Molten Drop Deposition and the Dynamics of the Molten Contact Line

by

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B.S.E. in Mechanical Engineering, Princeton University, 1992
S.M. in Mechanical Engineering, Massachusetts Institute of Technology, 1995

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Abstract

The development of many advanced manufacturing technologies requires a basic understanding of how molten materials spread over cold, solid surfaces. Of particular interest are molten drop deposition processes in which the drops arrest by solidification before they reach an equilibrium configuration on the solid. Central to this spreading process is the molten dynamic contact line problem, which involves the relationship between the speed of the contact line and the apparent (visible to the observer) contact angle of the molten liquid.

This thesis examines the deposition of millimeter-scale molten drops on cold, solid surfaces. Arrest angle data are obtained for solder drops deposited on oxidized solid solder, octacosane ($C_{28}H_{58}$) on solid octacosane, and octacosane on glass coated with different types of self-assembled monolayers (SAMs). Direct measurements of the velocity-angle relationship are obtained for microcrystalline wax drops deposited on wax targets, both horizontal and inclined, and for water drops deposited on ice. The observations are consistent with Schiaffino and Sonin's (e.g. 1997, *Phys. Fluids*, 9 (8), 2217-2226 and 2227-2233, and 9 (11), 3172-3187) molten contact line model, except for the depositions on inclines, which reveal that the molten contact line may experience "stick-slip" motion and arrest with apparent contact angles that are inconsistent with existing empirical correlations.

A theoretical model for quasi-steady molten contact line motion is developed using a simple piecewise approximation of the shape of the solidification front based upon Schiaffino and Sonin's calculations. By considering the flow field very near the contact line, the relationship between the apparent contact angle, the dimensionless advance speed, and other relevant system parameters is established. When the molten contact line is very close to arrest this relationship reduces to a simple analytical expression, denoted the near-arrest law. Considering its approximations, the model provides surprisingly good agreement with the experimental data, provided the data meet the requirements of quasi-steady, inertia free flow near the contact line.

Thesis Supervisor: Professor Ain A. Sonin

Title: Professor of Mechanical Engineering
To my family, my friends, and my teachers.

Thank you.
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Chapter 1

Introduction

When a drop of liquid spreads over a solid surface, the line that demarcates the junction between the liquid and the solid is known as the contact line. The angle the liquid free surface makes with the solid is referred to as the contact angle, and we distinguish between the molecular, or true, contact angle and the apparent contact angle. The molecular contact angle is the slope of the free surface on a nanoscopic length scale (just larger, say, than molecular dimensions), and the apparent contact angle is the slope of the free surface measured at a microscopic length scale (that is, visible to an observer aided by a conventional optical instrument). These angles are approximately equal for a drop at rest on a horizontal surface. However, the apparent contact angle becomes larger than the molecular contact angle when the drop advances, and smaller when the drop recedes. The solution of a dynamic contact line problem centers around the relationship between the velocity of the contact line and the apparent contact angle.

The majority of the experimental and theoretical work on the dynamic contact line focuses on the isothermal problem, in which a liquid held at constant temperature advances or recedes over a solid maintained at the same temperature (larger than the fusion point of the liquid). In this case the liquid spreads until it reaches an equilibrium contact angle, whose value is controlled by the balance of interfacial forces at the contact line. The isothermal problem is fundamentally different from the molten dynamic contact line problem, in which, say, a small molten drop spreads over a large solid initially held at a temperature lower than the fusion point of the drop. This process is inherently a non-equilibrium one, because the molten contact line arrests due to solidification dynamics. In day-to-day terms this problem closely resembles the flow of molten wax down the side of a dripping candle.

In this thesis we focus upon molten drop deposition processes and the investigation of the molten dynamic contact line problem. The work builds upon the theoretical and experimental knowledge base developed by previous researchers of these topics (e.g. Gao and Sonin, 1994; Gao, 1995; Schiaffino, 1996; Schiaffino and Sonin, 1997a, b, c, and d). We begin by discussing the importance of this research in various industrial applications and in the scientific community, presenting the thesis objectives, and outlining the organization of the thesis.
1.1 Applications of the Molten Contact Line Problem

Molten dynamic contact lines are important elements of numerous industrial processes, and they will likely become even more prevalent as several emerging technologies gain acceptance in the marketplace. The sections below discuss the following processes and applications as examples: 1. three-dimensional microfabrication, 2. microelectronics device packaging, 3. rapid prototyping, 4. coating and casting flows, 5. free surface solidification, and 6. other advanced manufacturing technologies.

1.1.1 Three-Dimensional Microfabrication

A broad range of advanced fabrication and materials processing technologies require improved understanding of the fundamental physics of molten material spreading and solidification. Among these processes is a novel 3D microfabrication process investigated by Gao and Sonin (1994), which facilitates the precise manufacturing of small scale objects using 50 micrometer (μm) diameter drops as the fundamental building block. In this process an adapted drop-on-demand ink jet print head ballistically delivers precisely metered drops to a target (Figure 1.1). The drops impact the target and solidify into a final shape that depends primarily on the target thermal state before impact. Gao and Sonin demonstrated several fundamental building techniques using molten wax as their working fluid.

![Figure 1.1](image)

Figure 1.1 Gao and Sonin used an adapted ink jet print head to dispense 50 μm drops of molten wax. The drops solidified after impact, thereby forming precise three-dimensional structures.
This technique may, in principle, be extended to a wide variety of manufacturing applications that require the precise formation of small scale structures. Schiaffino and Sonin's work on molten drop deposition and the molten contact line problem followed from research on this process at MIT.

1.1.2 Microelectronics Device Packaging

The semiconductor manufacturing giants are currently shifting from conventional wire-bond to "flip-chip" type packages for many of their high performance microchips. The flip-chip packages use small bumps of solder to form a direct electrical connection between the microchip and a high resistance substrate under the microchip (Figure 1.2). Shifting from a wire-bond to a flip-chip package leads to higher clock speeds, smaller footprints, and improved thermal performance. One possible way to cost-effectively apply the solder bumps to the electrical connector is by "printing" with an adapted ink jet print head. The microdrops would impact the specially prepared target, spread under the influence of inertial and capillary forces, and arrest by solidification (Figure 1.3).

Solder microdrop deposition technology is gradually coming of age. Duthaler (1995) met with some difficulty in successfully designing and building a drop-on-demand ink jet that would dispense solder drops of 50 μm diameter, but a system built by engineers at MicroFab, Inc. (see Hayes, et al, 1992) is currently under investigation at the University of Chicago (Xiong, et al., 1998). Another solder microdrop deposition system employing magnetohydrodynamic solder drop ejection was built by scientists at IBM (Schiesser, et al., 1994; see also Duthaler, 1995).

1.1.3 Rapid Prototyping

Molten contact line research has direct applications in the quickly evolving field of rapid prototyping (RP). This field has grown enormously in recent years, and will continue to do so as companies seek to improve their competitive position by reducing the time required for new product development. The RP industry was revolutionized in the late 1970s by stereo lithography, a technique that builds a solid model in a layer-by-layer fashion using a laser to fuse a liquid resin. These systems allow engineers and manufacturers to rapidly build parts or molds directly from CAD (computer aided design) data. As a lower cost alternative to stereo lithography systems, several companies have developed RP machines that precisely dispense molten thermoplastics to form the layers of the solid model (e.g. 3D Systems of Valencia, California; Stratasys of Eden Prairie, Minnesota). Z Corporation of Somerville, Massachusetts, manufactures a 3D printer that uses an ink jet head to dispense microdroplets of resin onto a powder bed. The resin binds the powder and solidifies to form layers of the solid model.
Figure 1.2 Schematic of the electrical interconnects in a flip-chip semiconductor package. The solder bumps might be "printed" using an a solder microdrop dispenser.

Figure 1.3 An individual solder bump would be positioned on a specially prepared electrical connection site. Figure adapted from Kuleza and Estes (1992).

1.1.4 Coating Flows

Other more conventional industrial processes are linked to the molten contact line problem as well. Steen and Karcher (1997) describe the planar flow casting problem, illustrated in Figure 1.4.
In this process molten material (typically molten metal) is forced under pressure through a small gap onto a rapidly rotating, large chill wheel. The molten material solidifies into a ribbon and peels away from the wheel far downstream of the gap. There are two molten contact lines in this process: one at the contact line where the liquid first contacts the wheel (the advancing molten contact line), and another on top of the solidified ribbon (the retreating molten contact line). This problem is different from our drop deposition problem for three reasons: 1. spin casting is characterized by enormous thermal gradients which are simply not present in our experiments, 2. the velocities associated with spin casting are much larger than those of capillarity driven drop spreading, and 3. the spin cast material does not adhere to the chill wheel whereas the deposited drops generally adhere to the target.

![Diagram of spin casting process](image)

**Figure 1.4** In spin casting processes a molten contact line is maintained between the molten liquid and the chill wheel. The Figure is not to scale and was adapted from Steen and Karcher (1997).

1.1.5 Free Surface Solidification

Variations on the molten dynamic contact line problem also appear in the literature on containerless free surface solidification processes (Anderson, *et al.*, 1996). As depicted in Figure 1.5, the molten contact line demarcates the junction between the gaseous environment, the liquid, and the solid material. The contact line is dynamic because the solidification front moves upward at a speed $V$, given by the solidification rate. The physics of free surface solidification is relevant in many materials processing technologies in which the microstructural characteristics of the solid are important.
1.1.6 Other Advanced Manufacturing Technologies

Ink jet technology has progressed from a research lab experiment, to a niche market printing technology, to a mass produced printing technology, to a niche market flexible manufacturing technology. This trend will continue, as many new applications for microdroplet deposition loom on the horizon. In addition to the areas already discussed, the technology will likely have significant impact in the following areas, to name just a few: near net-shape forming, polymer jetting, precision coating, monodisperse powder formation, flat panel display manufacturing, microlens formation, photonics component assembly, combinatorial drug and materials discovery, clinical diagnostics of biological samples, and controlled drug delivery. Innovation by engineers and scientists will likely create many more uses for this and other related technologies, and many of these new applications will require a fundamental understanding of the physics of the molten dynamic contact line.

1.1.7 Scientific Importance of the Molten Contact Line Problem

The molten contact line problem plays an important role in a wide spectrum of industrial applications, but it is also important to the scientific community. Chapter 2 will show that the continuum formulation of the problem features singularities at the contact line in both fluid shear stress and heat flux. Researchers acknowledge that for the isothermal contact line problem a synthesis of molecular and continuum dynamics will result in the mitigation of the shear stress singularity. However, the mechanism that bounds the heat flux singularity at the molten dynamic contact line is still undetermined at this time. The problem is at the state-of-the-art of fluid dynamics, heat transfer, and materials processing research.
1.2 Thesis Objectives

The first work on the molten contact line problem was presented by Schiaffino and Sonin (1997a, b, c, and d; see also Schiaffino, 1996). They developed scaling laws that describe a broad range of drop deposition experiments, demonstrated that the advancing molten contact line arrests at an apparent angle which depends primarily on the dimensionless thermal sub-cooling of the target, showed that under certain conditions that the velocity-angle relationship for the molten dynamic case resembles that of the isothermal case, and posited the first theoretical framework for the arrest of a molten contact line. They also showed that the conventional formulation of the thermal problem associated with a molten dynamic contact line is singular in heat flux at the contact line.

