix I: Mathematica Code

This section provides a line-by-line description of the code used to model possible liquid configurations. The code presented was used for systems with a liquid entrapped between two rough surfaces. The surface features were assumed to be continuous along one axis, as described previously. The code operates by testing many possible triple-line boundary coordinates, calculating the resulting liquid/volume interface and the corresponding surface areas. Multiple tests are used to determine if the liquid configuration is physically possible. The result of the model is a large matrix with the remaining physically-possible liquid configurations, descriptions of their geometry, and the resulting total-interfacial energy.

To begin with, it is useful to have a user-definable equation for the profile of a surface. The command "Surf" accepts a set of parameters as an input, which define the amplitude, wavelength, phase shift, and vertical translation for a simple sinusoidal profile. The output of the "Surf" command will be a height value, based upon the input parameters included in 'set', and a horizontal coordinate, 'x'.

\[
\text{Surf}[\text{set}, \ x] := \text{set}[1] \times \sin[2 \pi \times \text{set}[2] \div \text{set}[3]] + \text{set}[4]
\]

set = {amplitude, wavelength, phase shift, vertical shift}

The following command, "Young", calculates the Young's contact angle based upon the input of three interfacial energies. \( \gamma_\text{sl} \) is the solid/liquid interfacial energy, \( \gamma_\text{sv} \) is the solid/vapor interfacial energy, and \( \gamma_\text{lv} \) is the liquid/vapor interfacial energy. This is used later to compare the contact angles of liquid configurations to the Young's contact angle.

\[
\text{Young}[\gamma_\text{sl}, \ \gamma_\text{sv}, \ \gamma_\text{lv}] := \frac{\arccos((\gamma_\text{sv} - \gamma_\text{sl}) \div \gamma_\text{lv}) \times 180}{\pi}
\]

The command 'Dist' calculates the distance between any two pair of \{x,y\} data points. This comes into play in a number of ways, but notably in determining the possible radii of curvature.

\[
\text{Dist}[\text{xa}, \ \text{ya}, \ \text{xb}, \ \text{yb}] := \sqrt{(\text{xa} - \text{xb})^2 + (\text{ya} - \text{yb})^2}
\]

'MxBT' outputs the equation of a line that passes through two points, \{xa, ya\} and \{xb, yb\}. The line is critical to determine the area enclosed within a possible liquid geometry.

\[
\text{MxBT}[\text{xa}, \ \text{ya}, \ \text{xb}, \ \text{yb}, \ x] := \\
\text{If}[\text{xa} = \text{xb}, 100000 \times (\text{x} - \text{xa}) + \text{ya}, \ (\text{yb} - \text{ya}) \div (\text{xb} - \text{xa}) \times (\text{x} - \text{xa}) + \text{ya}]
\]

'Vec' determines the unit vector that is perpendicular to the line connecting point \{xa, ya\}, to point \{xb, yb\}. When used with the origin of a circle, and a point on the circle, this vector has the same orientation as the tangent to the circle. For this model, the circular geometries define the liquid/vapor interface. The orientation of the vector tangent to the circle is therefore aligned with the liquid/vapor interface. This helps in calculating the local and macroscopic contact angles of a specific liquid configuration.

\[
\text{Vec}[\text{xa}, \ \text{ya}, \ \text{xb}, \ \text{yb}] := \text{Normalize}[\text{xb} - \text{xa}, \ \text{yb} - \text{ya}]
\]

The following commands ('PerpBi', 'xCent', and 'yCent') define the origin of a circle, used to calculate many aspects of circular segment later.

