

Pulsed-Laser Induced Dewetting of Metallic Nanostructures

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Dedication

I would like to dedicate this dissertation to my Mom and Dad, my siblings Abby, Emmy, Kara, Connor, and Liam, my Grandparents, and to all the places I called home.

My friends thank you for the time we spent together, especially Yao and Ryan.

I love you all very much!

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Abstract

This dissertation explores the fluid dynamics of nano and microscale liquid metal filaments, with an emphasis on experimentally investigating the influences and causes of filament breakup and metallic nanostructure formation. Understanding and manipulating the liquid state properties of materials, especially metals, have the potential to advance the development of future technology, particularly nanoscale technology. The combination of top-down nanofabrication techniques with bottom-up, intrinsic self-assembly mechanisms are a powerful fusion, because it permits new and unusual nanostructures to be created, whilst revealing interesting nanoscale physics.

In fluid dynamics, wetting and dewetting is the spontaneous natural process that occurs when a liquid supported on a substrate seeks to minimize its systems energy. Either by covering the substrate surface, in the case of wetting, or by rupturing and assembling into a collection of smaller liquid fragments; typically droplets, with minimal contact and surface area with the substrate and the surrounding gaseous environment. Due to metal's unique liquid state properties, like low viscosity and high surface energy, the dewetting phase is the prescient realm to experimentally access and study the governing dynamics, instabilities, and mass transport behind metallic nanostructure formation.

The work contained in this dissertation seeks to address some basic scientific questions, such as: How to develop reasonably simple but predictive models to describe the competition between instability mechanisms that result in filament coalescence or fragmentation, as a function of filament extent? How to manipulate the intrinsic material properties of liquid metals, like surface energy, to initiate instabilities, like those similar to the Rayleigh-Plateau instability, to encourage self-assembly at the nanoscale? A focused and collaborative approach is contained herein where experiments will be used to drive theoretical and computational simulations and vice versa.

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Chapter 1.

Physics of Wetting and Literature Review

Understanding the fundamental physics of liquids at the nanoscale, especially liquid metals, have the potential to extend the rich field of fluid mechanics and inform new advances in technology, especially nanoscale technology. For instance, metallic nanostructures are demonstrably important features in the research of plasmon resonances,^{1, 2} surface-enhanced Raman spectroscopy (SERS),^{3, 4} biosensing and biondiagnostics,^{5 6} photovoltaics,^{7, 8} and spintronics.^{9, 10} Therefore, by harnessing the underlying liquid state dynamics it will be possible to create new and unusual nanostructures whilst revealing interesting nanoscale physics. The science begins at an interface...

1.1 Interfaces, Surface Energy and Minimal Surfaces

The interface of a liquid with its surroundings, typically a gas like air, will spontaneously deform as it seeks to minimize the system energy. The interfacial energy is the result of broken or unsatisfied atomic, or molecular, bonds at the surface. A molecule or atom prefers to completely bond with another, attracting one another to satiate the available electronic bonds, the attraction is why the interface changes shape. When the interfacial energy per unit area is minimized (i.e. the fewest unoccupied bonds) the morphology is typically geometrically

simple, for instance a spherical bubble - however more complicated geometries can exist.

The interfacial energy can be approximated as, $\sigma \sim U/2a^2$, where U is this energy per atom or molecule and a^2 its area. Note that the interfacial energy increases as the intermolecular/atomic attraction increases and the molecular/atomic size decreases. For example, oils have interactions that are the van der Waals (vdW) type and near the thermal energy, $U_{oils} \sim kT$. At a temperature of 25 °C, $kT \sim 25$ meV, the interfacial energy is around 20 mJ/cm². For comparison the interfacial energy of water at room temperature is 72 mJ/cm² – it is higher due to its hydrogen bonding. Higher still are liquid metals. Mercury, which is a strongly cohesive liquid metal, and the only room temperature liquid metal, has an interfacial energy near 500 mJ/cm². The study of interfaces and interfacial energies between immiscible fluids is capillarity.¹¹

As a liquids interface is traversed, for instance, the curved surface of an oil droplet in water (two immiscible fluids) a change in pressure occur, see Figure 1.1(a). To minimize the interfacial energy the drop takes on the spherical shape with radius of curvature, R . Therefore, the work done by the surface when displaced by an amount dR can be written as, $\delta W = -p_o dV_o - p_w dV_w + \sigma_{ow} dA$. And the change in volume of one is the negative change in the other, $-dV_o =$

$dV_w = 4\pi R^2 dR$, where $dA = 8\pi R dR$. The constraint for equilibrium is $\delta W = 0$, resulting in an expression for the overpressure in the droplet, $\Delta p = p_o - p_w = 2\sigma_{ow}/R$. The result is the product of the interfacial energy and the radius of curvature.

However, curvature at an interface is often more complex. To define the curvature at a point, M , on an arbitrary surface, say, a piece of fruit, as in Figure 1.1(b), the surface normal has to be intersected by two orthogonal planes to define two radii of curvature, R and R' . If the center of the circle lies inside the surface the radius is defined as positive, otherwise it is negative. The increase in pressure that occurs when traversing the boundary is, analogously, the product of the interfacial energy and the, now arbitrary, surface curvature, κ . Equation (1.1) is also known as the Young-Laplace equation.^{12, 13} As a result of energy minimization some interfaces can possess complex and interesting surface curvature depending on the geometry of the supporting substrates, for example, those in Figure 1.1(c).

$$\Delta p = \sigma \left(\frac{1}{R} + \frac{1}{R'} \right) = \sigma \kappa \quad (1.1)$$

When the Laplace pressure is multiplied by a surface area element a force per unit length is present, an interfacial surface tension, or simply surface tension, and is expressed in units of Newtons per meter. The units of surface tension are

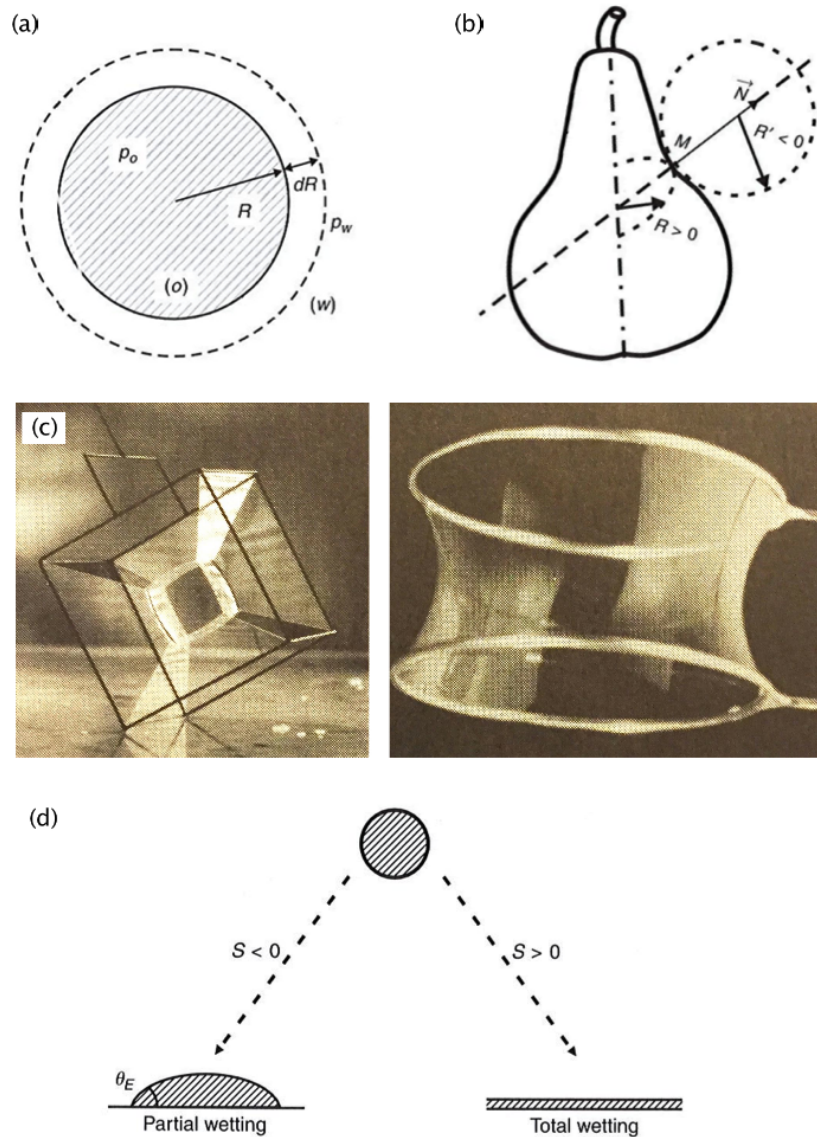


Figure 1.1. Surfaces with interfacial curvature, (a) a spherical oil droplet in water, two immiscible fluids, a change in pressure occurs when the interface is traversed, (b) complicated surface of a complex object, (c) interesting minimal surfaces, interfaces minimize their surface area depending on the supporting structure, (d) the spreading parameter, S , indicates whether a liquid will wet, or dewet (partial wetting), a surface depending on the interfacial energies of the system (liquid-solid, liquid-air, and solid-air energies), a liquid drop partially wets a substrate with a characteristic, equilibrium wetting angle, θ_e , at the triple phase contact line.¹¹

analogous to interfacial energy, and the two are used interchangeably. When the surface tension acts along a line element on the surface, a force is present, the capillary force, therefore surface tension resists the creation of new interfacial area and spontaneously minimizes it. Finally, two fluids that do not have a surface tension are said to be miscible.

1.2 Wetting and Dewetting

1.2.1 Total Wetting

Whether a liquid wets a substrate is captured by the, so-called, spreading parameter, S , and it depends on the differences in interfacial energies between the component materials that comprise the wetting system, Equation (1.2). When $S > 0$ spontaneous wetting happens and the liquid spreads and completely covers the substrate surface. This is due to the liquid-air interfacial energy being energetically favorable compared to the bare substrate-gas interfacial energy. On the other hand, if $S < 0$ then wetting is not energetically favorable and the liquid does not spontaneously cover substrate but forms droplets instead, partially wetting the substrate.

$$S = [E_{\text{substrate}}]_{\text{dry}} - [E_{\text{substrate}}]_{\text{wet}} = \sigma_{sg} - (\sigma_{sl} - \sigma_{lg}) \quad (1.2)$$

1.2.2 Partial Wetting - Dewetting

Dewetting is the natural process that occurs when liquids partially wet a substrate, often forming droplets. The droplets are created when an initially wetting condition, typically a liquid thin-film or filament, breaks apart and self-assembles through natural, energy minimization mechanisms (detailed in the following sections). As a result of dewetting a unique line exists, the triple-line, where all three phases (liquid, solid, gas) of the system meet. The perimetric triple-line changes shape as the droplet evolves through the dewetting process until the competing interfacial energies are in equilibrium with one another. The equilibrium condition is characterized by an angle the droplet surface at the triple-line makes with the substrate, the equilibrium-wetting angle, θ_e , see Figure 1.1(d). The spreading parameter can be recast in terms of the equilibrium-wetting angle and the liquid-gas interfacial energy, σ_{lg} . The expression is called Young's relation for the spreading parameter, $S = \sigma_{lg}(\cos \theta_E - 1)$.

1.3 Hydrodynamics

1.3.1 Free Jets and Rayleigh-Plateau Instability

When turning on the sink faucet in the lab it is a common site to observe the falling cylindrical water column break into droplets. This seemingly ordinary

occurrence is the consequence of some interesting physics. To begin with, volume conservation dictates that a cylinder of water with initial radius, R_o , and length, L , will break up into, n , number of droplets with radius, r . Therefore, $\pi R_o^2 L = 4/3 \pi r^3 n$. It is evident that the total surface area of all drops is less than that of the original cylinder when $r > 3R_o/2 = 1.5R_o$. Physicist Joseph Plateau lead the investigation into how a free, falling column of fluid spontaneously distorts its free surface in order to minimize the interfacial energy.¹⁴ He noticed that what began as a small surface perturbation, a sinusoidal-like fluctuation in the fluid column diameter, grows in amplitude with time. Eventually the amplitude grows so large that it pinches off from the fluid column forming a droplet.

Lord Rayleigh later extended the work of Plateau and mathematically demonstrated that not just any surface perturbation would grow in amplitude with time. He explained the phenomenon by correctly formulating the kinetic and potential energies of the fluid system and then used Lagrangian mechanics to solve for the dynamical equations.¹⁵ What he found is that there exists a preferred, natural perturbation wavelength that grows fastest in time. Equation (1.3) is the dispersion relation that expresses the dependence of the perturbation's growth rate, ω , to its wavelength, aka wavenumber, $k = 2\pi/\lambda$.¹⁶

$$\omega^2 = \frac{\sigma}{\rho R_o^3} k R_o \frac{I_1(k R_o)}{I_0(k R_o)} (1 - k^2 R_o^2) \quad (1.3)$$

Where I_0 and I_1 are the modified Bessel functions, R_o is the initial radius of the fluid column, and ρ is the fluid density. Unstable modes have positive growth rates and are only possible when $k R_o < 1$. Stable modes, therefore, decay in amplitude with time and have negative growth rates, $k R_o > 1$.

Figure 1.2 is a plot of the dispersion relation that illustrates the dependence of the growth rate on the wavenumber. Two important quantities are the maximum growth rate and wavelength, which are $\omega_m = 0.34 \sqrt{\frac{\sigma}{\rho R_o^3}}$ and $k R_o = 0.697$, respectively. In his own words, Rayleigh described the solution as, “The corresponding value of λ is given by $4.508 \cdot 2R_o$ which gives accordingly the ratio of wave-length to diameter for the kind of disturbance which leads most rapidly to the disintegration of the cylindrical mass.”¹⁵ Whereas Plateau investigated a falling column in the presence of gravity, Rayleigh distinguished his theoretical solution by stating, “In the case just considered, the cause of instability is statical, and the phenomena are independent of the general translatory motion of the jet.”¹⁵ In recognition of the contributions from both men the phenomena has come to be known as the Rayleigh-Plateau instability or Plateau-Rayleigh instability.

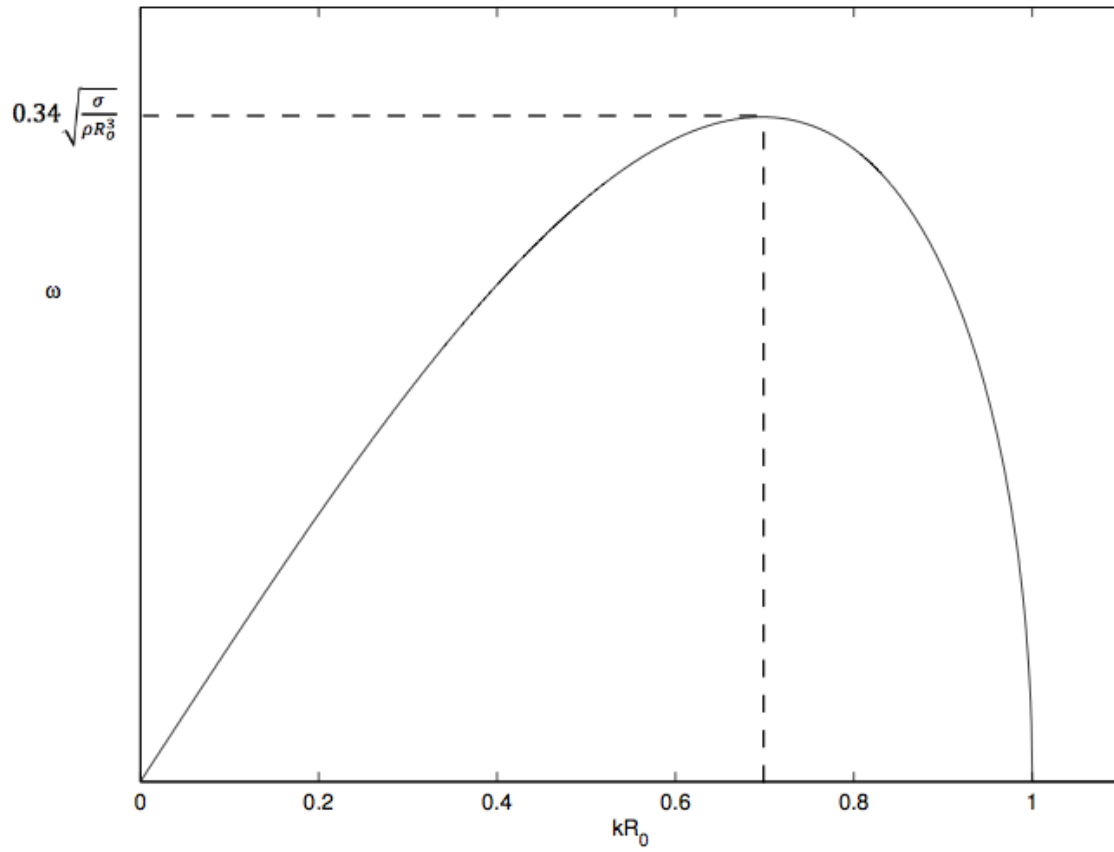


Figure 1.2. Plot of the dispersion relation, Equation (1.3), illustrating the dependence of the growth rate, ω , on the dimensionless wavenumber, kR_0 , for the Rayleigh-Plateau instability mechanism.¹⁶

Inverting the instability growth rate gives the characteristic breakup time. For example, a column of water with a diameter of 1 cm, approximately the diameter of a sink faucet, has a characteristic breakup time of $\sim 1/8$ s, which is consistent with the observation of breakup in a sink. Rayleigh's solution showed that the breakup of the fluid column is the result of capillary forces. A supplemental way to comprehend breakup is to conceptually understand how the surface curvature (i.e. perturbation) produces competing pressures, both stabilizing and destabilizing, inside a fluid column. This is done by taking inventory of the radii of curvature of the fluid column, Figure 1.3, then applying the Laplace pressure equation, Equation 1.1.

The circumferential radii, r and r' , inside the fluid column produce two regions of positive pressure, at the peak and trough, respectively. However, since the radius of the peak is larger than that of the trough the pressure in the peak is lower, therefore the higher trough pressure wants to squeeze fluid into the lower pressure peak region. As a result the trough amplitude seeks to grow in time. Additionally, the radii of curvatures and resulting pressures associated with the surface wavelength also contribute to the dynamics. The axial radii, R and R' , at the peak and trough, respectively, give rise to opposing pressure regions. The pressure is positive in the peak region, where as, the pressure in the trough is negative. The negative pressure would like to lessen the curvature of the trough

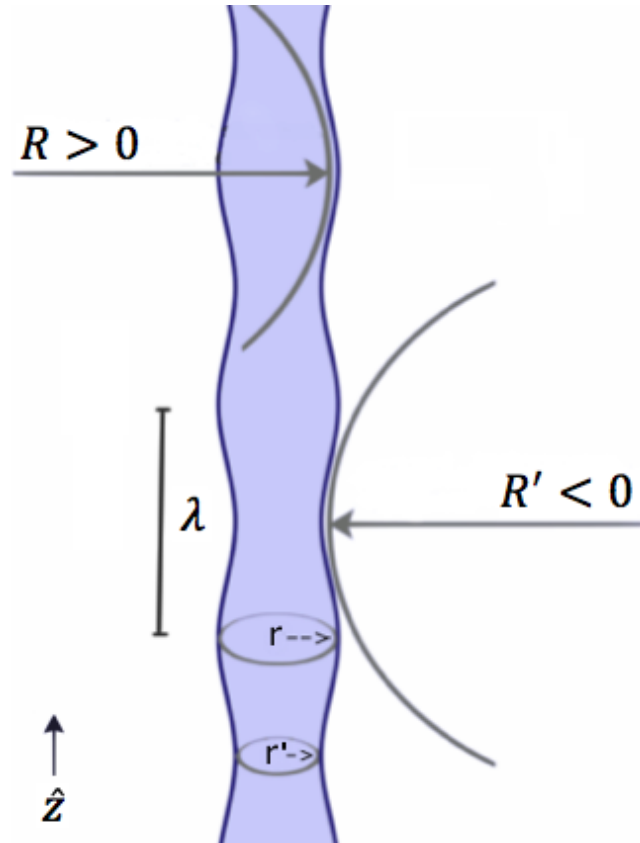


Figure 1.3. A free, fluid column distorts itself spontaneously due to the capillary force, which seeks to minimize the surface energy. A critical wavelength exists because of competing pressures, the circumferential and axial pressures. The stabilizing force is the axial capillary pressure associated with the radius R' , and the destabilizing force is the circumferential capillary pressure associated with the radii, r and r' .¹⁷

and diminish its amplitude with time. The confluence of the circumferential and axial pressures do not always cancel each other and one will eventually exert greater influence, depending on growth rates. Inevitably though, if the amplitude of the perturbation grows large enough troughs will touch, pinching off from the filament to form droplets.

1.3.2 Equation of Motion

To illuminate the fundamental physics beneath fluid dynamics it is worthy to construct, from first principles, the general, mathematical description for the equation of motion. From there it is possible to extend, or simplify, the theory in any number of directions, to best suit the need of a specific fluid dynamic system.

The following derivation is a macroscopic description of the motion of fluids; the fluid is regarded as a continuous system. That is, any small element of fluid volume is presumed to be sizable, so as to consist of a great number of molecules or atoms, whilst being considered a fluid-particle, or a fluid-point, in the flow. In other words, an elemental volume is small when compared to the volume of the fluid body, but large compared to the distances between the constituents. Even nanometric liquids can fall under this auspice, which is pertinent for this work. For example, a droplet of liquid copper just 100 nm in

diameter contains 10^8 atoms, which could fill 10^5 volume elements, each containing 10^3 atoms.

The state of a moving fluid follows from the functions that give the distribution of the fluid velocity, $\mathbf{u} = \mathbf{u}(x, y, z, t)$, and any two thermodynamic quantities related to the fluid, for instance the pressure, $p(x, y, z, t)$, and density, $\rho(x, y, z, t)$.¹² All the thermodynamic quantities are established by the values of any given two along with the equation of state – which provides a relationship between two or more state functions, such as pressure, temperature, volume or internal energy.¹⁸ If the three components of the velocity and the pressure and density are known then the state of the fluid is completely known. It is important to point out that the equations are functions of space and time at a particular point in the fluid, and are not actually affixed to moving particles; the same applies for the density and the pressure.

The derivation begins with the fundamental principle of the conservation of mass, pertaining to some volume of space, V_o , having a density, ρ . When integrated over the spatial extent it has a mass, ρV_o . The mass of fluid flowing per unit of time through a differential area element, $d\mathbf{f}$, bounding the volume is $\rho \mathbf{u} \cdot d\mathbf{f}$. The unit vector of $d\mathbf{f}$ is normal to the volume surface and pointed outward, its magnitude is equal to the area element. The unit vector sign convention

therefore prescribes that fluid flowing out of a volume is positive and mass flowing into a volume as negative. It follows then, that the total mass of fluid flowing out of a closed volume has to be equal to the decrease in mass leaving with time,

$$\oint \rho \mathbf{u} \cdot d\mathbf{f} = -\frac{\partial}{\partial t} \int \rho dV \Rightarrow \int \nabla(\rho \mathbf{u}) dV = -\frac{\partial}{\partial t} \int \rho dV. \quad (1.4)$$

The surface integral has been transformed into a volume integral using the Divergence theorem of vector calculus.¹⁹ Since both sides of Equation (1.4) are identically integrated over the same arbitrary volume the integrands are equal. This equivalence, between the divergence of mass (i.e. mass flux density) and the change in density with time, is known as the continuity equation.¹²

$$\frac{\partial \rho}{\partial t} + \nabla(\rho \mathbf{u}) = 0 \Rightarrow \frac{\partial \rho}{\partial t} + \rho \nabla \mathbf{u} + \mathbf{u} \cdot \nabla \rho = 0 \quad (1.5)$$

A pressure, p , acting on the volume is causing the mass to flow. The total pressure acting on the volume, when integrated over the bounding surface, produces a force, Equation (1.6) – the negative sign is due to the pressure acting inward, recall the differential area element was chosen to be positive when directed outward, normal to the surface.

$$-\oint p d\mathbf{f} = -\int \nabla p dV \quad \Rightarrow \quad \rho \frac{d\mathbf{u}}{dt} = -\nabla p \quad (1.6)$$

Again, the Divergence theorem was used to transform the surface integral into a volume integral. The right hand side tells us that a force is acting on the unit volume of fluid, hence the density.

Recall, what is of interest is a point in space in the fluid and not the moving particles, or elements, themselves. Newton's law, Equation (1.6), is the force on the unit volume, as if it were a particle (i.e. the continuum argument). It is therefore necessary to transform the time derivative in Equation (1.6) to refer to a fixed point in space. This is accomplished by recognizing that the change in velocity, $d\mathbf{u}$, of the fluid particle during the time, dt , is the combination of two components (i.e. the total derivative). Firstly, the change in velocity, $d\mathbf{u}$, at a fixed point in space, during the time, dt , and secondly, the difference in the velocities at two points, $d\mathbf{r}$, apart during the same time, dt . The first is given by, $(\partial\mathbf{u}/\partial t)dt$, where the partial derivative is taken with respect to constant spatial variables (x, y, z) , naturally, and the second is given by, $(d\mathbf{r} \cdot \nabla)\mathbf{u}$.¹² When combined, divided by dt , and equated to the pressure force, Newton's law, Equation (1.6), becomes,

$$\frac{d\mathbf{u}}{dt} = \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} = -\frac{1}{\rho}\nabla p + \mathbf{F}. \quad (1.7)$$

This is Euler's equation and it is a fundamental equation of fluid dynamics, and it has units of Newtons per unit volume. Extra terms can be added to take into account additional body forces, $\mathbf{F}$, acting on the fluid; for example, the force due to a gravitational field, $\mathbf{g}$.

So far, the derivation has not taken into account any energy dissipation processes, like heat transfer between different regions, or the consequences of viscosity, the internal friction resulting from the fluid moving. Equation (1.7) therefore describes the motion of an adiabatic, ideal fluid. However, ideal fluids are not an experimental reality. Energy dissipative processes, like viscosity, play an important role during the motion of a fluid, on the motion itself – the result of thermodynamic irreversibility. Real fluid are viscous fluids. The trajectory of the derivation for the viscous flow equation of motion largely follows from the venerable work of Landau and Lifshitz.¹²

Where the energy of a moving mass changes, a change in momentum is requisite. Therefore the derivation begins by finding an expression for the momentum flux with time. Equation (1.5), the mass flux density, (the amount mass diverging from a unit volume) has momentum, $\rho\mathbf{u}$, and a time rate of

change of $\partial(\rho \mathbf{u})/\partial t$; for illustrative purposes, it is recast in vector component notation (summation over the indices values $i = 1, 2, 3$ is understood and corresponds to the axes x, y, z , respectively),

$$\frac{\partial(\rho \mathbf{u})}{\partial t} = \rho \frac{\partial \mathbf{u}}{\partial t} + \frac{\partial \rho}{\partial t} \mathbf{u} \Rightarrow \frac{\partial(\rho u_i)}{\partial t} = \rho \frac{\partial u_i}{\partial t} + \frac{\partial \rho}{\partial t} u_i. \quad (1.8)$$

Using the continuity equation, Equation (1.5), and the equation of motion, Equation (1.7), to substitute in for the terms $\partial \rho / \partial t$ and $\partial u_i / \partial t$, respectively, gives,

$$\frac{\partial(\rho u_i)}{\partial t} = -\rho u_k \frac{\partial u_i}{\partial x_k} - \frac{\partial p}{\partial x_i} - u_i \frac{\partial(\rho u_k)}{\partial x_k} = -\frac{\partial p}{\partial x_i} - \frac{\partial(\rho u_i u_k)}{\partial x_k}. \quad (1.9)$$

The pressure can be rewritten using a Kronecker delta,²⁰ δ_{ik} , as $(\partial p / \partial x_k) \delta_{ik}$, then combined with the velocity term to produce,

$$\frac{\partial(\rho u_i)}{\partial t} = -\frac{\partial}{\partial x_k} (p \delta_{ik} + \rho u_i u_k) = -\frac{\partial \Pi_{ik}}{\partial x_k}. \quad (1.10)$$

Equation (1.10) is the required momentum flux expression for the fluid, written in terms of the momentum flux density tensor, Π_{ik} , a second rank tensor – a second rank tensor can be best thought of as a matrix, with on and off diagonal

components, representing viscous interactions on and off axes, respectively. Thus Π_{ik} is the i th component of the amount of momentum flowing, in unit time, through an area perpendicular to the x_k axis.¹² The left hand side is the time rate of change of the i th component of the momentum contained in the volume.

Viscosity is the internal friction due to the irreversible transfer of momentum from faster moving particles to slower moving particles. Therefore, a viscous term, $-\sigma'_{ik}$, the viscosity stress tensor, can be added to the momentum flux density tensor, Π_{ik} , to account for the momentum transfer. The viscosity stress tensor's form will have to satisfy a couple conditions. First, that the internal friction in a fluid occurs only when fluid particles move with different relative motions, thus σ'_{ik} must depend on the spatial derivatives of the velocity, including a linear combination of them; supposing the velocity gradients are small they will depend only on the first derivatives. Second, it must vanish for $v = \text{constant}$, including for uniform circular motion, where $\mathbf{u} = \boldsymbol{\Omega} \times \mathbf{r}$. A constructed, rank two tensor that satisfies these conditions is,¹²

$$\sigma'_{ik} = \mu \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} - \frac{2}{3} \frac{\partial u_l}{\partial x_l} \delta_{ik} \right) + \zeta \frac{\partial u_l}{\partial x_l} \delta_{ik} \quad (1.11)$$

Where μ and ζ are the coefficients of viscosity (μ is called the dynamic viscosity and has units of [Pa·s]), which can, in general, be functions pressure, p , and

temperature, T . The term in the parenthesis vanishes under contraction with respect to i and k (Levi-Civita permutation). What is important, according to Equation (1.10), is the spatial derivative of the viscosity stress tensor,

$$\begin{aligned}\frac{\partial \sigma'_{ik}}{\partial x_k} &= \mu \left(\frac{\partial^2 u_i}{\partial x_k^2} + \frac{\partial}{\partial x_i} \frac{\partial u_k}{\partial x_k} - \frac{2}{3} \frac{\partial}{\partial x_i} \frac{\partial u_l}{\partial x_l} \right) + \zeta \frac{\partial}{\partial x_i} \frac{\partial u_l}{\partial x_l} \\ &= \mu \frac{\partial^2 u_i}{\partial x_k^2} + \left(\zeta + \frac{1}{3} \mu \right) \frac{\partial}{\partial x_i} \frac{\partial u_l}{\partial x_l}\end{aligned}\quad (1.12)$$

Equation (1.12) is therefore the force per unit volume generated by the viscosity stress tensor. When recast in vector form and added to the Euler equation for an ideal fluid, Equation (1.7), it becomes the equation of motion for viscous fluids.

$$\rho \left[\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right] = -\nabla p + \mu \nabla^2 \mathbf{u} + \left(\zeta + \frac{1}{3} \mu \right) \nabla (\nabla \cdot \mathbf{u}) + \sigma \kappa \delta_s \mathbf{n} \quad (1.13)$$

Equation (1.13) will be foundation for all the following equations of motion in this dissertation. It will be reduced, extended, recast and computationally modeled in order to investigate the underlying physics in the accompanying experimental results. Further more, extra terms can be added to account for additional forces acting on the fluid. For example, the force associated with surface tension was added, which did not appear in the derivation of the Eulerian equation of motion.

This is because it is not a continuum body force (i.e. force per unit volume), but rather a force associated with a boundary condition, the interface at the fluids free surface. Therefore, its form follows the Laplace equation, $\sigma\kappa$, Equation (1.1), and is appropriately restricted to the free surface by a delta function, δ_s , whose direction is normal to the surface.

Lastly, if it is assumed that the fluid is incompressible, that is, the divergence of the velocity is zero, $\nabla \cdot \mathbf{u} = 0$, and the surface energy term is not important, the last two terms of the right side of Equation (1.13) drop out, and the equation reduces to the well known Navier-Stokes (N-S) equation of motion for an incompressible, viscous fluid flow, Equation (1.14).

1.3.3 Thin-Film Approximation

Equation (1.13), or its derivative, the Navier-Stokes equation, is difficult to solve. This is due to the inclusion of a term for turbulent convective flow, $(\mathbf{u} \cdot \nabla)\mathbf{u}$. In fact, it has not been proven whether a three dimensional solution always exists; interestingly, since 2001 the Clay Mathematics Institute has offered a six-figure cash prize to anyone who shows solutions do.²¹ It is therefore necessary to reduce Equation (1.13) to a simpler form, and for fluid flow in very thin-films this reduction is called the thin-film approximation, or the lubrication approximation²².

The first assumption is that one dimension of the fluid flow is much smaller than the other dimensions. This is certainly the case for thin-films, where the thickness ($\hat{z}$), h , is much smaller than any in-plane ($\hat{x}, \hat{y}$) length, L . For example, in this work with metallic thin-films, thicknesses are on the order of $h \sim 10$ nm, where as, lateral dimensions range from $L \sim 10^2 - 10^5$ nm. It follows then that their ratio, $\epsilon = h/L$, becomes a very small parameter. The starting point for the approximation is the Navier-Stokes equation,

$$\rho \left[\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right] = -\nabla p + \mu \nabla^2 \mathbf{u}. \quad (1.14)$$

The fluid velocity, $\mathbf{u} = (\mathbf{v}, w)$, can be split into the in-plane and out-of-plane components, $\mathbf{v}$, and, w , respectively, and the velocity has a scale of, U .

The in-plane length and velocity scales can be used to calculate the Reynolds number, $Re = UL\rho/\mu$, which is a dimensionless number comparing a fluid's inertia to its viscosity. A large Reynolds number is indicative of an inertial regime, a regime where the dynamics are controlled by the rate at which surface energy is converted to kinetic energy of the liquid, where as, a small Reynolds number is indicative of a viscous regime, a regime where viscous dissipation is the important hydrodynamic quantity. For the lubrication approximation it is

assumed that the Reynolds number is small, therefore the inertial terms on the left side of Equation (1.4) can be ignored. The equation then becomes,

$$0 = -\nabla p + \mu \nabla^2 \mathbf{u} \quad (1.15)$$

$$0 = -\nabla p + \mu \left(\frac{1}{L^2} \frac{\partial^2}{\partial \bar{x}^2} + \frac{1}{L^2} \frac{\partial^2}{\partial \bar{y}^2} + \frac{1}{h^2} \frac{\partial^2}{\partial \bar{z}^2} \right) \mathbf{u}$$

In the second line, the Laplace operator was expanded and dimensionless variables used for a comparison to smallness; they are defined using the characteristic length scales from the system, $\bar{x} = x/L$, $\bar{y} = y/L$, $\bar{z} = z/h$. It can be seen that the second derivatives of the in-plane $(\hat{x}, \hat{y})$ coordinates can be ignored due to their smallness, since $L \gg h$. Omitting these terms, Equation (1.15) can be reduced to,²²

$$\nabla_2 p = \left(\frac{\partial}{\partial x} \hat{x} + \frac{\partial}{\partial y} \hat{y} \right) p = \mu \frac{\partial^2 \mathbf{v}}{\partial z^2} \quad (1.16)$$

$$\frac{\partial p}{\partial z} \hat{z} = \mu \frac{\partial^2 w}{\partial z^2} \hat{z} \approx 0 \quad (1.17)$$

Here, the in-plane and out-of-plane components have been separated, and the normal component of the velocity, $w \ll |\mathbf{v}|$, so it can be safely neglected. Equation (1.17) can easily be integrated to find the pressure, p . There is an

important boundary condition at the liquid-air interface, $z = h(x, y)$, the Young-Laplace equation states there is a change in pressure at the interface, $p(h) = -\sigma\kappa$, a product of the interfacial energy and surface curvature. Equation (1.16) can be integrated twice to find the velocity function, $\mathbf{v}(z)$,

$$\mathbf{v}(z) = \frac{1}{\mu} \nabla_2 p \frac{z^2}{2} + \mathbf{A}z + \mathbf{B} \quad \Rightarrow \quad \mathbf{v}(z) = \frac{1}{\mu} \nabla_2 p \left(\frac{z^2}{2} - zh \right) \quad (1.18)$$

The integration constants can be found by applying the boundary conditions. At the substrate interface, $z = 0$, a no slip condition is specified, that is, the velocity goes to zero, yielding $\mathbf{B} = 0$. Additionally, the stresses at the free surface interface have to be continuous, $(\partial \mathbf{v} / \partial z)_{z=h} = 0$, therefore, $\mathbf{A} = -\nabla_2 p h / \mu$. Importantly, the next step is to average the velocity over the thickness of the thin-film to remove the z -dependence.

$$\langle \mathbf{v} \rangle = \frac{1}{h} \int_0^h \mathbf{v}(z) dz = \frac{1}{h} \int_0^h \frac{1}{\mu} \nabla_2 p \left(\frac{z^2}{2} - zh \right) dz = -\frac{1}{3\mu} \nabla_2 p h^2 \quad (1.19)$$

Going forward, ∇_2 , will be written, ∇ , with the assumption that the spatial derivative be over the in-plane coordinates. Lastly, conservation of mass dictates that, $\partial h / \partial t + \nabla \cdot (h \langle \mathbf{v} \rangle) = 0$, and therefore the result is the desired thin-film equation,

$$\frac{\partial h}{\partial t} = -\frac{1}{3\mu} \nabla \cdot [\sigma h^3 \nabla \nabla^2 h + h^3 \nabla \Pi(h)] \quad (1.20)$$

Where the pressure takes the form, $p(h) = -(\sigma \nabla^2 h + \Pi(h))$, and the surface curvature can be approximated by, $\kappa \approx \nabla^2 h$. The additional pressure term, $\Pi(h)$, - discussed in the next section - is the so-called disjoining pressure, which describes the interaction between the particles in the fluid and solid substrate upon which it wets. It is a van der Waals (vdW) type interaction, including both an attractive and repulsive term between the thin-film and the substrate.

1.3.4 Substrate Interactions

The preceding sections on the equations of motion and Rayleigh-Plateau theory accurately describe the dynamics for a free, incompressible fluid. For real systems, like the experiments considered in this dissertation, it is important to extend the fluid dynamic description to take into account interactions with a supporting substrate. To describe the breakup of liquid thin-films and filaments on surfaces, like liquid metals on oxide, additional terms have to be included in the governing equations. Recall, the thin-film approximation of the Navier-Stokes equation is a spatial simplification, the rationale being that flows generally have one dimension that is much smaller than the others, in this case, the height of the liquid (metal). This approach leads to the dynamical equation,

Equation (1.20), describing the height h as a function of time. A new term was introduced, the disjoining-pressure, $\Pi(h)$, which represents the interaction between the substrate and the liquid via a potential,^{23, 24 25}

$$\begin{aligned}\Pi(h) &= \xi f(h) = \xi \left[\left(\frac{h_*}{h} \right)^n - \left(\frac{h_*}{h} \right)^m \right] \\ &= \frac{(n-1)(m-1)(1-\cos\theta_E)}{(n-m)h_*} \sigma \left[\left(\frac{h_*}{h} \right)^n - \left(\frac{h_*}{h} \right)^m \right]\end{aligned}\tag{1.21}$$

Where $h(x, y, t)$ is the height of the liquid, η is its viscosity, σ is the surface tension of the liquid-gas interface. The scale of the interaction, $\xi = s/Mh_*$, where $M = (n-m)/((n-1)(m-1))$, and $s = \sigma(1-\cos\theta)$, is related to the Hamaker constant, $A = 6\kappa h_*^3$, which is a material dependent constant that defines the vdW interaction.^{26, 27}

The form of Equation (1.21) is a form similar to the Lennard-Jones potential,²⁸ which is often utilized in physics as a description for the vdW interaction between atoms and/or molecules²⁹ – and is convenient because of its computational and physical simplicity, yet elegantly revealing. The first term represents liquid-solid repulsion, and the second term, liquid-solid attraction.^{30, 31} A characteristic of the equation is an equilibrium distance, a thin-film thickness, h_* , known as the precursor layer, at which attraction and repulsion cancel each other out.

The use of the disjoining pressure in the description of dewetting is important because of its repercussion in the governing equation, Equation (1.20). It is a mechanism that seeks to collapse the thin-film thickness to that of the equilibrium height. In essence, generating instability in its pursuit, a very important requirement in thin-film breakup phenomenon. Typical values for the pair interaction exponents are, $(n, m) = (3, 2)$.³² When the disjoining pressure is included, a very thin-film, a precursor film, wets the substrate, equal to the equilibrium thickness. This is because the precursor film is maintained in a state of equilibrium due to the intermolecular forces between the liquid and the substrate. As Diez³⁰ explains it, in this frontal film (i.e. near the contact line) there is excess, or “disjoining”, pressure that is due to the fact that the intermolecular forces experienced by a volume element in the interior of the precursor film are different from those acting on an identical element in the interior of the bulk phase of the same fluid. Figure 1.4 illustrates how the inclusion of the disjoining pressure affects the equilibrium-wetting condition of a droplet on a substrate by the necessity of the precursor film.