This thesis advances the knowledge base for molten drop deposition processes and the dynamic contact line problem. The work is both experimental and theoretical in scope, and focuses on the dynamics of the deposition of individual millimeter scale molten drops onto cold, solid targets. Table 1.1 summarizes the experiments completed as part of this work.

<table>
<thead>
<tr>
<th>Material System</th>
<th>Deposition Surface Target Description</th>
<th>Inclination Target Above Horizontal</th>
<th>Data Obtained Post-Arrest</th>
<th>Full Spreading Dynamics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solder on solid solder</td>
<td>Oxidized</td>
<td>0°</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Octacosane on solid octacosane</td>
<td>Rough</td>
<td>0°</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Octacosane on glass</td>
<td>Smooth</td>
<td>0°</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Coated with SAMs</td>
<td>0°</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Microcrystalline wax on solid wax</td>
<td>Smooth</td>
<td>0°, 28°, 68°</td>
<td>X, X</td>
<td></td>
</tr>
<tr>
<td>Water on ice</td>
<td>Smooth</td>
<td>0°</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

The experiments for which only the post-arrest information was obtained serve to supplement the data presented in Schiaffino and Sonin. The solder experiments were conducted to gain further insight into the importance of oxidation on solder drop deposition, as this effect will likely be an important consideration in certain microdrop-based manufacturing operations (see §1.1.2). Octacosane was selected as a deposition material because it has well-known and well-defined thermal properties (fusion temperature, latent heat, specific heat capacity, thermal conductivity, etc.). As such, these experiments serve an important role in the development of theories for drop spreading and arrest. The deposition on the self-assembled monolayer (SAM) coated surfaces illustrates another novel way in which molten drop arrest geometry may be manipulated. These tests
depart from the study of the homologous drop deposition problem, in which the drop and target material are the same.

A large portion of this thesis is devoted to tests that examine the full spreading dynamics for homologous molten drop deposition. These experiments provide direct measurements of the velocity-angle relationship for molten drop deposition events. These are the first data of their kind: to the author's knowledge no one has reported complete transient measurements of spreading rate and apparent contact angle for the deposition of molten drops on sub-cooled solids of the same material. We also develop and apply a simple theoretical model for the quasi-steady velocity-angle relationship for the molten contact line. The model generally requires a numerical solution, but we develop an asymptotic solution that applies near molten contact line arrest. Considering the simplicity of the model, the numerical solutions provide surprisingly good agreement with the inertia-free, viscous-dominated empirical data.

The experiments in which wax drops were deposited on wax inclines are not fully explained by existing theories. In these experiments the downhill arrest contact angle depends upon parameters other than the dimensionless thermal sub-cooling of the target. Also, under some conditions drops deposited on inclines undergo stick-slip motion. A simple mechanism for stick-slip motion is described, and calculations suggest that this behavior may result from solidification processes that occur on a length scale of order $\alpha/U$ from the contact line ($\alpha$ is the thermal diffusivity, $U$ is the spreading velocity, and $\alpha/U$ is an important dimensionless length scale for these problems).

This work involves free surfaces undergoing large, unsteady deformations, unsteady heat transfer and phase change, and coupled convection and diffusion. The molten dynamic contact line problem is an extremely difficult one, and this thesis will hopefully serve as a guide for those who work on the problem in years to come.

1.3 Thesis Organization

The remainder of the thesis is organized as follows. Chapter 2 discusses previous work done on the isothermal contact line problem, and delves into some depth on the work of Schiaffino and Sonin on the molten dynamic contact line problem. It sets the stage for Chapter 3, which presents the results for experiments in which only the post-arrest conditions are obtained (see Table 1.1). Chapter 4 reviews the derivation of the Hoffman-Tanner-Voinov law (using the techniques of Voinov, 1976, 1978) and presents the new theory for the quasi-steady velocity-angle relationship for the molten dynamic contact line. Numerical solutions of the new result are presented, and the importance of various dimensionless parameters is discussed. The description and results for the "full spreading dynamics" experiments are presented in Chapter 5, along with discussion of the results in
the context of Schiaffino and Sonin's theories. In Chapter 6 the data of Chapter 5 are compared with the molten contact line theory developed in Chapter 4. Chapter 7 summarizes the conclusions and presents several suggestions for future work. Appendix A lists the relevant material properties used in the thesis, and Appendix B presents the numerical data for the velocity-angle relationships obtained using the new molten contact line model.
Chapter 2

Background on Molten Drop Deposition and the Molten Contact Line Problem

The continued development of many of the advanced fabrication and materials processing technologies described in Chapter 1 requires improved understanding of the physics of molten material spreading and solidification. Modeling these processes requires analysis of the molten dynamic contact line problem, in which a molten material spreads over a subcooled solid and arrests by solidification mechanisms. This Chapter reviews the key aspects of the isothermal moving contact line (§2.1), discusses the key implications of Schiaffino and Sonin's theory of the molten dynamic contact line (§2.2), and describes the fundamental physics relevant to the drop deposition experiments of this thesis (§2.3).

2.1 Summary of Previous Work on the Isothermal Dynamic Contact Line Problem

The majority of work on the moving contact line focuses on the isothermal case, in which the liquid and solid are both held at a constant temperature above the fusion point of the liquid (see Dussan, 1979 for an excellent review). The fluid advances over the solid until it reaches its equilibrium angle \( \theta_e \), which is determined by the balance of interfacial stresses at the contact line. A horizontal force balance on the isothermal contact line at equilibrium gives the well-known result

\[
\sigma \cos \theta_e = \sigma_{sg} - \sigma_{sl},
\]

where \( \sigma_{sg} \), \( \sigma_{sl} \), and \( \sigma \) (the surface tension coefficient) are the interfacial energies associated with the solid/gas, solid/liquid, and liquid/gas interfaces, respectively. For a moving isothermal contact line the apparent contact angle \( \theta_a \) (the contact angle at a very small height \( H \) above the surface) differs from \( \theta_e \) for non-zero contact line speed. This dependence is qualitatively illustrated in Figure 2.1 for a quasi-steady flow with reference frame fixed at the contact line.

Modeling the flow field in the wedge-shaped region near the contact line using continuum theory produces the well-known shear stress singularity at the contact line. This non-physical result occurs because the continuum equations break down at molecular dimensions, and the solution of the dynamic contact line problem ultimately requires a synthesis of continuum and molecular hydrodynamics (e.g. deGennes, 1985; Blake, 1997). The singularity is traditionally circumvented or mitigated using one of two techniques: 1. truncation of the continuum equations at a molecular scale cut-off length, or 2. introduction of a small "slip length" over which velocity-slip occurs. The first
method is arguably the simplest and was used by Voinov (1976, 1978) and Tanner (1979) (see also Boender et al, 1991; Chesters and van der Zanden, 1993). Their results for the velocity-angle relationship has come to be known as the Hoffman-Tanner-Voinov law (denoted hereafter as Hoffman's law), given by

\[ Ca = \kappa_H \left( \theta_a^3 - \theta_m^3 \right). \] (2.2)

The capillary number \( Ca \) \((Ca=\mu U/\sigma)\) where \( \mu \) is the absolute viscosity and \( \sigma \) is the surface tension of the fluid) measures the relative importance of viscous forces compared to capillary forces. \( \theta_m \) is the slope of the free surface evaluated at the molecular scale cut-off length \( h_m \). Although a weak dependence of \( \theta_m \) on \( Ca \) may exist, it is usually assumed that \( \theta_m = \theta_a \). The molecular cut-off length scale is usually taken to be \( h_m = 1 \text{ nm} (=10^{-9} \text{ m}) \), which is just larger than typical molecular dimensions (e.g. Voinov; van der Zanden and Chesters, 1994). The coefficient \( \kappa_H \) weakly depends upon the length scale \( H \) of the observation of \( \theta_a \), and Voinov suggests that

\[ \kappa_H = \frac{1}{9 \ln \left( H/h_m \right)}. \] (2.3)

Hoffman's name is associated with the law because he used the functional form of (2.2) in his much-cited 1975 study. His empirical data correlates with (2.2) over a wide range of conditions for a value of \( \kappa_H \) of about \( 1.3 \cdot 10^{-2} \text{ rad}^3 \).
The slip length technique was investigated by many researchers, including Huh and Scriven (1971), Dussan (1976), Hocking (1992), and Bazhlekov and Chesters (1996). Huh and Scriven suggested that when flow dimensions approach the mean free path of the liquid, a slip model should be used to replace the no-slip condition along the solid boundary. They suggested the application of a Navier slip condition (i.e. where the shear stress is directly proportional to the slip velocity) and offered some preliminary work on the importance of long-range forces for this problem. Dussan showed that three different slip profiles lead to nearly identical results for the macroscale flow field. Hocking performed a lubrication analysis of the near contact line region by applying a linear slip condition over a small distance from the solid surface (see also Hocking and Rivers, 1982). He also applied this technique to the flow of a viscous fluid sheet in a 1990 paper. Bazhlekov and Chesters compared the solutions obtained using various slip models to that obtained by applying Moffatt's (1964) analytical wedge flow solution as a boundary condition along a surface at a small radial distance from the contact line. They found that all techniques investigated produced similar results on the macroscale; only on the scale of the slip length do the differences in any of these models become evident.

Shikhmurzaev (1996, 1997) employed a Navier slip condition and postulated the existence of a microscopic precursor film that extends from the liquid into the gaseous phase along the solid surface. The interested reader should consult the references for technical details of the analysis and for further description of the advantages and disadvantages of this technique.

A number of studies attempt to model the spreading dynamics of liquid drops, but few properly treat the near contact line region. Bechtel, et al. (1981) used a Lagrangian formulation and a truncated sphere approximation to model the impact of a drop on a flat surface, but did not make special consideration for the velocity-angle relationship at the contact line. Hatta, et al. (1995) used linear extrapolation of the macroscopically computed free surface shape to estimate the transient position of the contact line during drop spreading. Fukai, et al. (1993, 1995) recognized the need to incorporate dynamic contact angle physics into their computational model of drop impact and did so semi-empirically. Their measurements of dynamic advancing and receding angles were obtained from drops sliding under their own weight down an incline and were admittedly made at spreading speeds much slower than those characteristic of their drop spreading experiments. They were able to improve their numerical results by simply using "...constant values for the dynamic contact angles, both in the spreading and recoiling stages" (1995, p. 238).