\[
\text{PerpBi}[\text{x}, \ \text{y}, \ \text{x2}, \ \text{y2}, \ x] := \text{If}[\text{y} = \text{y2}, 10000 \times (\text{x} - (\text{x1} + \text{x2}) \div 2) \div (\text{y1} + \text{y2}) \div 2, \ (-\text{x2} - \text{x1}) \div (\text{y2} - \text{y1}) \times (\text{x} - (\text{x1} + \text{x2}) \div 2) \div (\text{y1} + \text{y2}) \div 2]
\]

\[
\text{xCent}[\text{x}, \ \text{y}, \ \text{x2}, \ \text{y2}, \ r, \ \text{sign}] := \text{If}[\text{r} = "\text{Flat}" , (\text{x1} + \text{x2}) \div 2 , \ \text{Quiet}[\text{Chop}([\text{sign} \times \text{SignD}([\text{PerpBi}[\text{x}, \ \text{y}, \ \text{x2}, \ \text{y2}, \ \text{x1}], \text{r}] \div \text{r} \div 2 , \text{r} , \text{sign} , \text{sign} , \text{x1}])] ; \text{If}[ \text{y} = \text{y2} , (\text{x1} + \text{x2}) \div 2 , \ \text{x} , \ \text{FindRoot}[(\text{x} - \text{x1}) \times 2 \div (\text{y1} - \text{PerpBi}\{\text{x} , \ \text{y} , \ \text{x2} , \ \text{y2} , \ \text{x1} \}^2 - 2 \div 2) \div (\text{x} , (\text{x2} + \text{x1}) \div 2 - \text{sign} \times \text{r} )])])]
\]

\[
yCent[\text{x}, \ \text{y}, \ \text{x2}, \ \text{y2}, \ r, \ \text{sign}, \ \text{xc}] := \\
\text{If}[\text{r} = "\text{Flat}" , (\text{y1} + \text{y2}) \div 2 , \ \text{Chop}[\text{If}[\text{Chop}[\text{y} - \text{y2}] = 0 , \ \text{y1} - \text{sign} \times \text{Sqrt}[(\text{r}^2 - ((\text{x2} - \text{x1}) \div 2)^2) \div (\text{PerpBi}[\text{x}, \ \text{y}, \ \text{x2}, \ \text{y2}, \ \text{xc}])]])]
\]
Using the vectors defined by the liquid/vapor interphase and either a horizontal line or the local slope of the surface, it is possible to calculate the macroscopic and local angles using "Angle". The result is expressed in degrees, not radians.

\[
\text{Angle}[\text{data}, \text{surf}_1, \text{set}_1, \text{surf}_2, \text{set}_2] := \text{With}[[\phi_T = 90 - \arctan[\text{data}[[2, 1]] - \text{data}[[3, 1]] / \text{data}[[3, 2]]] \times 180 / \pi, \\
\phi_B = \text{ArcTan}[\text{surf}_1[\text{set}_1, x] / x \to \text{data}[[2, 1]]] \times 180 / \pi, \\
\phi_S = \text{ArcTan}[\text{surf}_2[\text{set}_2, x] / x \to \text{data}[[3, 1]]] \times 180 / \pi], \\
\text{With}[[\phi_B = 180 - \phi_T], \text{Which}[[\text{data}[[7, 1, 1]] = 0, ((\phi_T, \phi_T - \phi_S), (\phi_B, \phi_B + \phi_S))], \\
\text{data}[[7, 1, 1]] = 1 && \text{data}[[7, 1, 2]] = 1, \\
((\phi_T + \text{Theta}[[\text{data}[[4]], \text{data}[[7, 2]]]], \phi_T + \text{Theta}[[\text{data}[[4]], \text{data}[[7, 2]]]], \\
\text{data}[[7, 1, 1]] = 1 && \text{data}[[7, 1, 2]] = 1, \\
((\phi_T - \text{Theta}[[\text{data}[[4]], \text{data}[[7, 2]]]], \phi_T - \text{Theta}[[\text{data}[[4]], \text{data}[[7, 2]]]], \\
\text{data}[[7, 1, 1]] = -1 && \text{data}[[7, 1, 2]] = 1, \\
((\phi_T - \text{Theta}[[\text{data}[[4]], \text{data}[[7, 2]]]], \phi_T - \text{Theta}[[\text{data}[[4]], \text{data}[[7, 2]]]], \\
\phi_B - \text{Theta}[[\text{data}[[4]], \text{data}[[7, 2]]]] + \phi_S), \\
\phi_B - \text{Theta}[[\text{data}[[4]], \text{data}[[7, 2]]]] + \phi_S)), \\
\phi_B - \text{Theta}[[\text{data}[[4]], \text{data}[[7, 2]]]], \\
\phi_S - \text{Theta}[[\text{data}[[4]], \text{data}[[7, 2]]]], \\
\phi_B - \text{Theta}[[\text{data}[[4]], \text{data}[[7, 2]]]] + \phi_S))]]
\]