1.3.5 Linear Stability Analysis

Equation (1.20) is a nonlinear equation, it is a fourth-order diffusion equation, carrying with it mathematical peculiarities. For instance, the maximum principle

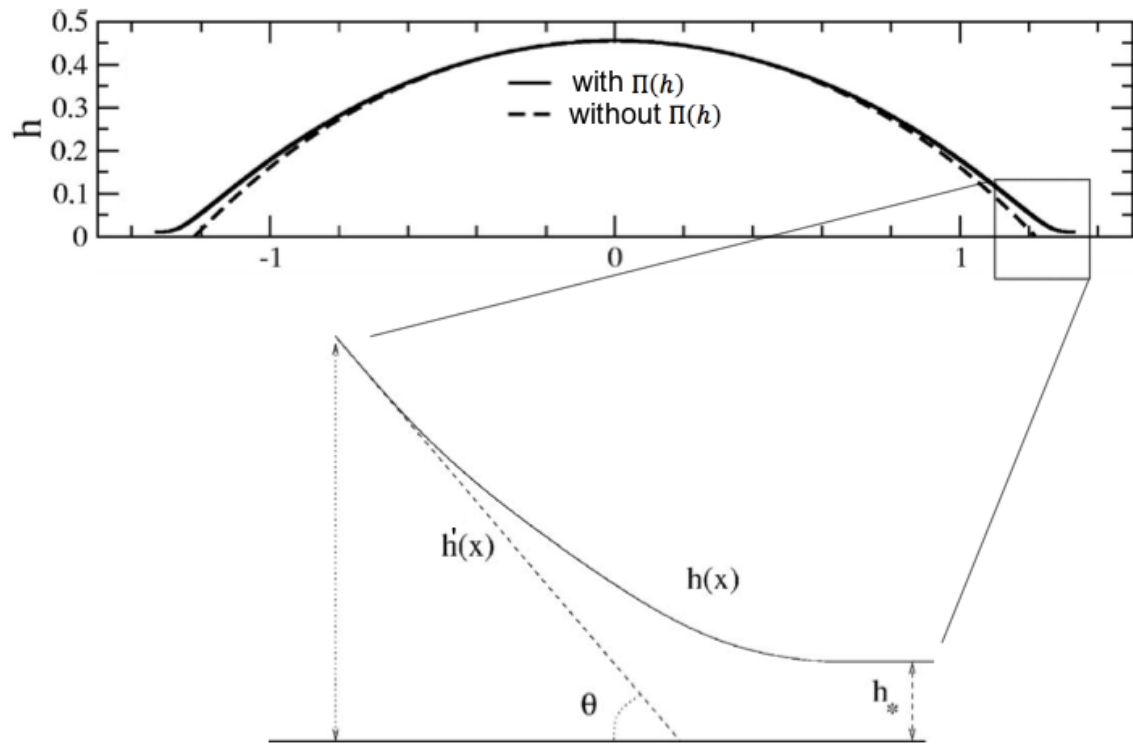


Figure 1.4. Profile of a droplet partially wetting a substrate with and without the disjoining pressure term. This is for a disjoining pressure with interaction exponents $(n, m) = (3, 2)$, equilibrium height $h_* = 0.1h$, and a wetting angle, $\theta = 50^\circ$.³⁰

is not guaranteed,³³ meaning, the solution is not guaranteed to be bounded from above and below by its initial conditions; in contrast to a second-order diffusion equations in which it is. As a result, even if the initial conditions are nonzero everywhere (i.e. the fluid covers the entire domain) there is no guarantee that a solution will remain bound.²² Therefore, solutions to Equation (1.20) need to be well-posed, weak solutions; namely, that a solution exists but whose derivatives may not all exist but nonetheless deemed to satisfy the equation in some precisely defined sense.³⁴ Additional properties, and idiosyncrasies, of the fourth-order diffusion equation are explored by Bertozzi.³³

As a result, a preferred technique for finding a descriptive solution has been to approach the problem from a linear stability analysis (LSA) direction. LSA supplies a fundamental understanding of the instability mechanism, including useful insight regarding the development of the instability from an initially flat thin-film, and by construction it applies to the early stages of evolution.²⁴

To begin, Equation (1.20) should be non-dimensionalized, this step serves to simplify and parameterize the governing thin-film equation.³⁰ If the equation, for instance, had numerous terms this process provides a sense of scale, that is, a means by which the relative importance of the terms can be determined. The

non-dimensional variables are defined as, $h = \bar{h}h_c$, $x = \bar{x}x_c$, $y = \bar{y}x_c$, $t = \bar{t}t_c$, and, $t_c = 3\mu x_c^4 / \sigma h_c^3$. Upon substitution, Equation (1.20) becomes,

$$\frac{\partial \bar{h}}{\partial \bar{t}} = -\nabla \cdot (\bar{h}^3 \nabla \nabla^2 \bar{h}) - K \nabla \cdot (\bar{h}^3 f' \nabla \bar{h}) \quad (1.22)$$

where $f' = \partial f / \partial h$, and $K = \kappa x_c^2 / \sigma h_c = (1 - \cos \theta_E) / M h_*$; for nanoscale metallic thin-films the constant non-dimensional length scales are typically chosen so that, $x_c = h_c = h_o$, the initial thin-film thickness, and h_* is in units of h_c . For plainness and intelligibility, from this point forward, the bars over the variables signifying non-dimensionality will be dropped.

The solution is constructed by taking an initially flat thin-film with thickness, h_o , the simplest base solution, and disturbing it with small perturbations in height, ϵ . It is supposed that, $\epsilon \ll 1$, and the perturbations are distinguished by having a characteristic wavenumber, $k = 2\pi/\lambda$, and frequency, ω , (i.e. growth rate). For instance,

$$h = h_o + \epsilon h_o \exp(ikx + \omega t) \quad (1.23)$$

Upon plugging in Equation (1.23) into Equation (1.22), and collecting terms linear in ϵ , a dispersion relation is generated that relates wave number to growth rate,

$$\omega = k^2 h_o^3 (k_c^2 - k^2) \quad (1.24)$$

where,

$$k_c^2 = K f'(h_o) = -\frac{K}{h_o} \left[n \left(\frac{h_*}{h_o} \right)^n - m \left(\frac{h_*}{h_o} \right)^m \right] \quad (1.25)$$

It is evident there's a critical wavenumber, such that, if $k_c^2 < 0$ the thin-film is linearly stable, $\omega < 0$, for all values of wavenumber, k , therefore, within this regime any instability will decrease in amplitude with time. However, when, $k_c^2 > 0$, and the wavenumber is in the range, $0 < k < k_c$, the film is unstable, $\omega > 0$, and instabilities will grow in amplitude with time, leading to thin-film breakup and the formation of droplets on the substrate surface.

It is important to point out that when, $k_c^2 = 0$, (i.e., no intermolecular forces present between the liquid and the solid substrate), the dash-dotted line in Figure 1.5(b), all instabilities decay in amplitude with time, and the thin-film is linearly stable for all wavenumbers. Therefore, the disjoining pressure, Equation (1.25), is the underlying mechanism by which thin-films experience dewetting.

Figure 1.5(a) illustrates the dependence of the critical wave number, k_c^2 , on the thickness of the precursor, h_* . It is apparent that k_c^2 is not positive for all values of h_* , the functionality turns negative as the precursor thickness approaches the thickness of the initial film, h_o . As a result, the amplitude of the perturbation, at

that wavenumber, will decrease with time and the thin-film will be linearly stable, the intermolecular forces, at these thickness of h_* , stabilize the film. However, there is a domain of h_* where k_c^2 is positive, therefore instabilities will grow with time, in Figure 1.5(a), this occurs when $0 < h_* < 0.65$. For nanoscale metallic dewetting the precursor thickness is typically chosen to be in the range, $0.001 < h_* < 0.1$, which leads to reasonable time and length scales for the breakup mechanism, and is supported by experimental observation.^{26, 30}

Figure 1.5(b) is a plot of the dispersion relation, Equation (1.24), the growth rate, ω , as a function of wavenumber, k . In the unstable region, $\omega > 0$, there exists a maximum growth rate when $d\omega/dk = 0$, given by

$$\omega_m = \frac{h_0^3 k_c^4}{4}, \quad (1.26)$$

at the wavenumber,

$$k_m = \frac{2\pi}{\lambda_m} = \frac{k_c}{\sqrt{2}}. \quad (1.27)$$

Where the wavelength, λ_m , is the length scale associated with the fastest growing instability, see dispersion curve in Figure 1.5(c). Therefore, this wavelength should dominate and be evident in dewett experiments. Indeed, this

Figure 1.5. (a) Plot of the square of the critical wavenumber, k_c^2 , Equation (1.25), as a function of the precursor thickness, h_* . Instabilities will grow in time when, $k_c^2 > 0$. (b) Growth rate, ω , of the instability as a function of wavenumber, $k = 2\pi/\lambda$, (solid line) for a thin-film with base height, $h_0 = 1$, wetting angle, $\theta = 69^\circ$, $(n, m) = (3, 2)$, and precursor thickness, $h_* = 0.1$. The fastest growth rate occurs for the wavenumber k_m . (c) Wavelength, λ , as a function of the growth rate. The maximum growth rate, ω_m , has an associated wavelength, λ_m , this wavelength should be experimentally measurable. When, $k_c^2 = 0$, (i.e., no intermolecular forces present between the liquid and the solid substrate) (dash-dot line) all instabilities decay in amplitude with time, the thin-film is linearly stable for all wavenumbers.

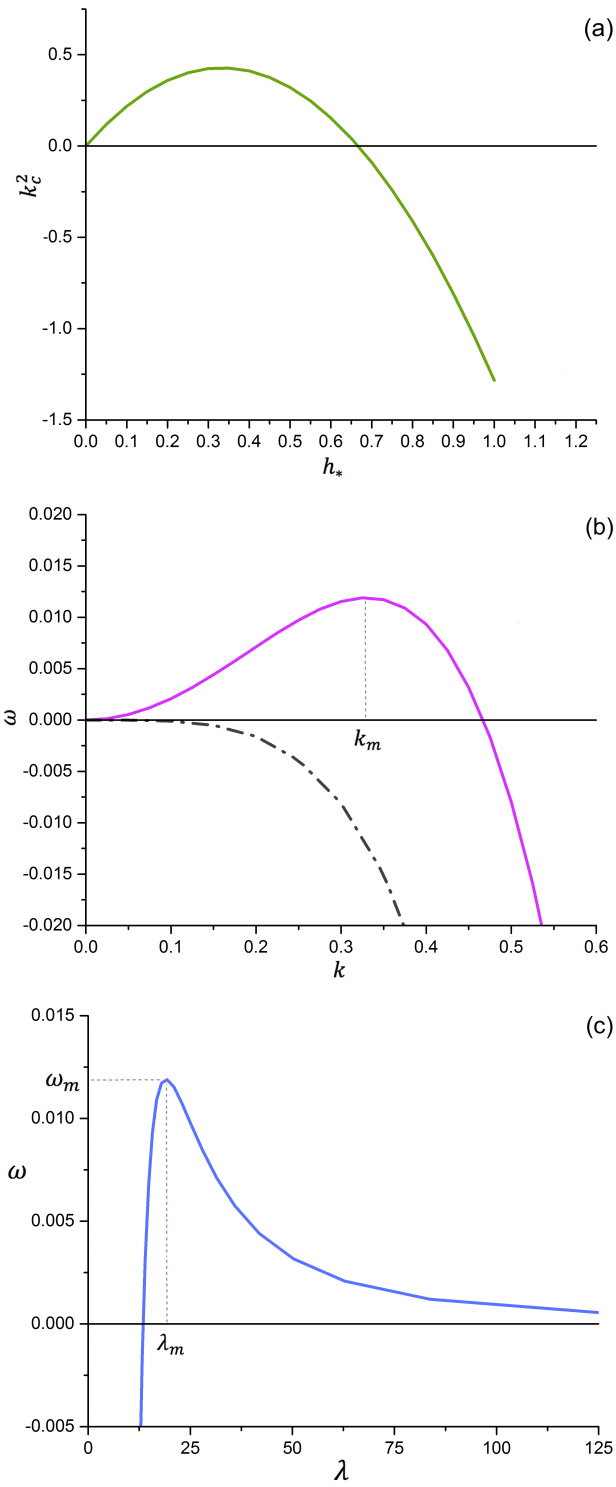


Figure 1.5. Continued.

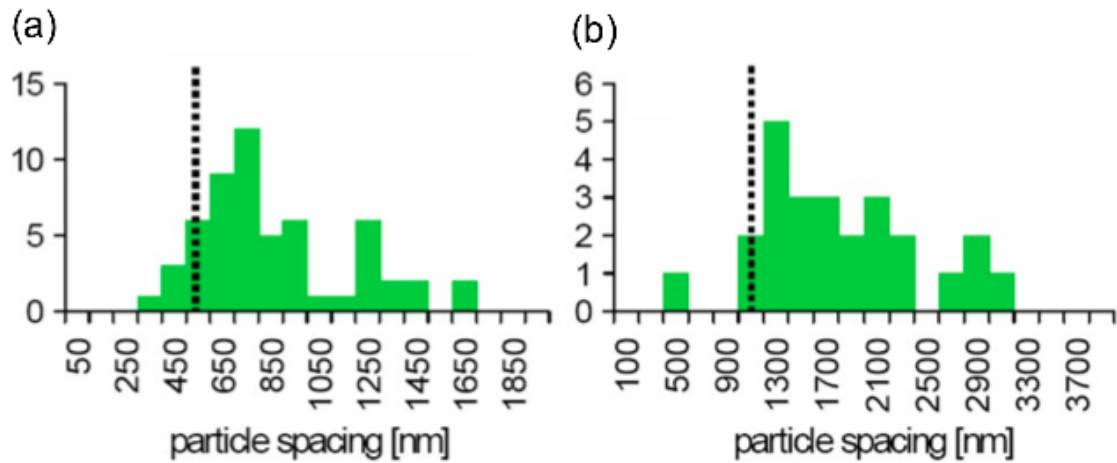


Figure 1.6. Particle spacing histograms for PLiD Ni thin-film lines, 420 nm wide, and heights of (a) 13 nm and (b) 55 nm. The shapes of the distributions are similar to the dispersion curve and the dominant particle spacing is near that predicted by LSA (dotted lines). LSA parameters used were, $(n, m) = (3, 2)$, $\theta = 90^\circ$, $x_c = 1 \mu\text{m}$, and $h_* = 0.001$.

is the case. The length scale, λ_m , is seen experimentally discernible, Figure 1.6 compares the measured spacing between droplets (particles) to that predicted by LSA, for pulsed-laser induced dewet (PLiD) Ni thin-film lines, 13 and 55 nm thick and 420 nm wide.³⁵ The resultant particle spacing is quantized in histogram bins, whose distribution not only exhibits a similar shape to the LSA dispersion curve, but a dominant spacing very near that predicted by LSA. Our research group has shown that LSA is applicable across several PLiD nanoscale metallic geometries, including, elemental thin-films,^{36, 37} binary alloy thin-films,³⁸ patterned thin-films,^{24, 32, 39, 40, 41, 42} circular ring structures,^{43, 44, 45} and square-wave patterns^{46, 47} – more regarding these in subsequent sections.

1.3.6 Selective Instability Control – Directed Self-Assembly

Figure 1.7 is a simple, informative illustration of the dewetting process of a metallic thin-film under laser melting, and the growth of naturally occurring instabilities that lead to dispersive breakup. With an understanding of the instability mechanism it is now possible, and desirable, to harness specific instabilities for specific purposes before other naturally occurring ones have time to develop. The choice to influence the natural evolution of liquid phase instabilities to create a desired structure is called directed-self assembly. It is a simple idea but a very powerful tool. Not only does it permit a deeper

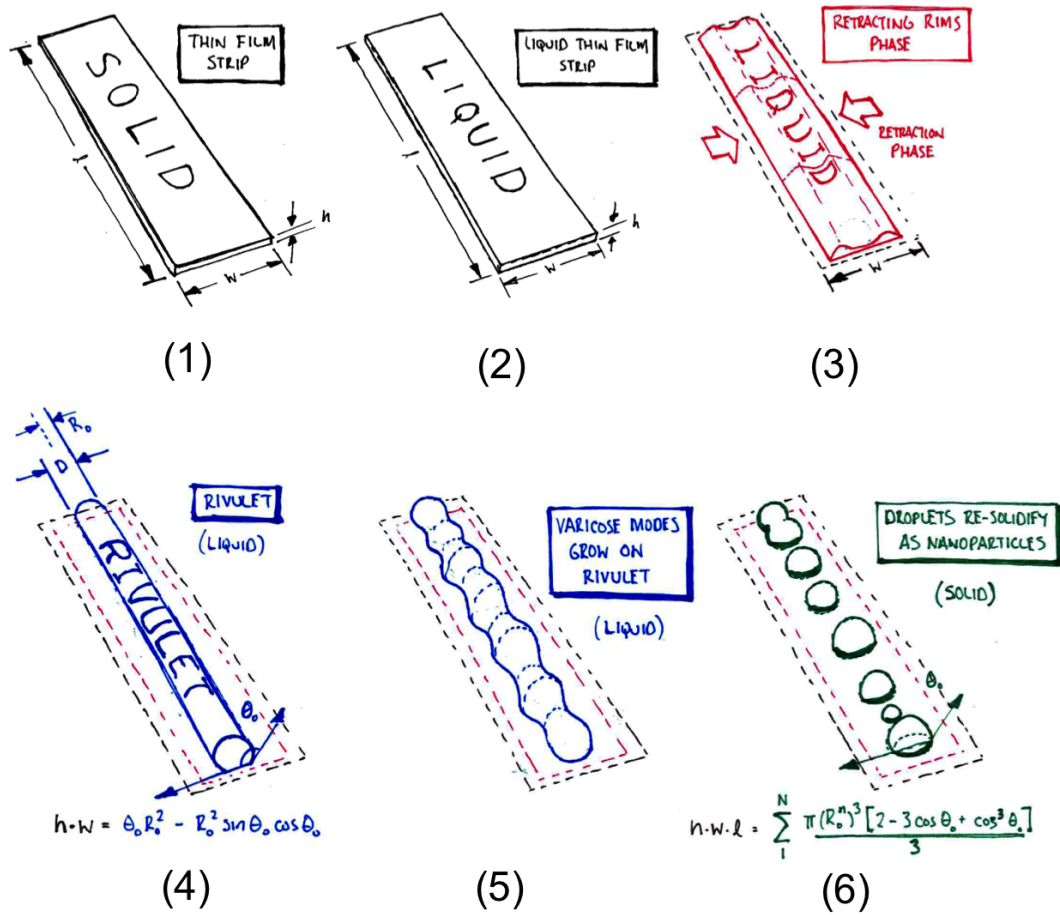


Figure 1.7. Progression of the dewetting process, steps (1)-(6), of a metallic thin-film under laser melting, and the growth of naturally occurring instabilities on a liquid filament (rivulet) that lead to dispersive breakup.

understanding of the underlying fluid dynamics, but also it is an applicable tool. For instance, by controlling the dewetting of Ni thin-films it is possible to create Ni nanoparticles that serve as catalyst sites for subsequent carbon nanofiber growth.⁴⁸

An inventive pathway to directed self-assembly is the use of lithographic patterning. It is possible to use electron beam lithography (EBL) techniques to create metallic thin-film strip(s) (TFS) patterns with instabilities of choice written directly into the initial geometry, prior to laser melting. For example, Figure 1.8(a) shows the selection of two wavelengths, one stable and one unstable, from the LSA dispersion curve and their patterning onto the edges of two thin-film strips of Ni on SiO₂, Figure 1.8(c) and (d), respectively. Upon laser melting the strips collapse to form liquid filaments and the chosen instability has rendered to the surface, giving it a head start in amplitude. Subsequently, as the instabilities evolve in time, the unstable mode decays in amplitude, forming a wire, where as, the unstable mode grows in amplitude and leads to filament breakup. Comparing Figure 1.8(d) to (e) highlights the sensitivity of the instability control. By patterning just one additional period of the unstable wavelength it leads to one additional particle.⁴⁰

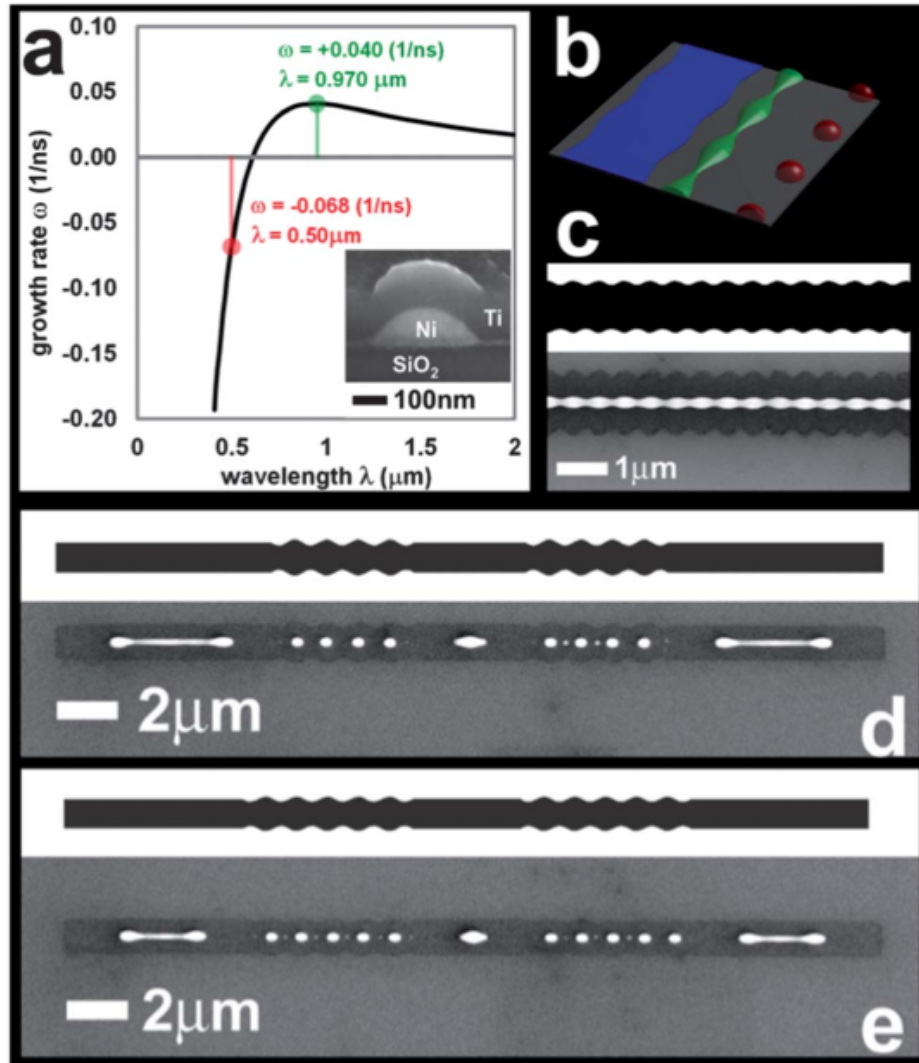


Figure 1.8. The lithographic patterning of instabilities onto metallic thin-films (a) selection of stable, $\omega < 0$, and unstable, $\omega > 0$, from the LSA dispersion relation (b) illustration of the edge patterned, sinusoid instability, its collapse to a liquid filament under laser melting, and finally breakup into droplets (c) stable instability wavelength patterned on thin-film strip (d) unstable instability wavelength patterned on thin-film strip (four periods) in series with rectangular strips with no instability (e) unstable instability wavelength patterned on thin-film strip (five periods) in series with rectangular strips with no instability. This image, when compared to (d), highlights the sensitivity of the instability control, by patterning one additional period of the unstable wavelength leads to one additional particle.⁴⁰

Figure 1.9. Experimental examples of selective instability control, directed self-assembly. (a) hierarchical droplet formation, multiple generations of droplets are formed by the patterning of a single unstable instability, Ni thin-film strip on an oxide surface³⁹ (b) Ni thin-film strips patterned with a square-wave instability on the edges (instead of a sinusoid like in (a)) was able to produce droplet spacing below that predicted by LSA and an unperturbed thin-film (blue histogram)⁴⁶ (c) 2D patterning of perturbations on top of a thin-film using geometric shapes (squares, circles, triangles) permits highly-ordered arrays of droplets across multiple dimensions, Cu on oxide.²⁴

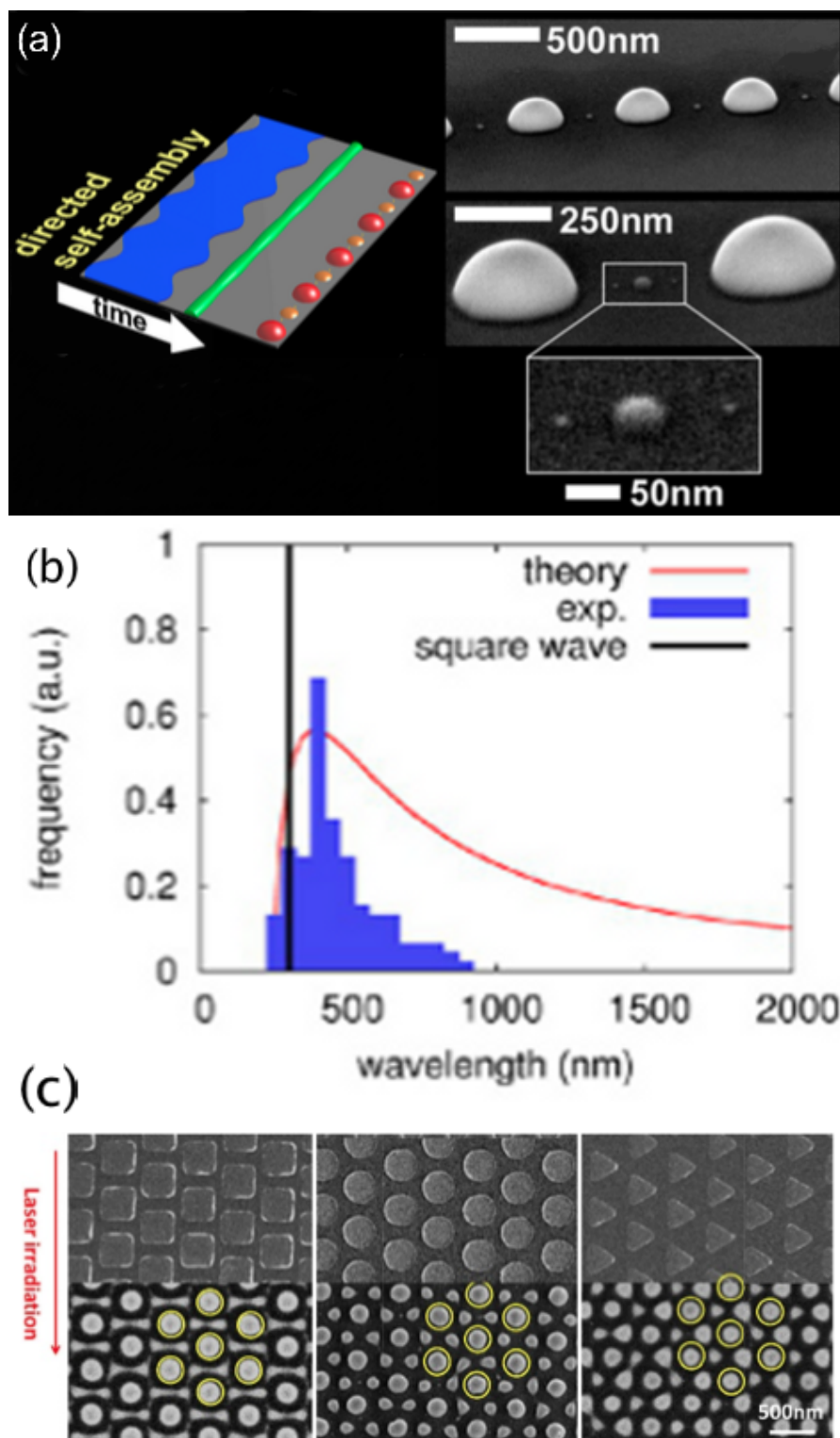


Figure 1.9. Continued.

Subsequent experiments, using a similar approach, have shown it is possible to create multiple generations of droplets by the patterning of a single perturbation. These, so-called, satellite droplets form between the larger order droplets, Figure 1.9(a), as a result of liquid filament pinch off.³⁹ Additionally, alternative instability pattern types have been explored, for example, instead of a sinusoidal variation on the thin-film strip edge, a square-wave pattern was explored and shown to produce droplet spacing below that of predicted by LSA, Figure 1.9(b).⁴⁶ Furthermore, this approach can be extended into multiple dimensions by patterning 2D perturbations, which can create arrays of droplets, Figure 1.9(c).

Experiments such as these are important for several reasons. Firstly they corroborate the theoretical framework used to study and understand the fluid dynamic system, they also provide an avenue for applied work, potentially leading to new technology, and lastly, they are a steak in the ground for the development of additional tools, an important example would be computational simulation.

1.3.7 Marangoni Effect and Thermocapillarity

If a surface varies in chemical composition from point-to-point, or varies in temperature, so does the surface tension. As a result a shear surface force

develops which transports liquid in a direction parallel to the surface from low surface tension regions to high. A very often cited example of this type of transport phenomena is the tears of wine, or wine curtains.⁴⁹ In a glass of wine, a mixture of mostly alcohol and water, it is observed that a thin liquid film will climb up the inside wall of the glass, reach a terminal height, forms a bulge-like ridge, then break down under its own weight into “tears of wine” that fall back down into the glass. This is due to the combination of alcohol modifying the surface tension of water, by lowering it, and its high vapor pressure. Alcohol evaporates very quickly at the bulge-like ridge, leaving the water behind. The high surface tension of the remaining water then draws more of the lower surface tension mixture, mostly alcohol, up the side of the glass. When fluids flow from areas of low surface tension to areas of high surface tension, because of the presence of two fluid, this is known as the Marangoni effect.⁵⁰

Besides chemical inhomogeneity there is an additional way to induce mass transport by way of an interfacial flow. For instance, surface tension has temperature dependence. Therefore, by differential heating a liquid it is possible to generate surface energy gradients that initiate flow, this is called the thermocapillary effect, or thermocapillarity. Spatial differences in temperature create a shear force what moves mass from hot regions, with lower surface tension, to colder regions, with higher surface tension. Ample research has

experimentally validated and characterized thermocapillary flows in ordinary liquids on substrates, like thermal gradients in silicon oils on hydrophobic surfaces,⁵¹ but knowledge of, or more importantly manipulation of, thermocapillarity in liquid metal dewetting is limited and needs to be further investigated.

Thermocapillarity or Marangoni effects⁵² can be modeled by augmenting the hydrodynamic equation to include a term for a spatially varying surface tension, $\nabla\sigma$, due to thermal gradients,

$$\nabla\sigma = \sigma_T T_h \nabla h = \frac{\partial\sigma}{\partial T} \frac{\partial T}{\partial h} \frac{\partial h}{\partial x} \quad (1.28)$$

The surface tension has a linear dependence of temperature; this functionality is addressed in the next section. Equation (1.28) can be added to governing thin-film equation, Equation (1.20), giving,

$$\frac{\partial h}{\partial t} = -\frac{1}{3\mu} \nabla \cdot \left[\sigma h^3 \nabla \nabla^2 h + h^3 \nabla \Pi(h) + \frac{3}{2} h^2 \nabla \sigma \right] \quad (1.29)$$

which, for LSA purposes, is then recast in non-dimensional form,

$$\frac{\partial h}{\partial t} = -\nabla \cdot (h^3 \nabla \nabla^2 h) - K \nabla \cdot (h^3 f' \nabla h) - D \nabla \cdot (h^2 \nabla h) \quad (1.30)$$

where the dimensionless constant, $D = 3\sigma_T T_h h_c / \sigma_m$, and recall that $K = \kappa x_c^2 / \sigma h_c = (1 - \cos \theta_E) / M h_*$, for nanoscale metallic dewetting the constant, non-dimensional length scales are typically chosen so that, $x_c = h_c$, and h_o is the initial thin-film thickness. Employing LSA, the dispersion relation is found to be,

$$\omega = k^2 h_o^3 \left(k_c^2 - k^2 + \frac{D}{h_o} \right) \quad (1.31)$$

This dispersion relation, which is similar to Equation (1.24), however now has a new term, one that is proportional to a spatially varying surface tension due to thermal gradients. Figure 1.10(a) and (b) are plots, based on the dispersion relation, for the growth rate of the fastest growing instability, ω_m , and the wavelength, λ_m , corresponding to the maximum growth rate, respectively, as a function of thin-film thickness, h_o . For comparison, there are three plots, one with only the thermocapillary term (Marangoni), D/h_o , a second with only liquid-solid substrate interaction term (vdW), k_c^2 , and a third with both terms. What is evident is that the Marangoni effects could be relevant because they are comparable to the liquid-solid interaction, at least on the level of linear stability. The capability to access thermocapillary effects in the dewetting of metallic thin-films would be

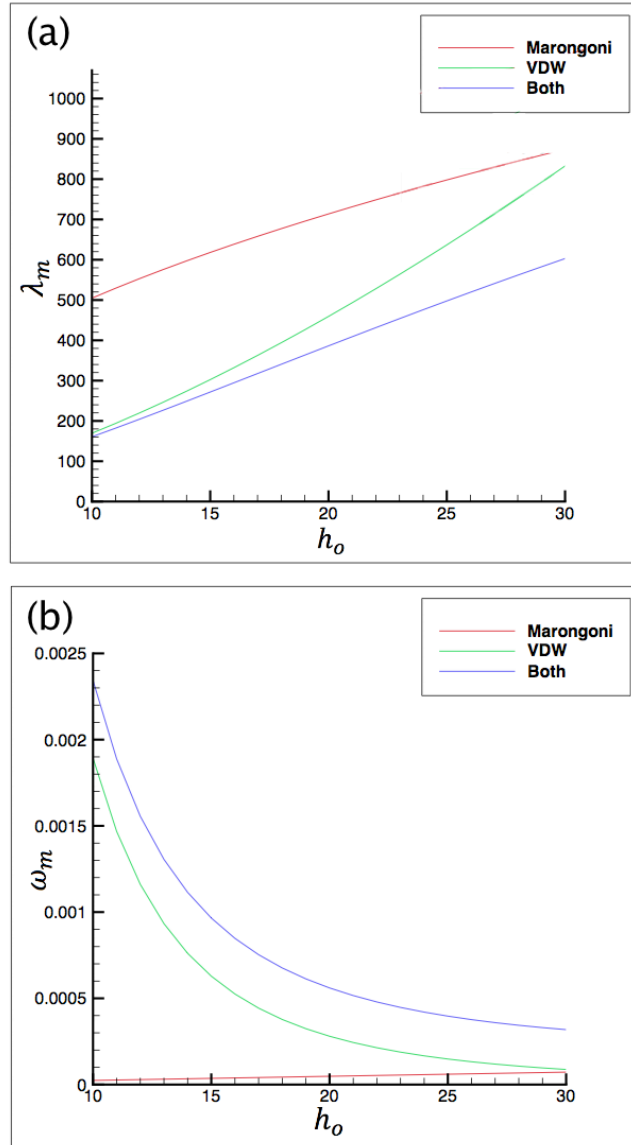


Figure 1.10. Dispersion relation, Equation (1.31), plots for the growth rate of the (a) fastest growing instability, ω_m , and (b) the wavelength, λ_m , corresponding to the maximum growth rate, as a function of thin-film thickness, h_o . Plotted are three curves one with only the thermocapillary term (Marangoni), D/h_o , a second with only liquid-solid substrate interaction term (vdW), k_c^2 , and a third with both terms. The Marangoni effects could be relevant because they are comparable to the liquid-solid interaction, at least on the level of linear stability. Model parameters, $\sigma_m = 1349$ mN/m, $\sigma_T = 0.21$ mN/K m, $T_m = 13.3$ K/nm, $h_* = 1$, $\theta = 79^\circ$, $(n, m) = (3, 2)$.

and innovative approach to directed self-assembly. This topic is discussed further in Chapter 4.

1.3.8 Physical Properties of Liquid Metals

The intrinsic physical properties of (liquid) metals important for dewetting are the melting temperature, density, viscosity, and surface tension – these are the variables in the hydrodynamic equations above. Table 3 lists the physical parameters, and how they change with temperature, for several metals used during the experiments and for simulations. Reference volumes like the prodigious Smithell's Metal Reference Book⁵³ and other investigators (listed below Table 3 for individual metals), that have directly measured the properties with temperature, conclude that the changes are well represented by linear equations for the density and surface tension and an exponential function for viscosity, which are given by Equations (1.32), (1.33) and (1.34), respectively.

$$\rho(T) = \rho_m + \frac{d\rho}{dT}(T - T_m) \quad (1.32)$$

$$\sigma(T) = \sigma_m + \frac{d\sigma}{dT}(T - T_m) \quad (1.33)$$

$$\mu = \mu_m \exp (E/RT) \quad (1.34)$$

It is evident that the metal's material properties decrease with increasing temperature. For density this makes sense, at the melting phase transition, after the absorption of the enthalpy (heat) of fusion, the metals atoms are no longer confined to the lattice. As a result, once the metallic atoms are free to move the viscosity, which is quantity expressing the magnitude of internal friction, should also decrease accordingly. The lowering of surface tension is influenced by their being fewer atoms per unit area near the surface as a result of the thermal motion of the metal atoms. Figure 1.11 is a plot illustrating the behavior of the material properties with temperature for copper.

It should be noted that, the effect of pressure on the properties of the liquids, or solids, is small, if not negligible, and therefore it is not considered here. This assumption follows as reasonable given that we have already assumed that the fluid is incompressible, that is, $\nabla \cdot \mathbf{u} = 0$, during the derivation of governing equations and approximations.

Table 1. Physical Properties of Liquid Metals⁵³

	Melt. Temp T_m [K] (T_{vap})	Density ρ_m [kg m ⁻³] (ρ_{solid})	$\frac{d\rho}{dT}$ [kg m ⁻³ K ⁻¹]	Surface Tension σ_m [N m ⁻¹]	$\frac{d\sigma}{dT}$ [mN m ⁻¹ K ⁻¹]	Viscosity μ_m [mPa s]	μ_o [mN s m ⁻²]	E [kJ mol ⁻¹]
Ni	1728 (3003)	7810 (8908)	-1.160	1.778	-0.38	4.90	0.166	50.2
Cu	1357 (2835)	8020 (8960)	-0.801	1.285	-0.13	4.0	0.301	30.5
Au	1337 (3243)	17360 (19300)	-1.50	1.140	-0.52	5.0	1.132	15.9
Ag	1234 (2435)	9320 (10490)	-0.907	0.903	-0.16	3.88	0.453	22.2
Al	933 (2743)	2385 (2700)	-0.280	0.914	-0.35	1.30	0.149	16.5
Co	1768 (3200)	7760 (8900)	-0.988	1.873	-0.49	4.18	0.255	44.4

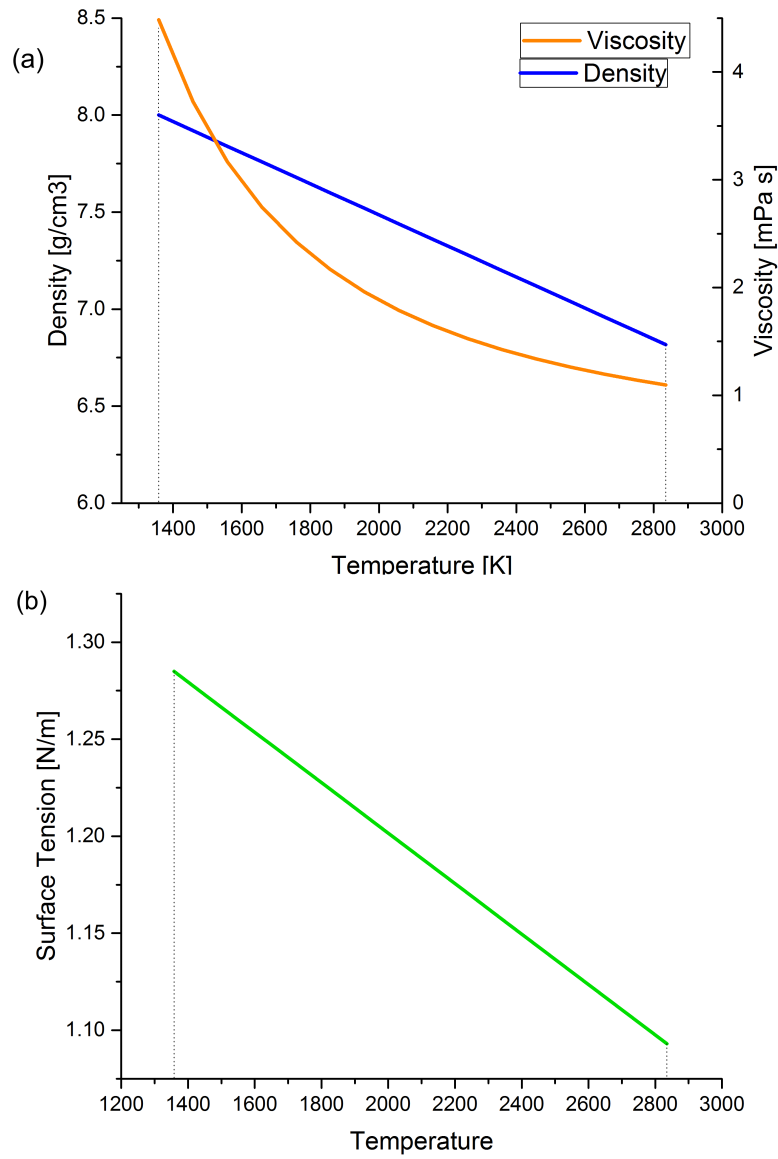


Figure 1.11. Material properties of Cu as a function of temperature, from the melting point, 1357 K, to vaporization, 2835 K. (a) density, $\rho(T)$, and viscosity, $\mu(T)$, (b) surface tension, $\sigma(T)$.⁵³

Chapter 2.

Experimental Procedure, Characterization and Analysis

The experiments performed in this dissertation can be summarized into three steps: 1) nanofabrication of the solid metal/substrate system 2) laser processing of the sample and 3) characterization and analysis. Nanofabrication includes the lithography and metal thin-film deposition. Prior to the start of the experimental process a 100 ± 0.5 mm diameter Si wafer is prepared, this will be the substrate upon which the sample will be fabricated. The wafers used are prime, single-sided polished, <100> Si wafer, n-type, phosphorous doped, with resistivity $10 - 20 \Omega \cdot \text{cm}$, and thickness of $500 \pm 50 \mu\text{m}$, sourced from WRS Materials. The silicon wafers are first cleaned in an RCA process, a multi-bath immersion procedure (named after the RCA Corporation, where the procedure was developed) to remove any organic matter and particulates, thin native oxide layers, or ionic contamination on the surface. Following the RCA clean the wafer is placed inside high-temperature furnace with a water vapor atmosphere to thermally grow 100 nm of SiO_2 , silicon dioxide. The resulting wafer has a very high-quality oxide surface with surface roughness of approximately ± 1 nm; see Figure 2.1 image for before and after oxide growth images.