Other researchers have been more fastidious in their treatment of the physics of the moving contact line. Seaver and Berg (1994) developed simple analytical models for drop spreading and confirmed that their models are consistent with Hoffman's law. Pasandideh-Fard, et al. (1996) dealt with the effect of surfactant addition on drop dynamics. They obtained transient contact angle measurements from drop deposition experiments that closely matched the conditions to be
simulated, and applied the empirical velocity-angle relationship as a boundary condition in their numerical analysis.

Still others worked on very specific aspects of the drop spreading problem, but did not focus on the details of the moving contact line problem. Elliot and Ford (1972) reported measurements of the apparent dynamic contact angle for water and alcohol drop deposition on wax surfaces prepared in various manners. Stow and Hadfield (1980) focused their experimental work on surface roughness and the transition to splashing. Chandra and Avedisian (1991) studied the impact of \( n \)-heptane (\( C_7H_{16} \)) drops on targets whose temperatures ranged from room temperature to 250\(^\circ\)C (above the Leidenfrost point of the liquid). Anderson and Davis (1995) dealt with thermocapillarity and volatile drop evaporation.

A tremendous amount of work in the literature addresses various aspects of the isothermal moving contact line problem, but the challenging technical issues associated with the problem are far from resolved. On one hand, an approximate velocity-angle relationship may be obtained in a straight-forward manner by truncating the continuum equations at a molecular length scale. While this approach may be appropriate for an engineering analysis, this technique is somewhat lacking in rigor. Employing a slip velocity profile near the contact line moves the modeling one level closer to molecular dynamics. However, since the macroscale is insensitive to the exact nature of the boundary condition employed at the contact line, there is no \textit{a priori} justification for choosing one slip profile over another. Recent efforts to synthesize molecular and continuum dynamics for the moving contact line problem have met with some success (Hadjiconstantinou, 1998) and much related work will likely be completed in the coming years.

2.2 The Advancing Molten Contact Line Problem

The molten dynamic contact line problem is fundamentally different from the isothermal one because it is inherently controlled by non-equilibrium processes. Solidification mechanisms play the deciding role in determining the conditions at molten contact line arrest, and specifically, in determining the value of the apparent contact angle at arrest. This implies that the velocity-angle relationship for the molten dynamic contact line is fundamentally different than that for an isothermal contact line.

The first treatment of the molten dynamic contact line appeared in Schiaffino and Sonin (1997a, b, c, and d; see also Schiaffino, 1996). They developed scaling laws that describe a broad range of drop deposition experiments, demonstrated that the advancing molten contact line arrests at an apparent contact angle that depends primarily on the difference between the fusion temperature and the target temperature, and posited the first theoretical framework for the arrest of a molten contact line. They attempted to solve the conventional formulation of the heat transfer
equations associated with this problem, and discovered that the heat flux at the contact line (an important quantity in their theoretical framework) is singular. Unable to identify a rate-limiting mechanism, they calculated the length scale $\lambda$ at which the conventional solution must be cut-off in order to make consistent their theory, calculations, and experiments. They also showed that under certain circumstances the velocity-angle relationship appears to obey a particular form of Hoffman's law.

Other works have investigated non-isothermal drop spreading and impact processes, but none adequately addressed the near contact line physics. Ehrhard (1993; see also Ehrhard and Davis, 1991) focused on the effects of thermocapillarity on drop spreading, and Macklin and Payne (1967) dealt with ice accretion processes. For containerless solidification processes Anderson, et al. (1996) did not address the heat flux singularity, but did show that inclusion of a dynamic contact angle was necessary to match their theory and experiment. Steen and Karcher (1997) presented some simple discussion on the basic physics associated with spin casting. They suggested that a heat transfer coefficient be used to limit the growth of the solidification front under the molten liquid. Xiong, et al (1998) employed a thermal contact resistance as an adjustable parameter in their model of solder microdrop impact and spreading. This technique is also used to align rapid solidification calculations with experiment (e.g. Clyne, 1984). Employing a thermal contact resistance is reasonable for spreading in which the ambient gas may become trapped in between the liquid and the solid (say, spreading over rough surfaces with $Ca \sim 10^{-2}$ to $10^{0}$) or for spreading over surfaces that are poorly wetted by the molten liquid. In the present drop deposition experiments molten contact line arrest generally occurs when $Ca$ is small (say $Ca \sim 10^{-5}$ to $10^{-2}$). The surfaces are reasonably smooth and are wetted by the molten liquid, so it is inappropriate to employ a thermal contact resistance in the analysis.

2.2.1 Summary of the Problem Formulation

At the heart of the molten dynamic contact line problem is the calculation of the shape of the solidification angle $\theta_s$, which is the slope of the solidification front immediately behind the molten contact line (Figure 2.2). Molten contact line arrest occurs, according to Schiaffino and Sonin's arrest hypothesis, when the apparent contact angle $\theta_a$ falls to $\theta_s$. The conventional formulation of the thermal problem associated with the near contact line region, however, is singular in heat flux at the contact line. This implies that the only mathematical solutions for the solidification angle are $\theta_s = \pm \pi/2$, which is in clear contradiction with experimental results.

As discussed by Schiaffino and Sonin, the singularity resembles those discussed in Anderson and Davis' (1994) paper on fluid and heat flow near contact lines. The liquid "wedge" near the molten contact line has a flux boundary condition (say, $\partial T / \partial n = 0$) along the gas interface and a
constant temperature \( (T=T_f) \) along the solidification front. The solid "wedge" spans from the horizontal target ahead of the molten contact line to the solidification front and has similar boundary conditions. Anderson and Davis analyzed the temperature field \( T(r, \theta) \) on a wedge domain subject to such conditions using the steady-state energy equation (for \( U=0 \)), which satisfies

\[
\nabla^2 T = 0. \tag{2.4}
\]

They showed that the solution in polar coordinates \((r, \theta)\) for a wedge with \( T=T_f \) on \( \theta=0 \) and \( \partial T/\partial \theta=0 \) on \( \phi=\phi \) takes the form

\[
T = T_f + B_m r^m \sin \theta, \tag{2.5}
\]

where \( B_m \) are coefficients to be determined using an additional boundary condition and the separation constant \( \tau \) is

\[
\tau = (m+1/2) \pi/\phi, \quad m = 0, 1, 2, \ldots. \tag{2.6}
\]

Equations (2.5) and (2.6) imply that the heat flux (either \( \partial T/\partial r \) or \( r^{-1} \partial T/\partial \theta \)) at the contact line is singular when \( \phi>\pi/2 \) and vanishes when \( \phi<\pi/2 \). Anderson and Davis also showed that when the no-flux condition is applied to both boundaries \( \theta=0 \) and \( \theta=\phi \), the heat flux is singular when \( \phi>\pi \). The inclusion of a non-zero flux condition (i.e. a convection boundary condition) instead of an adiabatic condition does not remove the singularity because the leading-order behavior near the corner remains
unchanged (Anderson and Davis, p. 233). Anderson and Davis also considered adjacent wedges that communicate through various fluid (solid wall and free surface) and thermal (constant temperature and no-flux) boundary conditions.

The molten contact line case is different from the situations considered in Anderson and Davis because material passes through the fusion interface, releases its latent heat, and translates away from the molten contact line region (refer back to Figure 2.2). This behavior led Schiaffino and Sonin to include in their analysis the energy balance (the Stefan condition) across the solidification front,

\[ q_s - q_l = \rho U L \sin \theta_s \theta_l, \quad (2.7) \]

where \( q_s \) is the heat flux from the fusion interface to the solid, \( q_l \) is the heat flux from the liquid to the fusion interface, \( \rho \) is the density (assumed equal for liquid and solid), and \( L \) is the latent heat. Here \( \theta_s, \theta_l(x) \) is the local slope of the solidification front at a horizontal distance \( x \) from the contact line, whereas the solidification angle \( \theta_s = \theta_s(0^+) \) is the slope of the solidification angle immediately behind the advancing molten contact line.

To calculate \( \theta_s, \theta_l \), and hence the supposed arrest angle \( \theta_s \), the heat fluxes \( q_s \) and \( q_l \) must be calculated. Schiaffino and Sonin considered the case where the molten liquid temperature \( T_s \) is sufficiently close to the fusion temperature \( T_f \), and argued that in this limit the liquid and solid problems decouple and \( q_l \) may be dropped from (2.7) in deference to \( q_s \). This approximation is consistent with Anderson and Davis' findings, which suggest that as \( r \to 0, q_s \to \infty \) and \( q_l \to 0 \) when both \( \theta_s, \theta_l \geq 0^+ \) and \( -\pi/2 \leq \theta_s, \theta_l \leq \pi/2 \).

For the decoupled problem, Schiaffino and Sonin showed that the transient term \( \partial T / \partial t \) may be dropped from the full energy equation for length scales \( x/R \ll 1 \) and \( x/R \ll Pe_R^{-1/2} \) (\( Pe_R = U/R/\alpha \) is a Peclet number based on molten drop footprint radius \( R \), and its relevance is further discussed in Chapter 6). The quasi-steady energy equation valid in the solid material is then

\[ (U \cdot \nabla) T = \alpha \nabla^2 T, \quad (2.8) \]

where \( \alpha \) is the thermal diffusivity. Equation (2.8) is solved for the domain and boundary conditions pictured in Figure 2.3. For this problem the heat flux \( q_s \) is singular at the contact line, due to the discontinuous change in geometry and boundary conditions at the contact line. Thus, (2.7) and (2.8) strictly give \( \theta_s = \pm \pi/2 \) as the only acceptable mathematical solutions for the solidification angle.

To bring their calculations in line with their arrest hypothesis and experimental results, Schiaffino and Sonin suggested that an unidentified mechanism bounds the heat flux near the contact line, and that \( \theta_s \) is constant up to a cut-off distance \( r = \lambda \). For larger distances their calculated solutions for the shape of the solidification front remain valid. The cut-off length \( \lambda \) is estimated to

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be of the order of 0.1 to 1.0 μm for microcrystalline wax, mercury, and water drop deposition. This scale is several orders of magnitude larger than the molecular length scale and about 10^{-2} to 10^{-1} times the convective thermal length scale ω/U for their experiments. This thesis does not present a mechanism that mitigates the heat flux singularity; however, it uses Schiaffino and Sonin's estimates for λ in its model for the fluid dynamics of the near contact line region (Chapters 4 and 6).