When calculating the interfacial areas, the command "ArcLength" determines the solid/liquid interfacial area (per unit depth).

\[
\text{ArcLength}[\text{surf}_1, \text{set}_1, \text{left}_1, \text{right}_1] := \\
\text{NIntegrate}[\sqrt{1 + (D[\text{surf}[[\text{set}_1, x]]]^2]}, \{x, \text{left}_1, \text{right}_1\}]
\]

As described earlier, the model determines the preferred liquid/vapor interfacial curvature with a multi-stage process. The first step of this process is to define a certain volume of liquid. For an arbitrary liquid/vapor interface, the volume can be calculated using two integrals, described in Section 3.6.1. The first integral is calculated using the command "IntRec" which calculates the liquid volume from a reference point x0 to a defined coordinate x1.

\[
\text{IntRec}[x_0, x_1, \text{surf}_1, \text{set}_1, \text{surf}_2, \text{set}_2] := \\
\text{Chop}[\text{NIntegrate}[\text{surf}_1[\text{set}_1, x] - \text{surf}_2[\text{set}_2, x], \{x, x_0, x_1\}]]
\]

The second integral required is calculated using "IntTri". This calculates the area of a triangular region defined by the line connecting x1 and x2 and the bottom surface.

\[
\text{IntTri}[x_1, x_2, \text{surf}_1, \text{set}_1, \text{surf}_2, \text{set}_2] := \\
\text{Which}[[x_1 = x_2, 0, x_2 > x_1, \text{Chop}[\text{NIntegrate}[\text{surf}_1[\text{set}_1, x] - \\
\text{MesBT}[x_1, \text{surf}_1[\text{set}_1, x], x_2, \text{surf}_2[\text{set}_2, x], \{x, x_2, x_1\}], x_1 < x_2, \\
\text{Chop}[\text{NIntegrate}[\text{MesBT}[x_1, \text{surf}_1[\text{set}_1, x_1], x_2, \text{surf}_2[\text{set}_2, x_2], x] - \\
\text{surf}_2[\text{set}_2, x], \{x, x_1, x_2\}]]]]
\]

In order to efficiently simulate many possible liquid configurations, it is important to avoid repeating calculations. The commands "TableRec" and "TableTri" create tables of possible values of integral1 and integral2 that can then be called upon to avoid repetitive calculations.
Similarly, the solid/liquid interfacial areas involved are a function of the contact points x1 and x2, not of the specific liquid/vapor interfaces. A table of possible surface areas can therefore be created to avoid repetitive calculations.