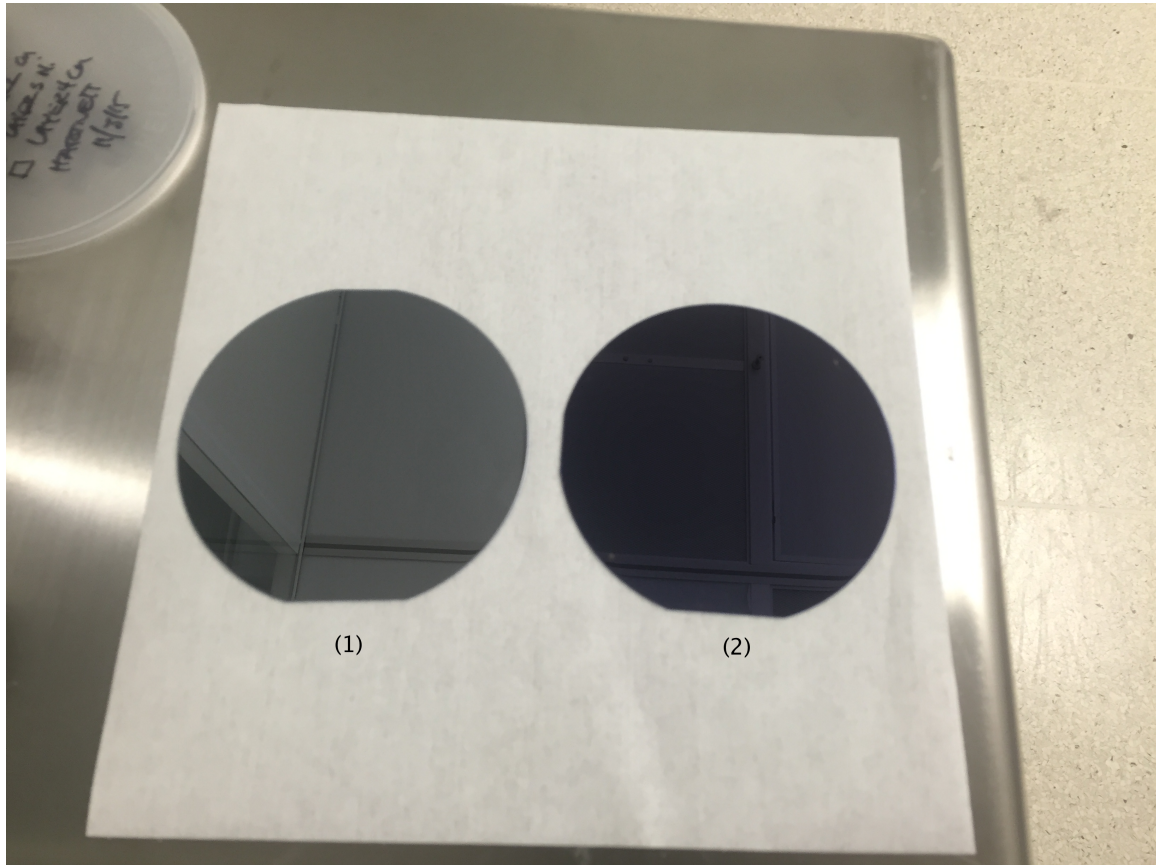


Figure 2.1. (1) New, single-sided polished, $\langle 100 \rangle$ Si wafer, n-type, phosphorous doped, with resistivity $10 - 20 \Omega \cdot \text{cm}$, and thickness of $500 \pm 50 \mu\text{m}$ (2) After the growth of 100 nm of SiO_2 , silicon dioxide, in a thermal growth process.

2.1 Electron Beam Lithography

A computer controlled, focused beam of electrons (e-beam) scans across the surface of a wafer coated with a thin layer of electron-sensitive material called photoresist (resist); typically a long chain organic polymer, like poly(methyl methacrylate) (PMMA) $(C_5O_2H_8)_n$, suspended in a solvent. Exposure to the e-beam causes polymer chain scissions (de-cross linking), which changes its solubility and allows for removal with a chemical developer. The unexposed areas are not susceptible to the chemical developer and therefore remain on the surface. The result is a positive-image representation of the shapes or pattern in the resist media layer. Negative resists are also available and behave in an opposite fashion under e-beam exposure; that is, chemical developers remove the areas not exposed to the e-beam. Choice of resist depends on the application; however, positive resists are exclusively used in this work.

A JEOL 9300FS Electron Beam Lithography System is used for EBL, with an extraction voltage set to 100 kV, which extracts and accelerates electrons from a ZrO/W thermal field emission source forming an e-beam column, the diameter and current settings are 4 nm and 2 nA, respectively. The e-beam is computer controlled by a pattern file (.v30), which is generated in the CAD-like software, Layout Editor and Layout Beamer. The series of steps a wafer takes during the EBL process is largely the same across all experiments, with differences being in

the dosage used (electrons per unit area delivered by the e-beam, measured in $\mu\text{C}/\text{cm}^2$) and thickness of resist, depending on the size and shape of the features in the pattern file. For instance, thicker resist layers typically need reduced dosages, due to the increased interaction volume and probability the electron scissions a polymer chain while traversing the thicker resist layer, saving EBL write time. However the tradeoff is feature fidelity, for a larger interaction volume effects resist areas adjacent to feature boundaries, scissioning adjacent polymer chains, leading to reduced edge sharpness, or ‘blowout’. Experience and trial and error produces the right combination of dose and resist thickness for the desired feature size. Figure 2.2 is an illustration of the EBL process, including the subsequent metallization and liftoff steps.

The following is the experimental procedure for EBL, performed on a JEOL 9300FS Electron Beam Lithography System; pictures of the tool can be found in Figure 2.3.

- 1) Spin Coat Wafer – PMMA 495 A4 resist is spun on the wafer at 3000 or 4000 rpm for 45 seconds, resulting in resist thicknesses of 160 or 120 nm, respectively.
- 2) Bake Resist – lay on a 180 °C hotplate for 60 seconds to set the PMMA 495 A4, driving off the volatile, suspending solvent from the resist.

- 3) Expose Wafer – EBL pattern writing and dosage dictated by size of pattern features and resist layer, typically in the range of 800-1200 μCcm^{-2} .
- 4) Chemical Development – immersion soak for 90 seconds in a 1:3 ratio MIBK:IPA developer (Methyl Isobutyl Ketone:Isopropyl Alcohol).
- 5) Rinse and Dry – Rinse using IPA for 15 seconds, blow dry with nitrogen (N_2) gas for 20 seconds.
- 6) Descum – 6 seconds O_2 plasma clean, removing any residual resist remaining on the surface of the wafer from the development step.

2.2 Metallic Thin-Film Deposition

Two physical vapor deposition (PVD) techniques were used to deposit thin-films of metal onto a sample, electron-beam evaporation and DC magnetron sputtering, a variant of DC sputtering. Sputtering is different from evaporation, in that atoms are ejected from the surface of the target through the collision with gaseous plasma ions, typically Ar^+ . The primary goal for these two techniques is to control film composition and thickness uniformity, both offer satisfactory deposition rates, controllable to better than 1 nm/min. Both methods utilize high vacuum ($> 10^{-6}$ Torr) systems and are a way to controllably transfer atoms from a source, referred to as the target, onto a substrate located a distance away,

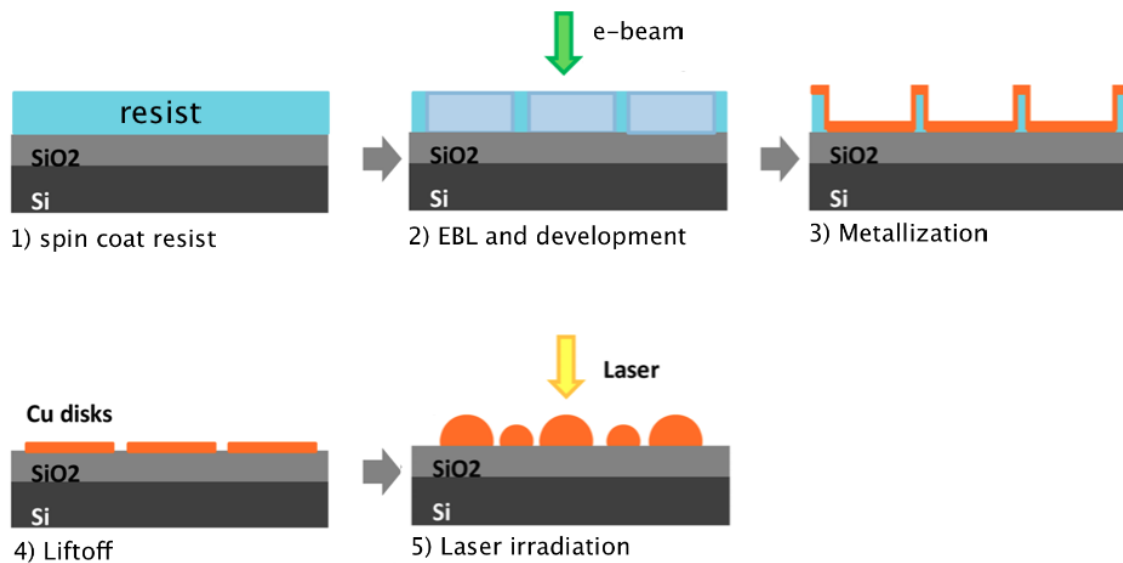


Figure 2.2. Sequential illustration of the electron beam lithography (EBL) process and the subsequent metallization, liftoff and pulsed laser induced dewetting; in this instance, Cu discs were patterned into the resist, however, the pattern can be any arbitrary, extended 2D pattern.³²

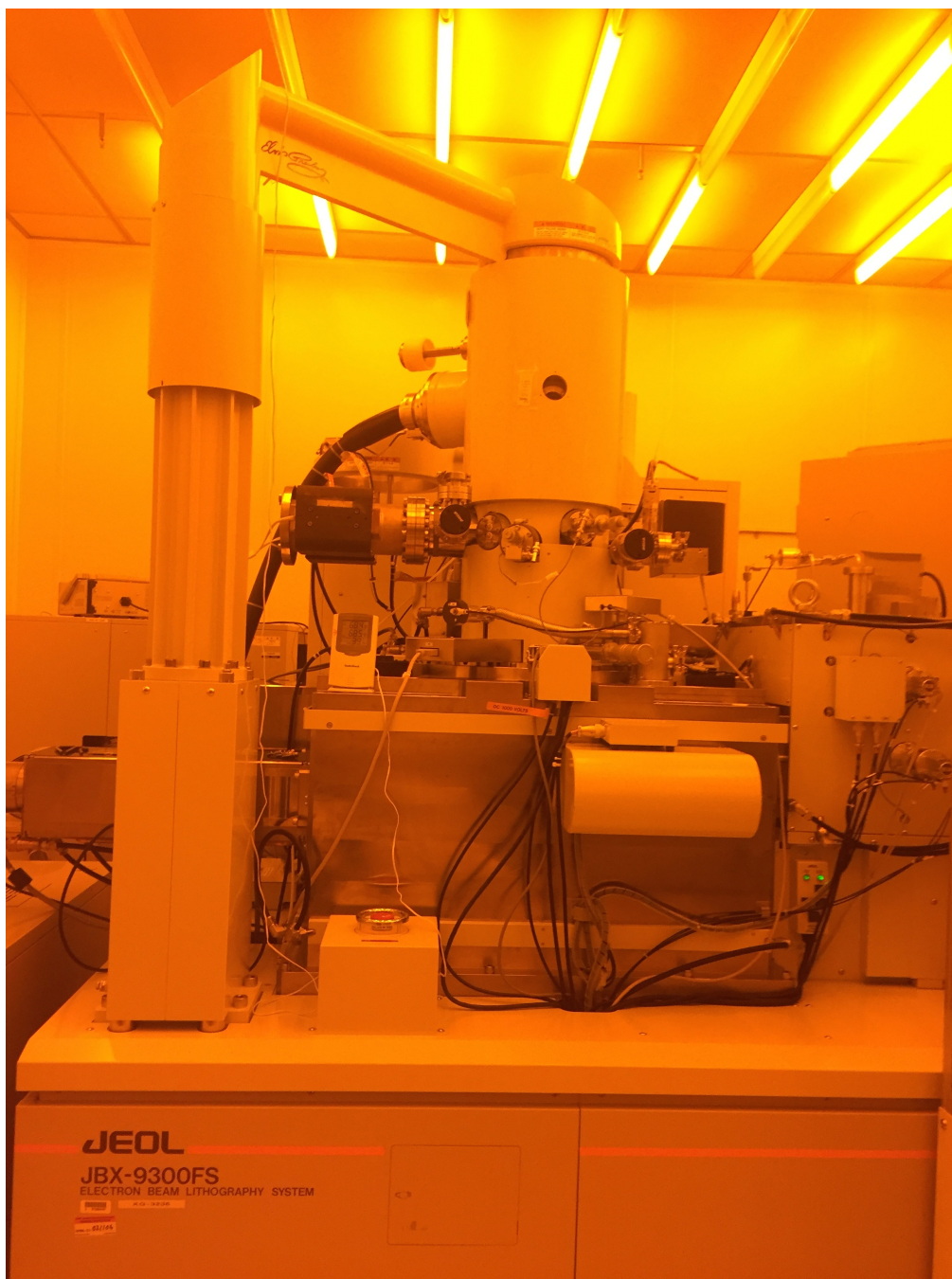


Figure 2.3. JEOL 9300FS Electron Beam Lithography System, inside the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory.

where the growth of the thin-film proceeds atomistically.⁵⁴ Targets are commercially available for practically every solid material important to the microelectronic and nanofabrication industries; for example, metals, oxides, nitrides, carbides and silicides.

2.2.1 Electron Beam Evaporation

The technique of electron beam evaporation (EBE) is very simply the action of imparting thermal energy to a material by electron bombardment, such that the target material temperature is raised to the point where evaporation (from a liquid) or sublimation (from a solid) occurs. For instance, metals largely evaporate as atoms and sometimes as clusters of atoms, this occurs for Au and Cu from the liquid phase (evaporation) and for Cr from the solid phase (sublimation). Evaporative methods have seen widespread use because of its applicability to many materials and classes of materials.⁵⁴

The evaporant material is placed in a crucible, typically made from heat resistant material like graphite or aluminum oxide, Al_2O_3 . Purity is maintained due to only a small area at the surface of the material melting, or subliming, and the surrounding unmelted material is in contact with the cooled crucible. Electrons are thermionically emitted from a heated cathode filament, usually tungsten,

which is shielded from the line of sight of the material so as to not contaminate the filament. The cathode is negatively biased in order to accelerate the emitted electrons, typically in the 10 kV range with respect to the ground anode - the evaporant material/crucible. A magnetic field is applied in the transverse direction to the velocity of the emitted electrons. The Lorentz force acts on the negative charges, bending the electron beam in a circular arc and directing it into the crucible, see Figure 2.4. The beam's position and spot size can be controlled, as well as the ability to scan the beam over the source in order to prevent splattering of a liquid state evaporant, or deep drilling into materials that sublime; in this way the source material is efficiently consumed.

Figure 2.4 is an illustration of the evaporation dynamics during deposition. The material vapor just above the crucible behaves like a hot, dense, high-pressure viscous cloud of evaporant. The transport and kinetic motion of the particles inside the viscous cloud, and their effect on material flow to the substrate, has been modeled by Balakrishnan, et al.⁵⁵ This region, located above the crucible and closer to the substrate plane, acts like an effective virtual source and particles appear to emanate from the viscous cloud boundary in all directions. The virtual source distance to the substrate, h_v , depends on the evaporation rate of the material, and its ratio to the crucible-plane-to-substrate distance, h , is typically around 0.7.⁵⁴ Outside the viscous cloud is a lower pressure region and

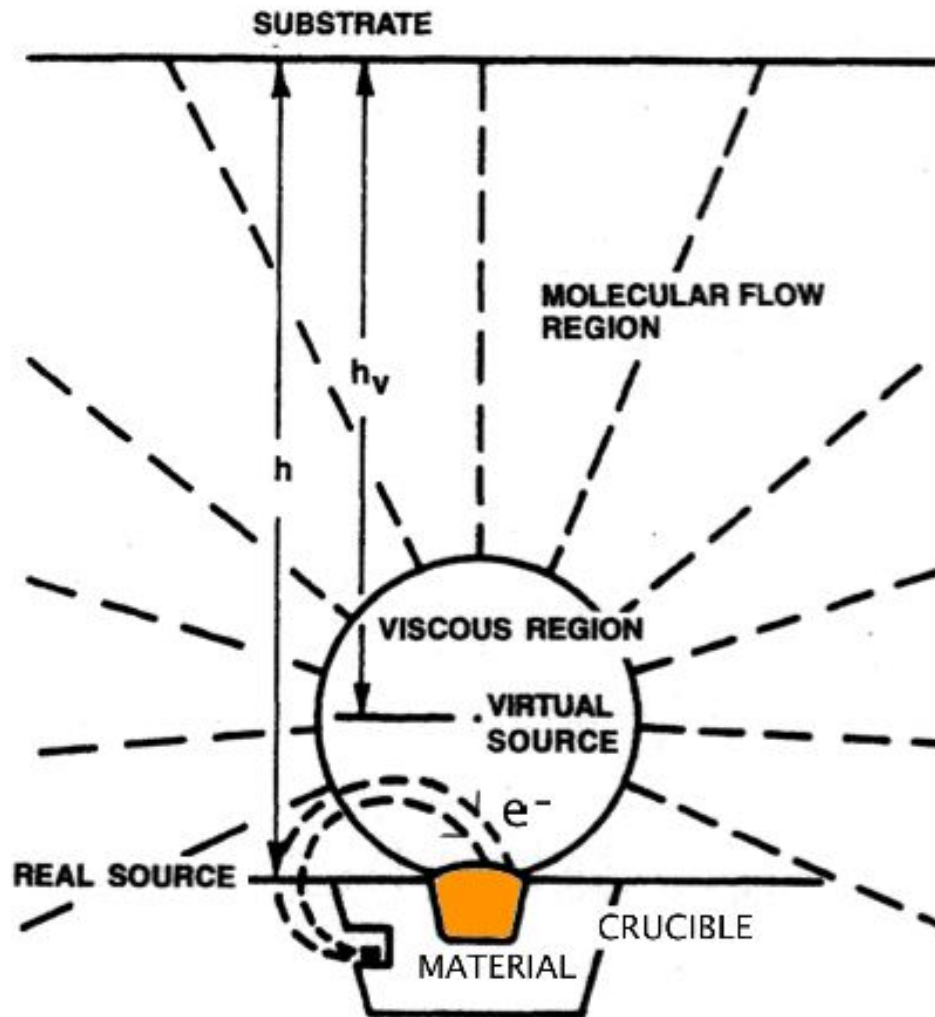


Figure 2.4. Illustration of the physical vapor deposition technique of electron beam evaporation, a beam of energetic electrons bombards a crucible containing the evaporant material, the kinetic energy of the electrons is transferred to the material through collisions, causing it to heat up and evaporate away which then deposits on an adjacent substrate coating it. ⁵⁴

molecular flow is assumed to exist, and the evaporative particles travel unimpeded to the substrate where they are deposited.

Knowledge of the underlying physics of EBE helps to deepen the understanding of the physical process occurring. An important phenomenon affecting the evaporation rates is the connection between the temperature and equilibrium vapor pressure of the source material. The connection can be expressed through the Clausius-Clapyeron equation, for both the liquid-vapor and solid-vapor, Equation (2.1).⁵⁴

$$\frac{dP}{dT} = \frac{\Delta H(T)}{T\Delta V} \approx \frac{P\Delta H}{RT^2} \quad (2.1)$$

Where the enthalpy, $\Delta H(T)$, and volume, ΔV , refer to the difference between the vapor and the condensed phase, whether liquid or solid, and T is the temperature at which the transformation occurs. If the volume of the vapor phase is much larger than the volume of the liquid or solid phase, which is a reasonable assumption, then $\Delta V \approx V_v = RT/P$, in conformity with the ideal gas law. The enthalpy $\Delta H(T)$ can be taken, to a first approximation, to be a constant, and the latent heat of evaporation, ΔH_e . Equation (2.1) can be integrated and the solution describes the temperature dependence of the vapor pressure; the value of P_o is usually with reference to 1 atm for P , and the boiling point for T .

$$P = P_o \exp\left(-\frac{\Delta H_e}{RT}\right) \quad (2.2)$$

Equation (2.2) adequately describes the temperature dependence of the vapor pressure for many materials.⁵⁴ Table 2 catalogs several of the important characteristics mentioned regarding the EBE technique, like state of evaporation and recommended crucible material, and importantly the dependence of the sputter rate on vapor pressure and temperature.

$$\Phi_e = \frac{\alpha_e N_A (P - P_h)}{(2\pi MRT)^{1/2}} \quad (2.3)$$

Equation (2.3) is the express relation between the vapor pressure and temperature of the evaporant and the evaporation flux, in units of [atoms/cm² · s]. Where α_e is the coefficient of evaporation, having a value between 0 and 1, P and P_h are the equilibrium vapor pressure and hydrostatic pressure, respectively, acting on the evaporant and M its mass.

The following experimental procedure for the deposition of metallic thin-films was performed on a Thermionic Laboratory VE-240 Vacuum Evaporation System; pictures of the tool can be found in the Figure 2.5.

- 1) Open Evaporation Vacuum Chamber – Turn off the vacuum turbo pump and flow nitrogen into the evaporation chamber until atmospheric pressure is reached, 7.6×10^2 torr, then turn off the N₂ supply.
- 2) Load Sample – Open the chamber door, load the sample onto the substrate carrier and locate it above the appropriate source material crucible.
- 3) Pump Down Evaporation Vacuum Chamber – Close chamber door and turn on the vacuum roughing pump, then the turbo pump when 1×10^{-1} torr is reached. Allow time for the chamber to reach a base pressure of 5×10^{-6} torr.
- 4) E-beam – Turn on the power supplies for the thermionic emitter (tungsten filament), the electrostatic accelerating voltage, and the beam scanner.
- 5) Evaporation – Locate the beam onto the crucible and increase beam current until the source material either melts or sublimes. Monitor the evaporation rate on rate monitor device – which is simply a membrane resonator located near the substrate whose frequency changes as material is deposited, the materials atomic weight/density is selected on the device prior to deposition.
- 6) Evaporation Off and Unload – Ramp down the beam current and turn off the power supplies. Allow time for the turbo pumps to reach a vacuum

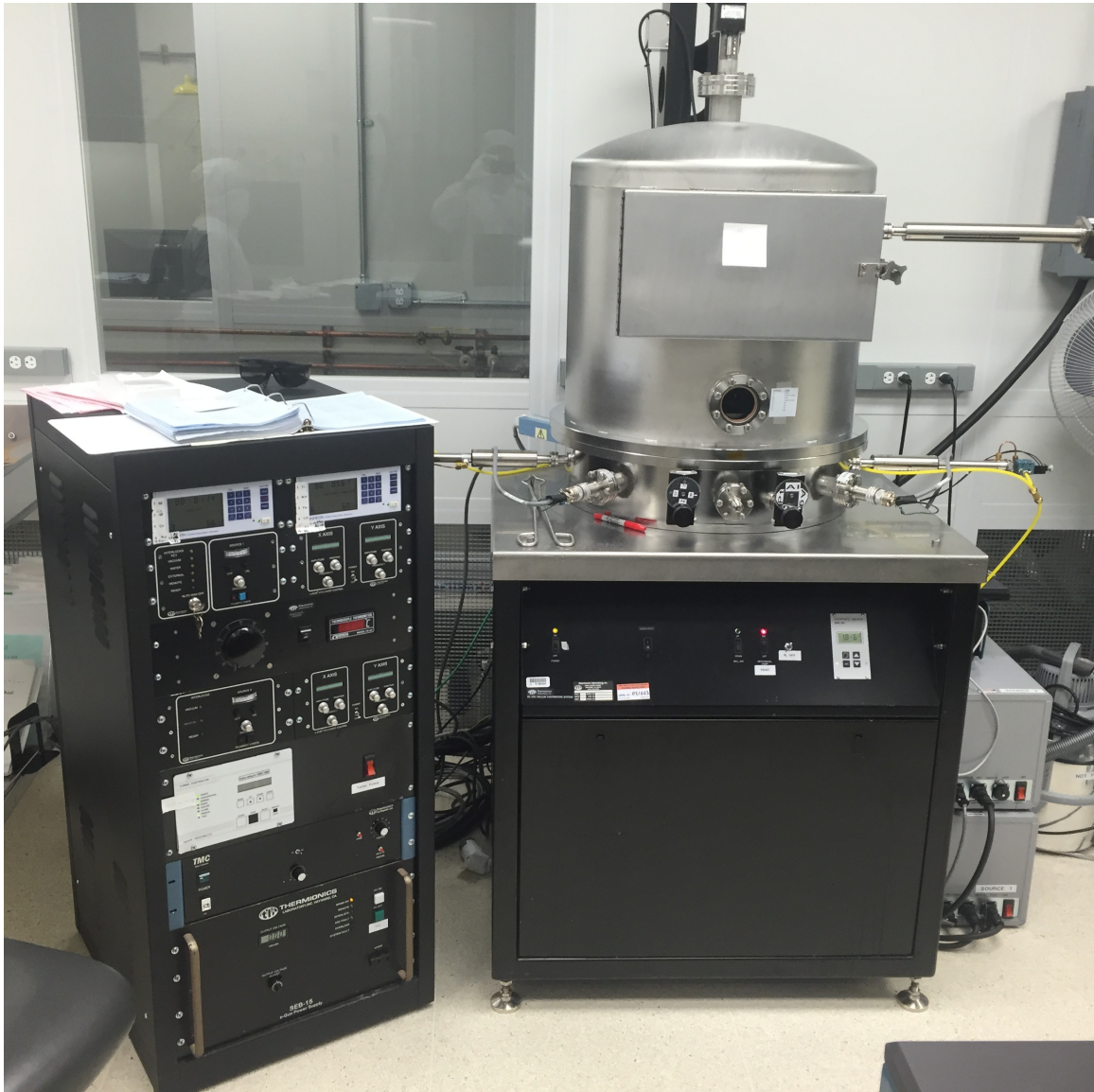


Figure 2.5. Electron-Beam Thermionic Laboratory VE-240 Vacuum Evaporation System

Table 2. Electron-Beam Evaporation Sputtering Parameters

Material	Minimum Evaporation Temperature ^a [°C]	State of Evaporation	Crucible Material	Deposition Rate [Å/s]	E-beam Power ^b [kW]
Aluminum	1010	Melts	BN	20	5.
Carbon	2140	Sublimes		30	1
Chromium	1157	Sublimes	W	15	0.3
Cobalt	1200	Melts	Al ₂ O ₃	20	2
Copper	1017	Melts	Al ₂ O ₃	50	0.2
Gold	1132	Melts	BN	30	6
Iron	1180	Melts	Al ₂ O ₃	50	2.5
Nickel	1262	Melts	Al ₂ O ₃	25	2
Platinum	1747	Melts	Graphite	20	4
Silicon	850	Melts	BeO	15	0.15
Titanium	1453	Melts		20	1.5
Zirconium	1987	Melts	W	20	5

^aTemperature (°C) at which the vapor pressure is 10^{-4} torr, ^bfor a 10 kV accelerating potential and a source-substrate distance of 40 cm. ^{56, 57}

pressure of 5×10^{-6} torr before following the first step to open the evaporation chamber and remove the sample.

2.2.2 DC Magnetron Sputtering

The need for elemental and alloy films with stringent requirements, like stoichiometry, in microelectronics encouraged the development and widespread use of sputtering. Elemental metallic targets, like those used in this work, have purities of 99.99% or greater. Sputtering has become the dominant technique for the deposition of films by plasma methods.

In basic DC sputtering a neutral, sputtering gas, like argon or krypton, is maintained at low-pressure between two electrodes (cathode and anode) with an applied potential difference between the plates. The electric field, typically on the order of 100 V/cm,⁵⁴ accelerates a free electron which collides with a neutral gas atom, ionizing it. The ionization reaction, $e^- + \text{Ar} \rightarrow \text{Ar}^+ + 2e^-$, is the beginning of a cascade, the two product electrons move on to ionize two further atoms, and so forth. The positively charged Ar^+ species are accelerated toward the negative cathode plate, striking the target material and sputtering target atoms.

DC magnetron sputtering is a variant of the simpler DC sputtering technique. Rare earth, permanent magnets are arranged behind the target, for instance in a circular ring, the magnetic field lines confine free electrons and plasma ions to near the surface of the target, see Figure 2.6. The confinement increases the likelihood of plasma ionization reactions, which in turn increases ion current and deposition rate. DC magnetron sputtering has the advantages of higher deposition rates at reduced operating pressures. At such pressures, typically a few mTorr, atoms travel ballistically from the target to the substrate, avoiding the collisions and scattering that occur at high pressures.

A look at the physics underlying sputtering helps to make clear the physical process taking place. As the Ar^+ ions move closer to the target surface electron exchange occurs when they are angstroms apart. The work functions of most solids are less than the ionization energy of gases, and the recoiled and scattered gas species are largely neutral. As the distance shrinks even further, electronic repulsion and the Pauli exclusion principle become dominate, resulting in collisional reionization of the gas neutrals. This may be considered the instant of impact, and the ion collision initiates a cascade of impacts leading to the ejection of one or more of the target atoms, i.e. sputtering. The sputter yield, S , is a measure of efficiency (target atoms ejected/incident ion) and ranges from 10^{-1} to 10 for most sputtering processes.⁵⁴

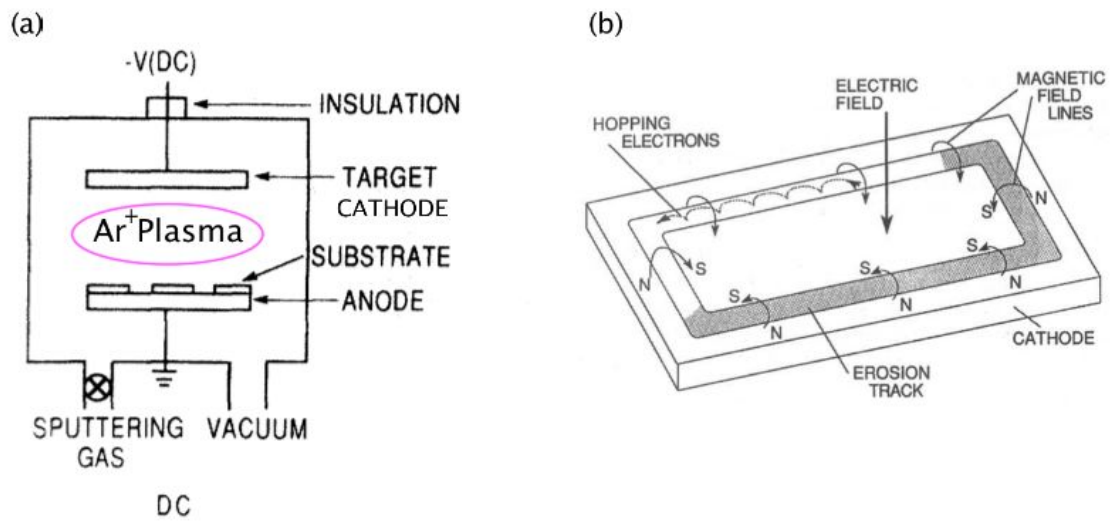


Figure 2.6. Illustration of the physical vapor deposition technique of DC magnetron sputtering system. (a) sputtering chamber view.⁵⁴



Figure 2.7. AJA International ATC2000 Sputtering System

The ejection of target atoms from the surface is a result of momentum transfer during the knock-on collisions. The threshold energy, E , is the minimum ion energy required to remove a target atom and overcome the binding energy, U , of the target material, its work function. The threshold energy E depends on the incident ion and on the atomic number and mass of the target material, and typical values range from 5 to 40 eV.

$$S = \frac{\text{\# of sputtered atoms}}{\text{incident particle}} = \frac{3\alpha M_1 M_2 E}{4\pi^2 (M_1 + M_2)^2 U} \quad (2.4)$$

Sigmund⁵⁸ theoretically modeled sputtering as a linear cascade phenomenon and his expression for the sputtering yield is widely acknowledged. Equation (2.4) is the low energy limit for energies $E < 1\text{keV}$, the appropriate limit for this work, where M_1 and M_2 are the masses of the ion and target atoms respectively, and $\alpha(M_2/M_1, \theta)$ can range from 0.1 to 1.4 depending on the ratio of masses and angle of impact, often taking a value of 0.2 to 0.4.

The following experimental procedure for the deposition of metallic thin-films was performed on an AJA International ATC2000 Sputtering System; pictures of the tool can be found in the Figure 2.7.

- 1) Open Sputter Vacuum Chamber – Close Adaptive Pressure Controller cryo-pump line and open nitrogen supply line, bringing chamber up to atmospheric pressure, 7.6×10^2 torr, then close nitrogen supply line.
- 2) Load Sample – Place sample on wafer carrier and beneath appropriate sputter target.
- 3) Pump Down Sputter Vacuum Chamber – Open vacuum chamber roughing pump, bring chamber down to 1×10^{-1} torr. Close vacuum chamber roughing pump and open Adaptive Pressure Controller cryo-pump, allow time for the chamber to reach a base vacuum pressure of 6×10^{-7} torr.
- 4) Ar Gas Supply – Turn on Mass Flow Controller to flow 25 sccm of Ar into the sputter chamber. Set Adaptive Pressure Controller to regulate flow of Ar for a sputtering pressure of 3×10^{-3} torr.
- 5) Plasma and Pre-Sputter – Set power supply to an appropriate value for target material. Turn on Power Supply and spark plasma, pre-sputter target for 3 minutes to remove any target surface contaminants or thin native oxide layer.
- 6) Thin-film Deposition – Open the shutter to expose the sample to the sputtering target. Close the shutter after the appropriate exposure time.
- 7) Sputter Off and Unload – Turn off the Power Supply and Ar Mass Flow Controller. Open the Adaptive Pressure Controller cryo-pump, pump

down to a vacuum pressure of 1×10^{-6} torr before following the first step to open the chamber and remove the sample.

2.3 KrF Laser Processing

Liquid-state dewetting of metals necessitates a thermal processing technique that can deliver a substantial amount of energy in a very short period of time. This is due to the combination of extremely high melting temperatures and fast cooling rates, high thermal conductivities, inherent to metals. For comparison, the temperature and timescales for the dewetting of nanoscale polymer polystyrene⁵⁹ are ~ 400 K and $\sim 10^2$ s, respectively, contrasting that to nickel's requirement of ~ 2000 K and $\sim 10^{-8}$ s, which are orders of magnitude different.

This relegates the conventional thermal-annealing chambers, like commercially available rapid thermal processors (RTPs), to be used for polymer or solid-state dewetting. RTPs are not suitable for liquid-state metallic dewetting. To achieve the temperatures and energy delivery timescales necessary high-powered, nanosecond pulsed lasers offer the requisite performance characteristics; for instance, a ultra-violet krypton-fluoride (KrF) excimer laser with a wavelength of 248 nm is a capable tool. Such a laser system produces a Gaussian temporal

beam profile at pulse-widths of less than 20 ns and energy densities on the order of 10^2 mJ/cm^2 , sufficient to melt metals.

Understanding how metals, like nickel and copper, absorb laser light energy, melt, then solidify is very important to the work of nanosecond liquid metal dewetting. Knowledge of a material's temperature changes with time during irradiation is critical for the discernment of other material properties that depend on temperature, like density, viscosity, and surface tension. A mathematical, thermal model can help elucidate the underlying physics. Equation (2.5) is a 1-D differential equation that describes the heating, and subsequent melting and solidification, of a semi-infinite, metallic thin-film by a pulsed-laser beam. The laser pulse is assumed to be incident normal to the surface of the thin-film ($\hat{z}$), have a spatially uniform, Gaussian temporal energy profile, Equation (2.6).⁶⁰

$$\rho_m C_m \frac{\partial T}{\partial t} = k_m \frac{\partial^2 T}{\partial z^2} + \alpha_m [1 - R(h)] f(t) \exp(-\alpha_m(z + h)) \quad (2.5)$$

$$f(t) = \frac{E_o}{\sigma\sqrt{2\pi}} \exp\left(\frac{-(t - t_p)^2}{2\sigma^2}\right) \quad (2.6)$$

Where $T(z, t)$ is the temperature of the metallic thin-film as a function of time, ρ_m is the density, C_m is heat capacity (the subscript m denotes metal), k_m is the

thermal conductivity, α_m is the absorptivity of the metal at a given wavelength, $R(h)$ is the thickness dependent reflectivity, and $f(t)$ is the Gaussian temporal profile of the energy, E_o , that is delivered by a laser pulse. Below the metal thin-film is 100 nm of SiO_2 , an insulating oxide layer, and beneath the oxide layer is 25 μm of Si. The vacuum-thin-film interface is located at $z = -h$, and $z = 0$ is the thin-film-oxide interface.

As beam energy is absorbed it is transformed into thermal motion of the metal atoms, the temperature increases quickly and at sufficient fluence approaches the melting phase change (or the subsequent solidification phase change during cooling, heat loss occurs through conduction with the underlying substrates). Considerations for the latent heat of fusion and parameter changes in Equation 2.5 are taken into account to for the phase transformation during the temporal evolution. Figure 2.8 is the modeled thermal behavior for several thicknesses of a Cu thin-film, 10 – 30 nm in 5 nm increments, irradiated with a fluence of 200 mJ/cm^2 . The duration of time above the melting point is the “liquid-lifetime” of the metal, and is typically on the order of ~ 20 ns. All dewetting dynamics therefore happen within this short temporal window.

The following experimental laser processing procedure was performed on a Lambda-Physik LPX300cc Excimer Laser; pictures of the tool and process can

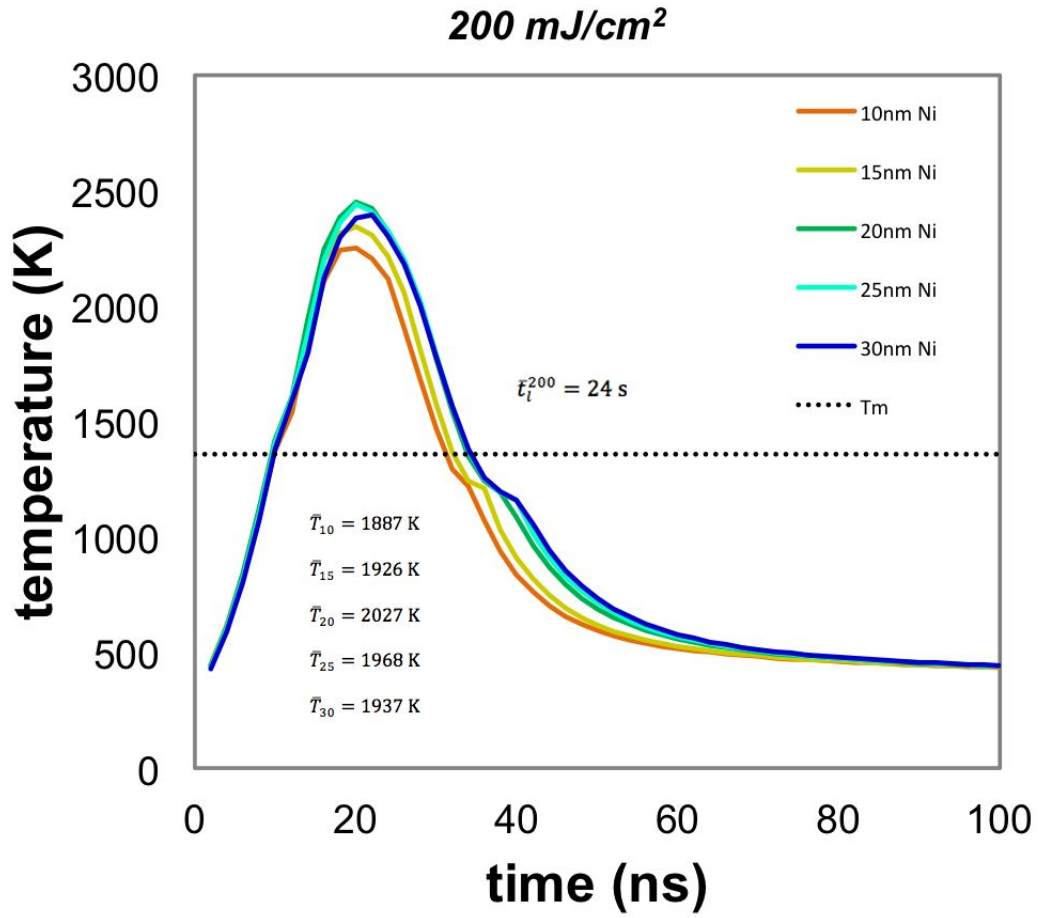


Figure 2.8. The simulation of the temperature with time for a copper thin-film on 100 nm oxide on silicon, of varying thickness, before, during, and after laser irradiation with a single laser pulse, 248 nm KrF laser, having an energy fluence of 200 mJ/cm².

be found in the Figure 2.9.

- 1) Laser On – Power on the laser control computer and start the control program. Ensure the interlock sensor coupled to the laboratory door is in position - the laser system will not function without interlock continuity. Turn on the laser coolant flow pump.
- 2) Energy Calibration – Place the Scientech Astral AD30 energy meter in the beam line and measure the energy per pulse (mJ), take an average of multiple individual pulses.
- 3) Fluence Calibration – Adhere thermal paper to the sample carrier and place in the beam line, the laser will blacken the paper and the visible spot allows for the measurement of the spot area (cm²). Move the converging, plano-convex lens along the beam line to either increase or decrease the spot size to attain the desired fluence (mJ/cm²).
- 4) Irradiation – Adhere the experimental sample to the sample carrier and place in the beam line, then fire the desired number of laser pulses.
- 5) Laser Off – Allow the laser coolant flow pump to cool the laser for an additional time after the last laser shot. Exit the laser control program and power off the control computer.



Figure 2.9. Lambda-Physik LPX300cc KrF Excimer Laser with optical table, converging lens, and sample chamber, in the foreground. The wavelength of the laser is 248 nm and the experimental energy range, depending on the experiment, was $E = 150 - 250 \text{ mJ/cm}^2$.

2.4 Characterization and Analysis Techniques

The following is a listing of the characterization and analysis techniques employed during the experiments contained in this dissertation. A reference has been included for each in case additional information regarding the technique is desired.

2.4.1 Scanning Electron Microscopy

The imaging of all samples was performed on two scanning electron microscopes (SEM), the Zeiss Auriga SEM in the microscopy laboratory at UT, and the FEI Novalab 600 SEM located in the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL). During operation an Everhart-Thornley secondary-electron detector was used to capture a still image of the sample under study, including a scale bar.⁶¹

2.4.2 Analysis Techniques

- Composition - When it was necessary, a sample's material composition was analyzed using the EDAX energy-dispersive x-ray spectroscopy (XDS) system on the FEI Novalab 600 SEM at ORNL.⁶²

- Particle Size and Spacing – Two methods were used to discern particle size and spacing, direct measurement using an SEM image and the associated scale bar, and a custom Matlab script that analyzes the image for particles by a coded, random walk process, then bins the particle spacing and size to produce a histogram.
- Filament Instability Development– A spatial correlation function is used to analyze the varicose perturbations on the surface of a filament, providing a spectrum of wavelengths that constitute the perturbation.
- Thin-Film Thicknesses – The height of thin-films and nanostructures were measured using a Veeco stylus profilometer, in addition to a Veeco Atomic Force Microscope (AFM).⁶³
- Optical Properties – A JA Woollam M-2000U ellipsometer was used to measure the optical properties of thin-films, namely the refractive index and extinction coefficients.⁶⁴

Chapter 3.