The ω/U length scale mentioned above plays an important role in the molten dynamic contact line problem. This characteristic dimension provides an order of magnitude estimate of the penetration depths of the thermal fronts associated with the fusion interface (which is exactly at T=T_f, if we disallow the possibility of under-cooling) into the liquid and solid near the advancing molten contact line. During quasi-steady spreading the thermal front that advances ahead of the molten contact line is roughly of thickness ω/U and resembles a traditional thermal boundary layer far behind the contact line (Figure 2.4). Outside the thermal layer the target temperature tends toward its far-field value T_r. The penetration of the T_f thermal layer into the liquid is considerably more complex, because the details of the fluid flow and geometry of the fluid "wedge"
are important in determining the temperature field in the liquid. As sketched in Figure 2.4, the thickness of the layer along the free surface is $\alpha/U \cdot f(\theta_0, \theta_1)$, where $f(\theta_0, \theta_1)$ is an undetermined geometric function. The $T_f$ thermal layer in the liquid transitions to a boundary layer type behavior far from the contact line. The temperature approaches $T_o$ in the liquid far from the fusion interface.

2.2.2 The Velocity-Angle Relationship for the Molten Contact Line

Schiaffino and Sonin showed that their force-fed microdrop deposition experiments appear to obey a restricted form of Hoffman's law. In these experiments a modified ink-jet print head was used to dispense a barrage of molten microcrystalline wax ($T_f=90^\circ$C) drops onto a large wax target maintained at $T_i=80^\circ$C. They measured the footprint radius $R(t)$ of the "puddle" formed by the microdrops, and estimated the apparent contact angle $\theta_0(t)$ during spreading by assuming the drops were perfectly hemispherical during spreading. The empirical velocity-angle relationship ($\theta_o$ vs. $dR/dt$) for their experiments appears in Figure 2.5. The solid line in the Figure represents Hoffman's law with $\theta_e=0^\circ$ and $\kappa_f=1.3 \cdot 10^{-2}$ rad$^3$. 

Figure 2.4 During quasi-steady flow the penetration of the thermal front associated with the fusion interface into the liquid and solid scales with the $\alpha/U$ length scale.
Figure 2.5 Schiaffino and Sonin's data for force-fed microcrystalline wax drop deposition appear to obey Hoffman's law with $\theta_r=0^\circ$. $T=80^\circ\text{C}$ for the experiments, and the drops were assumed to maintain perfect hemisphericity during the spreading process.

This plot represents the first attempt to quantify the velocity-angle relationship for the molten dynamic contact line and requires several comments. First, the velocity and angle measurements for these experiments are not independent. Measurement independence is important because the advancing apparent contact angle should differ slightly from that of a perfect hemisphere (an equilibrium configuration). Second, Hoffman's law should not apply when the molten contact line is near arrest. In the near-arrest limit $\theta_a \to \theta_c$, so the geometry of the near contact line region is markedly different from that considered in the derivation of Hoffman's isothermal law.

Any new theory for the velocity-angle relationship for the molten dynamic contact line must take into account the shape of the solidification front, especially near the contact line where viscous forces are large. Unfortunately, this is exactly where the calculations for the shape of the solidification front break down due to the heat flux singularity. In this thesis we assume, as did Schiaffino and Sonin, that the solidification front has a constant angle $\theta_i$ to a distance $r=\lambda$ from the molten contact line. This assumption greatly simplifies the geometry of the molten contact line region, and facilitates the development of a the velocity-angle relationship for this case.

In general the governing differential equations that lead to the velocity-angle relationship require a numerical solution. However, when $\theta_a \to \theta_i$ (the near-arrest limit) an analytical asymptotic expression for the velocity-angle relationship is derived. When $\theta_a \gg \theta_i$ the governing equations
reduce to Hoffman's law. The new theoretical results compare favorably with data obtained for millimeter scale molten drop deposition experiments.

2.3 Fundamentals of Molten Drop Deposition Experimentation

In our experiments individual molten drops with radii on the order of 1 mm are deposited onto large, solid, subcooled targets of the same material. Upon impact with the target, the drop spreads outward under the influence of inertial and capillary forces until the footprint arrests due to solidification. The bulk of the drop solidifies over a much longer time scale.

Relevant dimensionless parameters for the molten contact line problem are discussed in Schiaffino and Sonin (1997a). The parameters most relevant to this work are: 1. the Bond number $Bo (Bo=\rho ga^2/\sigma$, where $\rho$ and $\sigma$ are the fluid's density and surface tension, $g$ is the acceleration of gravity, and $a$ is the drop radius), 2. the Weber number $We (We=\rho V^2 a/\sigma$, where $V$ is the drop freefall velocity at impact), 3. the Ohnesorge number $Z (Z=\mu/(\rho \sigma a)^{1/2}$ where $\mu$ is the absolute viscosity of the fluid), 4. the Stefan number $S (S=c(T_f-T_s)/L$, where $c$, $T_f$, and $L$ are the solid's specific heat capacity, fusion temperature, and latent heat of fusion, and $T_s$ is the target temperature), and 5. the dimensionless parameter $\beta (\beta=(T_s-T_f)/(T_f-T_s)$, where $T_s$ is the drop temperature). The capillary number $Ca (Ca=\mu U/\sigma$, where $U$ is the spreading velocity) was introduced earlier in this Chapter.

In the present experiments $Bo$ ranges from order $10^{-1}$ to $10^0$, $We$ ranges from order $10^{-2}$ to $10^0$, and $Z$ is always smaller than $10^{-1}$. This set of parameters generally places the experiments completely inside or just on the border of Schiaffino and Sonin's "inviscid, capillarity-driven" spreading regime (1997a). In this regime the characteristic (inertial) spreading time is $\tau_\text{inertial}=(\rho a^3/\sigma)^{1/2}$ and the associated spreading velocity is of order $U_\text{inertial}=(\sigma/\rho a)^{1/2}$. The thermal parameter $S$ is the primary control parameter for the experiments and ranges from 0 to about 0.7. Since Schiaffino and Sonin found that $\beta$ has only a weak affect on the arrest conditions for a molten contact line, we generally kept $T_s-T_f$ constant during the experiments and allowed $\beta$ to vary as $S$ was adjusted. The characteristic time associated with complete drop solidification is $\tau_{\text{solidification}}=(a^2/\alpha)S^{-1}$ ($\alpha$ is the thermal diffusivity), which is typically several orders of magnitude longer than the time scales for spreading and arrest.

Millimeter scale drops were dispensed from one of three devices: a heated glass pipette, a pendant drop deposition system, or a microsyringe. Detailed descriptions of these devices and their use appear later in the thesis, but several general features of these systems deserve comment here. The heated glass pipette, which is essentially a thermally controlled eye-dropper, performs well over an exceptionally wide temperature range. It produces well-formed drops for fluids that do not wet glass, but the drop size and impact $We$ are difficult to control. The pendant drop dispenser is a heated
crucible with a small drain hole that allows molten drops to fall under their own weight toward the target below. It functions well over a wide range of temperatures, but works best for fluids that partially wet the crucible surface. The drop size is extremely repeatable and the impact $We$ may be controlled by adjusting the free-fall distance of the drop. The microsyringe is reliable for dispensing fluids at moderate temperatures (say, $T_o<60^\circ$C). It produces repeatedly sized drops, and the impact $We$ may be controlled by adjusting the drop free-fall distance. However, some fluids (microcrystalline wax, in particular) wet the outer diameter of the syringe needle and did not detach from the needle. All of these techniques produce drops that spread "naturally" on the target; they spread under the influence of the forces associated with impact, capillarity, inertia, and gravity until they reached their arrest configuration.
Chapter 3

Molten Drop Deposition Experiments Part I: Experimentally Determining Drop Geometry After Arrest

Millimeter scale molten drops were deposited onto sub-cooled solid targets and the post-arrest drop geometry was measured. This Chapter discusses the experimental methods, presents the empirical results, and compares the findings to available data for these types of experiments. The Chapter is organized as follows: §3.1 molten solder on solid solder, §3.2 molten octacosane on solid octacosane, and §3.3 molten octacosane on glass, both clean and coated with various self-assembled monolayers (SAMs). In §3.1 and §3.2 the post-arrest measurements include the apparent contact angle $\theta_a^*$ and the dimensionless footprint size $R'/a$. In §3.3 only measurements of $\theta_a^*$ are presented.

3.1 Molten Solder on Solid Solder

A heated glass pipette was used to dispense small molten drops of eutectic solder (63 wt% Sn, 37 wt% Pb; material properties for 60 wt% Sn, 40 wt% Pb solder appear in Appendix A) onto an oxidized solid solder target (Figure 3.1). A charge of molten solder was drawn from below the surface of a pool of the molten liquid. The pipette was then positioned directly above the target and the molten drop was ejected onto the surface. The solder drop spread, arrested, and solidified. Photos of typical post-solidification drops appear in Figure 3.2. To slow the oxidation of the solder, the experiments were conducted inside a glove box filled with argon gas (oxygen concentration smaller than 5 ppb).

The temperature of the pipette was managed using an automatic temperature controller (Omega CN76000 1/16 DIN Auto-Tune), two cartridge heaters (each rated 100 W), and a type T thermocouple attached to the heated aluminum structure that intimately contacted the pipette. For the experiments the dispenser temperature was approximately 240°C.

The targets were formed in the argon environment of the glove box by over-filling with molten solder a small aluminum cup (about 2 mm deep and 12 mm diameter) cut into the surface of a 6.3 mm thick aluminum plate. The molten solder solidified, forming a slightly curved target that was typically 4 mm thick at its centerline. The targets were exposed to oxidizing environments for varying degrees of time before their use; some were used immediately after they cooled to the desired temperature, and others were removed from the glove box and placed on a 150°C hot plate in the open air for a fixed period of time (ranging from about 10 to 90 hours) before being returned to the
glove box for drop deposition. The target surface oxide thickness was estimated using Auger surface analysis after the experiments were completed (see below).

During an experiment the target was placed on a large aluminum hot plate (3 cm x 5 cm x 6 cm) whose temperature $T_p$ was measured using a type T thermocouple and controlled using a second
Omega controller and two additional cartridge heaters (rated at 100 W each). The thermal contact resistance between the hot plate and the aluminum target holder caused the measured value of the hot plate surface temperature to differ from the solder target surface temperature. Additional temperature measurements established the steady-state relationship between \( T_p \) and \( T_n \), and provided a correlation to estimate \( T_i \) for each experiment. Tests were completed for two values of \( S \) (\( S=c(T_f-T_i)/L=0.02 \) and 0.07) and at least seven distinct oxidation thicknesses.