The commands "Area" and "InvArea" are used to calculate the areas of circular segments. "Area" is used for circular segments that are less than a hemisphere, while "InvArea" is used for circular segments greater than a hemisphere.

\[ \text{Area}(c, R) := R^2 / 2 * (2 * \text{ArcSin}(c / (2 * R)) - \text{Sin}(2 * \text{ArcSin}(c / (2 * R))) \]

\[ \text{InvArea}(c, R) := \pi * R^2 / 2 / 2 * (2 * \text{ArcSin}(c / (2 * R)) - \text{Sin}(2 * \text{ArcSin}(c / (2 * R))) \]

To calculate the liquid/vapor interfacial area (which is related to the arclength of a circular segment), the commands 'CircLength' and 'InvCircLength' are used. Again, 'CircLength' is used when the circular segment is less than a hemisphere, while 'InvCircLength' is used for more than a hemisphere.

\[ \text{CircLength}(c, R) := R * (2 * \text{ArcSin}(c / (2 * R))) \]

\[ \text{InvCircLength}(c, R) := 2 \pi * R - R * (2 * \text{ArcSin}(c / (2 * R))) \]

The following two commands calculate the orientation of the circular segments, used later to define the contact-angle of the liquids.

\[ \text{Theta}(c, R) := \text{ArcSin}(c / (2 * R)) * 180 / \pi \]

\[ \text{ThetaInv}(c, R) := 180 - \text{ArcSin}(c / (2 * R)) * 180 / \pi \]

Using the previously calculated tables of Integrall and Integral2, the command "TableSort" compiles a large matrix with all liquid-volume/contact-point combinations that will be tested.
As described in Section 3, the curvature of the liquid/vapor interface is dependent upon the liquid volume and the contact points. Based upon the values of Integral1 and Integral2 (which together equal Area1), it is possible to find the required Area2. This area is a function of the distance between contact points and the curvature of the liquid/vapor interface. It is therefore possible to back-calculate the required curvature to fulfill the area requirement. The commands "FindR" and "TableR" take the compiled matrix of volume/contact-point combinations and determines the liquid/vapor interfacial curvature required. It also determines if the liquid/vapor interface is required to have positive or negative curvature, and if the circular segment involved will be more or less than a hemisphere.

\[
\text{FindR}[\text{data}_b] := \text{Quiet}[\text{Chop[With[\{\text{diff} = \text{Chop[data[5]]} - \text{data[6]}\},
\text{sign} = \text{If[\text{Abs[data[5]} - \text{data[6]}] < \pi \times (\text{data[4]} / 2)^2 / 2, 1, -1],
\text{Which[diff == 0, \{0, 0, 0\},
\text{diff > 0 \& sign == 1, \{1, sign\},
\text{diff > 0 \& sign == -1, \{-1, sign\}],
\text{R / FindRoot[Area[data[4], R] == diff, \{R, data[4] / 2 + 0.1\}],
\text{diff < 0 \& sign == 1, \{-1, sign\},
\text{diff < 0 \& sign == -1, \{1, sign\}],
\text{R / FindRoot[invArea[data[4], R] == -diff, \{R, data[4] / 2 + 0.1\}],
\text{invArea[data[4], R] == -diff, \{R, data[4] / 2 + 0.1\}]]]]]]]]
\]
\]

\[
\text{TableR}[\text{data}_b] := \text{Table[\{\text{data}[a, b, c, 1], \text{data}[a, b, c, 2], \}
\text{data}[a, b, c, 3]], \{\text{data}[a, b, c, 1], \text{data}[a, b, c, 3]\}, \{\text{data}[a, b, c, 5], \text{data}[a, b, c, 6]\},
\text{data}[a, b, c, 7]], \text{data}[a, b, c, 8], \text{FindR[\text{data}[a, b, c]]]}]
\]

Using the full set of geometric data (solid/liquid interfacial areas plus liquid/vapor interfacial geometry), the commands "SurfCirc" and "TableSurf" calculate all of the interfacial areas involved.