Instability of Nano and Microscale Liquid Metal Filaments: Transition From Single Droplet Collapse to Multi-Droplet Breakup

Christopher Hartnett, et al, originally published a version of this chapter.⁴⁷

Hartnett, C. A.; Mahady, K.; Fowlkes, J. D.; Afkhami, S.; Kondic, L.; Rack, P. D. Instability of nano and microscale liquid metal filaments: Transition from single droplet collapse to multi-droplet breakup. *Langmuir* **2015**, 31 (50), 13609-13617.

3.1 Introduction

Controlling the placement of metallic nanostructures is crucial. The potential applications for organized metallic nanostructures are wide ranging. The incorporation of plasmonic nanoparticles into photovoltaic devices has led to increased efficiency,^{7, 8} for photonic applications,⁶⁵ and plasmonics^{1, 66} – the surface plasmon resonance between metallic nanostructures depends on coordination, size, and spacing. One strategy to create organized structures at the nanoscale is by harnessing the inherent, liquid self-assembly mechanisms. The physical properties of liquid metals and the ability to lithographically pattern nanoscale features, create an intriguing platform to study the governing hydrodynamics,⁶⁷ such as liquid instabilities,⁴³ with the goal of directing the assembly of precise, coordinated nanostructures in one³⁹ and two⁴⁶ dimensions.

In this work we observe that liquid metal filaments below a critical length, l_c , collapse to a single droplet, however as a filament length increases a threshold is crossed where multi-droplet breakup results. As the breakup is a Raleigh-Plateau-like instability, this threshold is a function of the filament radius of curvature, R . Herein we focus on the unique spatial and temporal transition region between the two regimes. We show a competition is present between two fluid dynamic phenomena: 1) capillary-induced retraction of the filament axial ends promoting the collapse to a single droplet and 2) filament breakup into multiple droplets due to the growth of varicose instabilities (i.e. surface perturbations) similar to the Rayleigh-Plateau (R-P) mechanism.

To investigate this competition we utilize established nanofabrication techniques and pulsed laser induced dewetting (PLiD).⁴⁶ With these methods it is experimentally possible to precisely control the initial far-from-equilibrium geometry and the liquid lifetime via nanosecond laser melting. The finite extent of a filament's geometry and the temperature and liquid lifetime has profound effects on the dewetting dynamics. We first give an overview of the experimental results and then compare them with relevant hydrodynamic models. Finally, we compare the experimental results with direct numerical computations of the full Navier-Stokes equations based on the volume-of-fluid (VoF) interface tracking method.⁶⁸

3.2 Experimental Details

EBL was used to pattern a mask of rectangular strips of increasing width ($w = 136 - 665$ nm) and length ($l = 0.135 - 12.3$ μm) using a positive tone resist, polymethylmethacrolate (PMMA), on a 100 nm SiO_2 surface that was thermally grown on a prime, $\langle 100 \rangle$ Si wafer. Nickel (Ni) was subsequently deposited using DC magnetron sputtering with a thickness, h , and ranged from 10 ± 1 nm to 30 ± 1 nm, in 5 nm increments. Figure 3.1(a) illustrates the resultant Ni thin-film strip (TFS) geometry on oxide, characterized by the cross sectional area, hw .

A krypton fluoride (KrF) excimer laser, wavelength 248 nm, energy range $220 - 300 \pm 10$ mJ/cm², and pulse-width of 18 ± 2 ns FWHM, was used to melt the Ni TFS. Figure 3.1(b) demonstrates the substrate-supported, liquid metal filament geometry that results from the laser melting. The amount of time a Ni TFS is in the liquid state, its liquid lifetime, is dependent on the energy fluence delivered by a laser shot and the thermal and optical properties of the Ni, the supporting SiO_2 layer, and the underlying Si substrate. The area of the laser spot is ~ 1 cm², which is much larger than the ~ 1 mm² area containing the sample, thus ensuring a homogenous fluence. Figure 3.3 is a collection of numerical simulations modeling the surface temperature of the Ni thin-film supported on 100 nm SiO_2 on Si, exposed to one 250 mJ/cm² laser shot.⁴¹ Due to the finite liquid lifetime per laser pulse and rapid cooling, a series of individual laser pulses

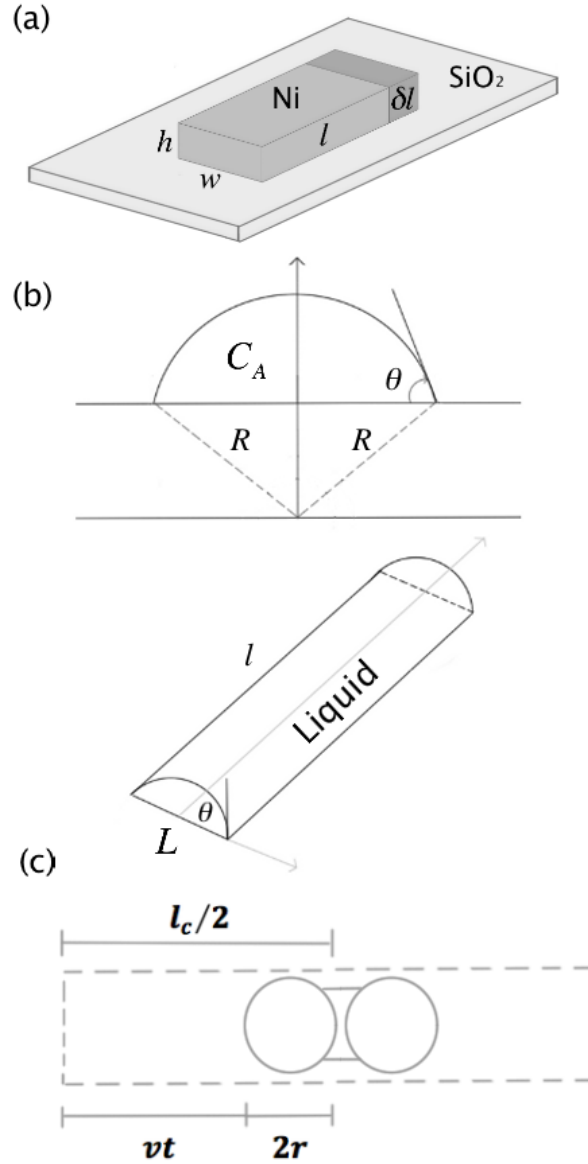


Figure 3.1. Illustration of the patterned Ni TFS on SiO₂, having thickness, h , width, w , and length, l , and increment length, $\delta l = w/2$. (b) Geometry of the substrate-supported liquid metal filament with cross sectional area, C_A , and radius of curvature, R . (d) Top down view of a retracting filament the instant before the accumulating edge droplets, of radius r and traveling at velocity v , merge to form a single droplet. The filament length where the end droplets do not have sufficient time to retract half the length and merge when breakup occurs is the critical length (breakup time equals collapse time); this time condition is expressed as Equation (3.1).

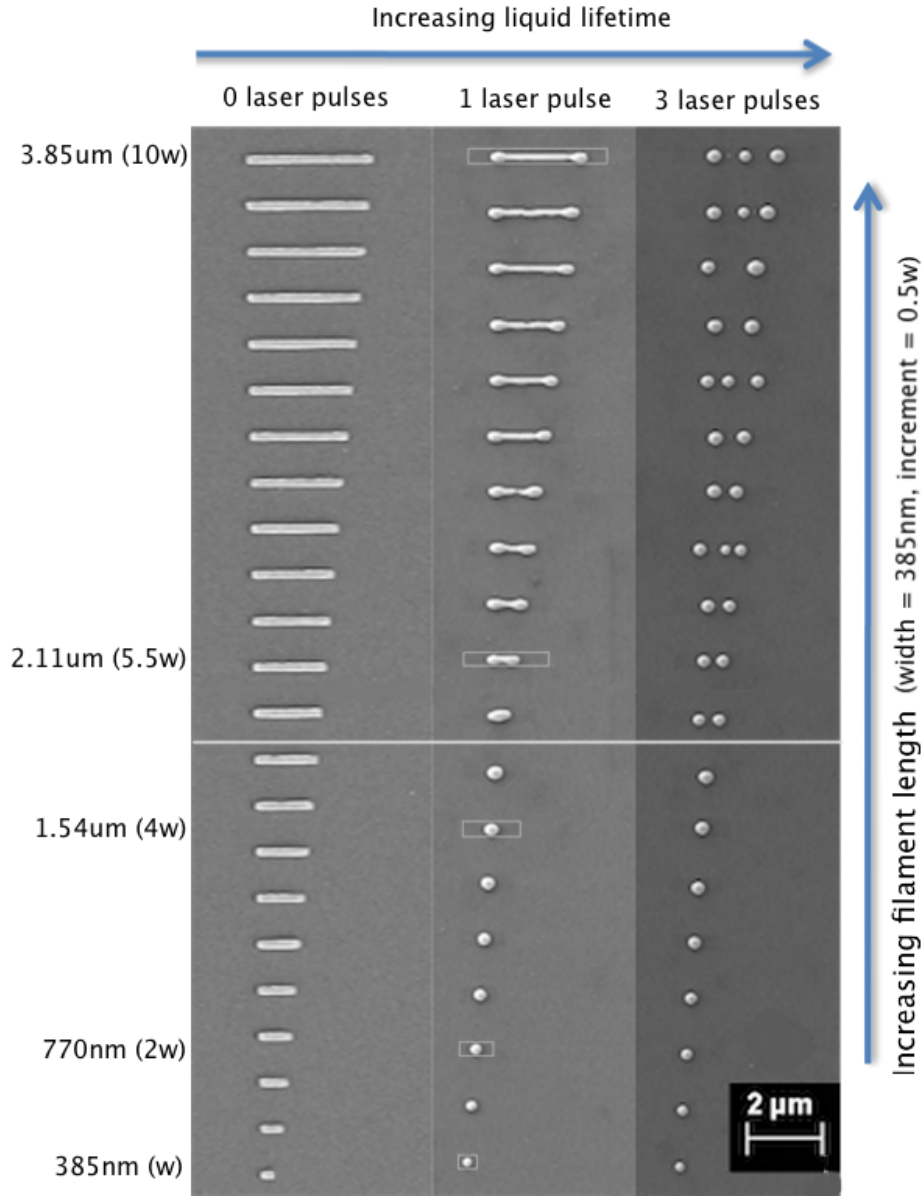


Figure 3.2. SEM images of the Ni TFS, increasing in length from bottom-to-top, initially square with sides, l_o , equal to the width. Liquid lifetime increases from left-to-right as a function of number of laser pulses. At a critical length, l_c , (horizontal line) the filament breaks into multiple droplets rather than collapsing into a single droplet. For this example $h = 20 \pm 1$ nm, $w = 437 \pm 12$ nm, $C_A = 8740 \pm 498$ nm², and l_c is ~ 2.1 μ m. Included are relevant material properties of Ni at the melting temperature, $T_m = 1728$ K, the equilibrium contact angle, θ ,¹³ the surface tension, σ ,¹⁸ the viscosity, μ ,¹⁹ and the density, ρ .²⁰

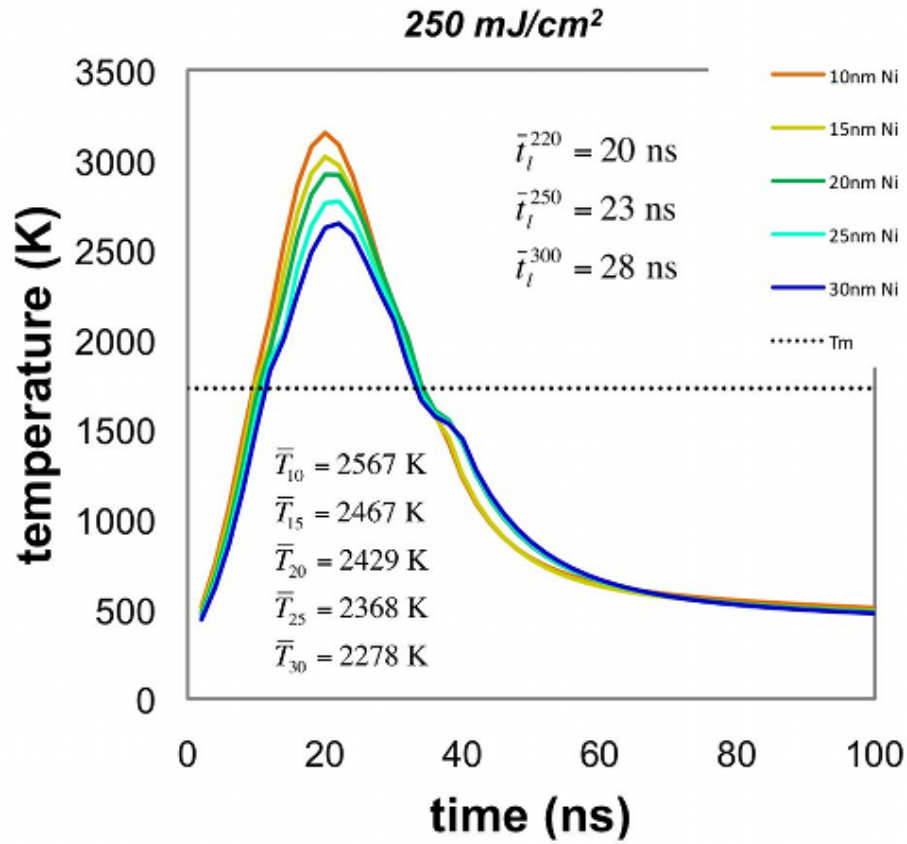


Figure 3.3. Simulated surface temperatures of a Ni thin-film on 100 nm SiO₂ on Si during and after the absorption of a single KrF laser pulse with a fluence of 250 mJ/cm². The liquid lifetime, t_l , is the amount of time spent at or above the Ni melting temperature, 1728 K (dotted line). Insets are the average liquid lifetimes at three laser fluences, 220, 250 and 300 mJ/cm², and the average temperatures during the liquid lifetime after a single laser pulse with a fluence of 250 mJ/cm².

can be used to control the dewetting evolution and interrogate morphological changes of the liquid filament.⁶⁹

3.3 Model and Simulation Methods

3.3.1 Model

We begin by calculating a few important fluid dynamic quantities for Ni to identify the relevant fluid regime for our experiments. As described, the operative experimental thicknesses are in the tens of nanometer range, widths at the hundreds of nanometer range, and lengths ranging from hundreds of nanometers to tens of micrometers. Such length scales are well below the capillary length,¹¹ $\lambda_c = \sqrt{(\sigma/\rho g)}$, which is ~ 1 mm for liquid Ni, therefore gravitational effects do not need to be considered. The Ohnesorge number, $Oh = \mu(\sigma\rho R)^{-1/2}$, is the ratio of viscous to inertial and surface tension forces, has a value of ~ 0.1 . The R-P instability is expected to be an influential, fluid dynamic mechanism within the range of $0.05 < Oh < 2$ for viscous filaments. Driessen et al.,⁷⁰ demonstrated that filaments dominated by inertia/surface tension have an $Oh < 0.05$, and breakup by end pinch-off. However if viscosity dominates, when $Oh > 2$, the filaments are stable with respect to the R-P instability and collapse to a single droplet, independent of length. For our experiments the variation of the

Ohnesorge number due to Ni's temperature dependent material properties (viscosity, surface tension, and density) at the filament radii min and max, [44 nm, 150 nm], at 1728 K (the melting temperature) are [0.185, 0.100], respectively, and at 2500 K are [0.103, 0.056], respectively. Based on the experimental Ohnesorge range it is expected that filament surface instabilities, like the R-P mechanism, will be operative. Consequently, it was opined that the transition from collapse to breakup of a filament would be sensitive to the aspect ratio ($\Gamma = l/2R$).

When a patterned Ni TFS melts, the initially rectangular cross sectional area, hw , forms a truncated cylinder of equal cross sectional area, $C_A = R^2 A(\theta)$, where the radius of curvature, R , depends on the equilibrium wetting angle between the liquid metal and the SiO_2 substrate and $A(\theta) = (\theta - \sin \theta \cos \theta)$, Figure 3.1(b).⁶⁷ It is assumed that during laser melting the amount of time it takes for a Ni TFS to initially melt and the lateral edges to retract to form a truncated cylinder occurs in ~ 2 ns, Figure 3.1(a) to (c).⁴³

At filament lengths smaller than where breakup occurs, retracting axial ends travel half the filament length and merge/collapse to form single droplets. For a filament to collapse to a single droplet the amount of time the filament axial ends have to travel and successfully merge must be less than the time necessary for

the development of varicose perturbations that lead to filament breakup, like those of the R-P instability. Accordingly, the time condition for collapse, and therefore breakup, can be expressed as a critical retraction time of the axial end. This rationale leads to a time constraint based on geometrical arguments; see Figure 3.1(c), that is,

$$t_c = \left(\frac{l_c}{2} - 2r \right) v^{-1} \quad (3.1)$$

Where, $l_c/2$, is half the filament length at the critical length where transition would occur, r is the radius of the accumulating droplet at the retracting axial end, and v is its velocity.

The capillary velocity, $v_c = (\sigma/\rho R)^{1/2}$, which depends on the surface energy of the liquid and the filament radius, can be used to estimate the retraction velocity. For Ni the capillary velocity, at the melting temperature, spanning from the filament radii maximum to minimum, 150 and 44 nm, respectively, ranges from $38 - 71 \text{ ms}^{-1}$. This is comparatively fast, capillary waves on water travel at $\sim 20 \text{ cms}^{-1}$. The capillary velocity for liquid metals is considerably larger, by a few orders of magnitude, a consequence of their high surface energy and lower viscosity. A quick calculation provides an estimate of the collapse time for a filament, for example, the length scale for filaments in the experiment is

~ 1000 nm, as stated above, and if the velocity is $\sim 50 \text{ ms}^{-1}$, then the collapse time should be ~ 20 ns. This timescale estimate is consistent with that for laser melting, PLiD, and the KrF laser pulse-width.

The retraction velocity can be experimentally estimated by measuring the distance the TFS retracts after a single laser pulse and normalized to the average, simulated liquid lifetime of 24 ns. The range of experimentally determined velocities, spanning the filament radii, 150 – 44 nm, was found to be, $36 - 19 \text{ ms}^{-1}$, respectively, with an average of 29 ms^{-1} , see Figure 3.4. The measured retraction velocities are smaller than what the capillary velocity equation predicts, however, the order of magnitude is consistent. In addition, it was also noted that the velocity dependence on filament radius is opposite to that of the capillary velocity at small radii, that is, the experimental velocities were seen to decrease at small filament radii, whereas, the capillary velocity equation at small radii predicts an increase.

The divergence of the experimental velocities and the behavior at small radii is presumed to be a result of real energy losses, as well as assumptions made in estimating material properties. The material properties of metal are temperature dependent; as temperature increases under laser melting the viscosity decreases. For Ni this amounts to a 5% decrease in the velocity between its melting and

maximum temperature. Add to that viscous dissipation at the filament-substrate interface, solidification effects as liquid changes phase to a solid (which will be discussed later in the section), and the effect that material accumulation at the filaments ends have during retraction. For these reasons, some of which are more difficult to quantify than others, it is reasonable that the experimentally measured velocities are smaller than the theoretical capillary velocity.

Furthermore, the velocity was also simulated via a VoF approach (described later in the section) at 1728 and 2500 K and radii range of 25 – 87 nm. The simulations resulted in average velocities of 34 and 41 ms⁻¹ at 1728 and 2500 K, respectively. Figure 3.4 compares the capillary, experimental, and VoF velocity data. Again, what is reassuring is that the capillary, experimental, and VoF velocities are of similar order. For simplicity the experimental velocity is assumed to be a constant, 30 ms⁻¹ for Ni in our analytical model below – for the Cu experiments, discussed later, its experimental velocity is 15 ms⁻¹.

The accumulating droplet at the retracting axial end creates a rim, the extent of which can be estimated by the Stokes length, $L_s = \mu^2/(\sigma\rho)$, and can have a stabilizing effect on the filament if it approaches half the filament length. That is, if the two droplet rims that form at opposite ends overlap they can induce

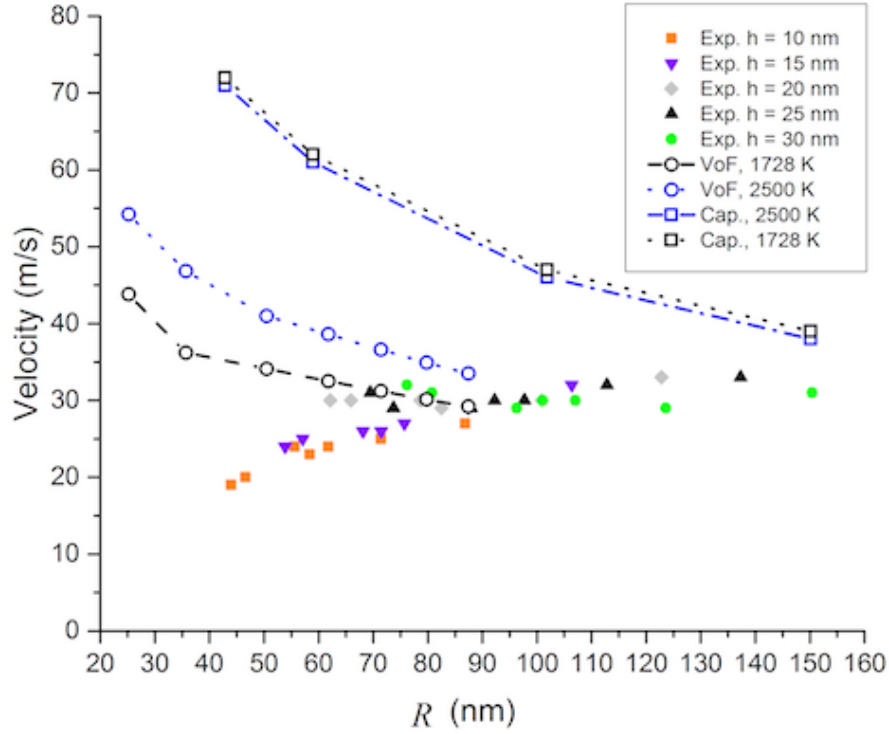


Figure 3.4. Experimental retraction velocities measured after one liquid lifetime, grouped by initial TFS thickness, and compared to the theoretical capillary velocity and VoF simulation estimates at two temperatures, 1728 and 2500 K. The average experimental retraction velocity is 29 ms^{-1} . For the analytical model, Equation (3.6), a value of 30 ms^{-1} was chosen to approximate the experimental results. The experimental velocities are noticeably lower at smaller filament radii, which is in contrast to the VoF and capillary velocity behavior. Future work should explore the reasons for this difference; we anticipate that temperature dependent material properties may play an important role in eventual explanation.

collapse of the filament homogeneously to a single droplet. The Stokes length for our experiments is, ~ 1 nm, much smaller than the filament lengths, so the retracting axial droplets are immune to rim interactions.

Driessen et al.,⁷⁰ outlined a similar argument for single droplet collapse for (nonmetallic) free viscous jets (filaments) (not supported on a substrate). To do so, Driessen utilized a convenient framework to describe the system, which we will modify and extend to include the effects of the supporting substrate. The filament is geometrically characterized in terms of a dimensionless aspect ratio, $\Gamma = l/2R$. At the critical length the retracting axial ends each accumulate half the volume of the filament, forming an end droplet with radius,

$$r = \left(\frac{3}{4}\Gamma_c\right)^{\frac{1}{3}} R \quad (3.2)$$

The critical retraction time, given by Equation (3.1), can be rewritten as a function of the aspect ratio and radius of curvature, R , by combining it with Equation (3.2),

$$t_c = R \left(\Gamma_c - (6\Gamma_c)^{\frac{1}{3}} \right) \nu^{-1} \quad (3.3)$$

It follows then that any instability on the filament surface must evolve with a time equal to or faster than the retraction time, Equation (3.3), if the instability is to be the mechanism by which the filament reaches its end state. The evolution of the surface instability can begin to be understood by starting from the framework of the R-P mechanism. For a free filament in air, of radius R_o , the varicose surface instability of maximum growth rate causes breakup. The fastest growing wavelength predicted by LSA for the R-P instability is,⁷¹

$$\Lambda_m = 2\pi\sqrt{2}R_o \quad (3.4)$$

As a consequence the resultant distribution of droplets should be spaced approximately equal to the wavelength Λ_m , that is, the final droplet distribution should scale with R_o . Assuming that LSA can be extended to the nonlinear regime (i.e. evolution times not near the initial stages of the instability development) the time needed for a R-P-like surface instability to grow to an amplitude comparable to that of the filament radius is,^{67, 70}

$$t_b = \frac{1}{\omega} \ln\left(\frac{R}{\delta}\right) \quad (3.5)$$

Where the initial amplitude of the surface instability is represented by a perturbation amplitude, δ , and ω is the growth rate of the fastest growing instability.

For the nanoscale liquid metals considered here, the initial perturbation amplitude is assumed to be the van der Waals radius; for example, Ni has a van der Waals radius, $\delta \sim 0.2 \text{ nm}$.⁷² This is in contrast to Driessen who chose their perturbation to be a function of radius, $\delta = \epsilon R$, with $\epsilon = 0.01$; this value was chosen as a fitting parameter to their experimental data. Alternatively, Diez et al.,⁶⁷ used an ϵ value of 0.001 as their initial, infinitesimal perturbation value in a fully nonlinear time-dependent simulation of finite length filaments, and found the breakup to be dominated by the pinching-off of droplets at the axial ends. Our constant δ value of the van der Waal radius, and filament radii range, yields effective ϵ values ranging from 0.0013 to 0.0045 for Ni, and commensurate to both approaches.

The transition from single droplets collapse to multiple droplet breakup can therefore be described as a competition between two fluid dynamic timescales, that of collapse due to axial end retraction and the instability development time for breakup. An expression for the critical aspect ratio can then be found by equating Equations (3.3) and (3.5),

$$\frac{R}{\nu} \left(\Gamma_c - (6\Gamma_c)^{\frac{1}{3}} \right) - \frac{1}{\omega_s} \ln \left(\frac{R}{\delta} \right) = 0 \quad (3.6)$$

However, the Dreissen description is that of a free filament, we extend their description to that of a filament supported on and partially wetting a solid surface. Therefore the growth rate, ω , is replaced with, ω_s , the growth rate of the fastest growing perturbation for liquid filaments supported on a solid substrate.

Brochard-Wyart and Redon⁷³ estimated the relaxation times of the varicose modes of a liquid filament with circular cross section on a flat solid surface, and found that modes below a wave vector, q , are unstable. They predicted the relaxation times of the instabilities in two regimes; a viscous regime, where viscous dissipation is the dominant hydrodynamic quantity, and the viscoinertial regime, appropriate for low viscosity and large contact angle fluids. For the viscous regime they determined the relaxation times for all q as,

$$\omega^{vis.} = \frac{\sigma}{3\mu c} \theta^3 \frac{q}{(1 + 4/q^2 L^2)} \left(-\frac{2}{Lq} + \tanh \frac{Lq}{2} \right) \quad (3.7)$$

where the substrate supported filament width is $L = 2R \sin \theta$, see Figure 3.1(b), and c is a logarithmic factor reflecting the singularity near the contact line, on the

order 10, and can be treated as a constant.⁷⁴ The fastest growing mode⁶⁷ occurs for $qL \sim 1.421$, therefore,

$$\omega_s^{vis.} = 0.379 \frac{\sigma}{30\mu} \frac{\theta^3}{2R\sin\theta} \quad (3.8)$$

For the viscoinertial regime, where surface energy is the important material property, it was determined that the relaxation time for all q is given by,

$$\omega^{viscoin.} = \left(\frac{\theta}{L}\right)^{\frac{4}{3}} \left(\frac{\sigma^2}{\mu\rho}\right)^{\frac{1}{3}} \frac{(-1 + (qL/2)\tanh(qL/2))^{\frac{2}{3}} (1 + qL/2)^{\frac{2}{3}}}{(1 + 4/q^2 L^2)^{\frac{2}{3}}} \quad (3.9)$$

Once again, utilizing that the fastest growing mode has a value of $qL \sim 1.421$, therefore,

$$\omega_s^{viscoin.} = 0.317 \left(\frac{\theta}{2R\sin\theta}\right)^{\frac{4}{3}} \left(\frac{\sigma^2}{\mu\rho}\right)^{\frac{1}{3}} \quad (3.10)$$

Equations (3.9) and (3.10), for the viscous and viscoinertial regimes, respectively, provide the complimentary temporal quantity to that provided by Equation (3.3) for the retraction timescale. A quick calculation can provide an estimate for the instability growth time, for example, plugging in a median radius

value of, 100 nm, and material properties for Ni at melt, the development time for the viscoinertial regime is, ~ 10 ns, and the viscous regime is, ~ 20 ns. These timescales are comparable to the retraction/collapse time estimate, and consistent with laser melting, PliD, and the KrF laser pulse-width.

3.3.2 Simulation Methods

We compare the experimental results with the ones obtained by fully nonlinear simulations utilizing a VoF method.^{25, 75} By directly solving the three-dimensional Navier-Stokes (N-S) equations, these simulations provide additional insight regarding the competing instability mechanisms. It is assumed that the fluid flow can be modeled as an isothermal Newtonian fluid obeying the N-S equations.

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p + \nabla \cdot (\mu(\nabla\mathbf{u} + \nabla\mathbf{u}^T)) + \sigma\kappa\delta_s\mathbf{n} \quad (3.11)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (3.12)$$

where $\mathbf{u} = (u, v, w)$ is the velocity field, p is the pressure, κ is the curvature of the fluid-vapor interface, and $\delta_s\mathbf{n}$ denotes the normal vector at the fluid-vapor interface. A contact angle of 90° is imposed during the simulations. Experimental results could not be reproduced without taking contact line slip and laser induced

melting/solidification effects into account. The contact line slip is represented by a slip condition,⁶⁸

$$(u, w)|_{y=0} = \lambda \partial_y (u, w)|_{y=0} \quad (3.13)$$

where, λ , denotes the slip length, and, (u, w) , are the in-plane components of velocity. To represent liquid solidification, we implement a simple model, such that the fluid motion completely stops after a liquid lifetime, t_l . Therefore, we put

$$\mathbf{u}(\mathbf{x}, nt_l) = 0, \quad \forall \mathbf{x} \text{ and } n \in \mathbb{Z} \quad (3.14)$$

After the ‘freeze’, the liquid is allowed to again evolve according to Equation (3.11), mimicking melting and solidification as a result of multiple laser pulses.

The open-source computational fluid dynamics software package, Gerris was used for the simulations.⁷⁶ Spatial discretization is accomplished using an adaptive octree, the adaptive mesh resolves the fluid-vapor interface with a resolution of ~ 1 nm and regions of high curvature are resolved to ~ 0.5 nm. The VoF approach tracks the fluid phase of each point in space by introducing a volume fraction function, which states the fraction of each computational cell occupied by the liquid phase. Viscosity and density depend on the volume

fraction function by assignment of the appropriate liquid and vapor values. In order to mitigate the effect of the surrounding vapor (i.e. air) we set $\mu_v = \mu/100$ and $\rho_v = \rho/20$.

3.4 Results and Discussion

3.4.1 Nickel

Figure 3.5(a) is a plot of average, critical breakup length, l_c , versus the filament radius of curvature, R , for different thickness and width combinations explored in the experiment. For the 65 data points that were explored (five thicknesses ranging from 10 – 30 nm thick and for each thickness 13 widths ranging from 135 to 665 nm) each data point represents an average of six measurements. We observe that the critical breakup length follows a similar phenomenological scaling law to that expected for the R-P instability, Equation (3.4). As is evident in Figure 3.5(a) the linear best-fit line, forced through the origin, is applied to the data; the fit is described by, $l_c = \alpha R = \alpha R \sqrt{A(\theta)^{-1} C_A} = \alpha' \sqrt{C_A}$. This is encouraging because we have reasoned the critical length to be dependent on instabilities similar in nature to the R-P mechanism. However this is an oversimplification, because the equation for the R-P instability wavelength, Equation (3.4), is void of any important experimental realities, like those related

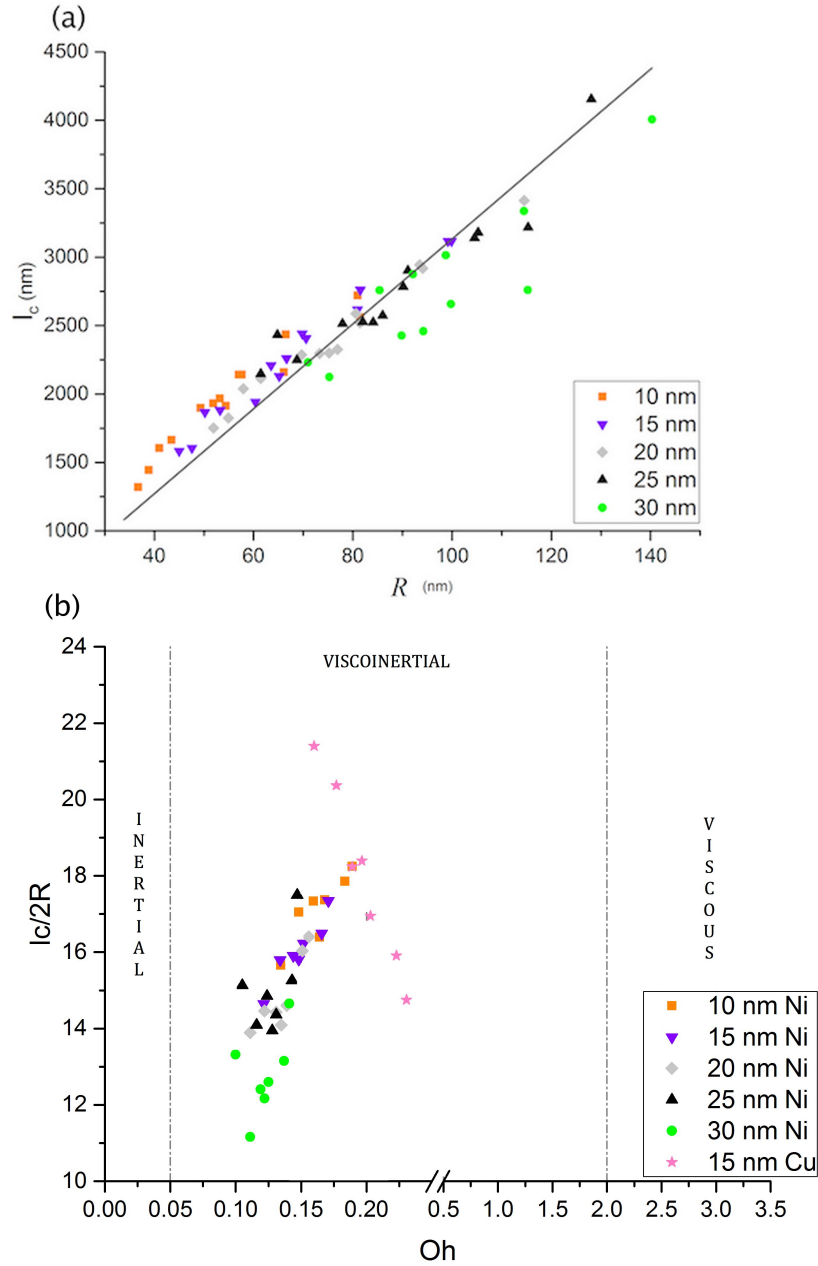


Figure 3.5. (a) Average experimental l_c colored by initial film thickness. Samples were irradiated with 5 laser pulses using a KrF laser (wavelength 248 nm) at a fluence of 250 mJcm^{-2} , to ensure final droplet morphology (sufficient cumulative liquid lifetime). The linear best-fit parameter is $\alpha' = 31.27$, with 95% confidence bounds $[30.52, 32.02]$. (b) Critical aspect ratio ($\Gamma_c = l_c/2R$) versus the Ohnesorge number (Oh), calculated at the melting temperature and the Oh range for the operative regimes.

to the wetting of the substrate or any material property dependency. Also, it appears to underestimate the measured critical lengths at small radius and overestimate it at larger radius. We will discuss the origins of these trends at the end in the chapter.

Figure 3.5(b) is a plot of the aspect ratio, $\Gamma_c = l_c/2R$, versus the Ohnesorge number, Oh , for filaments at the critical length. Included are vertical lines delineating the important fluid dynamic regimes; the viscous regime, $Oh > 2$, the inertial regime, $Oh < 0.05$, and separating the two, the intermediate, visco-inertial regime, $0.05 < Oh < 2$. Recall, that R-P-like instabilities are expected to be an influential mechanism within the visco-inertial range.⁷⁰ The experimental data points fall within the visco-inertial range, closer to the inertial boundary. Accordingly, there should be an expectation that the prediction of critical lengths by the analytical model should come from the visco-inertial framework.

In Figure 3.6 we plot solutions to the governing, competing timescale equation, Equation (3.6), the predicted critical breakup length, for both the viscous and the visco-inertial regime and compare them to the experimental data set for Ni. We use the average measured retraction velocity of 30 ms^{-1} and an equilibrium wetting angle of 69° , consistent with the measured contact angle for liquid Ni on SiO_2 .³⁶ As mentioned earlier, the initial amplitude of the surface instability is

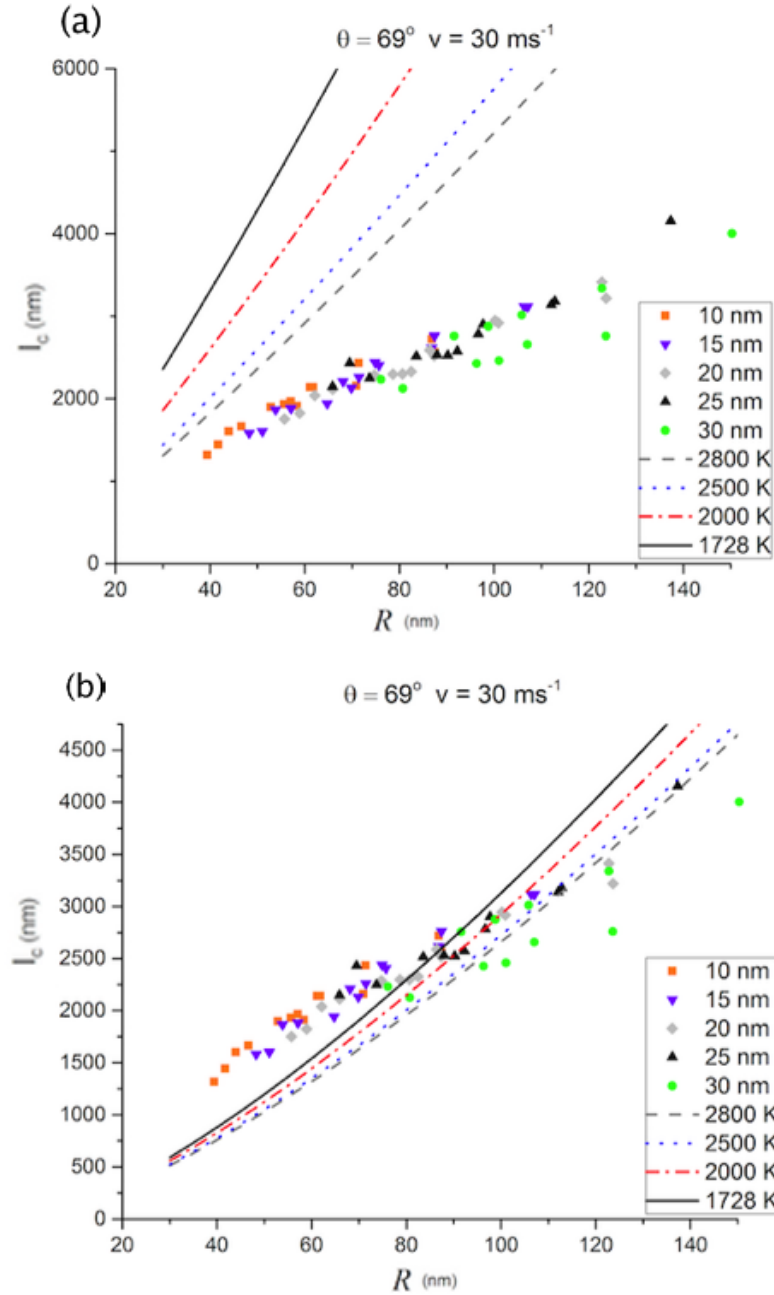


Figure 3.6. Experimentally measured critical lengths, grouped by initial TFS thickness, compared to the solutions of Equation (3.6), at several temperatures. (a) viscous regime solution, (b) visco inertial regime solution. In both cases, (a) and (b), the viscosity and surface tension (and density in (b)) vary with temperature, the contact angle, 69° , and velocity, 30 ms^{-1} , remain constant.

chosen to be $\delta = 0.2$ nm. Additionally, to illustrate how changes in temperature, which modify material properties, alter predicted critical lengths three additional temperature solutions are plotted, 2000 K, 2500 K, and 2800 K.

Noticeably, agreement with the viscous regime solution, Figure 3.6(a), is not very good. It does improve at higher temperature, the slope and l_c both decrease, however it fails to reach any of the data points. Higher temperature solutions could succeed in reaching the experimental data, but those predictions would be unrealistic. The temperatures necessary would be beyond those simulated in our thermal model (Figure 3.3) and there is also the evaporation threshold (3003 K) to consider. Also, the range of Ohnesorge numbers for Ni is not supportive of the viscous regime. Therefore it is not surprising that the viscous framework does not fit the experiments well.

On the other hand, the experimental data does fit well with the viscoinertial solution, at constant velocity, Figure 3.6(b). Such a finding is reasonable, based on the Ohnesorge number, and generally validates the hypothesis that the length at which breakup occurs, for nano and microscale liquid metal filaments, can be described as a competition between timescales, that of a R-P-like instability and the axial retraction/collapse of the filament. However there is disagreement, for instance, at larger filament radii the model overestimates the critical length

relative to the experimental data. This could be due to a decrease in velocity because of larger filament radius. While at small radius it underestimates it, this and other issues will be discussed below. Additionally, as will be shown below, the VoF simulations reveal that the solidification of the filament quenches the inertia of the dynamic collapse. For larger radii filaments, which require multiple laser pulses, this decreases the average velocity and leads to a shorter critical lengths. For example, at 1728 K, VoF simulations reveal that solidification reduces the average velocity by 40%.