The arrest angle \( \theta_a^* \) and footprint size \( R^* \) were measured for each of the solidified drops. We were unable to obtain acceptable measurements of the radius \( a \) of the spherical solder drop during free fall, so could not immediately write the footprint size in dimensionless form \( R^*/a \). An estimate of \( a \) for each experiment was obtained using

\[
a = \left[ \frac{R^*}{4} \left( \frac{1 - \cos \theta_a^*}{1 + \cos \theta_a^*} \right)^{3/2} \right]^{1/3},
\]

which assumes that the drops do not contract upon freezing and are perfect hemispheres resting atop a flat target. For the solder drop experiments the value of \( a \) calculated from (3.1) ranges from 1.0 to 1.7 mm. This value corresponds to \( Bo=\rho g a^2/\sigma=0.2 \) to 0.5, where \( \rho \) is the solder density, \( g \) is the gravitational constant, and \( \sigma \) is the surface tension coefficient. Since \( Bo \) is considerably smaller than unity, the assumption of hemispherical drops is reasonable and (3.1) may be recast as

\[
\frac{R^*}{a} = \left[ \left( \frac{1 + \cos \theta_a^*}{1 - \cos \theta_a^*} \right)^{3/2} \right]^{1/3}
\]

to estimate \( R^*/a \) for each experiment. The results for \( \theta_a^* \) and \( R^*/a \) vs. \( S \) appear in Figure 3.3 and 3.4. Schiaffino and Sonin's \( R^*/a \) data for mercury and water drop deposition are shown in Figure 3.4 for comparison. Additional data points are required to assess the appropriateness of a one-third power law fit for the solder.

An Auger surface analysis system (Perkin Elmer Model 660 Scanning Auger Microprobe) equipped with an ion sputtering gun was used to analyze the surface chemistry of the solid solder targets. Transport of the targets to the Auger system was accomplished with due caution: targets that were not subjected to the open air oxidation treatment were transported in a small, sealed environmental chamber directly from the argon environment to the ultra-high vacuum of the Auger system. Once inside the Auger system the surface chemistry of small regions on the target surface was analyzed to assess the elemental concentrations of lead, tin, and oxygen. Layers were progressively sputtered from the sample using a 2.0 keV Ar\(^+\) ion beam (current density=5 \( \mu \)A/cm\(^2\)), and the surface chemistry was re-evaluated after each sputter cycle. The procedure was repeated until the characteristic signature for oxygen vanished, thus indicating the maximum penetration.
Figure 3.3 $\theta^*$ vs. $S$ for solder drop deposition on a solid solder target in an argon environment.

Figure 3.4 $R^*/a$ vs. $S$ for solder drop deposition on solid solder targets in an argon environment. Schiaffino and Sonin's (1997a) $R^*/a$ data for mercury and water are shown for comparison.
depth of the oxide layer. Typical signature plots for tin- and lead-rich regions of the target appear in Figures 3.5 and 3.6.

Analysis suggests that tin oxide (SnO$_2$) forms on the surface of both the lead- and tin-rich regions. The absence of a lead signature on the surface suggests that lead oxide is not present in significant concentrations. In the tin rich region (see Figure 3.5) the dual peaks of the tin oxide signature shift to slightly higher energies as the surface chemistry shifts from tin oxide to elemental tin. The lead signature becomes visible once the oxide layer is sufficiently penetrated. The lead-rich region also shows the dual peaks of tin oxide on the surface (see Figure 3.6). As the oxide is sputtered away, the tin signature gradually vanishes as the lead signature grows in prominence. From these plots we estimate the number of sputter cycles required to penetrate the oxide for a given sample.

The sputter rate for pure SnO$_2$ may be estimated using correlations from the literature (see Kelly and Lam, 1973; Sigmund, 1969), but since the surface chemistry changes dramatically as a function of depth, it is risky to assume a constant sputtering rate for all sputter cycles. Recognizing this weakness, we estimate that for pure SnO$_2$ the sputter rate is about 0.34 nm/cycle, which suggests that the oxide layer is from 3 to 6 nm thick on the targets studied. These estimates and the surface composition results agree favorably with the oxide structure reported in Wassink (1989), who states that the oxide coating for 60 wt% Sn, 40 wt% Pb exposed to 250°C air for 15 minutes consists of three layers: "(i) a thin outer layer of SnO$_2$ of thickness about 2 nm; (ii) a layer of SnO, mixed with finely dispersed metallic lead; and (iii) a transition layer of SnO and metallic tin and lead." (p. 175)
Figure 3.5 Elemental signature plots for the tin-rich region of a typical solder target. The left third of each plot shows the peak for oxygen, the center third the dual peaks for tin, and the right third the peak for lead. The lower plot is identical to the upper one, except that the "Cycle" axis is reversed.
Figure 3.6 Energy signature plots for the lead-rich region of a typical solder target. The left third of each plot shows the peak for oxygen, the center third the dual peaks for tin, and the right third the peak for lead. The lower plot is identical to the upper one, except that the "Cycle" axis is reversed.
Figure 3.7 depicts the arrest angle $\theta_a^*$ as a function of the approximate number of sputter cycles required to penetrate the oxide layer. When the tin and lead rich regions of a single target require different numbers of sputter cycles to penetrate the oxide layer, the plot shows the average number of cycles required. Targets subjected to identical oxidation treatments are assumed to have equal oxide layer thicknesses. The plot suggests that the arrest angle $\theta_a^*$ is nearly independent of the oxide layer thickness over the range considered. Since interfacial properties are approximately constant for all samples (they all have nanometer-scale oxide layers), our findings imply that the oxide layer does not significantly affect the heat transfer from the molten drop to the target. Specifically, thermal diffusion through the thin oxide layer occurs much faster than other relevant transport processes, and the thermal resistance of the layer must be negligibly small.

![Graph showing $\theta_a^*$ vs. number of sputter cycles to penetrate oxide](image)

**Figure 3.7** $\theta_a^*$ vs. average number of sputter cycles required to penetrate the oxide layer on the solder target.

### 3.2 Octacosane on Solid Octacosane

Millimeter scale drops of molten octacosane ($C_{28}H_{58}$) were deposited onto solid octacosane targets, and the experiments were observed using a CCD camera outfitted with a microscope objective lens. For each test we obtained the values at arrest of the apparent contact angle $\theta_a^*$ and the footprint size $R^*$. Photos of typical post-solidification drops appear in Figure 3.8. The depression
of the tops of the drops (especially evident in the $S=0.29$ case) results from the difference in density between the liquid and solid phases of octacosane. The shape of the dimple depends on the dynamics of the formation and collapse of the solid skin that forms on the drop surface due to heat loss to the air.

To produce the molten drops, small grains of solid octacosane were placed in a heated aluminum crucible (Figure 3.9). As the material melted it flowed through a small hole at the bottom of the crucible and accumulated at the tip in the form of a pendant drop. The drop increased rapidly in size until it fell under its own weight toward the solid target. The snap-off process led to the formation of a satellite drop, whose consistent size and presence in all of the experiments suggests the high level of repeatability associated with the drop production method. The entire "melt and dispense" process took about 2 seconds to complete. If the drop did not fall in this allotted time, the flow of molten material to the cone tip was likely obstructed by an air bubble in the crucible and the test was aborted. The temperature of the crucible was controlled using an automatic temperature controller, a 100 W cartridge heater, and a type T thermocouple bonded to the surface of the aluminum near the cone tip.

One solid octacosane target was formed by filling with molten octacosane a shallow trough (2 mm x 22 mm x 70 mm) cut into the surface of a 6.3 mm thick aluminum plate. The molten liquid was allowed to solidify in open air, and the solidified surface was rough to the touch (quantification of the surface roughness appears below). For another target a small piece of an overhead transparency was placed on the surface of the molten pool of octacosane, and the octacosane was allowed to solidify. The transparency was then peeled away to expose a target surface that was smooth to the touch (quantification below).
During an experiment the target was placed on a large aluminum hot plate (1 cm x 9 cm x 21 cm) that was heated by flexible resistive heaters (delivered about 80 W total). Thermally conductive paste (GC Electronics Type Z9 heat sink compound) was applied between the aluminum target holder and the hot plate to ensure good thermal contact between the metal surfaces. At the time of drop deposition, the temperature of the crucible tip and the hot plate surface were recorded.

Since we are interested primarily in the target surface temperature $T_n$, additional temperature measurements were made to establish an empirical relationship between $T_p$ and $T_n$. The target surface temperatures predicted using this relationship agreed well with predictions made using a one-dimensional model for heat transfer from the hot plate to the target surface. The temperature drop across the octacosane, $T_p-T_n$, ranged from approximately 1°C at $T_p \sim 33^\circ C$ to nearly 4°C when $T_p \sim 61^\circ C$ (when the edges of the octacosane target in contact with the aluminum target holder were on the verge of melting).

For pendant drops $Bo$ is always approximately equal to unity so we may not safely use the hemispherical equation (3.2) to estimate $R' / a$ directly from the $\theta_0^*$ data. Instead, we measure $R'$ and independently calculate $a$ by measuring the increase in mass $\Delta m$ of a glass slide due to the deposition of $n$ octacosane drops on the slide. We then have that

$$a = \left( \frac{3}{4\pi} \frac{\Delta m / n}{\rho} \right)^{1/3},$$

(3.3)
where $\rho$ is the density of the liquid octacosane. Equation (3.3) assumes that the $n$ drops are equally sized, and that the total mass contributed by the satellite drops is negligibly small compared to the mass of the millimeter scale drops. Based upon two independent measurements ($n=20$ for one slide and $n=21$ for another), we estimate that $a=1.85$ mm, which corresponds almost exactly to $Bo=\rho g a^2/\sigma=1$.

The arrest angle $\theta_a^*$ and the dimensionless footprint size $R^*/a$ are shown in Figures 3.10 and 3.11 as functions of $S$. The plots suggest that the arrest variables are only weakly dependent on $S$ for the range considered. We expect that $\theta_a^*$ will decrease aggressively as $S\to 0$, but could not obtain any data for $S<0.06$ using this experimental set-up (the periphery of the octacosane target started to melt when $S\sim 0.05$). $\theta_a^*$ for octacosane is surprisingly large over the range of $S$ considered, compared to similar data for millimeter scale wax drop deposition (see §5.1). This disparity is likely related to the different thermal and interfacial properties of octacosane and wax. Octacosane is a pure substance and releases its latent heat at a distinct fusion temperature, whereas microcrystalline wax is an "alloy" of several materials and releases its latent heat over a wide temperature range (Torresola, 1998).
Figure 3.10 $\theta^*_o$ vs. $S$ for octacosane drops deposited on solid octacosane surfaces. $\theta^*_o$ vs. $S$ data for millimeter scale wax drop deposition from §5.1.3 are shown for comparison.

Figure 3.11 $R'/a$ vs. $S$ for octacosane drops deposited on solid octacosane surfaces.
Figures 3.10 and 3.11 suggest that the impact of surface roughness on the measured values of $\theta_0^*$ and $R'/a$ appears to be insignificant. To better understand the reasons for this observation, we examined the "rough" and "smooth" surfaces using a surface profilometer (Tencor model P10). The instrument precisely maps the surface topography of a sample using an extremely sensitive, diamond tipped stylus. A representative trace of the rough surface is shown in Figure 3.12. The data points are sampled at 8 $\mu$m intervals, and this point spacing is much smaller than the wavelengths of all relevant surface features.