\[
\text{SurfCirc[\text{data}_b]} := \text{Which[}
\text{data[9, 1]} = \{0, 0\}, \text{data[7]}, \text{data[8]}, \text{data[4]},
\text{data[9, 1]} = \{1, 1\}, \text{data[7]}, \text{data[8]}, \text{data[4]},
\text{CircLength[data[4]], data[9, 2]]}, \text{data[9, 1]} = \{-1, 1\},
\text{data[7]}, \text{data[8]}, \text{CircLength[data[4]], data[9, 2]}],
\text{data[9, 1]} = \{1, -1\}, \text{data[7]}, \text{data[8]}, \text{InvCircLength[data[4]], data[9, 2]}],
\text{data[9, 1]} = \{-1, -1\},
\text{data[7]}, \text{data[8]}, \text{InvCircLength[data[4]], data[9, 2]}]]]
\]

\[
\text{TableSurf[\text{data}_b]} := \text{Table[\{\text{data}[a, b, c, 1], \text{data}[a, b, c, 2], \text{data}[a, b, c, 3], \}
\text{data}[a, b, c, 4]], \text{data}[a, b, c, 5]], \text{data}[a, b, c, 6],
\text{data}[a, b, c, 7]], \text{SurfCirc[\text{data}[a, b, c]]]}, \{\text{a, 1, Length[data]}\},
\{b, 1, Length[data]\}, \{c, 1, Length[data]\}]]]
\]

Now that the interfacial areas are calculated, it is possible to calculate the total-interfacial energies. This is done using the command "TableEnergy"

\[
\text{TableEnergy[\text{data}_b, ysl1, ysv1, ysl2, ysv2, ylv]} := \text{Table[\{\text{data}[a, b, c, 1], \text{data}[a, b, c, 2], \text{data}[a, b, c, 3],
\text{data}[a, b, c, 4]], \text{data}[a, b, c, 5]], \text{data}[a, b, c, 6],
\text{data}[a, b, c, 7]], \text{data}[a, b, c, 8], \text{data}[a, b, c, 8, 1]} * (\text{ysl1} - \text{ysv1}) +
\text{data}[a, b, c, 8, 2] * (\text{ysl2} - \text{ysv2}) + \text{data}[a, b, c, 8, 3] * \text{ylv},
\{a, 1, Length[data]\}, \{b, 1, Length[data]\}, \{c, 1, Length[data]\}]]]
\]

To determine if a possible liquid configuration is physically possible, the command "SingleChecker" checks to see if the liquid/vapor interface (as previously defined) ever passes into a solid surface. If so the configuration is considered nonphysical. To do this, the command "SingleChecker" uses five commands ("CheckerRightLinear", "CheckerRightPP", "CheckerRightPN", "CheckerRightNP", "CheckerRightNN") depending upon the curvature of the interface and whether the circular segment is more or less than a hemisphere.
SingleChecker[data_, surf1_, set1_, surf2_, set2_] :=
If[data[[2, 1]] == data[[3, 1]] && data[[7, 2]] == 1, "Pass",
Which[
  data[[7, 1, 1]] == 0 &
data[[7, 1, 2]] == 0,
  CheckerRightLinear[data, surf1, set1, surf2, set2],
  data[[7, 1, 1]] == 1 &
data[[7, 1, 2]] == 1,
  CheckerRightPP[data, surf1, set1, surf2, set2],
  data[[7, 1, 1]] == 1 &
data[[7, 1, 2]] == -1,
  CheckerRightPN[data, surf1, set1, surf2, set2],
  data[[7, 1, 1]] == -1 &
data[[7, 1, 2]] == 1,
  CheckerRightNN[data, surf1, set1, surf2, set2]]]

CheckerRightLinear[data_, surf1_, set1_, surf2_, set2_] :=
If[data[[2, 1]] == data[[3, 1]], "Pass",
If[If[MinTable[surf1, x] - MxBT[data[[2, 1]],
  data[[2, 2]], data[[3, 1]], data[[3, 2]], x],
  {x, Min[data[[2, 1]], data[[3, 1]]], Max[data[[2, 1]], data[[3, 1]]],
  Abs[data[[2, 1]] - data[[3, 1]]] / 50}] < 0, "Fail", "Pass"],
  If[MinTable[MxBT[data[[2, 1]], data[[2, 2]], data[[3, 1]],
  data[[3, 2]], x] - surf2[set2, x], {x, Min[data[[2, 1]], data[[3, 1]]],
  data[[2, 2]], data[[3, 1]], Abs[data[[2, 1]] - data[[3, 1]]] / 50}] < 0,
  "Fail", "Pass"}) = {"Pass", "Pass", "Pass", "Fail"}]