We will now discuss the experimental data and the analytical model, focusing only on the viscoinertial solution for the reasons stated above. To begin with, the governing timescale equation can be solved using other pertinent velocities, for instance, the theoretical capillary velocity. The timescale equation, Equation (3.6), in the viscoinertial regime, can be recast to shows its dependence on the capillary velocity, $v_c = (\sigma/\rho R)^{1/2}$. The dependence appears in the second term, inside the instability growth rate.

$$\frac{R}{v} \left(\Gamma_c - (6\Gamma_c)^{\frac{1}{3}} \right) - \frac{1}{0.317} \frac{R}{v_c^{2/3}} \left(\frac{2 \sin \theta}{\theta} \right)^{4/3} \left(\frac{\mu}{\sigma} \right)^{1/3} \ln \left(\frac{R}{\delta} \right) = 0 \quad (3.15)$$

When the retraction velocity, $v = v_c$, is allowed to vary like the capillary velocity, with material properties that depend on temperature, and radius, R , larger critical

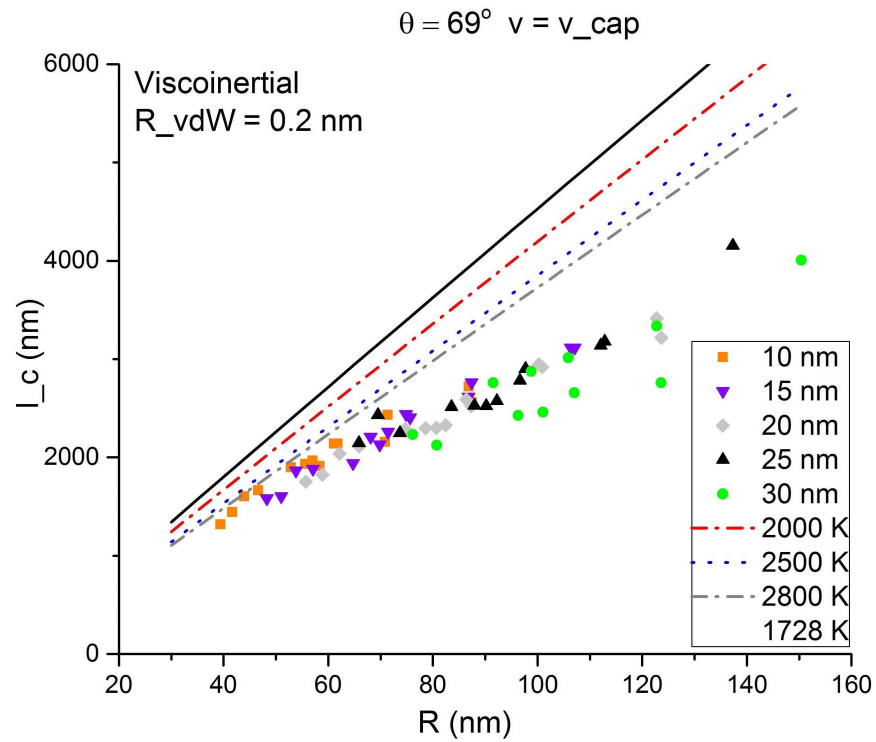


Figure 3.7. Plots of solutions to the analytical model with different values for the retraction velocity using experimentally measured velocities for the 15 nm Ni data, Figure (3.4). The viscosity, surface tension and density vary with temperature, and the contact angle, 69° , remains constant.

lengths are predicted, Figure 3.7. Clearly, the experimental data points fall below the model predictions. We speculate that the liquid lifetime of smaller radii filaments may be shorter than presumed, which were estimated by the KrF pulse-width and thermal simulations, and also shorter than for larger radii. This may be due to the filament substrate contact area to volume ratio at small radii filaments, i.e. a small thermal mass depositing heat more quickly into the substrate. For instance, a 40 nm radius filament has only 16 % the mass of a 100 nm radii filament, but shares ~ 40 % of contact area with the substrate. Furthermore, smaller filaments will be more susceptible to phase change effects, melting and solidifying, since the extent of the filament transitions in a shorter timeframe. Clearly the liquid lifetime as well as real energy loss effects can have dramatic ramifications on a retracting/evolving liquid filament, in contrast to the predictions using a theoretical capillary velocity that is not subject to finite liquid lifetimes constraints and losses.

Since the analytical model is dependent on material properties that change with temperature examination of Equations (3.6), (3.8) and (3.10) reveal the effects that temperature has on the predicted critical lengths. Nickel's surface tension decreases with temperature in a linear fashion, $\sigma(T) = \sigma_m - d\sigma/dT (T - T_m)$ Nm^{-1} , and viscosity also decreases with temperature, however it varies in an exponentially decreasing manner, $\mu(T) = \mu_o \exp(E/RT)$ $\text{Pa}\cdot\text{s}$, see Table 1 and

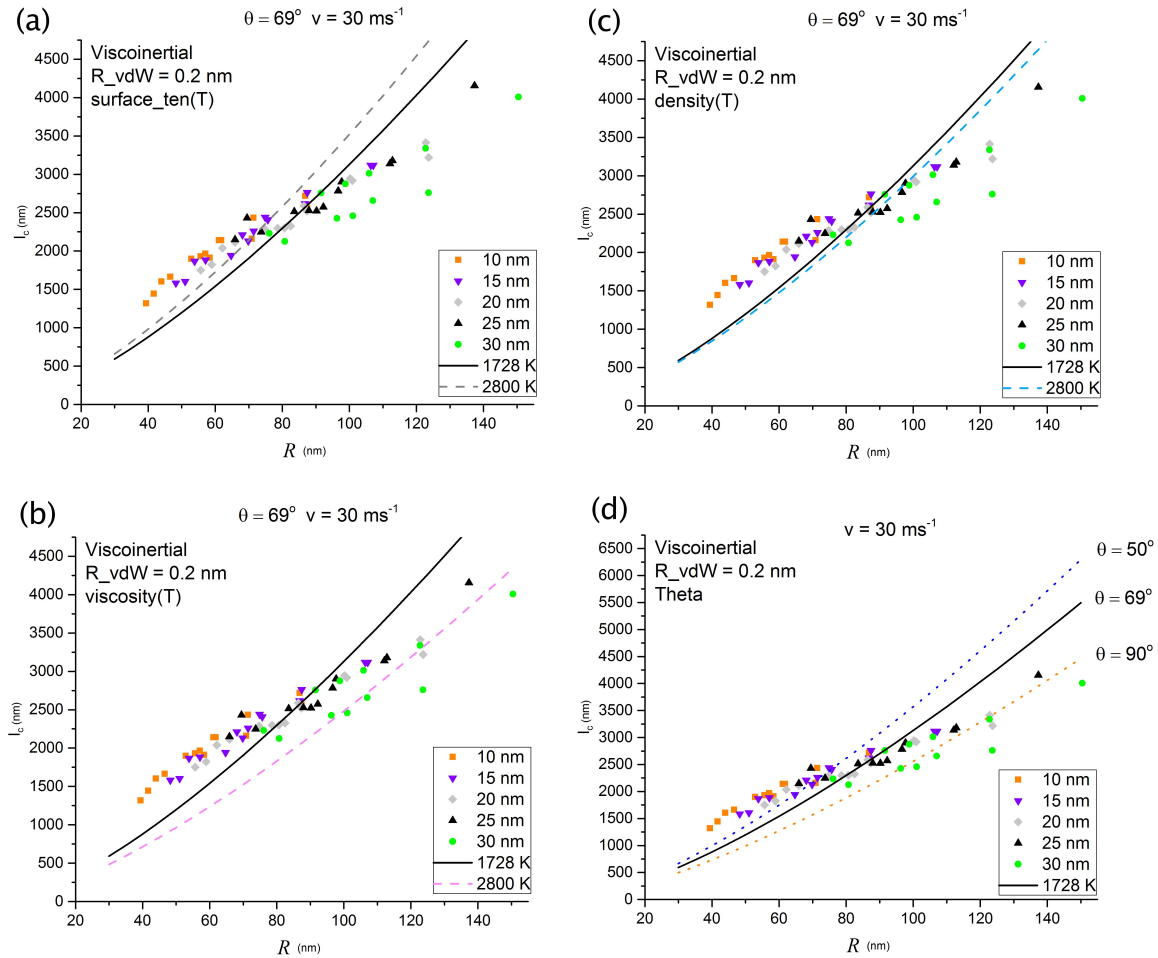


Figure 3.8. Plots of solutions to the analytical model showing the effects that temperature changes lengths (a)-(c) and wetting angle (d) have on the predicted critical lengths, (a) variation as surface tension changes with temperature, (b) variation as viscosity changes with temperature, (c) variation as density changes with temperature, (d) variation as the wetting angle changes, the retraction velocity, 30 ms⁻¹, and the contact angle, 69°, remain fixed for all.

Figure 1.11. As surface tension decreases at higher temperatures it has the effect of moving the predicted critical length, l_c , to longer lengths, Figure 3.8(a). Longer lengths mean longer development times for surface instabilities, and the retraction velocity has more of an opportunity to collapse a longer filament. This is due to the diminished surface energy at higher temperatures.

On the other hand, decreasing viscosity at higher temperature results in shorter predicted critical lengths, Figure 3.8(b). This is because lower viscosity fluids make it easier for surface instabilities to grow in amplitude with time, i.e. the lower the viscosity the less energy is dissipated in the fluid, making it easier for the instability to develop. The effect of density changes with temperature, Figure 3.8(c), is similar to changes seen with viscosity, adding to the shift to lower predicted critical lengths at high temperature. However, when all material properties are allowed to vary simultaneously with temperature, clearly, the most dominant effect is due to viscosity, which results in shortened critical lengths, as can be seen in any of the plots comparing the experimental data with the model solutions, Figures (3.6) and (3.7).

It should be noted, that the magnitude of change in the solutions for the critical length at higher temperatures is not as dramatic for the visco-inertial case as it is for the viscous, compare Figure 3.6(a) and (b). This is due to the temperature

dependent material properties largely balancing each other out in the visco-inertial regime, largely due to viscosity varying like, $\mu^{1/3}$, as it decreases. Whereas, in the viscous regime, the viscosity varies linearly, μ , as it decreases, and therefore smaller predicted critical lengths.

Increasing the laser fluence increases the average temperature of a filament, leading to a longer liquid lifetime and a reduced average viscosity and surface tension. Figure 3.9 is a plot of the measured critical lengths for a 20 nm thick Ni TFS irradiated at three different laser fluences. The plot illustrates that the measured critical length is longer with increased laser fluence. As noted above, for a constant retraction velocity, higher temperature decreases the predicted critical length. The experimental results here seem to be contrary to that prediction.

We attribute the longer critical lengths at higher laser fluence to two effects, namely, longer liquid lifetimes at higher temperature and higher retraction velocities due to decreased average viscosity. As will be shown below, the VoF simulations reveal that the solidification of the filament quenches the inertia of the dynamic collapse. For larger radii filaments, that require multiple laser pulses, this decreases the average velocity and leads to a shortening of the critical

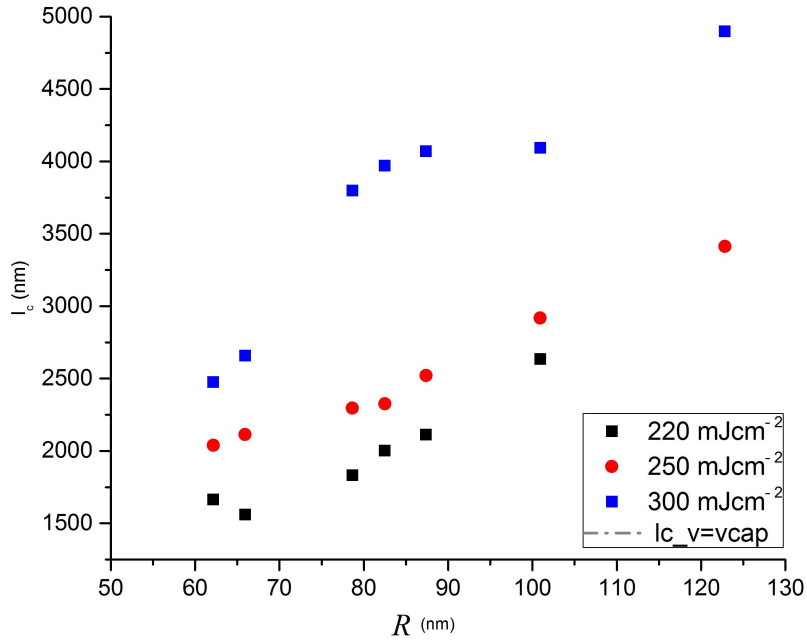


Figure 3.9. Measured critical lengths for a, 20 nm, thick Ni film irradiated at three laser fluences, 200, 250 and 300 mJcm⁻². The longer critical lengths at higher laser fluence are attributed to higher retraction velocities, similar to those of the capillary velocity, and longer liquid lifetimes at elevated temperature.

length. For example, at 1728 K, VoF simulations reveal that solidification reduces the average velocity by 40%.

3.4.2 Copper

A second metal was experimentally investigated, Cu, and it was selected for a few reasons, previous experience, amenability with the nanofabrication processes and PLiD, and for its differences in material properties to that of Ni, see Table 1. For instance, the melting temperatures differ by 20%, where, $T_m^{Ni} = 1728$ K and $T_m^{Cu} = 1357$ K, and importantly, the surface energies and viscosity are different by 27% and 18%, respectively, however their densities vary much less, at 3%. Additionally, the two metals have the distinction of being isomorphous, that is, their crystal lattice structure is similar, that of an FCC lattice – a feature that will be noted in next chapter on thermocapillary/Marangoni effects. Finally, copper and nickel have total solid and liquid solubility, thus in principle alloy films could be investigated to look at intermediate values. The differences in the important properties of melting temperature, viscosity, and surface energy make it a good candidate as an alternative metal for the analytical model.

Currently, only one thickness of Cu, 15 nm, has been explored. Additional thicknesses, similar to those for Ni, should be explored in the future; note, nanofabrication tool issues made it impossible to investigate more, however, the results for this singular thickness are encouraging and corroborate the general findings. The experiment spanned 6 widths from, 145 – 626 nm, which corresponds to filaments radii spanning, 43 – 89 nm, and each data point represents an average of six measurements.

The capillary length, $\lambda_c = \sqrt{(\sigma/\rho g)}$, for Cu is ~ 4 mm, which is much greater than the length scales of the experiment, thus, gravitational effects still do not need to be considered. At the filament radii considered the Ohnesorge number, $Oh = \mu(\sigma\rho R)^{-1/2}$, for Cu is similar to that for Ni, albeit slightly larger, ranging from, 0.16 – 0.23, at the melting temperature, and decreases as the temperature of the material dependent properties increase. Figure 3.5(b) is the plot of critical aspect ratio as a function of Ohnesorge number and includes Cu's experimental values, which can be compared to those for Ni. Albeit that the values for Cu are slightly shifted towards the viscous regime, they are solidly in the visco-inertial regime. Recall, that R-P-like surface instabilities are expected to be an influential fluid dynamic breakup mechanism within the range of $0.05 < Oh < 2$. Therefore, it is anticipated that the experimental results for Cu will follow more closely those predicted by the visco-inertial regime solution.

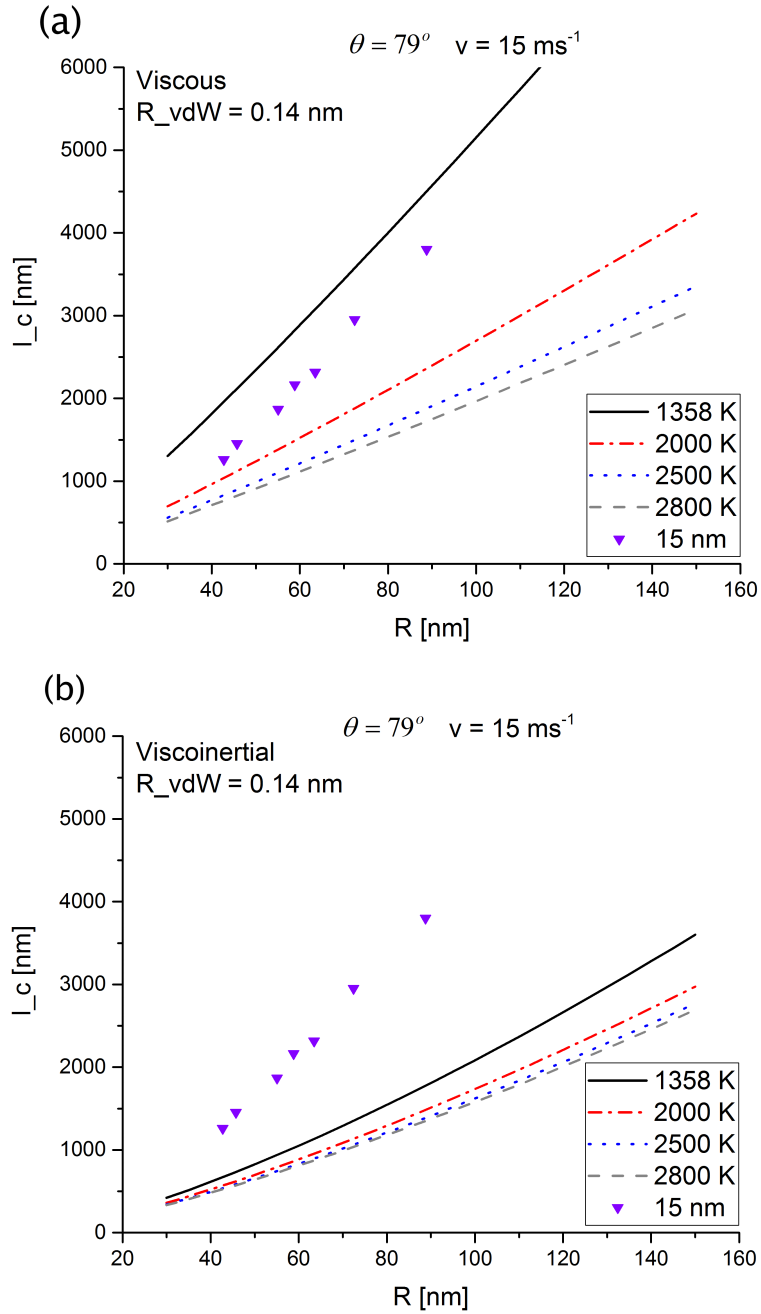


Figure 3.10. Experimentally measured critical lengths compared to the solutions of Equation (3.6) at several temperatures, (a) viscous regime solution, (b) viscoinertial regime solution. In both cases, (a) and (b), the viscosity and surface tension (and density in (b)) vary with temperature, the contact angle, 79° , and velocity, 32 ms^{-1} , remain constant.

The retraction velocity was also experimentally measured for Cu, the average value was found to be 15 ms^{-1} , which is smaller than that of Ni's 30 ms^{-1} . For comparison, the capillary velocity for Cu ranges from, $42 - 61 \text{ ms}^{-1}$, spanning the filament radii maximum and minimum, $89 - 43 \text{ nm}$. Furthermore, the velocity was simulated via the VoF approach at two temperatures, 1358 and 2000 K, and radii range of $29 - 92 \text{ nm}$. The simulations resulted in average velocities of 20 ms^{-1} and 30 ms^{-1} at 1358 and 2000 K, respectively. Again, what is reassuring is that the capillary, experimental, and VoF velocities are of similar order.

In Figure 3.10 we plot solutions to the governing, competing timescale equation, Equation (3.6), the predicted critical breakup length, for both the viscous and the viscoinertial regime and compare them to the experimental data set for Cu. We use an equilibrium wetting angle of, 69° , consistent with the measured contact angle for liquid Cu on SiO_2 .⁴³ The initial amplitude of the surface instability is again chosen to be the van der Waal radius of the metal, $\delta = 0.14 \text{ nm}$.⁷²

It is evident that the agreement with the viscous regime solution, Figure 3.10(a), is better than that seen for Ni. The data lies between the melt line, at 1358 K, and the next highest temperature plot line, 2000 K. The average temperature of 15 nm of Cu, from simulations was estimated to be 1926 K. The fact that the

viscous solutions is a better fit than Ni, to some degree, makes sense seeing as the Ohnesorge number is slightly larger. However, the Ohnesorge for Cu, at this length scale, it is not supportive of the viscous regime. A possible reason for this could be that the average, experimentally measured retraction velocity is not a good estimate. This could also explain why the experimental data does not fit well with the viscoinertial solution using the average velocity, Figure 3.10(b), as was the case for Ni. The viscoinertial prediction for the critical length is simply too small.

It is pertinent to make an additional comment about what else could cause the mismatch, and correct it, in the predicted length when using the experimental average estimate of 15 ms^{-1} . The wetting angle for Cu could be smaller than experimental data range, and bringing up the viscoinertial solution closer to the data.

It should be added to the discussion that, interestingly, the fit improves markedly when the theoretical capillary velocity, $v_c = (\sigma/\rho R)^{1/2}$, or a higher constant retraction velocity of, $\sim 45 \text{ ms}^{-1}$, is used in the viscoinertial regime solution, Figure 3.11(a) and (b), respectively; note, if the capillary velocity is used in the viscous regime solution the predicted critical lengths are far too long, this is because the viscous solution is not an inertial solution, where surface tension

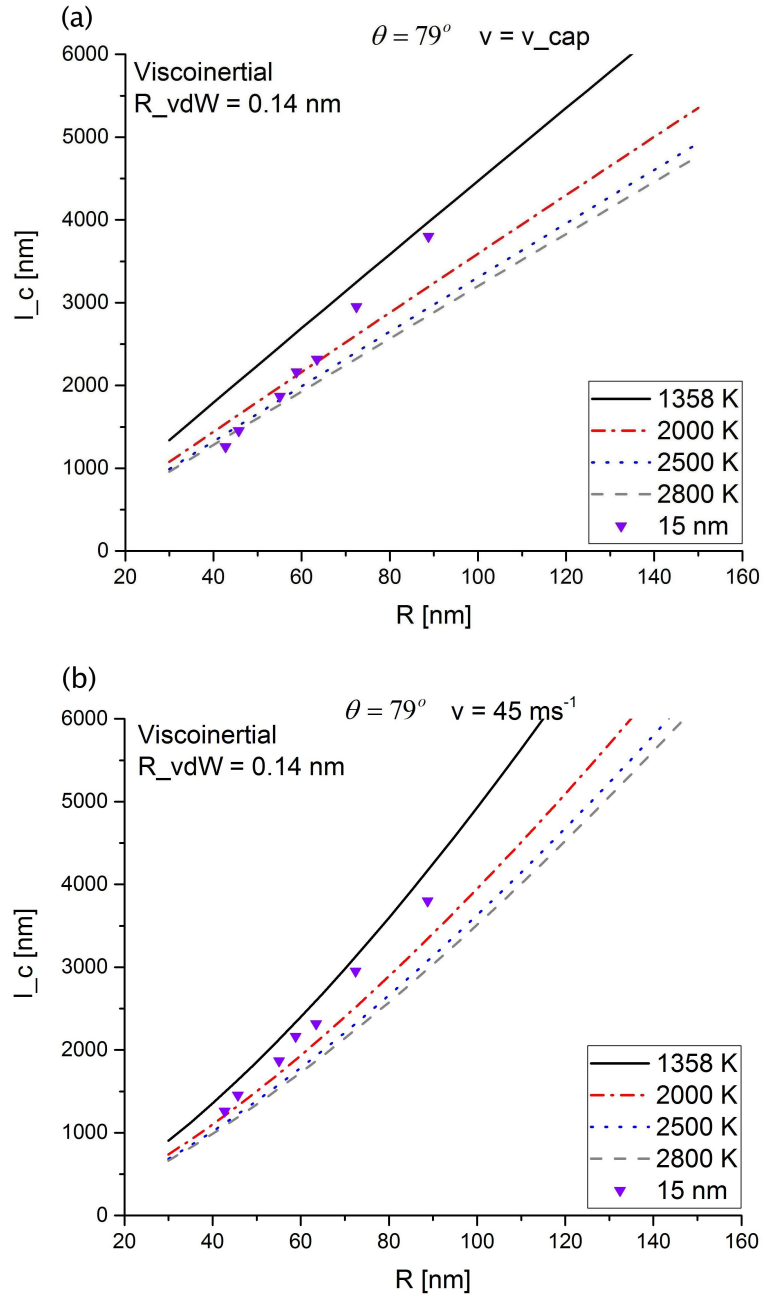


Figure 3.11. Plots of solutions to the viscoinertial model for 15 nm Cu using different values for the retraction velocity, (a) theoretical capillary velocity, where the surface tension and density vary with temperature (b) constant retraction velocity of 45 ms^{-1} . The contact angle, 79° , always remains constant.

and density are important, therefore the capillary velocity should not apply in the viscous case. The improved fit might be evidence that our estimate for the liquid lifetime used in the experimentally measured retraction velocity is too large, in order to achieve an average velocity of, 45 ms^{-1} , ranges from, 5 – 12 ns, for the smallest to largest radii filaments, respectively. Everything considered, the exploration of Cu generally validates, the hypothesis that critical length can be described as a competition between development timescales, Equation (3.6).

3.6 VoF Simulations

Here, we computationally investigate the dependence of the critical length on the filament radius curvature while varying the liquid lifetime. Initially, a semi-cylindrical liquid filament, with cross sectional area, $C_A = hw$, is placed on a solid surface with an imposed wetting angle of 90° . Recall, that between laser pulses the filament solidifies. Solidification is modeled by simply zeroing the fluid velocity field in the evolving filament after a specified liquid lifetime, t_l , then continuing the evolution to simulate further laser pulses. No evolution occurs while the filament is in the solid state.

Figure 3.12 illustrates the effects of varying the liquid lifetime, as well as a comparison to the 10 and 20 nm thick Ni experimental data. When the liquid

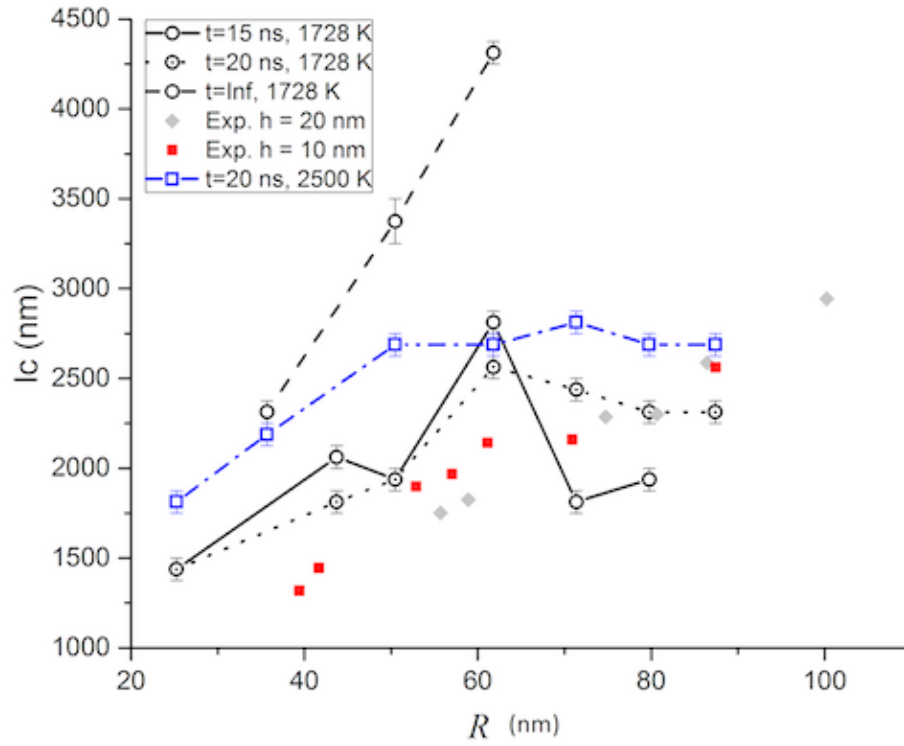


Figure 3.12. VoF simulations for critical length compared to experimental measurements for Ni, red squares and gray diamonds represent thicknesses of $h = 10$ and 20 nm, respectively. Circular symbols show the results of VoF simulations as the liquid lifetime is varied, with material properties set to the melting temperature. Square symbols represent the VoF results when the material properties are set to those at 2500 K and $t_l = 20$ ns. For clarity, solid lines represent the experiments and the dotted lines the simulations.

lifetime is simulated to be infinite, $t_l \rightarrow \infty$, i.e. no solidification, the simulations predict longer critical lengths compared to the experiments. This is expected, in similar fashion as to the presumption of increased critical lengths at higher laser fluence; infinite liquid lifetimes can be likened to laser irradiation at 100% duty cycle of the laser. What is evident is that the difference is particularly significant for larger values of R . The simulation results reveal that inertial effects are important when, $t_l \rightarrow \infty$, i.e. the retraction velocity is freer to collapse filaments to longer lengths. When solidification is included the resulting critical length predictions are much shorter and in good agreement with the experiment, Figure 3.12. This result suggests that the simulated liquid lifetimes in the range of ~ 20 ns provide the best agreement with the experimental results. This is encouraging because it is consistent with the timescales of the thermal simulations, KrF pulse-width, and instability growth rates. We note that in the simulations the slip length, λ , is fixed to 20 nm; we carried out an comprehensive study of the effect of slip length on critical length and obtained the best agreement with the experiments with this value.

Additionally, we carry out VoF simulations using the parameters that correspond to higher temperature, with the material properties of viscosity, density, and surface tension corresponding to 2500 K. The elevated temperature generally predicts longer critical lengths, Figure 3.12, which is consistent with the

experimental observation. When the VoF simulations include a change in the material properties with temperature the velocity profile of the retracing filament is similar to that of the capillary velocity, and agreeing qualitatively with the experimental results of longer critical lengths at higher laser energy.

Note, that the simulation results when solidification is modeled show that the critical breakup length is not necessarily a monotonously increasing function of filament radius, R . This unexpected behavior can be attributed to the particular retraction state the filament is when solidification takes place, for example, Figure 3.13 shows two representative examples. Early in the simulation both filaments begin to retract with accumulating end droplets, Figure 3.8(b), however, when solidification occurs, after one liquid lifetime, the central regions of the filaments are characterized by different geometry, Figure 3.8(c). For the, $l = 2.31 \mu\text{m}$, case (left panel), the central bulge collapses and the liquid is transported to the filament ends, leading to breakup and the formation of two droplets. For the, $l = 2.69 \mu\text{m}$ case (right panel), there is no liquid transport from the center bulges to the filament ends, so the retraction continues and a single drop results. This example therefore illustrates that, perhaps surprisingly, a breakup may occur for a shorter filament, length but not for a longer one. This process also explains why the simulations with very long liquid lifetimes, $t_l \rightarrow$, lead to a longer critical length, that is, the filament is able to continue retracting without freezing and so the two filament ends continue to move inward, eventually coalescing to a single

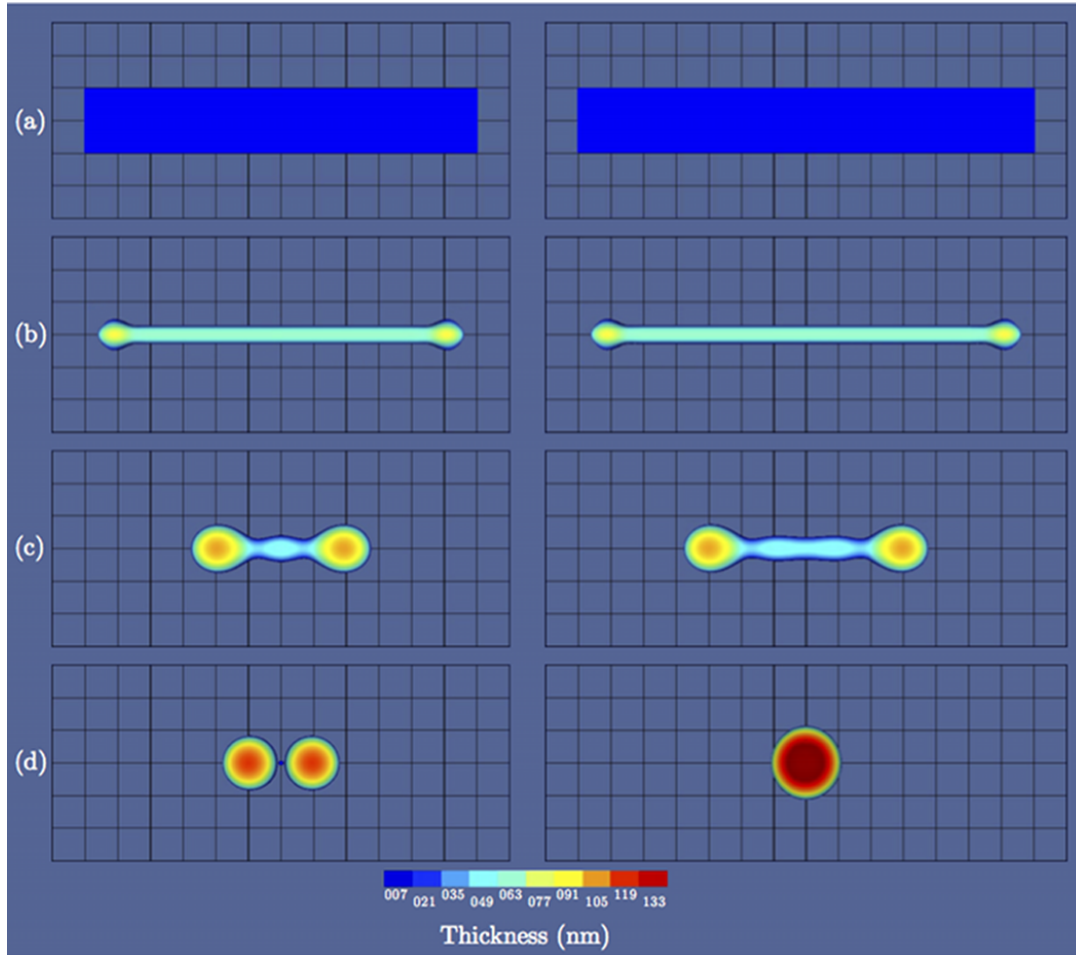


Figure 3.13. Snapshots of VoF simulation for a Ni filament with initial TFS geometry, $h = 20$ nm, $w = 385$ nm ($R \sim 100$ nm) and $l = 2.69$ μ m (left panel) and $l = 2.69$ μ m (right panel). (a) Initial geometry, $t = 0$ ns, (b) the strip has formed a truncated cylindrical filament and the axial ends have begun to retract, $t = 2.5$ ns, (c) at, $t = 20$ ns, one simulated liquid lifetime, the filament has 'frozen'. (d) The filament either breaks up (left, $t = 39$ ns) and multiple droplet formation occurs or edge droplets coalesce into a single droplet (right, $t = 52$ ns). The VoF simulations capture the dewetting dynamics seen during the experiment in Fig. 3.1c. Note, that in the absence of solidification the simulation predicts the filament will collapse into a single drop, for both values of l . Note, that in the absence of solidification the simulation predicts the filament will collapse into a single drop, for both values of l .

droplet. We also note that when ignoring the solidification the simulated critical lengths compare well with the viscous model presented in the previous section. Figure 3.14 compares VoF simulations of critical lengths to experimental measurements for a 15 nm thick Cu sample. The critical length predictions are in good agreement with the experimental values and a similar trend is apparent, the critical length increases with filament radius, R . The simulations use a liquid lifetime of 20 ns and a slip length of 20 nm, which are similar to those from the Ni VoF simulations having the best agreement. This being the case, across different material simulations, is encouraging because this timescale is consistent with those of the thermal simulations, the KrF pulse-width, and instability growth rates. Once more the simulated critical lengths are still not monotonously increasing functions of filament radius. This behavior is again attributed to the particular retraction state the filament is in when solidification takes place; this effect was discussed in the Ni simulation results, see Figure 3.13.

Additionally, the VoF simulations were carried out using parameters that correspond to higher temperature, with the material properties of viscosity, density, and surface tension corresponding to 2000 K. The elevated temperature simulations predict longer critical lengths at smaller filament radii, which is consistent with the experimental observation seen during the Ni experiment, however the simulated critical lengths flatten out at radii larger than 50 nm and

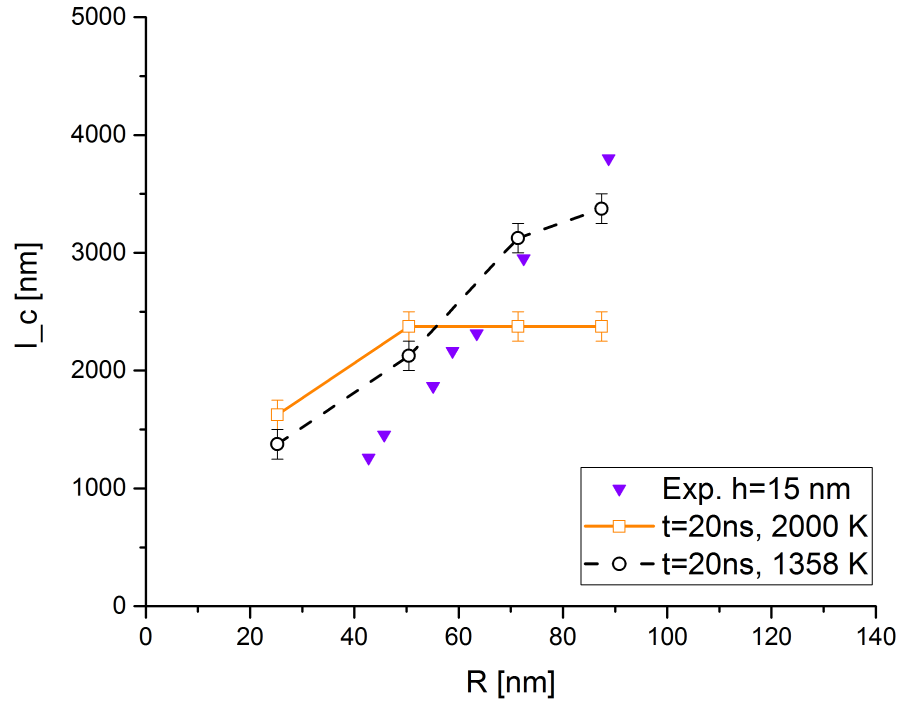


Figure 3.14. VoF simulations for critical length compared to experimental measurements of critical lengths for Cu, purple diamonds, at a thickness of $h = 15$ nm. Circular symbols show the results of VoF simulations with material properties set to the melting temperature, 1358 K. Square symbols represent the VoF results when the material properties are set to those at 2000 K. In both simulations the liquid lifetime is $t_l = 20$ ns.

fall below those of the 1358 K simulation predictions. The increase in simulated critical lengths at smaller radii and higher temperature can be attributed to the increase in the capillary velocity at higher temperatures due to a decrease in Cu's viscosity; which agrees qualitatively with the experimental results of longer critical lengths at higher laser energy seen for Ni. However the divergence at larger filament radii is interesting. The flattening out of the simulated critical lengths may again be due to changes in the retraction velocity, however now it may be due to the influence of a geometrical parameter, that of the filament's radius, and not solely a material property. In other words, the retraction velocity does indeed increase as the viscosity decreases with temperature however the capillary retraction is also inversely proportional to filament radius, and these two effects compete to raise and lower the simulated critical length, respectively. The flattening is suggestive that the onset of filament radius effects for Cu occurs at filament radii of 50 nm and larger.

3.7 Application

To demonstrate how understanding when to expect a liquid filament to collapse to a single droplet or breakup into multiple droplets can be useful, we utilize the insights to facilitate the directed assembly of metallic nanoparticle arrays. Figure 3.15(a)-(c) is a series of composite SEM images of a lithographically patterned Ni

thin-films (background) and the resultant nanoparticle array after ten laser pulses (foreground). The initial, so-called, 'square-wave' pattern contains two alternating side-amplitudes orthogonal to the central axis: 1) a shorter amplitude with a fixed length, which is below the critical length, therefore these side-amplitudes will collapse to a single droplet, 2) a slightly longer amplitude which progressively increases, as noted with the arrows in Figure 3.15a)-(c). As the side-amplitude increase a transition is observed, from collapse to a single droplet, Figure 3.15(a), then to mixed single and two droplet breakup, Figure 3.15(b); and finally to ordered breakup where two droplets are observed, Figure 3.15(c). The transition occurs at a side-amplitude of, $\sim 2.3 \mu\text{m}$, which correlates well with the, $2.1 \mu\text{m}$, estimate from the analytical model at constant retraction velocity for Ni. As a result, it is possible to direct the self-assembly of highly ordered, hierarchical metallic nanoparticle arrays by understanding the fluid dynamic regimes and instability/transport competitions. Figure 3.16 illustrates the robustness of the directed self-assembly over large length scales.

3.8 Conclusion

In this work we studied the critical breakup length, l_c , of partially wetting, liquid metal filaments supported on a solid substrate, under nanosecond laser heating. It was found that filament lengths less than a critical length, $l < l_c$, collapse to a

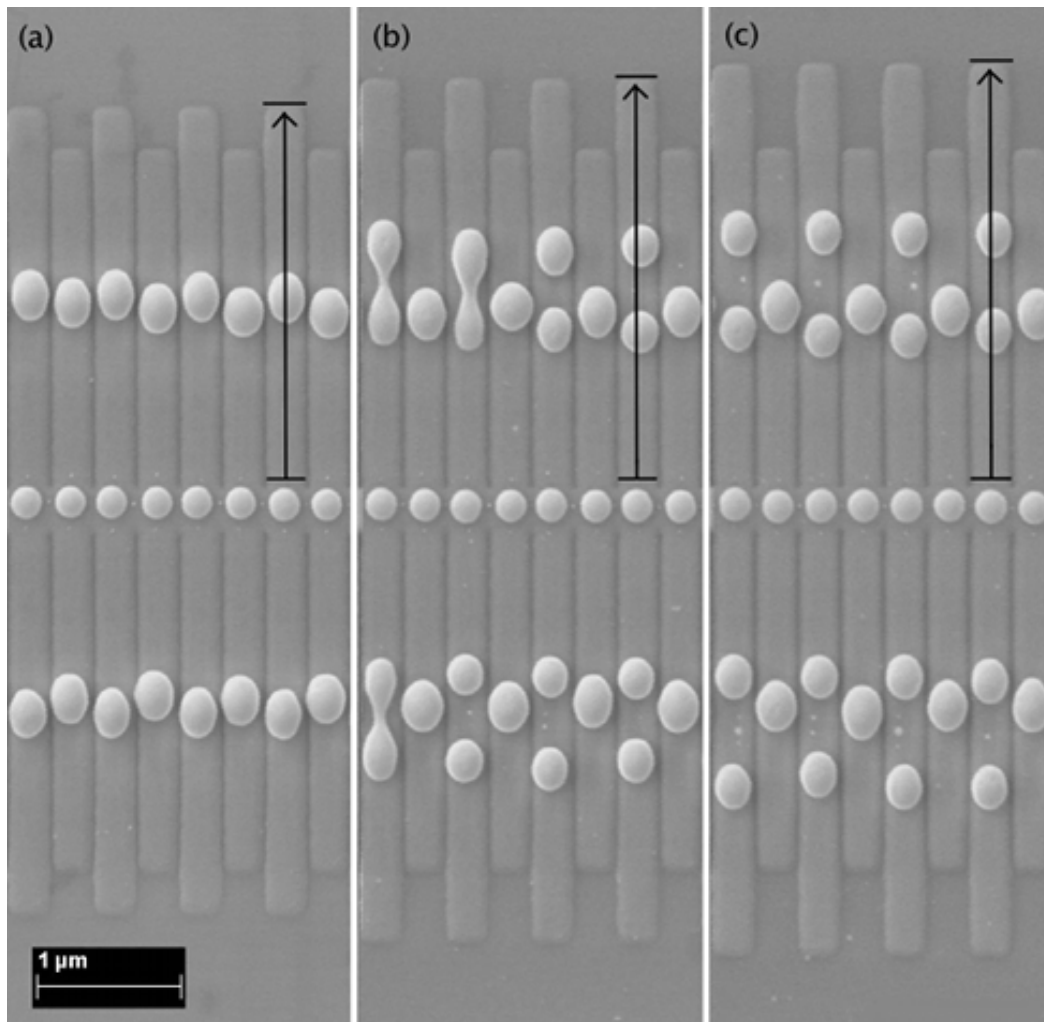


Figure 3.15. (a)-(c) Composite SEM images of a lithographically patterned Ni thin-film (background), and the resultant nanoparticle array after ten laser pulses (foreground). The transition from single droplet collapse to two droplet breakup is observed in the progression of the larger amplitude side-filaments of the 'square-wave' pattern.