From the $h$ vs. $x$ data the root-mean-square roughness, $R_{rms}$, is (see Slocum, 1992)

$$ R_{rms} = \sqrt{\frac{1}{L} \int_0^L y^2(x)dx}, $$

(3.4)

where $y(x)$ is the deviation of the data from a best fit straight line of length $L$. Splitting the 20 mm trace into five 4 mm segments (roughly the footprint size of a drop), Equation (3.4) gives $R_{rms}=7.7$ to 22 $\mu$m. For the five calculated values of $R_{rms}$, the average is 12.4 $\mu$m with a standard deviation of 5.0 $\mu$m.

The angle the surface makes with the horizontal at data point $i$ is approximately

$$ \theta_i = \tan^{-1}\left(\frac{h_{i+1} - h_{i-1}}{2\Delta x}\right). $$

(3.5)

The values of $\theta_i$ for the data of Figure 3.12 appear in histogram form in Figure 3.13. The average angle is 0.0032° (the target is not perfectly leveled) with a standard deviation of 4.2°; approximately 98% of all angles fall in the range ±10°.

Similar results for the "smooth" target appear in Figures 3.14 and 3.15. The 8 $\mu$m point spacing was small enough to resolve the salient surface features. Being careful to avoid the two cracks in the surface (near $x=3.5$ and 16 mm), the data are divided into four 4 mm segments. For these segments $R_{rms}$ ranges from 1.9 to 4.1 $\mu$m, with an average value of 3.0 $\mu$m and a standard deviation of 0.9 $\mu$m. The average angle that the surface makes with the horizontal is -0.0052° with a standard deviation of 0.54°; approximately 98% of all angles fall in the range ±1.6°.

Since the characteristic angles for both the rough and smooth surfaces are much smaller than the observed arrest angles, it is reasonable to expect that surface roughness will have only a small effect on the arrest conditions. For surface features characterized by large angles (say, 90°), Liu (1998) found that drop spreading dynamics are dramatically affected.
Figure 3.12 The profilometer provides $h$ vs. $x$ data for the "rough" target.

Figure 3.13 Histogram showing the distribution of surface angles (from the horizontal) for the data of Figure 3.12.
Figure 3.14 The profilometer provides $h$ vs. $x$ data for the "smooth" target.

Figure 3.15 Histogram showing the distribution of surface angles (from the horizontal) for the data of Figure 3.14.
3.3 Octacosane on Glass

The pendant drop dispenser described in §3.2 was used to dispense octacosane drops onto glass microscope slides. Some of the slides were simply cleaned with acetone before drop deposition, but others were chemically treated to produce a self-assembled monolayer (SAM) on the surface (Figure 3.16). The molecular structures of the SAM molecules after assembly appear in Figure 3.17, and we adopt the A, B, and C nomenclature of the Figure for our discussion. Since coatings A and B are both methyl terminated, their surface energies are similar. Coating C has a markedly different surface energy since the molecules are CF$_3$ terminated.

![Individual molecule](image)

**Figure 3.16** Chemical processing of the glass slide causes a close-packed monolayer to self-assemble on the surface. Figure adapted from Wasserman, et al (1989).

![Coating structures](image)

**Figure 3.17** Post-assembly molecular structure of the self-assembled monolayers applied to the glass targets. Coating A is formed by treating the glass with octadecyltrichlorosilane, B with methyl [(1-trichlorosilyl)undec-11-yl] triethylene glycol, and C with heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane (Lee and Laibinis, 1998; Lee, 1998).
The glass targets (1 mm thick) were placed on the large aluminum hot plate (1 cm x 9 cm x 21 cm). Thermally conductive paste was applied to ensure good thermal contact between the aluminum and the glass. Assuming one-dimensional heat transfer and perfect thermal contact between the aluminum and the glass, the steady-state surface temperature of the glass slide should be within a fraction of a degree of the hot plate surface temperature. Thus, \( T_p \) was used to control the temperature of the glass target, and it is acceptable to assume \( T_p = T_i \) in the calculation of \( S \). For all of the experiments \( T_o - T_f = 10^\circ C \) (\( \beta = 1 \) when \( S = 0.15 \)), and the ambient temperature ranged from 20 to 25\(^\circ\)C. The value of \( We \) was typically of the order of 0.01, and drop snap-off from the crucible occurred from 33 to 67 ms after impact. Arrest typically occurred about 100 ms after impact, visible surface skin formed over the bulk of the drop about 5 to 7 seconds after impact, and complete solidification occurred on much longer time scales.

The measured arrest angles for the octacosane on glass experiments appear in Figure 3.18. In many of the deposition experiments, the contact line "pinned" at various locations around the periphery of the drop, thus resulting in a slightly irregular footprint shape. We do not offer an explanation for this behavior, but note that it may be responsible for the large amount of scatter in the data. For data points with \( S < 0, \theta_a^* \) corresponds to the equilibrium angle \( \theta_e \) for molten octacosane on the glass target. The equilibrium angles range from 10 to 20\(^\circ\) on clean glass, coating A, and coating B. The equilibrium angle is approximately 79\(^\circ\) for the CF\(_3\) terminated coating C.

Figure 3.19 shows expected trends for the \( \theta_a^* \) vs. \( S \) data. In the limit of \( S \to 0 \), the arrest angle must approach \( \theta_e \), which is a function of the surface chemistry of the target. For these experiments surface chemistry plays an important role in determining \( \theta_a^* \) up to roughly \( S \approx 0.2 \). For \( S \) larger than about 0.2, the value of \( \theta_a^* \) is (except for scatter) nearly independent of \( S \).
Figure 3.18 \( \theta^* \) vs. \( S \) for millimeter scale octacosane drops deposited on glass surfaces. The fusion temperature is indicated by the vertical line \( S=0 \).

Figure 3.19 \( \theta^* \) vs. \( S \) for the octacosane on glass experiments. Expected trends are sketched over the data.
3.4 Summary of Experiments Part I

This Chapter presents experimental results for the arrest geometry of millimeter scale molten drops for solder on solid solder, octacosane on rough and smooth octacosane targets, and octacosane on glass targets prepared with different surface chemistries.

The solder experiments show that the presence of a thin (~3 to 6 nm) oxidation layer on the surface of the target does not significantly affect the arrest angle \( \theta_a^* \) and dimensionless footprint radius \( R^*/a \). The interfacial properties of the oxidized targets should be approximately constant, so our findings suggest that the oxide layer has a negligible effect on heat transfer from the molten drop to the solid target.

The octacosane on octacosane experiments show that octacosane, which has a distinct fusion temperature and latent heat, arrests when the apparent contact angle is large compared to that of wax drops deposited under the same conditions. Detailed surface analysis of the octacosane targets reveals that both the "rough" and "smooth" surfaces are characterized by surface angles that are small compared to the measured arrest angles. Consequently, we do not observe significant differences between the arrest angles and footprint sizes for the two different targets.

The deposition of octacosane drops on glass treated with various self-assembled monolayers suggests that under certain conditions, surface chemistry plays an important role in determining molten drop arrest conditions. For roughly \( S<0.2 \) the equilibrium angle \( \theta_e \), which is a property of the octacosane/SAM system, is important in determining the drop arrest conditions. For larger \( S \), however, the arrest angles are nearly independent of both \( S \) and \( \theta_e \).
Chapter 4

Theoretical Investigation of the Velocity-Angle Relationship for the Molten Contact Line

In the past two decades a significant body of literature has addressed the motion of a liquid’s contact line over a solid. These works sought to develop and verify the relationship between the apparent contact angle $\theta_a$ of a free surface (the observed angle measured at a small height $H$ above the solid surface) and the speed of motion $U$ of the contact line. Several forms of this spreading law have been suggested, one of the simplest being the one suggested in the works of Hoffman, Tanner, and particularly Voinov (Hoffman, 1975; Tanner, 1979; Voinov, 1976, 1978; see also Chesters and Van der Zanden), who proposed that

$$Ca = \kappa_H \left( \theta_a^3 - \theta_m^3 \right).$$

(4.1)

Here $Ca = \mu U/\sigma$ is the capillary number, $\theta_m$ is the slope of the free surface evaluated at the molecular scale $h_m$, and $\kappa_H$ is a coefficient that depends weakly upon the length scale of the observation of $\theta_a$. Voinov’s analysis gives the $\kappa_H$ dependence as

$$\kappa_H = \frac{1}{9\ln(H/h_m)}.$$  

(4.2)

For Hoffman’s empirical data a "universal" value of $\kappa_H = 1.3 \cdot 10^{-2}$ rad$^3$ may be used to obtain good agreement over a wide range of conditions. The Hoffman-Tanner-Voinov law has found wide applicability in moving contact line theory and experiment, and variations of it appear throughout the literature on moving contact lines, drop spreading, and rivulet flows.

This Chapter develops an analog to Hoffman’s law for the advancing molten contact line. We derive the governing equations for a simple model of the near contact line region, and develop analytic expressions that describe limiting behavior of these equations. The governing equations are also solved numerically to examine the sensitivity of the equations to relevant dimensionless parameters.

4.1 Order-of-Magnitude Scaling Analysis of the Isothermal Dynamic Contact Line Problem

To better understand the fundamental physics that underpins (4.1), we investigate the two-dimensional wedge flow near the contact line (see Figure 4.1). We focus on the region between the contact line and the point (a) where the liquid surface angle is $\theta_a$ and the fluid height is $H$. $H$ is the
minimum length scale at which $\theta_e$ may be seen by an observer. We assume a quasi-steady contact line advance speed $U$, and fix our reference frame on the contact line so that the solid sweeps to the left (refer to the close-up of the near contact line region in the Figure). The fluid obeys the continuity and momentum equations,

$$\vec{V} \cdot \vec{V} = 0$$

(4.3)

and

$$\rho \frac{D\vec{V}}{Dt} = \rho \ddot{g} + \vec{V} \cdot \tau_y.$$  

(4.4)

As shown in Figure (4.1), we affix the 2-D polar coordinate system $(r, \varphi)$ at the contact line and write the continuity equation as

$$\frac{1}{r} \frac{\partial}{\partial r}(rv_r) + \frac{1}{r} \frac{\partial}{\partial \varphi}(v_\varphi) = 0.$$  

(4.5)

The $r$ momentum equation is

$$\rho \frac{Dv_r}{Dt} = \rho g \sin \varphi - \frac{\partial P}{\partial r} + \mu \left( \nabla^2 v_r - \frac{v_r}{r^2} - \frac{2}{r^2} \frac{\partial v_\varphi}{\partial \varphi} \right),$$  

(4.6)

Figure 4.1 The flow field in the wedge domain close to the isothermal contact line.
where
\[ \nabla^2 = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \varphi^2} \] (4.7)

\[ \frac{Dv_r}{Dt} = \frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\varphi}{r} \frac{\partial v_r}{\partial \varphi} - \frac{v_\varphi^2}{r}. \] (4.8)

Introducing the two-dimensional form of the Young-Laplace relationship, which relates the pressure drop \( P - P_\infty \) across the free surface to the curvature \( q \) of the surface, gives
\[ P - P_\infty = q\sigma. \] (4.9)

Here, \( P_\infty \) is the ambient pressure and
\[ q = -\frac{\partial \theta}{\partial r} \] (4.10)

for a surface whose curvature varies weakly with distance from the contact line. Equation (4.10) is valid if \( h/\theta \cdot \partial \theta/\partial h << 1 \); the interested reader may consult the references (e.g. Voinov, 1976, 1978; Boender, et al, 1991) for further discussion of the wedge-flow assumption. Note that (4.9) defines \( P > P_\infty \) when \( q > 0 \), so that a drop at rest on a flat surface (\( \partial \theta_c/\partial r < 0 \)) is characterized by a positive curvature.