CheckerRightPN[data_, surf1_, set1_, surf2_, set2_] :=
With[{xc = xCenter[data[[2, 1]], data[[2, 2]], data[[3, 1]],
  data[[3, 2]], data[[7, 2]], data[[7, 1, 1]] * data[[7, 1, 2]]]},
  With[{yc = yCenter[data[[2, 1]], data[[2, 2]], data[[3, 1]],
  data[[3, 2]], data[[7, 2]], data[[7, 1, 1]] * data[[7, 1, 2]], xc]},
    If[data[[3, 2]] > yc,
      If[If[MinTable[Sqrt[(surf1[set1, x] - yc)^2 + (x - xc)^2],
        {x, data[[3, 1]], data[[2, 1]]}, Abs[data[[2, 1]] - data[[3, 1]]] / 50}] < data[[7, 2]], "Fail", "Pass"],
      If[MaxTable[Sqrt[(surf2[set2, x] - yc)^2 + (x - xc)^2], {x, data[[3, 1]],
        data[[2, 1]], Abs[data[[2, 1]] - data[[3, 1]]] / 50}] < data[[7, 2]],
    yC > data[[3, 2]], If[If[MinTable[Sqrt[(surf2[set2, x] - yc)^2 + (x - xc)^2],
      {x, xC - data[[7, 2]], data[[2, 1]]},
      Abs[data[[2, 1]] - (xC - data[[7, 2]])] / 50}] < data[[7, 2]], "Fail", "Pass"],
    If[MaxTable[Sqrt[(surf2[set2, x] - yc)^2 + (x - xc)^2], {x, data[[2, 1]],
      data[[3, 1]], Abs[data[[2, 1]] - data[[3, 1]]] / 50}] < data[[7, 2]],
      "Fail", "Pass"}) = {"Pass", "Pass", "Pass", "Fail"}]
  ]

CheckerRightNN[data_, surf1_, set1_, surf2_, set2_] :=
With[{xc = xCenter[data[[2, 1]], data[[2, 2]], data[[3, 1]],
  data[[3, 2]], data[[7, 2]], data[[7, 1, 1]] * data[[7, 1, 2]]}],
  With[{yc = yCenter[data[[2, 1]], data[[2, 2]], data[[3, 1]],
  data[[3, 2]], data[[7, 2]], data[[7, 1, 1]] * data[[7, 1, 2]], xc]},
    If[If[MinTable[Sqrt[(surf1[set1, x] - yc)^2 + (x - xc)^2], {x, xC - data[[7, 2]],
      data[[2, 1]]}, Abs[(xc - data[[7, 2]]) - data[[2, 1]]] / 50}] < data[[7, 2]], "Fail", "Pass"],
    If[MinTable[Sqrt[(surf2[set2, x] - yc)^2 + (x - xc)^2], {x, xC - data[[7, 2]],
      data[[3, 1]], Abs[(xc - data[[7, 2]]) - data[[3, 1]]] / 50}] < data[[7, 2]],
]
For a given system, the previously defined commands are used to compile a large list of liquid configurations, and the resulting interfacial energy. The commands 'PostCheck' and 'TableMin' sort these configurations, taking the lowest energy configuration first, and determine what the lowest total-interfacial energy physically-possible configuration is.

For the system, the commands are previously defined to have compiled a large list of liquid configurations, and the resulting interfacial energy. The commands 'PostCheck' and 'TableMin' sort these configurations, taking the lowest energy configuration first, and determine what the lowest total-interfacial energy physically-possible configuration is.