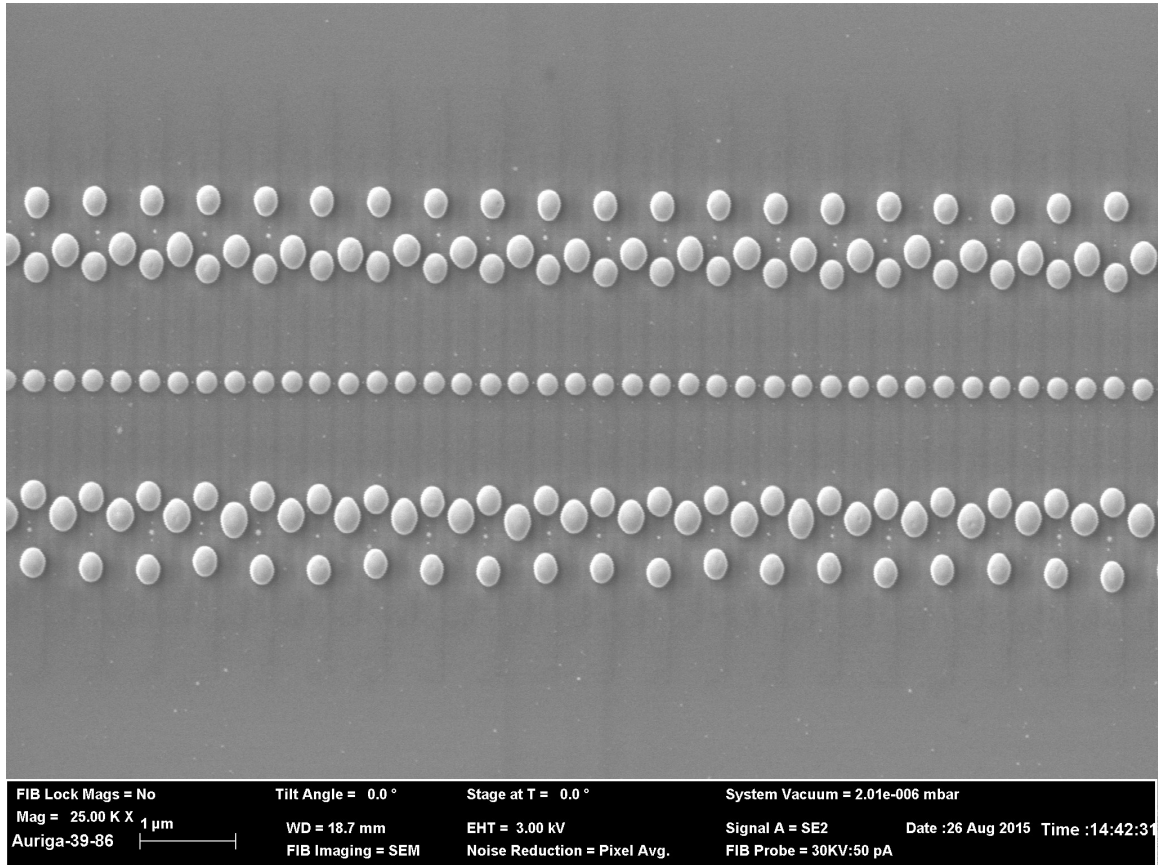


Figure 3.16. SEM image of a 17 nm thick Ni patterned “square-wave” after 10 laser pulses, with alternating side-amplitudes of 2.4 and 2.8 μm . The results illustrate the robustness of the directed self-assembly approach to create arrays of metallic nanoparticles over large extents.

single droplet, and lengths, $l > l_c$, result in filament breakup into two or more droplets. We show that the critical length can be understood by considering a competition between two fluid dynamic timescales: 1) capillary-induced axial end retraction and 2) filament breakup due to the growth of surface instabilities similar to the R-P mechanism. Furthermore, the competing timescale model was solved for the viscous and the visco-inertial regimes. The visco-inertial regime solution for the breakup length more closely matches the experimental results, which is consistent with the Oh number for the filaments studied. To complement the experimental and model results, fully nonlinear simulations were carried out based on a VoF method. To converge to the experimental length scales, thermal effects like liquid lifetime, solidification morphology, and the temperature dependent viscosity, surface energy, and density need to be considered. The comprehension and exploitation of fluid dynamic mechanisms, and timescales, permits new nanofabrication modalities, importantly the directed self-assembly of highly ordered and hierarchical nanoparticle arrays.

Chapter 4.

Investigation Into The Use of Marangoni and Thermocapillary Effects To Initiate Filament Instabilities

4.1 Introduction

The choice to influence the natural evolution of liquid phase instabilities to create a desired structure is a simple idea but a very powerful tool. Up to this point the directed self-assembly of liquid metal filaments has focused on the imparting of instabilities by patterning them on the edges of the initial TFS, like the previous sections square-wave pattern, Figure 3.15, or the sinusoidal pattern discussed in Chapter 1 and illustrated in Figure 1.8. Moving beyond the patterned edge approach to pursue a new pathway is an innovative next step. In this chapter we investigate a new approach to imparting instabilities by experimentally influencing the physical property of surface tension along the length of a liquid metal filament during PLiD. Additionally, imparting a step height variation in the same material can induce thermocapillary forces due to induced temperature variations in the film.

Recall, that if a surface tension gradient exists on a fluid's surface a force is present. Fluid is then transported in a direction parallel to the surface, from regions of low surface tension to high. When this gradient is due to variations in surface temperature it is referred to as the thermocapillary effect, and when it is

due to differences in chemical composition, for instance, between two different fluids, it is known as the Marangoni effect.⁵⁰ For liquids encountered every day the Marangoni effect is fairly easy to determine, for example the tears in a wine glass, however it is much harder to study in the dewetting of nanoscale liquid metals.

To begin with, the temperature and time scale at which metallic dewetting occurs make it difficult to precisely control and view what is occurring dynamically in a precise region of any surface. To explore these effects one must use a judicious choice of the metals as compositional gradients in some phase diagrams can complicate the resultant material flow induced during liquefaction. It is well known that phase diagrams of metal systems can be complicated, with many phases present over the range of compositions and temperatures. For example, the two familiar metals Ag and Pt have a very complicated binary phase diagram, especially in the intermediate compositions. So if the binary pair Ag and Pt was chosen several phases would be traversed during the rapid heating and cooling over the very short liquid lifetime during PLiD. It is unknown how passing rapidly through several phases would effect dewetting, not to mention its effects on the surface instabilities under study - this may be a new avenue for directed self-assembly, but that is for future research to determine. However, there are a couple ways to mitigate this issue, that is, by selectively using compositions at

the eutectic point, were the system would melt as a whole, or utilizing two metals that are fully miscible at all composition ratios.

In addition to any mentioned miscibility issues, the two metals should have melting temperatures (and evaporation points) that are not too disparate, so as to melt largely together, whilst having sufficiently different surface tensions in order to engender a Marangoni effect. Finally, there is the issue of amenability to the nanofabrication process, like sputter deposition. This list of requirements for material pairs is challenging and thus a search for metal pairs that met these requirements was undertaken, with an emphasis put on those that could work well with Ni, the metal with which we have a lot of experimental and simulation experience. The search effort identified three candidate elements, namely, copper (Cu), gold (Au), and aluminum (Al); the phase diagrams for Ni-Au and Ni-Al can be found in the Appendix. The best candidate material was Cu, for several reasons, which will be discussed. Of the three, Cu does not have the largest surface tension difference. Aluminum has the largest surface tension difference relative to nickel.

Figure 4.1 is the binary phase diagram for the Ni-Cu pair, it is apparent that the system is isomorphous, that is, the two metals are completely miscible in the solid and liquid phase for all compositions. Consistent with the Hume-Rothery

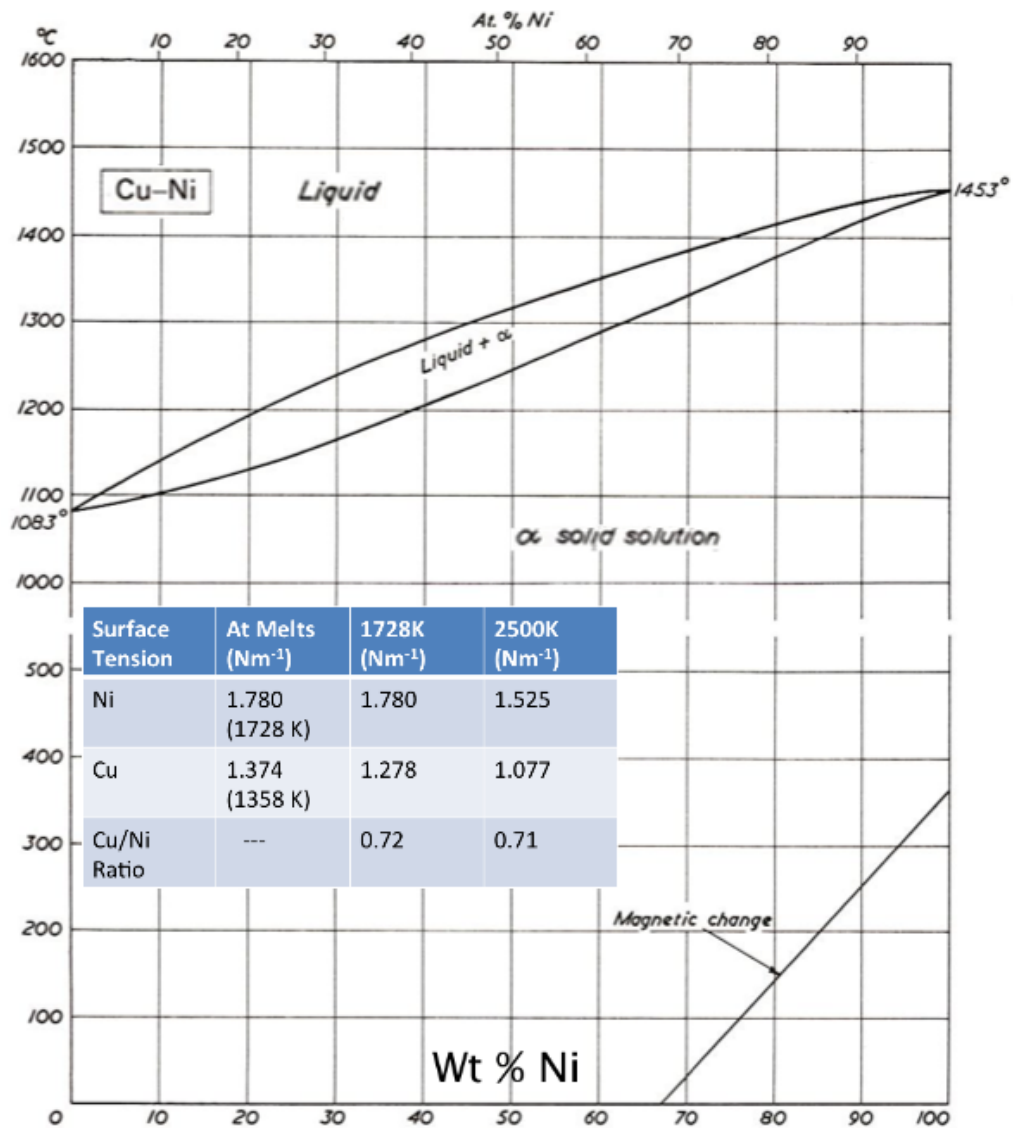


Figure 4.1. Nickel and copper binary phase diagram.⁵³ The two metals are fully miscible, at any composition. The inset is a comparison of the surface tensions at several temperatures for Cu and Ni. The surface tension of Cu is ~ 30% less than that of Ni.⁵³

rules for extended solid solubility, Ni and Cu are face centered cubic (FCC) crystal structures, and have similar lattice constants, 352 and 361 pm, and atomic radii, 149 and 145 pm, respectively. On the periodic table Ni and Cu are adjacent transition metals with atomic numbers, 28 and 29, respectively.

Therefore, it should then be possible to selectively pattern the surface of a Ni thin-film strip (TFS) with Cu to prescribe certain areas with lower surface tension, thereby creating a surface tension gradient with an adjacent Ni area during laser heating and over its liquid lifetime. Furthermore, if the Cu areas are spaced apart at distances similar to those of unstable surface instabilities, in accordance with the R-P mechanism, it could be possible to initiate liquid phase instabilities on the filament and drive breakup using the these effects. Figure 4.2 is an illustration of the establishment of a varicose, surface instability by means of surface tension differences along the length of a filament.

4.2 Experimental Details

A multi-process EBL approach was devised to create a, so-called, “stack” of metals for the TFS. The supporting substrate was a 100 nm SiO₂ surface that was thermally grown on an underlying prime, <100> Si wafer. For each lithography process, two total, (see Figure 2.2), a positive tone resist was used,

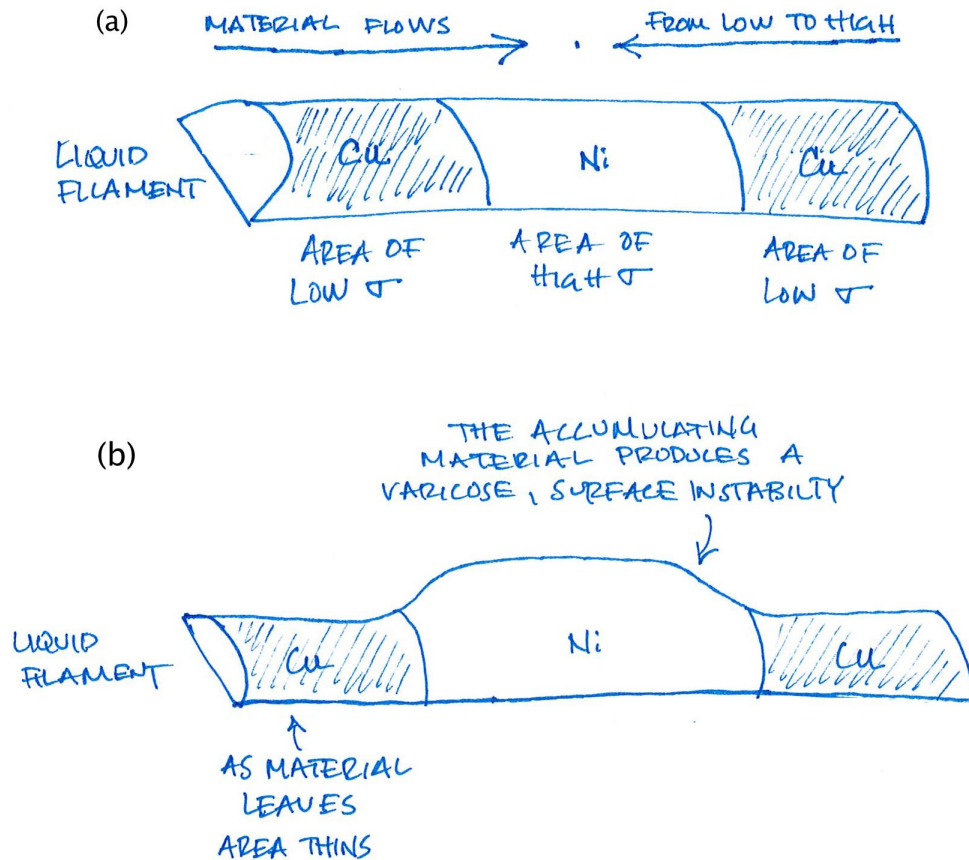


Figure 4.2. Illustration of the creation of a surface instability on a filament by way of the Marangoni effect, (a) the selective patterning of Cu on the surface of a Ni TFS creates areas with lower surface tension, σ , during PLiD, thereby creating a surface tension gradient with the adjacent Ni area, (b) material then leaves the Cu region and accumulates in the Ni region, thereby establishing a varicose surface instability; a novel way of producing surface instabilities, previously only achievable by lithographic edge patterning.

polymethylmethacrolate (PMMA), and an e-beam current density of 900 – 1000 $\mu\text{C}/\text{cm}^2$. The metals, Ni and Cu, were deposited using DC magnetron sputtering, at thicknesses of, $12 \pm 1 \text{ nm}$, for the principal Ni TFS, and, $2 \pm 1 \text{ nm}$, for the Cu and/or the Ni TFS perturbation material on top of the principal Ni TFS. The first lithography process patterned the principal Ni TFS in several widths, 185, 370, 555 and 740 nm. The EBL process was subsequently repeated and a perturbation pattern of Cu, and/or Ni, was lithographically patterned on top of the principal Ni TFS. Figure 4.3 is an illustration of the combinations of TFS stacks explored in the experiment, along with the nomenclature for the particular geometries; for instance, Ni_Cu refers to a principal Ni TFS, 12 nm thick, with Cu, 2 nm thick, patterned periodically along the length, acting like a perturbation on the surface. Figure 4.4 is an illustrative SEM image of the nanofabricated TFS of two metals on the supporting oxide substrate, in this case, the 370 nm width Ni_Cu geometry sample. The spacing of the perturbations follows that of the predicted fastest growing instability, λ_m , given by instability theory, and the extent of the perturbations is half the wavelength. Figure 4.5 is a plot of the predicted fastest growing wavelength as a function of TFS width for a 12 nm thick nickel strip; the inset tabulates the experimentally patterned perturbations spacing for each of the widths.

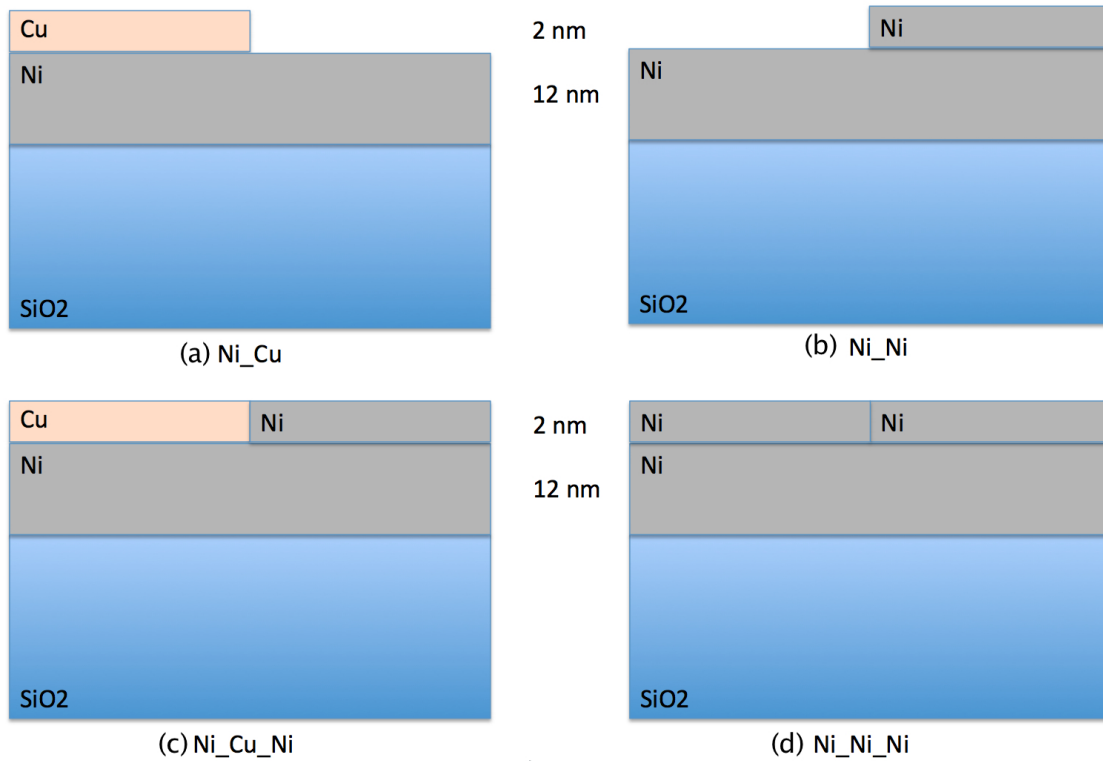


Figure 4.3. TFS geometries explored in the experiments and their nomenclature, the unit repeats to form a continuous filament, all start with an initial underlying 12 nm Ni TFS and on top of which is patterned different surface perturbations (a) 2 nm Cu, (b) 2 nm Ni, (c) 2 nm Ni and Cu, (d) 2 nm Ni and Ni. When repeated, the spacing of the perturbations is in accordance with the wavelength of the fastest growing instability.

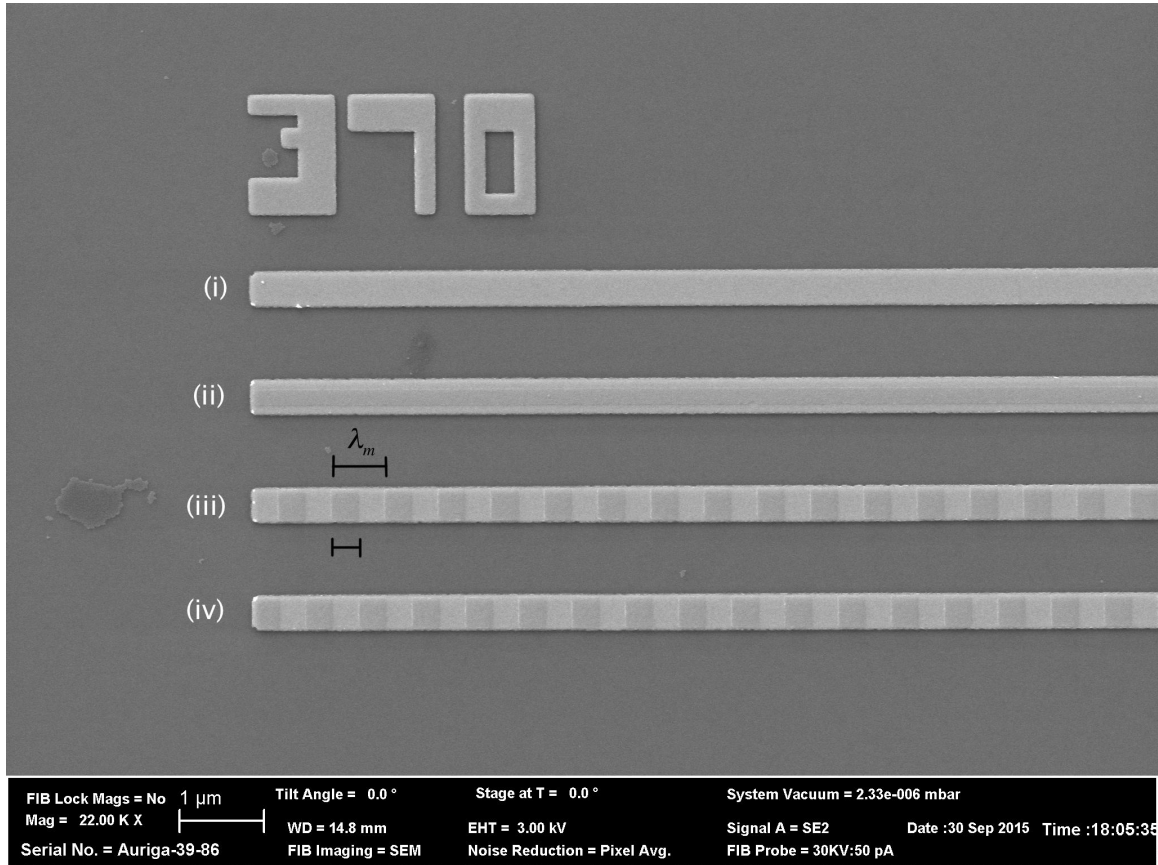


Figure 4.4. Illustrative SEM image of a sample area before PLID, Cu (darker material color) was lithographically patterned on top of the Ni TFS (light color) as a surface perturbation. The four TFS on the sample are, i) 12 nm thick pure Ni TFS with no perturbation, ii) 12 nm thick Ni TFS with a continuous 2 nm Cu TFS down the center, iii) 12 nm thick Ni TFS with patterned 2 nm Cu perturbations, the spacing of the Cu areas follows that of the fastest growing instability, λ_m , and whose extent is half that, for the 370 nm instance here, $\lambda_m = 634$ nm. (iv) same as (iii) only phase shifted by one pattern unit.

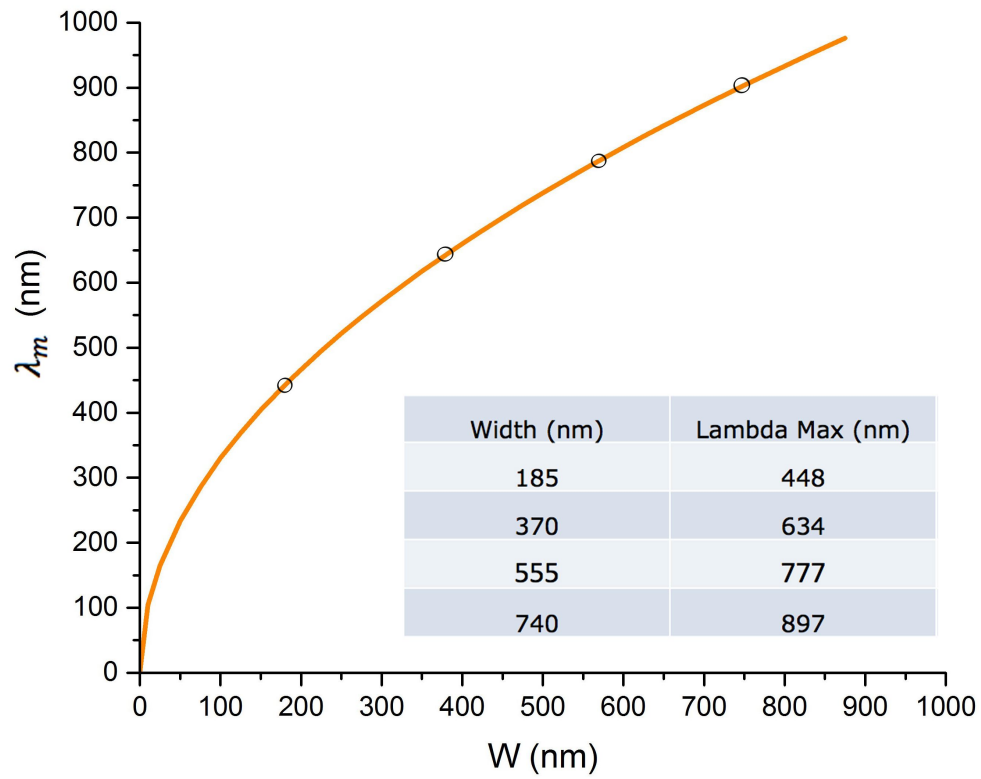


Figure 4.5. Prediction for the fastest growing instability wavelength as a function of TFS width according to R-P theory, the circles represent the experimentally explored TFS widths and their max wavelengths, the inset table conveniently lists these values.

Once again, a krypton fluoride (KrF) excimer laser, wavelength 248 nm, energy range 250 ± 10 mJ/cm², and pulse-width of 18 ± 2 ns FWHM, was used to melt the metal TFS. The amount of time the TFS stack is in the liquid state, its liquid lifetime, is dependent on the laser fluence delivered by the laser pulse and the thermal and optical properties of the metals, the supporting SiO₂ layer, and the underlying Si substrate. The area of the laser spot is very large, ~ 1 cm², compared the extent of the sample area, ~ 1 mm², thus a homogenous fluence over the sample area is assumed. Due to the finite liquid lifetime per laser pulse and rapid cooling, a series of individual laser pulses can be used to control the dewetting evolution and interrogate morphological changes of the liquid filament.⁶⁹

4.3 Model and Simulation Methods

Recall, that thermocapillarity and the Marangoni effect can be modeled by augmenting the governing thin-film equation, Equation (1.22), to include a term for a spatially varying surface tension, $\nabla\sigma$,

$$\frac{\partial h}{\partial t} = -\frac{1}{3\mu} \nabla \cdot \left[\sigma h^3 \nabla \nabla^2 h + h^3 \nabla \Pi(h) + \frac{3}{2} h^2 \nabla \sigma \right] \quad (4.1)$$

The surface tension gradient can be expressed as, $\nabla\sigma = \sigma_T T_x = \frac{\partial\sigma}{\partial T} \frac{\partial T}{\partial x}$, where, σ_T , and, T_x , are the variations of surface tension with temperature and temperature with space, respectively. The surface tension has a linear dependence on temperature, Equation (1.28). This corroborates the experimental objective of producing a spatially varying surface tension along the length of a liquid filament during PLiD.

Additionally, the experimental results are compared with fully nonlinear simulations. The simulations provide meaningful insight regarding the operative fluid dynamic mechanisms. Two simulation approaches were employed, a 2D method and a 3D method with a VoF technique.^{25, 75} Both approaches directly solve the Navier-Stokes (N-S) equations,

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p + \nabla \cdot (\mu(\nabla\mathbf{u} + \nabla\mathbf{u}^T)) + \kappa\sigma\delta_s\mathbf{n} + \nabla_s\sigma\delta_s \quad (4.2)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (4.3)$$

where $\mathbf{u} = (u, v, w)$ is the velocity field, p is the pressure, κ is the curvature of the fluid-vapor interface, and $\delta_s\mathbf{n}$ denotes the normal vector at the fluid-vapor interface. It is assumed that the flow can be modeled as an isothermal and incompressible fluid, Equation (4.3). The term, $\nabla_s\sigma$, represents the surface

gradient of the surface tension, which can be a function of concentration of different materials, for instance, two metals in the case of a Marangoni effect, or a function of temperature in the case of a thermocapillary effect. In either instance the concentrations are advected in the flow. It should be noted that for the 3D simulations the surface tension gradient is set to zero, only the constant surface tension term, σ , remains. This is because the 3D simulations here specifically simulate geometric effects without surface tension gradients. However, the 2D simulations are fully capable of simulating the effects of a spatially varying surface tension. Note, freezing is not taken into consideration in the simulations.

The open-source computational fluid dynamics software package, Gerris was utilized to solve the fully nonlinear N-S equations for both the 2D and 3D simulations.⁷⁶ The spatial discretization is accomplished using an adaptive octree for the 3D approach, and an adaptive quadtree for the 2D approach, the adaptive mesh resolves the fluid-vapor interface with a resolution of ~ 1 nm and regions of high curvature are resolved to ~ 0.5 nm.

The VoF method tracks the fluid phase of each point in space by introducing a volume fraction function, which states the fraction of each computational cell occupied by the liquid phase. Viscosity and density depend on the volume

fraction function by assignment of the appropriate liquid and vapor values. In order to reduce the effect of the surrounding vapor (i.e. air) we set $\mu_v = \mu/100$ and $\rho_v = \rho/20$. Specifically for the 3D simulation, a contact angle of 90° is imposed during the simulations and a contact line slip length of, $\lambda = 20$ nm, is used. The contact line slip is represented by a slip condition,⁶⁸

$$(u, w)|_{y=0} = \lambda \partial_y (u, w)_{y=0} \quad (4.4)$$

where, (u, w) , are the in-plane components of velocity and, λ , denotes the slip length; the contact line slip value was selected based on previous experience reliably simulating experimental results, see Chapter 3.⁴⁷

Establishing what the temperature and liquid lifetimes estimates are for the Ni and Cu during PLiD is important for setting the material properties, like density, viscosity, and surface tension. These material property values will be the inputs to the model and simulations. The temperatures for the metal TFS were again discerned using the 1-D laser heating model previously outlined in Chapter 1, Equation (2.5).

4.4 Results and Discussion

Since the experimental pathway to altering the surface tension of a filament is to pattern and deposit additional material on top of an initial TFS prior to PLiD, the first item to explore in this section shall be the effect that purely geometry would have on filament, its surface curvature, instability development, and subsequent filament breakup, in the absence of a surface tension gradient. For example, in Figure 4.6(a)-(b), the 2 nm thick perturbation on top of the 12 nm Ni creates a periodic TFS thickness difference. Because of the extra thickness the following geometric effects are postulated to occur, 1) immediately after laser melting the added material creates a maxima, the thicker region on the liquid filament will produce a varicose height perturbation, and 2) as the filament evolves with time, the maxima will grow, the filament will subsequently breakup, and the resultant droplets will be positioned at the locations of the original maxima.

Indeed, a purely geometric effect is observed in the simulations when the surface tension gradient is set to zero. Figure 4.6(a)-(d) are snapshots from simulations of the fully nonlinear N-S in 3D, Equation (4.2). The simulation results show the filament maxima remain located at the initially thicker region, and it did not matter if the extra thickness was as small as a mere 2 nm more than the initial TFS thickness, as was the case in the 3D simulations. Furthermore, the resultant droplets do locate at the maxima. In the absence of surface tension gradients,

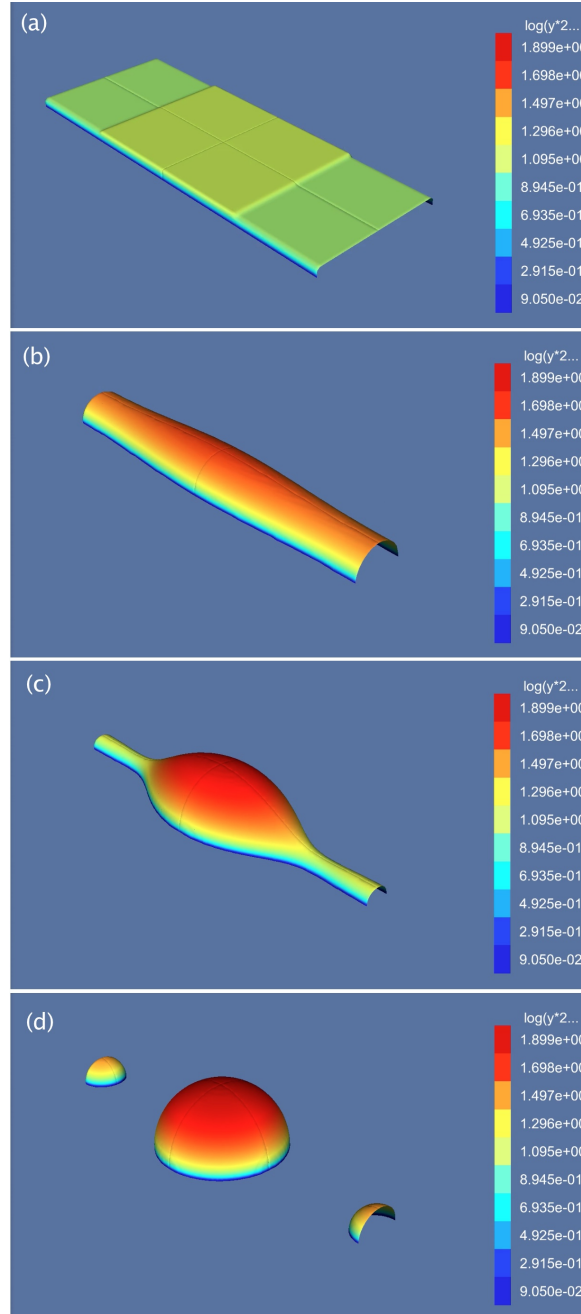


Figure 4.6. Snapshots from 3D simulations of the N-S equation, without the surface tension gradient term. The results show that droplets form and remain located in the initially thicker areas. The same result was found with and without the disjoining pressure.

why the maxima continues to accumulate more material with time can be better understood by considering the Laplace pressures in the filament. The difference of circumferential radii in the filament produces two regions of positive pressure, the thicker region has a larger radii than that of the adjacent thinner region so the pressure in the maxima is lower, therefore the higher pressure, thinner filament region seeks to move fluid into the lower pressure maxima; this is similar to the column of fluid evolution discussed in Chapter 1. The 3D simulations were also performed with and without the disjoining pressure and the results were the same, geometry affected the maxima and droplet location. The purely geometry influenced results were not seen experimentally, to reproduce the experimental results the effects of surface tension gradients must be taken into consideration.

The first TFS combination designed to explore the Marangoni effect was the Ni_Cu geometry, see Figure 4.3(a). Copper's surface tension is $\sim 30\%$ less than that of Ni, the effects of which, upon laser melting, should be experimentally evident in a couple of ways, 1) an inversion of thickness, the initially thicker, patterned Cu region on the TFS will thin out as material flows to the adjacent Ni region, 2) a surface perturbation will be created with maxima in the Ni region and minima in the Cu region, similar to Figure 4.2(b), the wavelength of the perturbation should be that of fastest growing instability, due to the patterning of

the Cu areas, and 3) the location of the resultant droplets should be in the regions with no copper pattern, as result of the continued thinning of the Cu region and ultimate filament pinching.

Figure 4.7(a) is an SEM image of the experimental results for the 370 nm wide, Ni_Cu TFS geometry after one laser pulse, during the first liquid lifetime, estimated to be 20 ns based on the thermal simulation (Figure 4.9). All the TFS have laterally collapsed, forming liquid filaments, and the ends have retracted. It is immediately apparent that varicose surface perturbations have been established on filaments (iii) and (iv). Figure 4.7(b) is an overlay with the as-patterned image (Figure 4.4) and it is clear that the surface perturbations coincide with the patterned Cu. The Cu regions, originally thicker (darker shade), have begun to thin out, and the lateral edges are retracting as if to pinch off the filament, this is due to material being forced out of the Cu area and into the adjacent Ni areas (lighter shade). Utilizing a spatial correlation function it is possible to analyze the varicose perturbation established on the filament. The analysis results reveal a perturbation wavelength of 627 nm, which is very close to the patterned Cu perturbation spacing of 634 nm. Combined, this experimental evidence is supportive of a surface force, due to a surface tension gradient between the Ni and Cu, the Marangoni effect, as being responsible for

Figure 4.7. Experimental results for the 370 nm wide, Ni_Cu TFS geometry after one laser pulse with fluence of 250 mJcm^{-2} and estimated liquid lifetime of 20 ns. The four TFS on the sample are, (i) 12 nm thick pure Ni TFS with no Cu, (ii) 12 nm thick Ni TFS with a continuous 2 nm Cu TFS down the center, (iii) 12 nm thick Ni TFS with patterned 2 nm thick Cu TFS perturbations, the spacing of the Cu areas follows that of the fastest growing instability, λ_m , and whose extent is half that, and for the 370 nm instance here is, $\lambda_m = 634 \text{ nm}$. (iv) same as (iii) only phase shifted by one Cu pattern unit. (a) original SEM image after PLiD, varicose surface perturbations have clearly been established in (iii) and (iv), (b) overlay with the before-PLiD image, Figure 4.4, the originally thicker Cu areas are thinner because material has been forced into the adjacent Ni area as a result of the Marangoni effect.

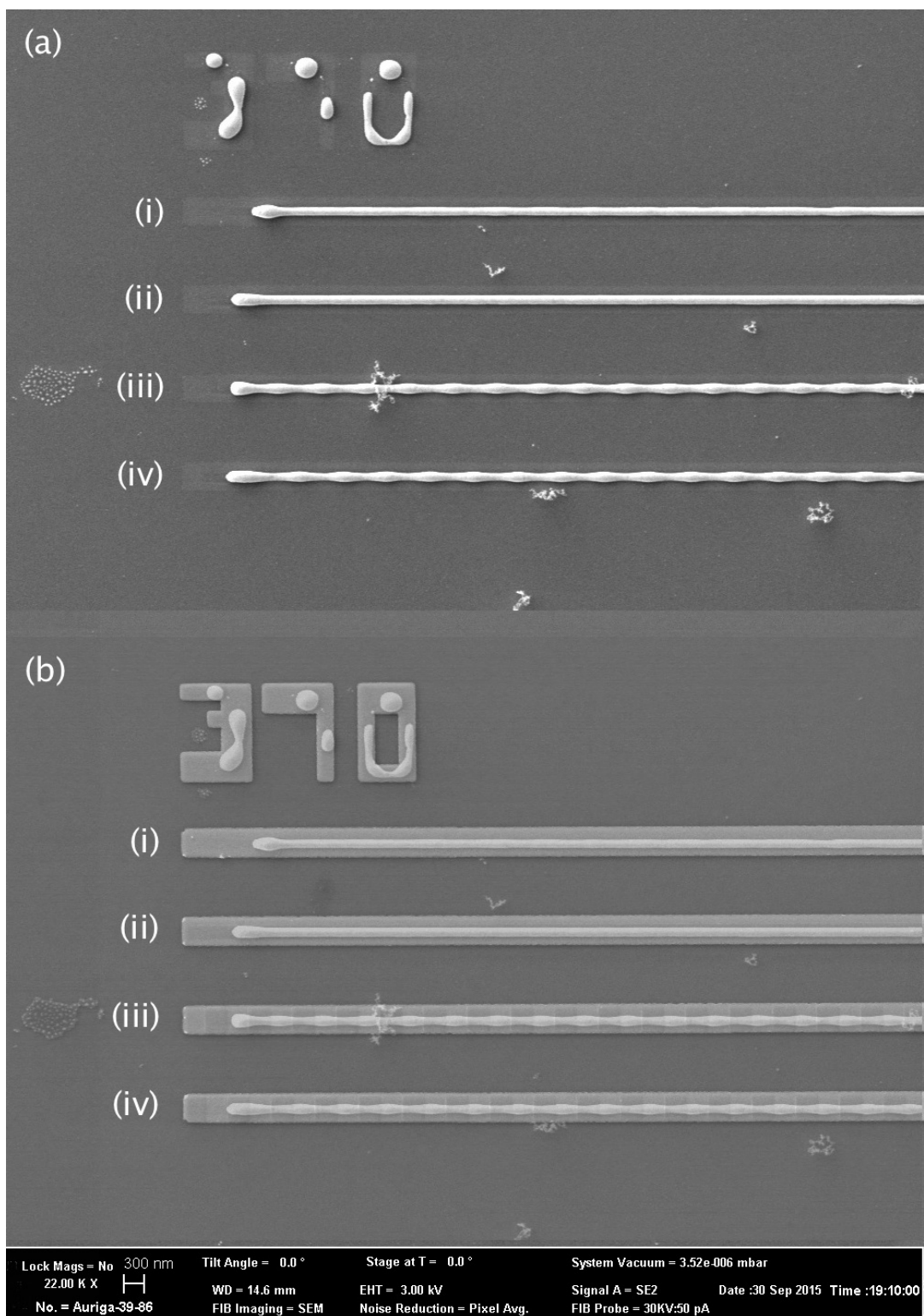


Figure 4.7. Continued.

establishing the filament instability, providing it a head start in its temporal evolution. Additional experiments follow to further investigate the phenomenon

Furthermore, the Ni-Cu experiment was simulated to investigate the establishment of the filament instabilities due to surface tension gradients. Figure 4.8(c)-(e) are the results of the fully non-linear, 2D N-S simulations that included the surface tension gradient term, Equation (4.2), for the 185 nm width Ni-Cu sample. Also included, for direct comparison, is the similarly specified experiment sample after one laser pulse, approximately 20 ns of liquid lifetime. At, $t = 0$ ns, the simulation snapshot is of the initial Ni-Cu TFS, 2 nm Cu on top of 12 nm Ni, represented by the red and blue color, respectively, and the spacing of the Cu perturbations is similarly the fastest growing surface instability wavelength, 448 nm.