We construct approximate scaling relationships for the governing equations by denoting "of the order of" by the symbol \( \sim \). Since \( \Delta \varphi \sim \theta_a \) (4.5) is (to an order of magnitude)
\[ v_r \sim \frac{v_\varphi}{\theta_a}. \] (4.11)

We further limit the order-of-magnitude analysis to small angles (\( \theta_a << 1 \)) so that \( \Delta r/H/\theta_a \) and \( v_r \sim U \). With these results we use (4.9), (4.10), and (4.11) to represent (4.6) as (to an order of magnitude)
\[ \rho \left[ \frac{U}{\tau} + \frac{\theta_a U^2}{H} + \frac{\theta_a U^2}{H} \right] \sim \rho \theta_a \frac{\sigma \theta_a^3}{H^2} + \mu \left[ \frac{\theta_a U^2}{H^2} + \frac{U}{H^2} + \frac{\theta_a U}{H^2} + \frac{\theta_a U}{H^2} \right] \] (4.12)

where \( \tau \) denotes a transient time scale. Since \( \theta_a << 1 \) the final convective term may be neglected with respect to the other convective terms, and the first, third, and fourth viscous terms may be neglected with respect to the second.

Of most interest is the case in which the second viscous term in (4.12) balances the surface tension term, and all other terms are negligible. For this situation to be valid, we require that 1. the
flow is quasi-steady on both local and system scale dimensions (i.e. \( \text{Re}_H = \rho U H / \mu \ll \theta_a \), \( \text{Re}_a = \rho U a / \mu \ll 1 \), \( \tau \rho H^2 / \mu \ll (\rho a^3 / \sigma)^{1/3} \)), and 2. the length scale \( H \) is much smaller than the capillary length (i.e. \( H / (\sigma / \rho g)^{1/2} \ll \theta_a, (Ca / \theta_a)^{1/2} \)). When these conditions are satisfied, we immediately obtain from (4.12) the scaling of the Hoffman-Tanner-Voinov law:

\[
Ca = \frac{\mu U}{\sigma} \sim \theta_a^3.
\]

The numerous restrictions imposed on (4.12) to produce (4.13) are, in fact, satisfied during a wide spectrum of moving contact line problems.

### 4.2 Modeling the Advancing Molten Contact Line

The molten contact line problem is fundamentally different from the isothermal one because the liquid is molten and the solid is initially maintained at a temperature below the fusion point of the liquid. The molten liquid therefore freezes from below as it spreads over the solid. As argued by Schiaffino and Sonin (1997b and 1997c), this situation leads to the formation of a solidification front underneath the liquid as it advances over the solid (Figure 4.2). Using the methodology of previous researchers (Voinov, Tanner, and Chesters and Van der Zanden), we construct a model for the flow in the liquid region near the moving molten contact line. The goal of this analysis is to develop a relationship that predicts the apparent contact angle \( \theta_a \) as a function of \( Ca \) and relevant system parameters.

![Figure 4.2](image)

**Figure 4.2** A solidification front forms underneath a molten liquid advancing at a quasi-steady speed \( U \) over a solid subcooled substrate. Drawing not to scale.

In constructing the model we use Schiaffino and Sonin's hypothesis about the geometry of the solidification front. In their work they performed a numerical calculation to determine the shape of the solidification front. They discovered that the conventional continuum equations and boundary
conditions resulted in an unbounded heat flux at the contact line. The singularity matched in form the one described by Anderson and Davis (1994). To offer a consistent explanation of their empirical findings, Schiaffino and Sonin hypothesized (for microcrystalline wax, water, and mercury) that an unidentified mechanism bounded the heat flux for distances from the contact line \( r \) smaller than \( \lambda \sim 10^{-7} \) to \( 10^{-6} \) m. In this inner region, they argued that the slope of the solidification front was constant and equal to \( \theta \); in the outer region the solidification front followed the shape predicted by continuum calculations.

We make use of the inner and outer regions suggested by Schiaffino and Sonin in formulating the molten contact line fluid dynamics model. In our model the inner region extends from a cut-off length \( h_m \) just larger than molecular dimensions to a point where \( r = \lambda \), and the outer region stretches from \( r = \lambda \) to observable length scales. The two domains are labelled in Figure 4.3. The model is further simplified by assuming that the solidification front has constant thickness in the outer region. This simplification is reasonable because the viscous forces are largest in the inner region (§4.2.1 shows that viscous stress \( \sim 1/r^2 \)), so the geometry of the outer region has only a minor effect on the calculations. The real solidification front has a smooth shape, but we employ a "wedge-step" geometry as a first attempt at understanding the fundamental fluid dynamics of the problem.

![Figure 4.3 Schematic of the near contact line region showing the "wedge-step" model of the solidification front.](image)

### 4.2.1 Derivation of the Differential Equations for \( \theta(h) \)

We begin the derivation of the governing equations by looking exclusively at the inner region. As is standard in isothermal contact line analysis, the lowest-order solution of the flow field
near the contact line is assumed to be well approximated by the solution for Stokes flow in a wedge domain. Following Moffatt (1964), such a flow may be described by similarity solutions of the biharmonic equation
\[ \nabla^4 \psi = 0, \]  
(4.14)
where \( \psi \) is the stream function. For the wedge geometry with polar coordinates \( (r, \varphi) \) the solution assumes the form \( \psi = U f(\varphi) \), where
\[ v_r = \frac{1}{r} \frac{\partial \psi}{\partial \varphi} = U \frac{\partial f(\varphi)}{\partial \varphi} \]  
(4.15)
and
\[ v_\varphi = - \frac{\partial \psi}{\partial r} = -U f(\varphi) \]  
(4.16)
are the velocity components. The boundary conditions for the inner region solution are a prescribed velocity at the solidification front,
\[ v_r \big|_{\varphi=\theta_s} = U \cos \theta_s \]  
\[ v_\varphi \big|_{\varphi=\theta_s} = -U \sin \theta_s , \]  
(4.17)
and vanishing shear and normal flow at the free surface,
\[ v_\varphi \big|_{\varphi=\theta} = 0 \]  
\[ \tau_{r\varphi} \big|_{\varphi=\theta} = 0 . \]  
(4.18)
As described in Moffatt's work, general solutions are limited to those of the form
\[ f(\varphi) = A \cos \varphi + B \sin \varphi + C \varphi \cos \varphi + D \varphi \sin \varphi, \]  
(4.19)
where \( A, B, C, \) and \( D \) are undetermined constants. Substituting (4.19) into (4.14) and applying the boundary conditions (4.17) and (4.18) yields the solution
\[ f(\varphi; \theta, \theta_s) = \frac{-\cos \varphi + 2(2\theta - \theta_s - \varphi) \sin \varphi + 2(\theta_s - \varphi) \sin(2\theta - \varphi) + \ldots}{4(\theta - \theta_s) - 2 \sin[2(\theta - \theta_s)]} . \]  
(4.20)
Figure 4.4 illustrates the dimensionless stream function \( \psi/UR = r/R f(\varphi) \) for typical wedge domains considered. It is important to note that substituting (4.20) into (4.15) and (4.16) gives \( v_r = v_r(\varphi; \theta, \theta_s) \) and \( v_\varphi = v_\varphi(\varphi; \theta, \theta_s) \); that is, the fluid velocity components are self-similar and independent of \( r \).
Figure 4.4 The contour lines indicate constant value of the dimensionless stream function \( \psi/UR = \eta/Re(\varphi) \) for the wedge flow solution on \( r/Re \in [0, 1] \) with \( \theta = \pi/3, \theta_s = \pi/6 \) (left) and \( \theta = \pi/3, \theta_s = 0 \) (right).

The equation of motion in the Stokes flow approximation gives the pressure gradient along the free surface as

\[
\frac{\partial p}{\partial r}_{\varphi=\theta} = \frac{1}{r} \frac{\partial \tau_{\varphi \theta}}{\partial \varphi} \bigg|_{\varphi=\theta},
\]

where

\[
\tau_{\varphi \theta} = \mu \left[ \frac{\partial}{\partial r} \left( \frac{v_{\varphi}}{r} \right) + \frac{1}{r} \frac{\partial v_r}{\partial \varphi} \right].
\]

Using (4.22) and the Stokes flow solutions for the velocities \( v_r \) and \( v_{\varphi} \), (4.21) becomes

\[
\frac{\partial p}{\partial r} \bigg|_{\varphi=\theta} = \frac{4\mu U}{r^2} \sin \theta \frac{\sin \theta}{2(\theta - \theta_s) - \sin[2(\theta - \theta_s)]},
\]

By integrating (4.23) we obtain the pressure distribution in the liquid just below the free surface, based upon the zeroth-order approximation of a wedge-like flow field. For this level of approximation we may safely take \( r = h/\sin \theta \) to obtain the pressure \( P(h) \) as

\[
P(\lambda) - P(h) = 4\mu U \left( \frac{\sin \theta}{h} - \frac{1}{\lambda} \right) \frac{\sin \theta}{2(\theta - \theta_s) - \sin[2(\theta - \theta_s)]},
\]

where \( P(\lambda) \) denotes the value of the pressure at \( r = \lambda \). From the Young-Laplace relationship we have

\[
P(h) - P_{\infty} \approx \sigma \sin \theta \frac{\partial \theta}{\partial h},
\]
so Equations (4.24) and (4.25) yield the following non-linear, first-order differential equation for \( \theta(h) \) for the inner region:

\[
\sin \theta \frac{\partial \theta}{\partial h} = 4Ca \left( \frac{\sin \theta}{h} - \frac{1}{\lambda} \right) \frac{\sin \theta}{2(\theta - \theta_s) - \sin 2(\theta - \theta_s)} + q_\lambda. \tag{4.26}
\]

Here \( q_\lambda = [P_\lambda - P(\lambda)]/\sigma \) is a measure of the curvature associated with the fluid pressure at \( r = \lambda \) and is used to match the inner with the outer solution. Equation (4.26) may be integrated numerically to obtain an expression for \( \theta(h) \) in the inner region for given \( Ca, \theta_s, \) and \( q_\lambda. \) The integration is valid only for \( h \geq h_m, \) because the continuum solution breaks down as the molecular scale is approached.