The material properties of viscosity and density for Ni and Cu are constant and set to those at Ni's melting temperature, 1728 K, values, 4.61 mPa s and 7905 kgm⁻³, respectively. Therefore only a surface tension gradient remains between the Cu and Ni regions, that of, 1.285 N/m and 1.778 N/m, respectively; a difference of $\Delta = 0.493$ N/m. This difference is excess force acting tangential to the surface and along the (circumferential arc) line separating the two regions on a filament. The magnitude of the force can be estimated by using an average

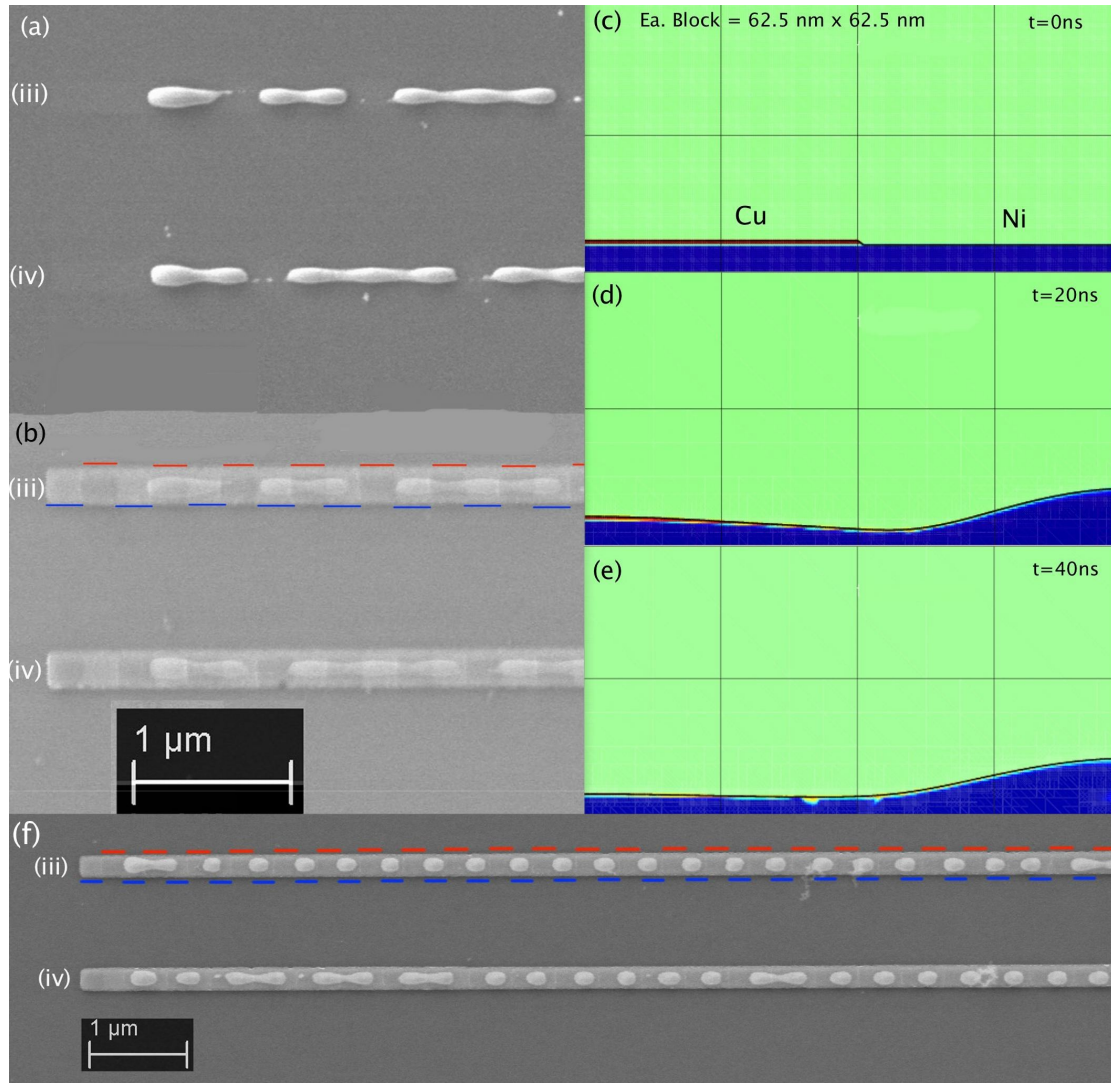


Figure 4.8. Experimental and 2D nonlinear N-S simulation results for the 185 nm width sample, (a) after one laser pulse, fluence of 250 mJcm^{-2} and estimated liquid lifetime of 20 ns, (iii) 12 nm thick Ni TFS with patterned 2 nm thick Cu TFS perturbations, the spacing of the Cu areas follows that of the fastest growing instability, λ_m , and whose extent is half that, here, $\lambda_m = 448 \text{ nm}$. (iv) same as (iii) only phase shifted by one Cu pattern unit, (b) overlay with the before PLiD image, red lines mark where the original Cu was and blue the Ni, it is apparent that the material has left the Cu region and moved into the Ni region. (c) initial geometry for the N-S simulation (d) filament profile after after 20 ns of liquid evolution (e) filament profile after after 40 ns of liquid evolution, again it is apparent that the material has moved from the initially thicker Cu region to the Ni region. (f) after several pulses the resultant droplets locate in the Ni region.

filament radius of 60 nm, therefore, $\pi R\Delta = \pi(60)(0.493) \cong 93 \text{ nN}$. For comparison, the force necessary to move a droplet of Ni, with an average radius of 130 nm, one perturbation wavelength of distance, $\sim 500 \text{ nm}$, in the time of one liquid lifetime, 20 ns, would require, $\sim 0.01 \text{ nN}$ of force, therefore the surface force is of sufficient magnitude to transport droplets of material. After one simulated liquid lifetime, $t = 20 \text{ ns}$, Figure 4.8(d), the results shows that a sizable amount of material has moved from the initially thicker Cu region into the Ni region, forming a new height maxima there. The appearance of the filament in the simulation looks very much like the filaments seen in the experiment after one laser pulse and a similar amount of liquid lifetime, Figure 4.8(a). As the simulation proceeds, $t > 20 \text{ ns}$, the maxima increases and the Cu region continues to diminish in thickness, a similar amount of thinning between the newly formed maxima can be seen in the experimental images, and a few have progressed to the point where the filament pinches off and individual droplets are close to being formed.

Figure 4.8(b) is a composite image with the initial TFS pattern, to aid the eye red lines demarcate where the original 2 nm Cu TFS were patterned and blue lines indicate the pure Ni areas. It is clearly evident that material has shifted, from what was the initially thicker Cu region and flowed into the Ni area. Spatial correlation analysis reveals that a wavelength of 446 nm has been established in the filament, which is very close to the target of 448 nm. After several laser

pulses the filament breaks apart and the droplets are seen to locate in the Ni region, Figure 4.8(f). Recall, that the spacing of droplets generated by a purely TFS geometry, discussed previously, locate oppositely than what is seen here. Analyses of the location of the droplets using a spatial correlation function shows a dominant droplet-droplet spacing of 475 nm, well in line with the patterned Cu perturbation spacing. Therefore, the experimental and simulation results are supportive of the proposition that Marangoni effects can be utilized to produce instabilities on the surface of liquid metal filaments and influence droplet formation. To bolster this claim additional TFS geometries and mechanisms will be explored.

Besides materials dissimilarities, temperature differences can create surface tension gradients, according to Equation (1.33), which as described is known as the thermocapillary effect. This pathway opens the door to the creation of surface tension gradients when only one material is used; for instance, the metal Ni. This is accomplished by using a similar lithographic approach to that previously discussed, by patterning additional thicknesses of material along the length of an underlying TFS, in this case 2 nm Ni on top of a 12 nm Ni TFS. The temperature imbalance is generated by laser energy absorption differences of the metal. In other words, the thicker regions absorb more of the lasers energy

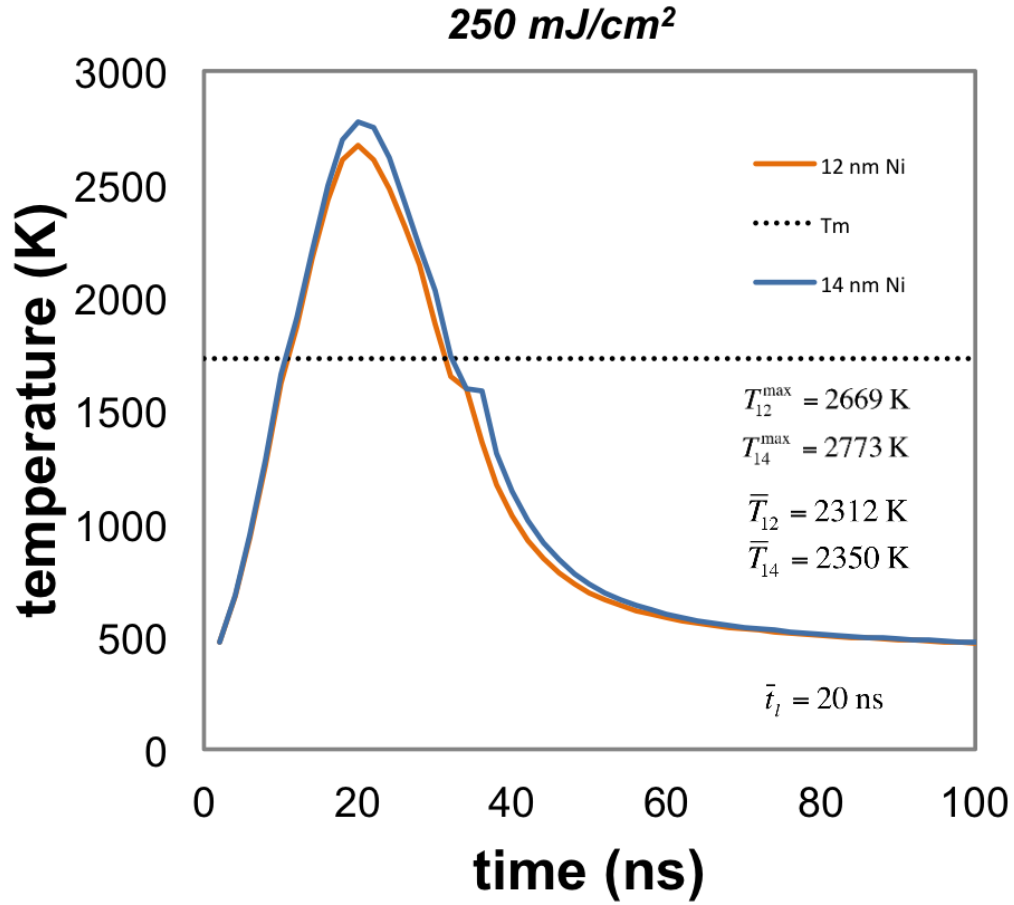


Figure 4.9. Simulated temperature vs. time profile for the two thickness of Ni, 12 and 14 nm, during the absorption of one laser pulse at a fluence of 250 mJ/cm⁻², the estimated liquid lifetime per pulse is 20 ns.

than the thinner regions, and the consequence is a lower surface tension in the hotter, thicker regions.

Figure 4.9 is a 1D thermal simulation for two thicknesses of Ni, 12 and 14 nm, during the absorption of one laser pulse with a fluence of 250 mJcm^{-2} . The maximum and average temperatures reached during PLiD were, 2669 K and 2316 K, for the 12 nm, and 2773 K and 2350 K, for 14 nm. The surface tension gradient at the max temperature is 0.0394 N/m, with an average, sustained gradient of 0.0355 N/m during the duration of the liquid lifetime. Experiments and simulations were carried out to validate whether a gradient of this magnitude, established as a result of thickness differences, is sufficient to create surface instabilities on a liquid filament. If so, the following results should be expected, 1) an inversion of thickness, the initially thicker 14 nm Ni region will thin out as material flows to the thinner 12 nm region, 2) a surface perturbation will be created with maxima in the thinner region and minima in the thicker region - similar to the previous Ni_Cu results - with a wavelength near that of the fastest growing instability, and 3) the location of the resultant droplets should locate in the originally thinner regions.

Figure 4.10(a) is an SEM image of the experimental results for the 185 nm wide, Ni_Ni TFS geometry after one laser pulse, the liquid lifetime is estimated to be

Figure 4.10. Experimental results for the 185 nm wide, Ni_Ni TFS geometry after one laser pulse at fluence of 250 mJcm^{-2} and estimated liquid lifetime of 20 ns. The four TFS on the sample are, (i) 12 nm thick pure Ni TFS, (ii) 12 nm thick Ni TFS with a continuous 2 nm Ni TFS down the center, (iii) 12 nm thick Ni TFS with patterned 2 nm thick Ni TFS perturbations, the spacing of the Cu areas follows that of the fastest growing instability, λ_m , and whose extent is half that, and for the 185 nm instance here is, $\lambda_m = 448 \text{ nm}$. (iv) same as (iii) only phase shifted by one Ni pattern unit. (a) original SEM image after one laser pulse, varicose surface perturbations are present in (iii) and (iv), (b) overlay of the before and after PLiD image, the initially thicker areas (marked by red lines) are now thinner because material has be forced into the adjacent area, initially thinner (marked by blue lines) as a result of the thermocapillary effect between the two different thicknesses.

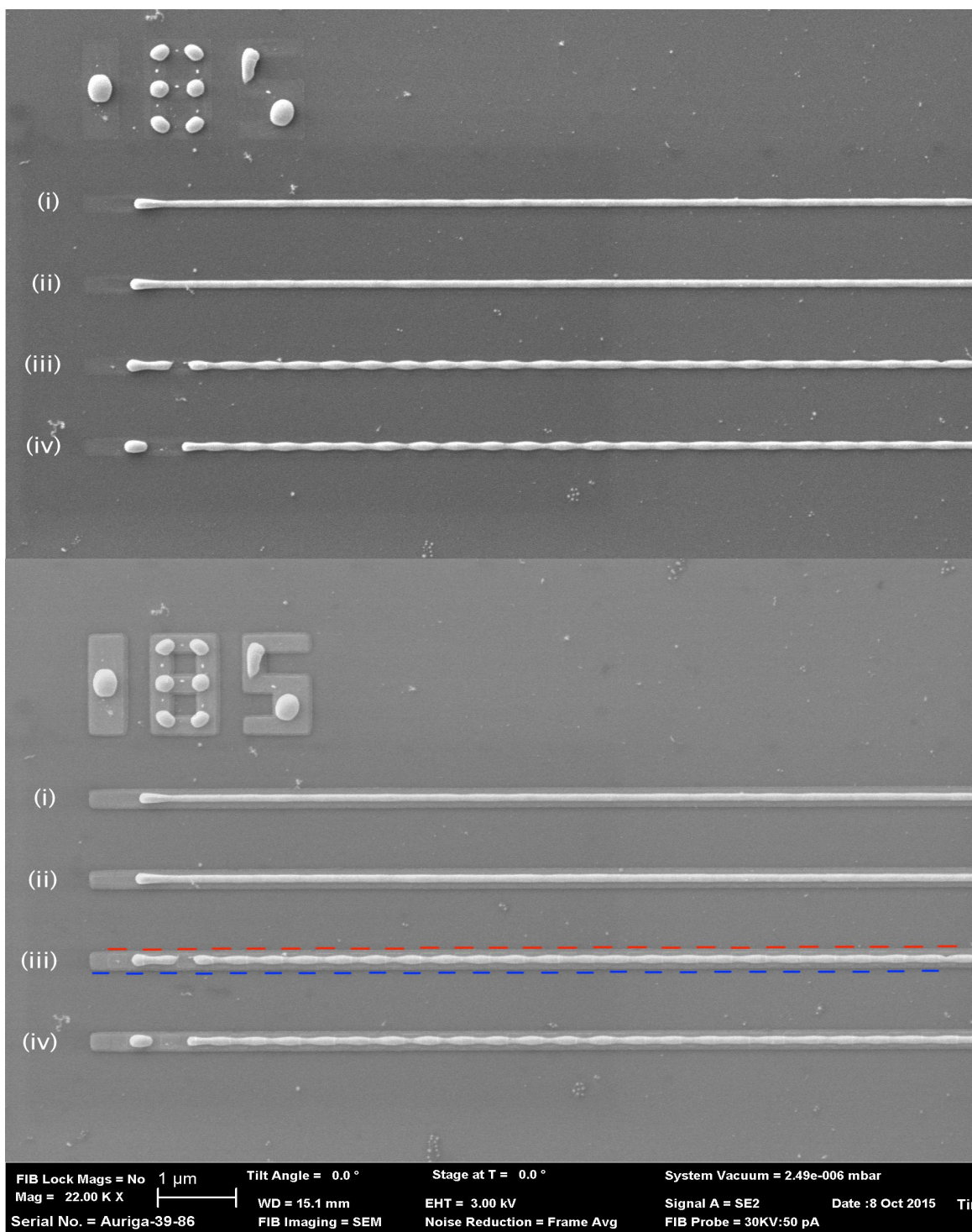


Figure 4.10. Continued.

20 ns based on the thermal simulations. Again, all TFS have laterally collapsed, forming liquid filaments, and the ends have begun retracting. It is evident that surface perturbations have been established on filaments (iii) and (iv). Figure 4.10(b) is an overlay with the before-PLiD pattern showing that the surface perturbation minima coincide with patterned 2 nm Ni regions, that is, the initially thicker 14 nm areas (red lines) have thinned and the lateral edges have retraced, this is because material has been forced into the adjacent, initially thinner, Ni areas (blue lines). The results are very similar in appearance to that of the Ni_Cu sample, which were supportive of a surface tension gradient effect. Therefore, the results here are supportive of the thermocapillary effect. Spatial correlation analysis reveals that a wavelength of 460 nm has been established in the filament, which is very close to the target of 448 nm.

In addition, 2D fully non-linear N-S simulations were carried out to substantiate the Ni_Ni experiment. The simulation thicknesses were similar to that of the experiment, 14 and 12 nm, and the TFS temperatures were set to 2773 K and 2669 K, respectively, thereby establishing the surface tension gradient of 0.0394 N/m. Viscosity and density, which also depend on temperature, were investigated to see their effects spanning the temperature range of the TFS, 1728 K, Ni's melting temperature, and 2773 K, the max temperature.

Figure 4.11. Experimental and simulation results for the Ni_Ni 185 nm width sample, (iii) 12 nm thick Ni TFS with patterned 2 nm thick Ni TFS perturbations, the spacing is that of the fastest growing instability, $\lambda_m = 448$ nm. (iv) same as (iii) only phase shifted by one Ni pattern unit, (a) after one laser pulse at a fluence of 250 mJcm^{-2} , the estimated liquid lifetime is 20 ns, (b) overlay with before image, (c) initial geometry for the N-S simulation, $t = 0$ ns, viscosity and density are those at 1728 K, (d) filament profile after $t = 20$ ns of liquid evolution, viscosity and density are those at 2773 K, (e) filament profile after $t = 20$ ns, viscosity and density are those at 1728 K, (f) filament profile after $t = 20$ ns, viscosity and density are those at 2773 K, (g) overlay with before image after several laser pulses at a fluence of 250 mJcm^{-2} , the resultant droplets locate largely the Ni region, red lines mark where it was initially 12 nm Ni thick and blue line where it was initially 14 nm, it is apparent that the material has moved from the initially thicker Ni region to the initially thinner Ni region.

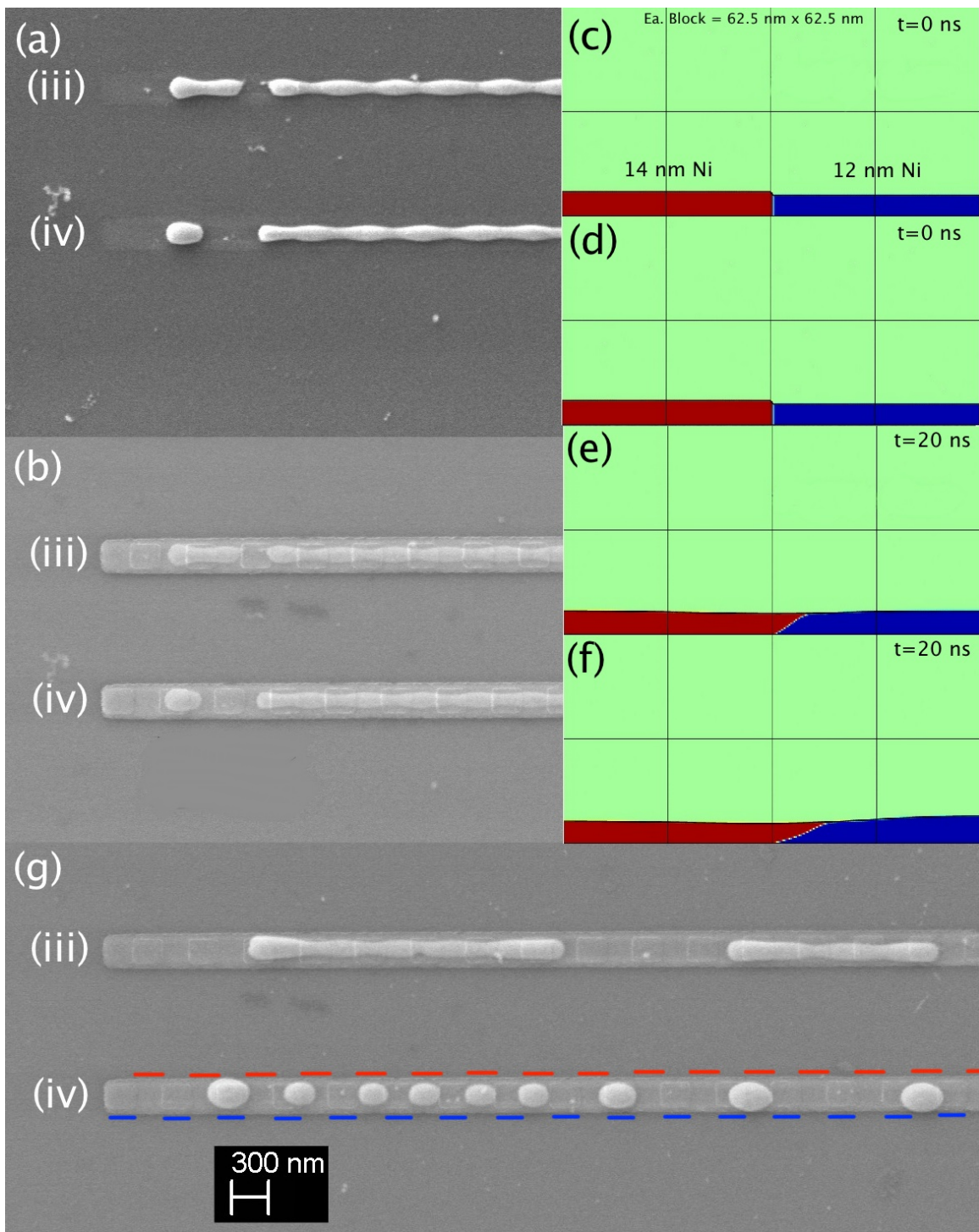


Figure 4.11. Continued.

After one liquid lifetime, $t = 20$ ns, Figure 4.11(e)-(f), the simulation results show material is in fact moving from the initially thicker region to the thinner region, under the influence of the surface tension gradient, and forming new height maxima. However, the magnitude of the perturbation height maxima in the simulation is much smaller than those seen in the experiment. The height of the maxima is assisted by reductions in viscosity and density values at higher temperature, this can be seen by comparing the simulation maxima heights, at the two temperatures, 1728 K and 2773 K, Figure 4.11(e) and (f), respectively. As the density and viscosity decrease at higher temperature the surface tension gradient is more efficient in moving material, less of the thermocapillary force is dissipated through internal losses, for instance, by viscous dissipation. Why the simulation maxima heights are smaller than those seen in the experiment could be due the underestimating of the thermocapillary effect, either in our description of the changes in surface tension with temperature, which are based on values taken from literature, or possibly in the thermal simulations of the temperatures reached by the TFS during PLiD.

Following several laser pulses, the Ni₂Ni TFS breaks apart and the droplets locate roughly in the initially thinner region, Figure 4.11(g), however their placement is more dispersive. Analysis of the location of the droplets using a spatial correlation function shows droplet-droplet spacing in the range 450 –

650 nm, largely in line with the patterned Ni perturbation spacing. A possible reason why their location is not as precise as those produced during the Ni_Ni experiment is the surface tension gradient magnitude is simply not as strong as the Ni_Cu. At least qualitatively, the simulation results support the experimental observations, that a surface tension gradient, created by a thermocapillary effect due to TFS thickness, is responsible for the flow of material from one region to the other.

Up to this point, the experiments and simulations have focused on geometries with patterned thickness differences along the length of the TFS, those of Ni_Cu and Ni_Ni. However, by incorporating an additional lithography step it is possible to eliminate any thickness difference to produce a constant height TFS, like those in Figure 4.3(c)-(d). For example, Ni_Cu becomes Ni_Cu_Ni, a constant height 14 nm TFS, with alternating regions of 2 nm Cu and Ni – this sample will be discussed later. By going to a constant height TFS it is possible to better elucidate whether the previous results were actually due to Marangoni and thermocapillary effects or not.

Take for instance the previous Ni_Ni results that were attributed to the thermocapillary effect. However, for the newly proposed Ni_Ni_Ni sample geometry, Figure 4.3(d), it becomes simply a constant height TFS. As a result

there should be no differential laser pulse absorption due to thickness differences, and therefore no filament perturbations should appear due to any thermocapillary effect. Indeed this was the case. No thermocapillary effect was seen in the Ni_Ni_Ni geometry across any of the TFS width samples. Figure 4.12 is a representative experimental SEM image showing that all the filaments in the sample are developing in a similar fashion, i.e. no perturbations are present. No simulations were conducted with this geometry, because no surface tension gradient is present for a TFS of constant height and material.

The final important pattern is the Ni_Cu_Ni geometry, a constant height 14 nm TFS, with alternating regions of 2 nm Cu and Ni, see Figure 4.3(c) – in essence, this is the constant height version of the previous Ni_Cu sample. This sample is important because no height differences are present, and if the material property differences, which are behind the Marangoni effect, are indeed responsible for the creation of the varicose filament perturbations then they should again be seen experimentally. Therefore, upon laser melting, this new geometry should preserve the experimental expectations from that of the Ni_Cu sample, those of 1) an inversion of thickness, the Cu region will thin out as material flows to the Ni region, 2) a surface perturbation will be created with maxima in the Ni region and minima in the Cu region, and the wavelength of the perturbation should be that of

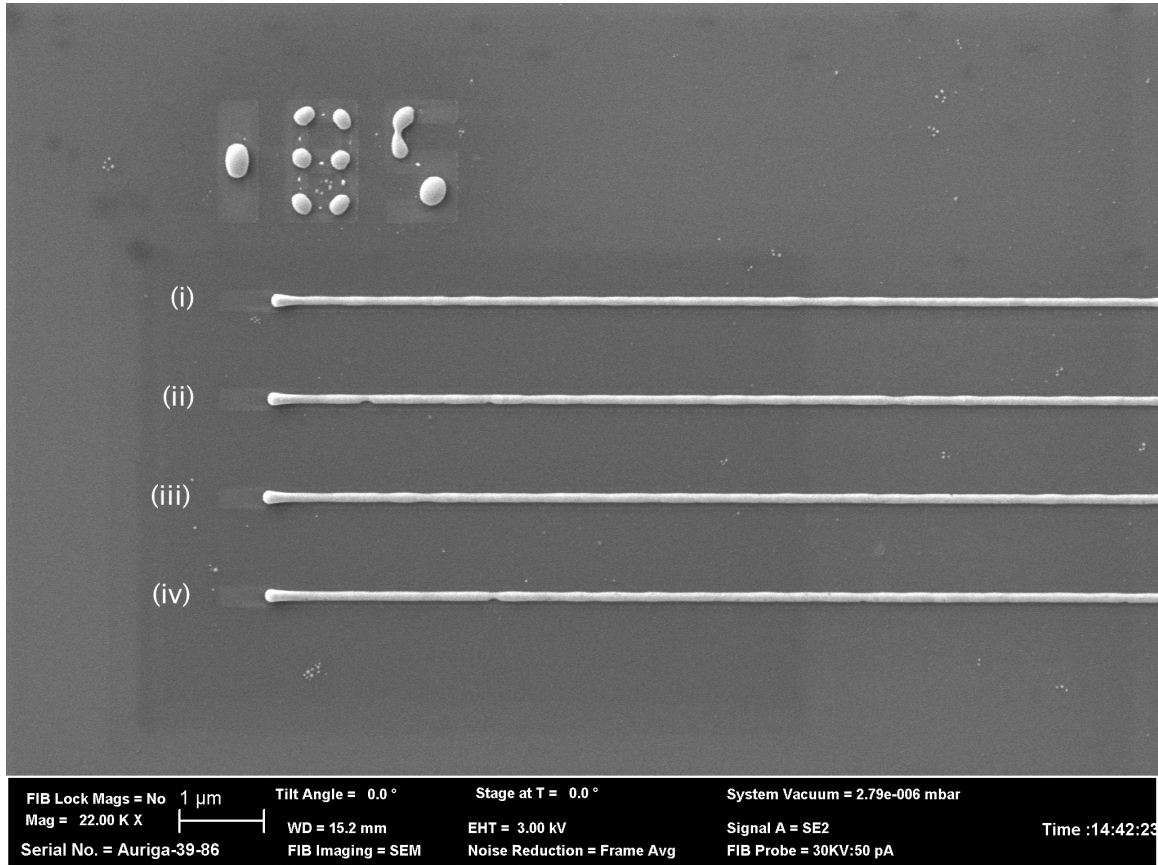


Figure 4.12. Experimental results for the 185 nm wide, Ni₂Ni₂Ni TFS geometry after one laser pulse at a fluence of 250 mJcm⁻² and estimated liquid lifetime of 20 ns. The four TFS on the sample are, (i) 12 nm thick pure Ni TFS, (ii) 12 nm thick Ni TFS with a continuous 2 nm Ni TFS down the center, (iii) 12 nm thick Ni TFS with patterned 2 nm thick Ni TFS perturbations continuously patterned down the length (iv) same as (iii). No varicose perturbations are present in (iii) or (iv).

fastest growing instability, and 3) the location of the resultant droplets should be in the initially Ni regions.

Figure 4.13 is SEM image showing the experimental results for the 370 nm wide, Ni_Cu_Ni geometry after one laser pulse and an estimated liquid lifetime of 20 ns. It is clearly observable that varicose surface perturbations are present on filaments (iii) and (iv), the filament's appearance is indeed similar to that of Ni_Cu, however the filament is noticeably thicker here due to the additional Ni material. The addition of material is evident in the Cu regions that haven't thinned as much or the lateral edge haven't contracted as far after one pulse. This may be due to the adjacent Ni areas being initially now thicker and reaching a higher temperature during PLiD, therefore having a lower surface tension, resulting in a reduced surface tension gradient and resultant surface force, affecting the flow of material. Figure 4.13(b) is an overlay with the before-PLiD image showing that the filament perturbation minima do in fact coincide with the patterned 2 nm Cu areas, marked with red lines; the initially Ni areas are marked with blue lines. Spatial correlation analysis reveals that a wavelength of 698 nm has been established on the filament, which is very close to the target of 634 nm.

In addition, 2D fully non-linear N-S simulations were carried out to substantiate the Ni_Cu_Ni experiment. Figure 4.14(c)-(e) are snapshots of the results of the

Figure 4.13. Experimental results for the 370 nm wide, Ni_Cu_Ni TFS geometry after five laser pulses at a fluence of 250 mJcm^{-2} , the four TFS on the sample are, (i) 12 nm thick Ni TFS, (ii) 12 nm thick Ni TFS with a continuous 2 nm Cu TFS down the center, (iii) 12 nm thick Ni TFS with patterned 2 nm thick Cu and Ni TFS perturbations, the spacing of the Cu areas follows that of the fastest growing instability, $\lambda_m = 634 \text{ nm}$, and whose extent is half that (iv) same as (iii) only phase shifted by one Cu pattern unit. (a) original SEM image after PLiD, varicose surface perturbations have clearly been established in (iii) and (iv), (b) overlay with the before-PLiD image, the Cu areas are thinner because material has been forced into the adjacent Ni area, as a result of the Marangoni effect between the two different materials with dissimilar surface tensions.

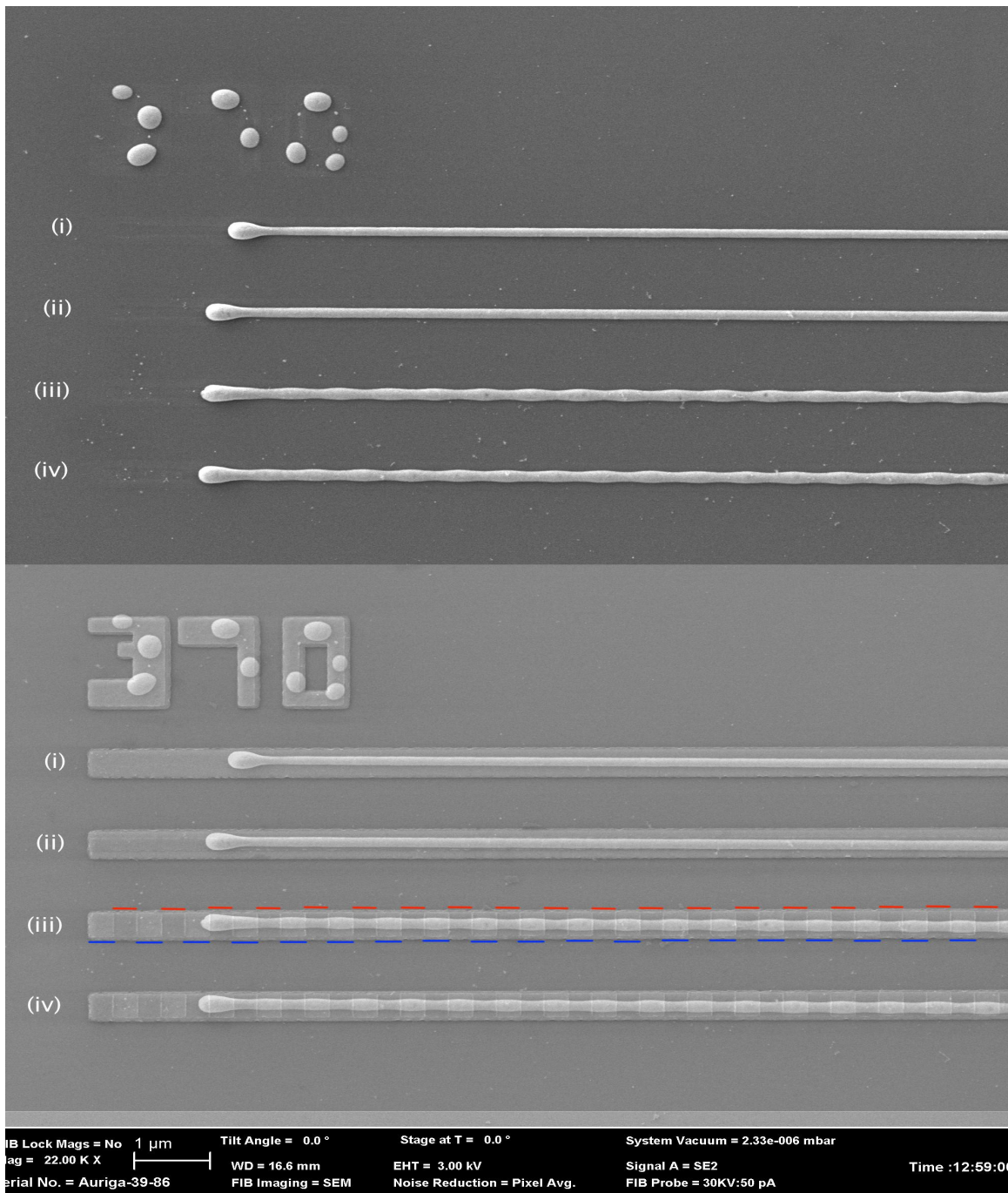


Figure 4.13. Continued.

for the 185 nm width Ni_Cu_Ni sample, the simulation thicknesses were similar to that of the experiment, 14 nm. The material properties were set to those of Ni at a temperature of 2773 K, the max temperature of the thicker TFS, and remained constant – again, the constancy of the material parameters is for the benefit of discerning the effects due to the surface tension gradient, and the magnitude of which is, 0.493 N/m, between these two materials.

A very important timeframe for the Marangoni effect is the early development period, these are the moments where the strength of gradient is at its peak. For instance, Figure 4.14(d) shows the simulation results at, $t = 1$ ns, and what is noticeable is the wave-like surface distortion that is created as the surface tension gradient immediately forces a material flow along the surface of the filament. It propagates towards the lower surface tension Ni region, moving material with it, and forming new height maxima as short as 1 ns later, Figure 4.14(e). The height of the maxima is again assisted by reduced viscosity and density values at higher temperature. The simulation compares favorably to the adjacent experimental images of the 185 nm, Ni_Cu_Ni sample seen in Figure 4.14(a)-(b). Additionally, spatial correlation analysis of the experimental filament reveals that a wavelength of 494 nm has been established on the filament, which is very close to the target of 448 nm.

Figure 4.14. Experimental and 2D nonlinear N-S simulation results for the 185 nm width Ni_Cu_Ni sample, (a) after one laser pulse at fluence of 250 mJcm^{-2} and estimated liquid lifetime of 20 ns, (iii) 12 nm thick Ni TFS with patterned 2 nm thick Cu and Ni TFS perturbations, the spacing of the Cu areas follows that of the fastest growing instability, $\lambda_m = 448 \text{ nm}$, and whose extent is half that (iv) same as (iii) only phase shifted by one Cu pattern unit, (b) overlay of the before PLiD image, red lines mark where the original Cu was and blue the Ni, it is apparent that the material has left the Cu region and moved into the Ni region, (c) initial geometry for the N-S simulation at $t = 0 \text{ ns}$ (d) filament profile after 2 ns of liquid evolution (e) filament profile after 2 ns of liquid evolution, it is apparent that the material is moving from the Cu region into the Ni region as a result of the Marangoni effect.

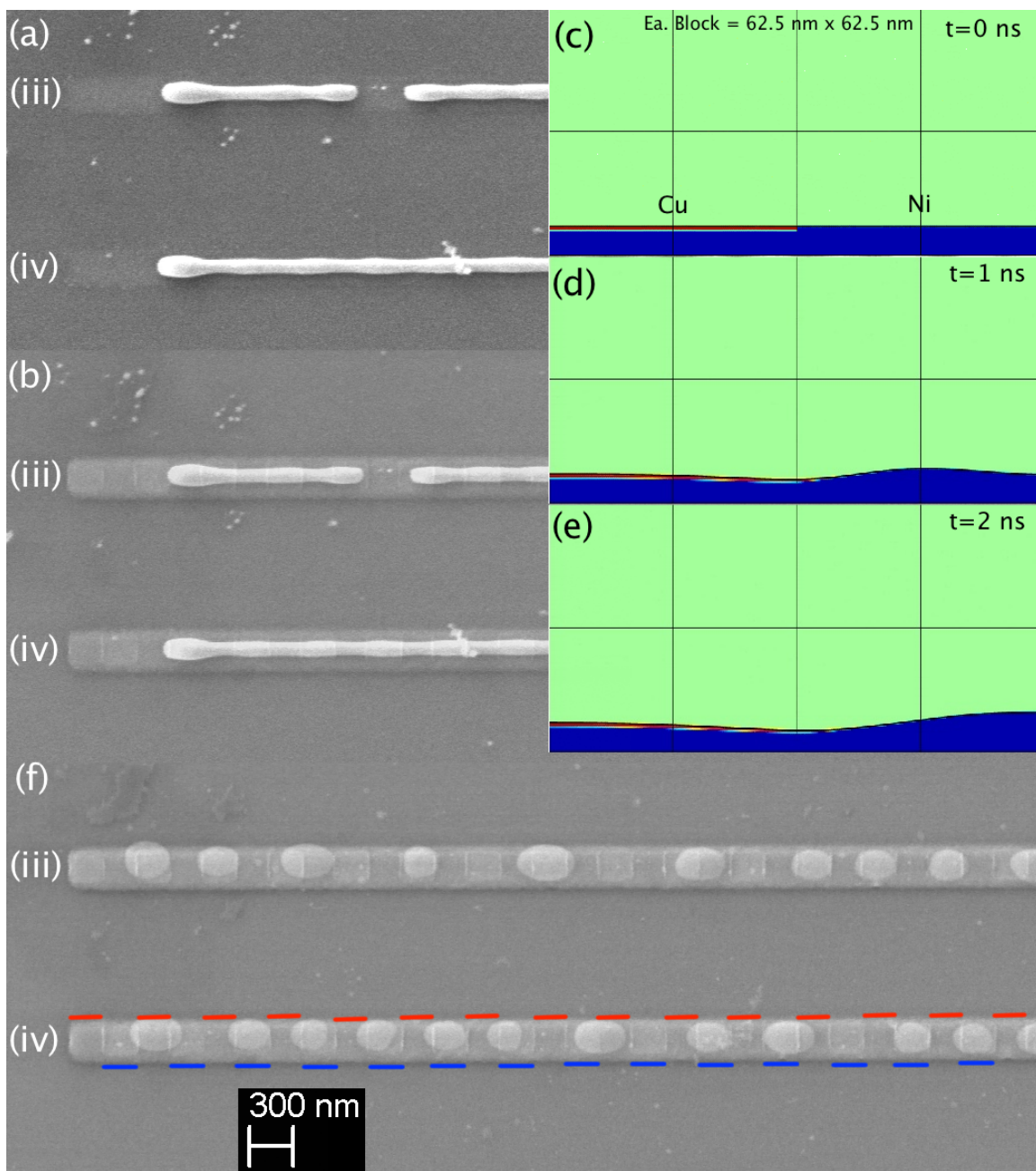


Figure 4.14. Continued.

Following several laser pulses, the Ni_Cu_Ni filament breaks apart and the droplets locate largely in the Ni region, this is seen in Figure 4.14(f). Analysis of the location of the droplets using a spatial correlation function shows droplet-droplet spacing in the range 450 nm, which agrees quite well with the patterned Cu perturbation spacing of 448 nm. The experimental results support the simulation results and vice versa. Therefore, they substantiate the proposition that Marangoni effects can be utilized to produce instabilities on the surface of liquid metal filaments and influence droplet formation.

4.6 Application

What the experimental and simulation results point towards is the development of a new tool for the creation of nanoscale, metallic structures by way of pulsed-laser induced dewetting. That is, the Marangoni or thermocapillary effect could be employed as a tool to precisely scission a liquid filament to create metallic droplets or filaments of any length. Figure 4.15 is an SEM image taken after an experiment where exactly the described was demonstrated. In this instance, by lithographically patterning areas of Cu along the top of a Ni TFS it was possible to prescribe exactly where one wanted the liquid filament to pinch and break apart. On the top filament Cu was patterned at random down the length, marked by black lines, contrast that to the placement of Cu at exact locations on the

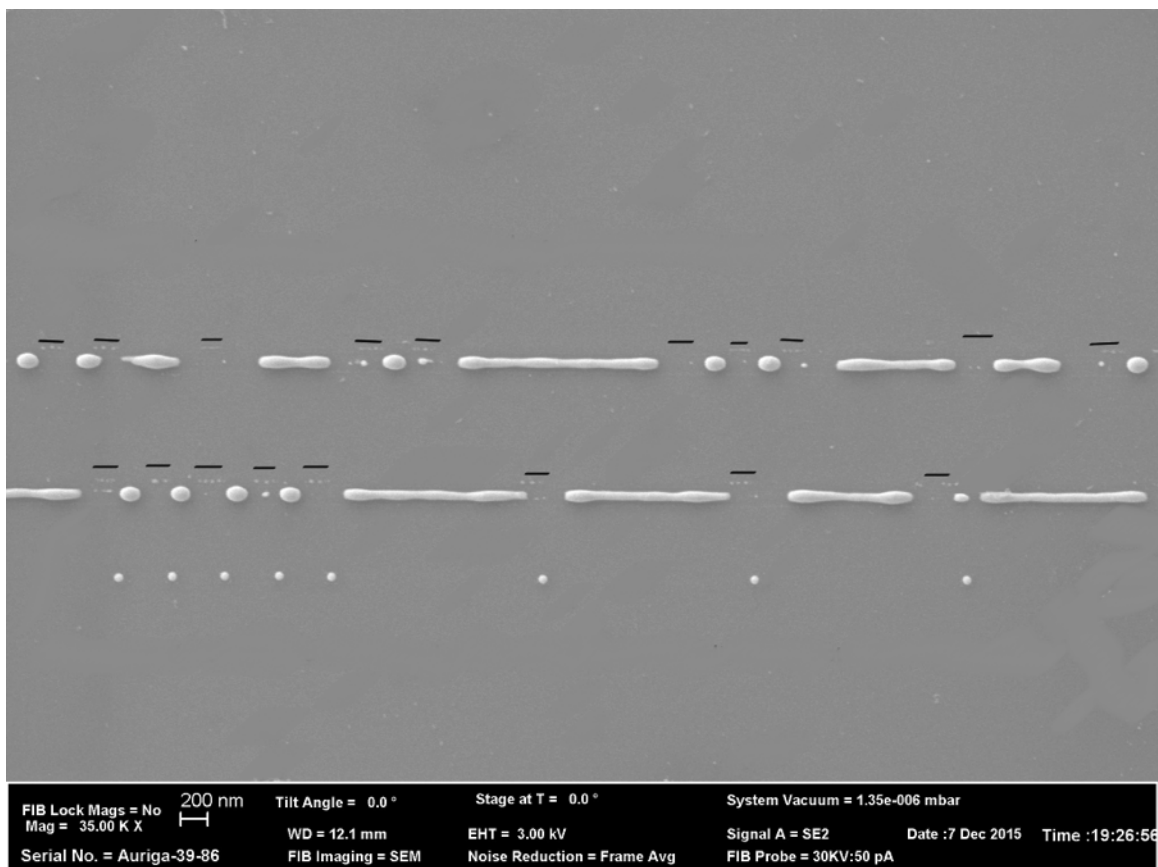


Figure 4.15. Two 12 nm Ni TFS after one laser pulse at a fluence of 250 mJcm^{-2} , the black lines indicate where 2 nm Cu TFS were placed during fabrication, on the top row they were randomly placed, on the bottom row they were placed at the location of the white dots, in essence the Marangoni effect was used to scission the filaments where ever desired, creating droplets or filaments on demand, this is a new pathway to directed self-assembly.

bottom filament, marked with white dots and black lines. After PLiD both filaments showed scissioning at precisely the locations where prescribed. Creating arrays or droplets and variable length metallic wires. Because the Marangoni effect makes use of the difference in material properties it could be a way to both prescribe exact scission locations as well as a way to alloy, or dope the resultant nanostructures. If purity needs to be maintained then the thermocapillary effect can be used. In any event, the harnessing of these two effects offers a new route to nanofabrication.

4.7 Conclusion

At the moment, the directed self-assembly of metallic nanostructures using pulsed-laser induced dewetting (PLiD) has focused on the imparting of fluid dynamic instabilities by lithographically patterning them onto the edges of thin-film strip (TFS) geometries. Moving beyond this approach and accessing a new mechanism would be an innovative next step. We investigate a new approach to imparting instabilities onto the surface of liquid metal filaments, by altering the inherent physical property of surface tension along the length of the filament during PLiD. When a surface tension gradient is due to variations in surface temperature it is referred to as the thermocapillary effect, and when it is due to differences in chemical composition it is known as the Marangoni effect. Two

mathematical models are considered, the thin-film equation and the Navier-Stokes equation, and are extended to incorporate surface tension gradients. Imparting surface tension gradients is explored experimentally, by selectively patterning the surface of Ni TFS with Cu and/or Ni, at distances similar to those of unstable surface instabilities, in accordance with the R-P mechanism, driving filament breakup. Additionally, these experiments are simulated using fully nonlinear 2D and 3D approaches using a VoF method. It was shown computationally and experimentally that surface tension gradients, created either by thermocapillary or Maragoni effects, can indeed be used to initiate filament instabilities at chosen length scales. Such an approach is a new and innovative way to fabrication nanostructures.

Chapter 5.

Dissertation Conclusion

The work contained in this dissertation sought to address some basic questions with regard to nanoscale metallic dewetting. How to develop reasonably simple but predictive models to describe the competition between instability mechanisms that result in liquid filament coalescence or fragmentation, as a function of filament extent? It was shown that the extent of the filament could be predicted, to a reasonable estimate, by equating two competing fluid dynamic instability timescales, 1) capillary-induced axial filament retraction and 2) filament breakup due to the growth of surface instabilities similar to the R-P mechanism, and solving for the equilibrium filament aspect ratio, which is proportional to the filament length, also known as the critical length. Furthermore, the competing timescale model was solved for the viscous and the viscoinertial regimes. The viscoinertial regime solution for the critical length more closely matches the experimental results, which is consistent with the fluid dynamic regime for the liquid metals. Fully nonlinear simulations were carried out based on a VoF method. To converge to the experimental length scales, thermal effects like liquid lifetime, solidification morphology, and the temperature dependent viscosity, surface energy, and density need to be considered.

Additionally, this dissertation asked another question. How to manipulate the intrinsic material properties of liquid metals, like surface energy, to initiate instabilities, like those similar to the Rayleigh-Plateau instability, to encourage self-assembly at the nanoscale? It was demonstrated that filament instabilities, similar in signature to the Rayleigh-Plateau instability, could be initiated, in a novel way, by altering the surface tension of a filament. This was accomplished through the selective addition of a second metal having a markedly different surface tension onto the surface of another, for instance Cu patterned on top of Ni. During PLiD the resultant surface tension gradient created a surface force, which initiated the surface instability, driving filament breakup. Additionally, these experiments are simulated using fully nonlinear 2D and 3D approaches using a VoF method. It was shown computationally that surface tension gradients, created either by thermocapillary or Marangoni effects, could certainly be the progenitor for filament instabilities. Such an approach is a new and innovative way to control the dewetting of liquid metals.

Directed self-assembly at the nanoscale is a prescient pathway forward. For instance, the use of surface forces was used to self-assemble planar 2D objects into 3D shapes,⁷⁷ or using self-assembling magnetic nanoparticles in ferrofluids to create lithography masks.⁷⁸ At the end of the day, the comprehension and exploitation of fluid dynamic mechanisms, timescales, and instabilities, permits

the underlying physics to be better understood, and importantly informs new nanofabrication modalities, importantly, the directed self-assembly of highly ordered and hierarchical nanoscale structures.

Chapter 6. Future Work

The study of pulsed-laser induced nanoscale metallic dewetting can be taken into several new and interesting areas. Additionally, the applicable use of metallic nanostructures is likely to grow, as nanotechnology increasingly becomes the dominant evolution path for devices. Below are a few interesting that can further the work explored in this dissertation.

6.1 Further Investigation into Marangoni Effects

Copper was a good choice for the second metal in the Marangoni experiments, for reasons discussed in Chapter 3, however there are other metals that would have worked in combination with Ni that are worth exploring that offer unique advantages, like Al and Au; the phase diagrams for Ni-Au and Ni-Al systems can be found in the Appendix. For instance, of the three, Al has the largest surface tension difference with Ni, a difference of nearly 60 %, at Ni's melting temperature, 1.78 N/m and 0.745 N/m, respectively. Alternatively, Au would be an interesting and attractive choice for several reasons. It has a fairly simple binary-phase diagram with Ni, a respectable surface tension gradient, but most interesting is the possibility of alloying with Ni to produce nanostructures with properties that may be useful in applications like surface enhanced Raman

spectroscopy and catalysis.⁷⁹ Furthermore, the demonstrated ability to scission liquid filaments at arbitrarily desired locations using the Marangoni effect is worthy of study. Such a technique could be used to create arrays of droplets and metallic nanowires, as seen in Figure 4.14.

6.2 Directed Self-Assembly for Plasmonics

Over the last decade there has been a lot of interest in the use of metallic nanoparticles in plasmonics. A plasmon is the collective oscillation of the free electron gas density – similar to phonons being the quantization of mechanical vibration. When at the interface of a conductor and a dielectric, like silica, they are surface plasmons (SP). At optical frequencies surface plasmons can couple with a photon to create a surface plasmon polariton, otherwise known as a surface plasmon resonance (SPR), and the coupled wavelength depends on the substance and geometry. When the substance is a metal, like Au, Ag, or Cu, and the geometry is a nanoparticle, they are distinguished as a localized surface plasmon resonance (LSPR). For example, a HeNe laser, whose emission is 633 nm, can excite a surface SPR at a Si-Ag interface with a wavelength of only 70 nm.⁸⁰ The ability of a SP to couple and manipulate to light is important, because information transfer in nanoscale structures by means of SPRs is referred to as plasmonics

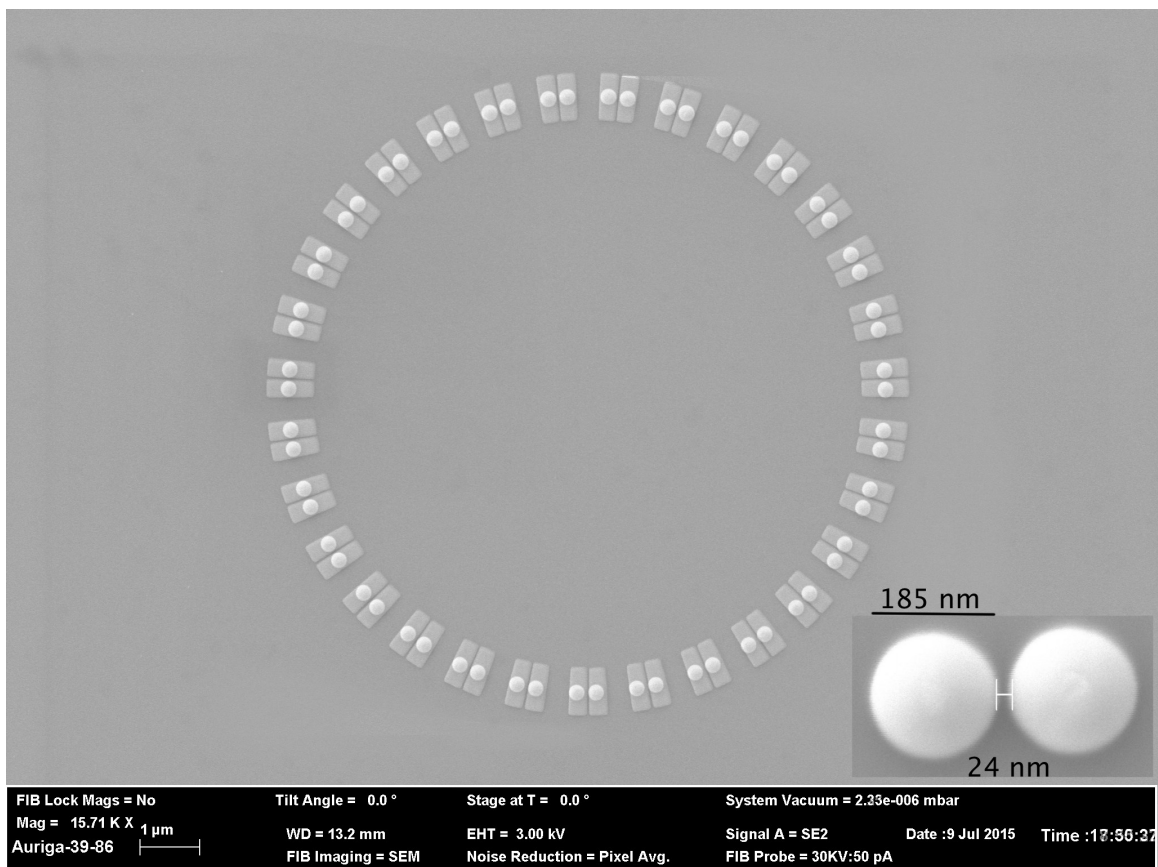


Figure 6.1. Circular ring of very closely spaced metallic nanoparticles, close enough for localized surface plasmon coupling between droplets, 25 nm Ni TFS, PLiD, 3 pulses, 250 mJcm⁻²,

(similar to photonics, where information is transferred using light).⁸¹ PLiD and directed self-assembly offer an innovative approach to fabricating metallic nanostructures for use in plasmonic research and applications. For example, Figure 6.1 is a ring of closely spaced metallic nanoparticles, sized appropriately for LSPR and spaced close enough for coupling between droplets. It is a real possibility that unique nanoparticle geometries like these could hold promise as plasmonic circuit elements. For instance, possibly as a filter or optical-converter, changing one wavelength to another by way of the droplet-droplet coupling between disparate materials. Such things need to be explored further, and the work contained in this dissertation would help.

6.3 Dewetting and Symmetry

The orderly outcomes of self-organization are pattern formation. When the initial conditions of a dewetting system have a high degree of symmetry the path toward the final end states have a better likelihood of being facile and anticipated. For instance, an isolated filament of small extent is very likely to collapse to a single droplet during PLiD (of course, the limit of the extent is now better understood thanks to the work in Chapter 3). But when the complexity of the system grows, if a high degree of symmetry is not maintained, then the

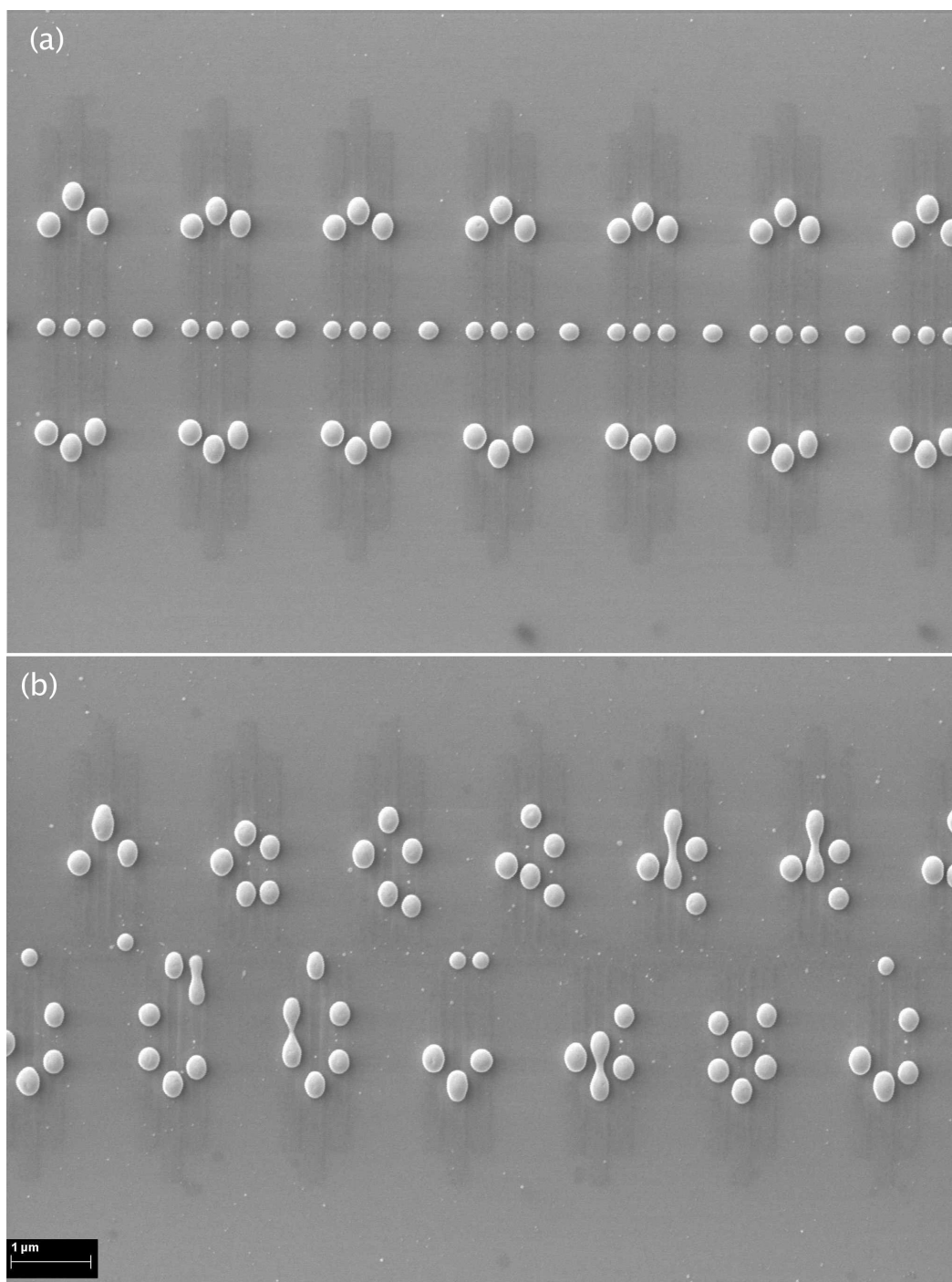


Figure 6.2. 20 nm Ni TFS, PLiD, 5 pulses, 250 mJcm^{-2} (a) TFS symmetry results in orderly droplet arrays (b) a simple shift in the pattern can drastically alter the final droplet arrangement.

expected outcomes are not necessarily preserved. For example, the PLiD pattern seen in Figure 6.2(a) is a 2D array of highly ordered single droplets, it is this way because of the symmetry of the original pattern, mirror imaged about the horizontal axis. However, if that symmetry is broken by a simple augmentation to the pattern, in this case by a shift by half a pattern unit, the result becomes quite disorderly and looks nothing like the previous highly ordered end state, Figure 6.2(b). Being able to simply go between ordered and unordered states, by design, could be a valuable and revealing tool to forward our understanding of not only the physics of dewetting but also those of nanofabrication techniques and computational modeling, all three are critically important.

List of References

1. Halas, N. J.; Lal, S.; Chang, W. S.; Link, S.; Nordlander, P. Plasmons in Strongly Coupled Metallic Nanostructures. *Chem Rev* **2011**, *111* (6), 3913-3961.
2. Magruder, R.; Wittig, J.; Zuhr, R. Wavelength tunability of the surface plasmon resonance of nanosize metal colloids in glass. *Journal of non-crystalline solids* **1993**, *163* (2), 162-168.
3. Anker, J. N.; Hall, W. P.; Lyandres, O.; Shah, N. C.; Zhao, J.; Van Duyne, R. P. Biosensing with plasmonic nanosensors. *Nat Mater* **2008**, *7* (6), 442-453.
4. Vo-Dinh, T. Surface-enhanced Raman spectroscopy using metallic nanostructures. *Trac-Trend Anal Chem* **1998**, *17* (8-9), 557-582.
5. Christopher, P.; Xin, H. L.; Linic, S. Visible-light-enhanced catalytic oxidation reactions on plasmonic silver nanostructures. *Nat Chem* **2011**, *3* (6), 467-472.
6. Rosi, N. L.; Mirkin, C. A. Nanostructures in biodiagnostics. *Chem Rev* **2005**, *105* (4), 1547-1562.
7. Atwater, H. A.; Polman, A. Plasmonics for improved photovoltaic devices. *Nat Mater* **2010**, *9* (3), 205-213.
8. Wu, J. L.; Chen, F. C.; Hsiao, Y. S.; Chien, F. C.; Chen, P. L.; Kuo, C. H.; Huang, M. H.; Hsu, C. S. Surface Plasmonic Effects of Metallic Nanoparticles on the Performance of Polymer Bulk Heterojunction Solar Cells. *Acs Nano* **2011**, *5* (2), 959-967.
9. Wolf, S. A.; Awschalom, D. D.; Buhrman, R. A.; Daughton, J. M.; von Molnar, S.; Roukes, M. L.; Chtchelkanova, A. Y.; Treger, D. M. Spintronics: A spin-based electronics vision for the future. *Science* **2001**, *294* (5546), 1488-1495.
10. Seneor, P.; Bernand-Mantel, A.; Petroff, F. Nanospintronics: when spintronics meets single electron physics. *Journal of Physics: Condensed Matter* **2007**, *19* (16), 165222.
11. Gennes, P.-G. d.; Brochard-Wyart, F. o.; Quéré, D. *Capillarity and wetting phenomena : drops, bubbles, pearls, waves*; Springer: New York, 2004. p xv, 291 p.
12. Landau, L.; Lifshitz, E. Fluid mechanics, vol. 6. *Course of Theoretical Physics* **1987**, 227-229.
13. Zhang, B.; Nakajima, A. Direct measurement of the Laplace pressure in a very thin liquid film. *Journal of colloid and interface science* **2002**, *245* (1), 215-218.
14. Plateau, J. The figures of equilibrium of a liquid mass. *The Annual Report of the Smithsonian Institution* **1864**, 338-369.
15. Rayleigh, L. On The Instability Of Jets. *Proceedings of the London Mathematical Society* **1878**, *s1-10* (1), 4-13.
16. Bush, J. W. M. MIT Lecture Note on Surface Tension, Lecture 5. <http://web.mit.edu/1.63/www/Lec-notes/Surfacetension/Lecture5.pdf> (accessed August 1, 2015).

17. Wikipedia. Plateau–Rayleigh instability [Online]. Published Online: December 2, 2015.
https://en.wikipedia.org/w/index.php?title=Plateau%E2%80%93Rayleigh_instability&oldid=693475710 (accessed January 1, 2016).
18. Wikipedia. Equation of state [Online]. Published Online: January 29, 2016.
https://en.wikipedia.org/w/index.php?title=Equation_of_state&oldid=702283484 (accessed February 3, 2016).
19. Wikipedia. Divergence theorem [Online]. Published Online: December 9, 2015.
https://en.wikipedia.org/w/index.php?title=Divergence_theorem&oldid=694489009 (accessed February 3, 2016).
20. Arfken, G. B.; Weber, H. J.; Harris, F. E. *Mathematical methods for physicists: A comprehensive guide*; Academic press 2011.
21. Wikipedia. Millennium Prize Problems [Online]. Published Online: January 11, 2016.
https://en.wikipedia.org/w/index.php?title=Millennium_Prize_Problems&oldid=699308630 (accessed February 5, 2016).
22. Kondic, L. Instabilities in gravity driven flow of thin fluid films. *Siam Review* **2003**, 45 (1), 95-115.
23. Mitlin, V. S. On dewetting conditions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1994**, 89 (2), 97-101.
24. Kondic, L.; Dong, N.; Wu, Y.; Fowlkes, J.; Rack, P. Instabilities of nanoscale patterned metal films. *The European Physical Journal Special Topics* **2015**, 224 (2), 369-378.
25. Mahady, K.; Afkhami, S.; Kondic, L. A volume of fluid method for simulating fluid/fluid interfaces in contact with solid boundaries. *J Comput Phys* **2015**, 294, 243-257.
26. Kondic, L.; Diez, J. A.; Rack, P. D.; Guan, Y. F.; Fowlkes, J. D. Nanoparticle assembly via the dewetting of patterned thin metal lines: Understanding the instability mechanisms. *Phys Rev E* **2009**, 79 (2).
27. De Gennes, P.-G. Wetting: statics and dynamics. *Reviews of modern physics* **1985**, 57 (3), 827.
28. Jones, J. E. In *On the determination of molecular fields. I. From the variation of the viscosity of a gas with temperature*, Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 1924; The Royal Society, pp 441-462.
29. Israelachvili, J. N. *Intermolecular and surface forces: revised third edition*; Academic press 2011.
30. Diez, J. A.; Kondic, L. On the breakup of fluid films of finite and infinite extent. *Physics of Fluids (1994-present)* **2007**, 19 (7), 072107.

31. Ruckenstein, E.; Jain, R. K. Spontaneous rupture of thin liquid films. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics* **1974**, *70*, 132-147.
32. Wu, Y. Y.; Dong, N. Y.; Fu, S. F.; Fowlkes, J. D.; Kondic, L.; Vincenti, M. A.; de Ceglia, D.; Rack, P. D. Directed Liquid Phase Assembly of Highly Ordered Metallic Nanoparticle Arrays. *Acs Appl Mater Inter* **2014**, *6* (8), 5835-5843.
33. Bertozzi, A. L. The mathematics of moving contact lines in thin liquid films. *Notices of the AMS* **1998**, *45* (6), 689-697.
34. Wikipedia. Weak solution [Online]. Published Online: May 5, 2015. https://en.wikipedia.org/w/index.php?title=Weak_solution&oldid=607163469 (accessed February 7, 2016).
35. Kondic, L.; Diez, J. A.; Rack, P. D.; Guan, Y.; Fowlkes, J. D. Nanoparticle assembly via the dewetting of patterned thin metal lines: Understanding the instability mechanisms. *Phys Rev E* **2009**, *79* (2), 026302.
36. González, A. G.; Diez, J. A.; Wu, Y.; Fowlkes, J. D.; Rack, P. D.; Kondic, L. Instability of liquid Cu films on a SiO₂ substrate. *Langmuir* **2013**, *29* (30), 9378-9387.
37. McKeown, J. T.; Roberts, N. A.; Fowlkes, J. D.; Wu, Y.; LaGrange, T.; Reed, B. W.; Campbell, G. H.; Rack, P. D. Real-time observation of nanosecond liquid-phase assembly of nickel nanoparticles via pulsed-laser heating. *Langmuir* **2012**, *28* (49), 17168-17175.
38. Wu, Y.; Fowlkes, J. D.; Rack, P. D. The optical properties of Cu-Ni nanoparticles produced via pulsed laser dewetting of ultrathin films: The effect of nanoparticle size and composition on the plasmon response. *Journal of Materials Research* **2011**, *26* (02), 277-287.
39. Fowlkes, J. D.; Roberts, N. A.; Wu, Y.; Diez, J. A.; Gonzalez, A. G.; Hartnett, C.; Mahady, K.; Afkhami, S.; Kondic, L.; Rack, P. D. Hierarchical Nanoparticle Ensembles Synthesized by Liquid Phase Directed Self-Assembly. *Nano Lett* **2014**, *14* (2), 774-782.
40. Fowlkes, J. D.; Kondic, L.; Diez, J. A.; González, A. G.; Wu, Y.; Roberts, N. A.; McCold, C. E.; Rack, P. D. Parallel assembly of particles and wires on substrates by dictating instability evolution in liquid metal films. *Nanoscale* **2012**, *4* (23), 7376-7382.
41. Fowlkes, J. D.; Kondic, L.; Diez, J.; Wu, Y. Y.; Rack, P. D. Self-Assembly versus Directed Assembly of Nanoparticles via Pulsed Laser Induced Dewetting of Patterned Metal Films. *Nano Lett* **2011**, *11* (6), 2478-2485.
42. Fowlkes, J.; Horton, S.; Fuentes-Cabrera, M.; Rack, P. D. Signatures of the Rayleigh-Plateau Instability Revealed by Imposing Synthetic Perturbations on Nanometer-Sized Liquid Metals on Substrates. *Angewandte Chemie* **2012**, *124* (35), 8898-8902.
43. Wu, Y.; Fowlkes, J. D.; Roberts, N. A.; Diez, J. A.; Kondic, L.; Gonzalez, A. G.; Rack, P. D. Competing Liquid Phase Instabilities during Pulsed Laser

- Induced Self-Assembly of Copper Rings into Ordered Nanoparticle Arrays on SiO₂. *Langmuir* **2011**, 27 (21), 13314-13323.
44. Nguyen, T. D.; Fuentes-Cabrera, M.; Fowlkes, J. D.; Diez, J. A.; González, A. G.; Kondic, L.; Rack, P. D. Competition between collapse and breakup in nanometer-sized thin rings using molecular dynamics and continuum modeling. *Langmuir* **2012**, 28 (39), 13960-13967.
 45. Wu, Y.; Fowlkes, J. D.; Rack, P. D.; Kondic, L.; Diez, J. On the breakup of patterned nanoscale copper rings into nanoparticles: Competing instability and transport mechanisms. *Langmuir* **2010**, 26 (14), 11972.
 46. Roberts, N. A.; Fowlkes, J. D.; Mahady, K.; Afkhami, S.; Kondic, L.; Rack, P. D. Directed Assembly of One- and Two-Dimensional Nanoparticle Arrays from Pulsed Laser Induced Dewetting of Square Waveforms. *Acs Appl Mater Inter* **2013**, 5 (10), 4450-4456.
 47. Hartnett, C. A.; Mahady, K.; Fowlkes, J. D.; Afkhami, S.; Kondic, L.; Rack, P. D. Instability of Nano- and Microscale Liquid Metal Filaments: Transition from Single Droplet Collapse to Multidroplet Breakup. *Langmuir* **2015**, 31 (50), 13609-13617.
 48. Randolph, S.; Fowlkes, J.; Melechko, A.; Klein, K.; Meyer III, H.; Simpson, M.; Rack, P. Controlling thin film structure for the dewetting of catalyst nanoparticle arrays for subsequent carbon nanofiber growth. *Nanotechnology* **2007**, 18 (46), 465304.
 49. Wikipedia. Tears of wine [Online]. Published Online: August 28, 2015. https://en.wikipedia.org/w/index.php?title=Tears_of_wine&oldid=678237280 (accessed January 22, 2016).
 50. Wikipedia. Marangoni effect [Online]. Published Online: August 6, 2015. https://en.wikipedia.org/w/index.php?title=Marangoni_effect&oldid=674814782 (accessed January 9, 2016).
 51. Brzoska, J.; Brochard-Wyart, F.; Rondelez, F. Motions of droplets on hydrophobic model surfaces induced by thermal gradients. *Langmuir* **1993**, 9 (8), 2220-2224.
 52. Trice, J.; Favazza, C.; Thomas, D.; Garcia, H.; Kalyanaraman, R.; Sureshkumar, R. Novel self-organization mechanism in ultrathin liquid films: theory and experiment. *Phys Rev Lett* **2008**, 101 (1), 017802.
 53. Gale, W. F.; Totemeier, T. C. *Smithells metals reference book*; Butterworth-Heinemann 2003.
 54. Ohring, M. *Materials science of thin films : deposition and structure*; 2nd ed.; Academic Press: San Diego, CA, 2002. p xxi, 794 p.
 55. Balakrishnan, J.; Boyd, I. D.; Braun, D. G. Monte Carlo simulation of vapor transport in physical vapor deposition of titanium. *J Vac Sci Technol A* **2000**, 18 (3), 907-916.

56. Graper, E. B. Evaporation characteristics of materials from an electron beam gun II. *Journal of Vacuum Science & Technology A* **1987**, 5 (4), 2718-2723.
57. Dorsinville, H.; Alfano, R.; Schiller, N. The Photonics Design and Applications Handbook (Laurin, Pittsfield, Mass., 1987), p. H-28.
58. Sigmund, P. Theory of Sputtering. I. Sputtering Yield of Amorphous and Polycrystalline Targets. *Physical Review* **1969**, 184 (2), 383-416.
59. Xie, R.; Karim, A.; Douglas, J. F.; Han, C. C.; Weiss, R. A. Spinodal Dewetting of Thin Polymer Films. *Phys Rev Lett* **1998**, 81 (6), 1251-1254.
60. Krishna, H.; Shirato, N.; Favazza, C.; Kalyanaraman, R. Energy driven self-organization in nanoscale metallic liquid films. *Phys Chem Chem Phys* **2009**, 11 (37), 8136-8143.
61. Goldstein, J.; Newbury, D. E.; Echlin, P.; Joy, D. C.; Romig Jr, A. D.; Lyman, C. E.; Fiori, C.; Lifshin, E. *Scanning electron microscopy and X-ray microanalysis: a text for biologists, materials scientists, and geologists*; Springer Science & Business Media 2012.
62. Van Grieken, R.; Markowicz, A. *Handbook of X-ray Spectrometry*; CRC Press 2001.
63. Binnig, G.; Quate, C. F.; Gerber, C. Atomic force microscope. *Phys Rev Lett* **1986**, 56 (9), 930.
64. Fujiwara, H. *Spectroscopic ellipsometry: principles and applications*; John Wiley & Sons 2007.
65. Ozbay, E. Plasmonics: Merging photonics and electronics at nanoscale dimensions. *Science* **2006**, 311 (5758), 189-193.
66. Le, F.; Brandl, D. W.; Urzhumov, Y. A.; Wang, H.; Kundu, J.; Halas, N. J.; Aizpurua, J.; Nordlander, P. Metallic nanoparticle arrays: A common substrate for both surface-enhanced Raman scattering and surface-enhanced infrared absorption. *ACS Nano* **2008**, 2 (4), 707-718.
67. Diez, J. A.; Gonzalez, A. G.; Kondic, L. On the breakup of fluid rivulets. *Phys Fluids* **2009**, 21 (8).
68. Mahady, K.; Afkhami, S.; Diez, J.; Kondic, L. Comparison of Navier-Stokes simulations with long-wave theory: Study of wetting and dewetting. *Phys Fluids* **2013**, 25 (11).
69. Favazza, C.; Kalyanaraman, R.; Sureshkumar, R. Robust nanopatterning by laser-induced dewetting of metal nanofilms. *Nanotechnology* **2006**, 17 (16), 4229-4234.
70. Driessen, T.; Jeurissen, R.; Wijshoff, H.; Toschi, F.; Lohse, D. Stability of viscous long liquid filaments. *Phys Fluids* **2013**, 25 (6).
71. Davis, S. H. Moving Contact Lines and Rivulet Instabilities .1. The Static Rivulet. *J Fluid Mech* **1980**, 98 (May), 225-242.
72. Batsanov, S. S. Van der Waals radii of elements. *Inorg Mater+* **2001**, 37 (9), 871-885.

73. Brochardwyart, F.; Redon, C. Dynamics of Liquid Rim Instabilities. *Langmuir* **1992**, *8* (9), 2324-2329.
74. Redon, C.; Brochardwyart, F.; Rondelez, F. Dynamics of Dewetting. *Phys Rev Lett* **1991**, *66* (6), 715-718.
75. Wikipedia. Volume of fluid method [Online]. Published Online: February 3, 2016.
https://en.wikipedia.org/w/index.php?title=Volume_of_fluid_method&oldid=703025599 (accessed February 26, 2016).
76. Popinet, S. An accurate adaptive solver for surface-tension-driven interfacial flows. *J Comput Phys* **2009**, *228* (16), 5838-5866.
77. Cho, J.-H.; Azam, A.; Gracias, D. H. Three Dimensional Nanofabrication Using Surface Forces†. *Langmuir* **2010**, *26* (21), 16534-16539.
78. Chang, C.-H.; Tan, C.-W.; Miao, J.; Barbastathis, G. Self-assembled ferrofluid lithography: patterning micro and nanostructures by controlling magnetic nanoparticles. *Nanotechnology* **2009**, *20* (49), 495301.
79. Sarkar, S.; Sinha, A. K.; Pradhan, M.; Basu, M.; Negishi, Y.; Pal, T. Redox transmetalation of prickly nickel nanowires for morphology controlled hierarchical synthesis of nickel/gold nanostructures for enhanced catalytic activity and SERS responsive functional material. *The Journal of Physical Chemistry C* **2010**, *115* (5), 1659-1673.
80. Polman, A.; Atwater, H. A. Plasmonics: optics at the nanoscale. *Materials today* **2005**, *8* (1), 56.
81. Wikipedia. Surface plasmon [Online]. Published Online: January 18, 2016.
https://en.wikipedia.org/w/index.php?title=Surface_plasmon&oldid=700427047 (accessed March 18, 2016).

Appendix

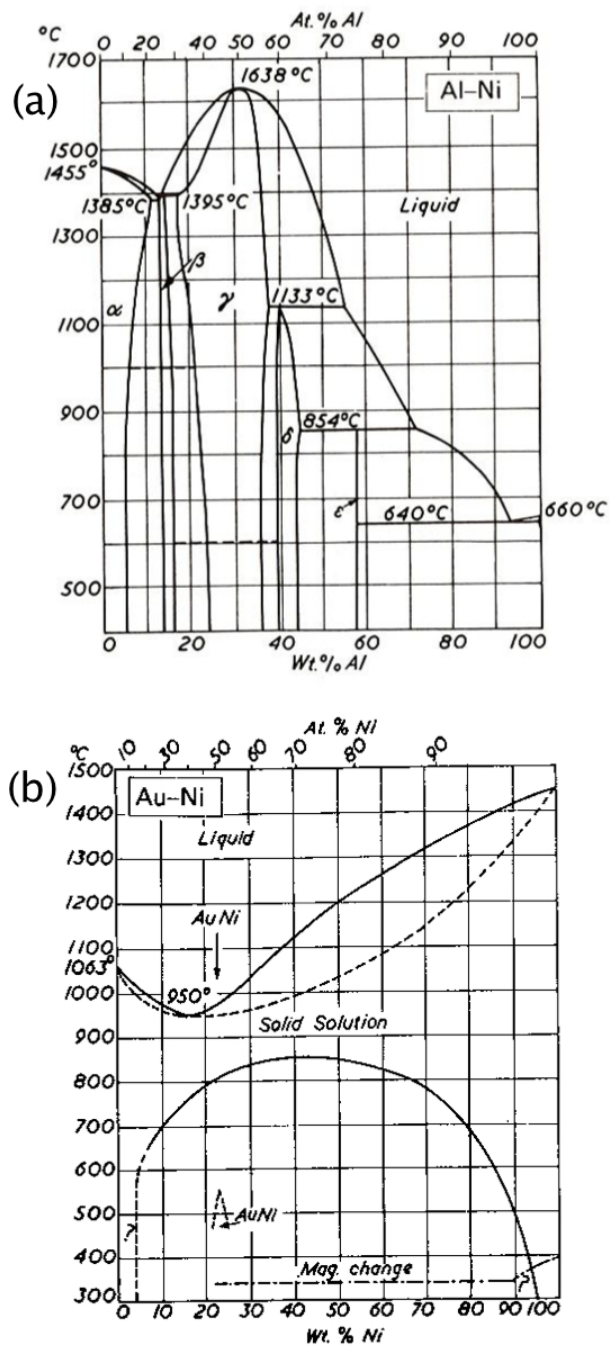


Figure A.1. (a) Al-Ni and (b) Au-Ni phase diagrams

Vita

Chris Hartnett was raised in the northern Chicago suburbs of Lake Bluff and Lake Forest, Illinois, and is the second of five children. After completing his undergraduate degree in physics from Northern Illinois University in DeKalb, Illinois, with a concentration in acoustics, he was recruited by an independent record label, Darwin Records, to be a recording engineer. After a year as a recording engineer he was hired by Shure Inc., a world-renowned audio electronics company, where he co-lead several product development teams in creating award winning dynamic and condenser microphone products. Following several years in industry Chris returned to academia to pursue a graduate degree in physics from the University of Tennessee, in Knoxville, Tennessee. His research interests are experimental, and in areas of nanomaterials and nanofabrication, specifically in the directed self-assembly of nanostructures and their potential uses. His academic research was conducted at the Nanofabrication Research Facility at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS). He believes the ability to manipulate materials and construct devices at the nanoscale is critical for the future of all advanced technology.