The technique used for determining the equation for \( \theta(h) \) in the inner region may easily be extended to the outer region. Since in the outer region we assume \( \theta = 0, \) by inspection we write the governing equation based upon our understanding of the derivation of (4.26). For the outer region

\[
\sin \theta \frac{\partial \theta}{\partial h} = 4Ca \left( \frac{\sin \theta}{h} - \frac{\sin \theta_a}{H} \right) \frac{\sin \theta}{2\theta - \sin 2\theta} + q_a, \tag{4.27}
\]

where \( \theta_a \) is the apparent contact angle and \( q_a = [P_\lambda - P(H)]/\sigma \) is a measure of the curvature associated with the fluid pressure evaluated at height \( H. \) Equation (4.27) may be integrated numerically to find \( \theta(h) \) on the outer region for given \( Ca, H, \) and \( q_a. \)

The integration of (4.26) and (4.27) must be completed in a piecewise manner. In one possible solution technique, the outer solution is first performed using given values of \( Ca, H, \theta_a, \) and \( q_a. \) At a distance \( r = h/\sin \theta = \lambda \) from the contact line, the outer solution is halted and the value of the curvature \( q_\lambda = \sin \theta \cdot \partial \theta/\partial h \) is recorded. The quantity \( q_\lambda \) is then input, along with \( \lambda \) and \( \theta_s, \) into (4.26) and the inner region solution is performed. At the molecular scale cut-off length \( h_m, \) the value of the free surface angle \( \theta_m \) is recorded. The final solution may be expressed in terms of dimensionless parameters as

\[
\theta_a = f(Ca; \theta_s, \theta_m, \frac{\lambda}{h_m}; \frac{H}{h_m}, Hq_a). \tag{4.28}
\]

To summarize, we use the Stokes flow solution for a wedge flow, obtain the pressure gradient from the (Stokes flow) equation of motion, and introduce the Young-Laplace equation to obtain a first-order differential equation for the angle of the free surface \( \theta(h). \) Following Voinov, we integrate the force balance before combining the result with the Young-Laplace relationship, and transform a second-order system into a first-order one. Chesters and Van der Zanden differentiated the Young-Laplace equation and then combined the result with the force balance to obtain a second-order differential equation for \( \theta(h). \) Both techniques are strictly valid only for weakly varying curvature and both require the same boundary conditions at the molecular cut-off and in the far-field. We use
the first-order method because it better lends itself to the derivation of approximate analytical solutions in limiting cases.

4.2.2 Two Limiting Solutions of the Velocity-Angle Relationship

Integrating (4.26) and (4.27) over the inner and outer regions produces the \( \theta_a \) vs. \( Ca \) relationship for the molten dynamic contact line. Before delving into full numerical solutions of the equations, we first study their behavior in two limits (Figure 4.5): 1. the case where the solidification angle is negligibly small compared to the apparent contact angle \( (\theta_s \gg \theta_i) \), and 2. the case where the molten contact line is near arrest \( (\theta_a \rightarrow \theta_i) \).

![Diagram of two limiting cases of the molten dynamic contact line model](image)

**Figure 4.5** The two limiting cases of the molten dynamic contact line model: 1. large fluid wedge angle compared to solidification angle, and 2. small fluid wedge angle compared to solidification angle.

4.2.2.1 Hoffman-Tanner-Voinov Law Limit \( (\theta_s \gg \theta_i) \)

First we examine the case where the solidification angle is negligibly small compared to the other angles in the system. In this limit \( \theta_i \) simply drops out of the inner region equation (4.26), and the outer region equation (4.27) may be used down to the molecular scale cut-off \( h_m \). For small far-field curvature \( q_a \) and \( H/h_m \gg 1 \), the \( \sin \theta_s/H \) term may be dropped with a negligible sacrifice in accuracy, and the equation transforms exactly into the one investigated by Voinov

\[
\int_{\theta_s}^{\theta_i} \frac{2\theta - \sin 2\theta}{\sin \theta} \, d\theta = \int_{h_m}^{H} 4Ca \frac{dh}{h}.
\]  

(4.29)

Voinov showed that an approximate solution for the left-hand side of (4.29) may be obtained using the first term of the series expansion of the integrand.
\[
\frac{2\theta - \sin2\theta}{\sin\theta} = \frac{4}{3} \theta^2 - \frac{2}{45} \theta^4 + O\left(\theta^6\right).
\] (4.30)

This first term approximation is valid when \(\theta \ll 30\) (it is exact when \(\theta = 0\)), and leads to Hoffman's law as given by (4.1) and (4.2). Voinov found that using only the first term of (4.30) in (4.29) gives error less than 1% up to \(\theta_a = 3\pi/4\).

### 4.2.2.2 Near-Arrest Law Limit \((\theta_a \to \theta_s)\)

We now develop the limiting solution for fluid wedge angle \(\theta - \theta_s\), that is small compared to the solidification angle \(\theta_a\). For simplicity we again investigate the case where the far-field curvature \(q_a\) is zero. To ensure that \(\theta - \theta_s \ll \theta_s\) the molten contact line must move at extremely small \(Ca\), that is \(Ca \ll 1\). In this limit the pressure in the outer region is approximately constant, so to a first-order \(\theta\) is constant for \(r > \lambda\). The inner region equation (4.26) may be written as

\[
\frac{\partial \theta}{\partial h} = 4Ca \left(\frac{\sin\theta}{h} - \frac{1}{\lambda}\right) \frac{1}{2(\theta - \theta_s)} \sin\left[2(\theta - \theta_s)\right] + \frac{q_{\lambda}}{\sin\theta},
\] (4.31)

and expanding the right hand side about \(\theta = \theta_s\) gives

\[
\frac{\partial \theta}{\partial h} = 3Ca \left(\frac{\sin\theta_s}{h} - \frac{1}{\lambda}\right) (\theta - \theta_s)^3 + 3Ca \frac{\cos\theta_s}{h} (\theta - \theta_s)^2 + O\left((\theta - \theta_s)^{-1}\right).
\] (4.32)

The \(q_{\lambda}\) term appears as a term of order \((\theta - \theta_s)^0\). Note also that in the limit \(\theta - \theta_s \ll \theta_s\) and \(\lambda/h>>1\), all terms in the expansion may be safely dropped near the contact line \(h \sim h_m\) in deference to the first. However, near the outer boundary of the inner region \(h \sim \lambda \sin\theta_s\), the first term vanishes altogether and the second term dominates (4.32). In order to produce a limiting analytical solution for the velocity-angle relationship, we approximate (4.31) using only the first term of (4.32) and recognize that an error of order \((\theta - \theta_s)^2\) has been introduced.

Using only the first term in the expansion, (4.31) may immediately be separated into

\[
(\theta - \theta_s)^3 d\theta = 3Ca \left(\frac{\sin\theta_s}{h} - \frac{1}{\lambda}\right) dh.
\] (4.33)

Integration over \(\theta \in [\theta_m, \theta_a]\) and \(h \in [h_m, \lambda \sin\theta_s]\) gives the desired \(\theta_s\) vs. \(Ca\) relationship

\[
Ca = \kappa_s \left[\sin\theta_s \left((\theta_a - \theta_s)^4 - (\theta_m - \theta_s)^4\right)\right],
\] (4.34)

where for \(\lambda/h_m>>1\).
\[
\kappa_s = \frac{1}{12 \ln \left( \frac{\lambda \sin \theta_s}{h_m} \right) - 1}.
\]  \hspace{1cm} (4.35)

The solution given by (4.34) and (4.35) describes behavior fundamentally different from the Hoffman-Tanner-Voinov law (4.1) and (4.2), and we denote this new result as the near-arrest law for a molten contact line. It applies strictly in the limit \( \theta - \theta_i << \theta_s \), which for \( \theta_m = \theta_s \) (more on this below) may be written approximately as \( \theta_o - \theta_i << \theta_s \). The law predicts that \( Ca \) varies as the 4th power of the small difference \( \theta_o - \theta_s \), and that the coefficient \( \kappa_s \) is a function of the inner region parameters \( \lambda/h_m \) and \( \theta_i \) independent of the observation length scale \( H \) (recall that in this limit \( \theta \) is approximately constant from the observation length scale \( H \) down to the edge of the inner region at \( h = \lambda \sin \theta_s \)).

Hoffman's law and the near-arrest law are limiting cases to the exact solution of the advancing molten dynamic contact line piecewise model. Hoffman's law applies when the apparent contact angle is much larger than the solidification angle (\( \theta_o >> \theta_i \)), but \( \theta_o \) may not be so large that the power series approximation (4.30) fails (\( \theta_o << 30^{1/2} \)). These conditions generally hold for moderate \( Ca \) (say, \( Ca > 10^{-4} \) or \( 10^{-3} \) spreading over a solid characterized by small subcooling (say, \( S \leq 0 \) to 0.2). The near-arrest law describes the final stages of quasi-steady motion before arrest of a molten contact line. The \( \theta_o - \theta_s << \theta_s \) restriction is satisfied for very small \( Ca \) spreading (say, \( Ca < 10^{-4} \)). The range of applicability of the limiting solutions is illustrated in the spreading law regime map shown in Figure 4.6. In the map the Hoffman's law region is characterized by \( \theta_o > 5 \theta_i \) and \( \theta_o < 6^{1/2} \). The near-arrest law region is characterized by \( \theta_o > 5(\theta_o - \theta_i) \). These boundaries are not strict limits. For example, we will see in §4.2.3 that the near-arrest law gives reasonable engineering approximations when \( \theta_o \sim 2(\theta_o - \theta_i) \).

Both Hoffman's law (4.1) and the near-arrest law (4.34) include terms involving the molecular contact angle \( \theta_m \). In isothermal dynamic contact line theory, the molecular angle \( \theta_m \) is commonly taken as the static, or equilibrium, contact angle \( \theta_e \). Molecular dynamic considerations may show that there exists a weak dependence of \( \theta_m \) on \( Ca \), but any such dependence will have a negligible effect on the observed value of \( \theta_o \). Whatever the correct answer for the isothermal case, the molten dynamic case is fundamentally different because it is inherently a non-equilibrium process.
Figure 4.6 Regime map showing the realms of applicability of Hoffman's law and the near-arrest law to the advancing molten contact line problem.

When considering $\theta_m - \theta_s$ for the molten dynamic case, we recall that empirical data suggests that a drop of fluid held just above the fusion point nearly completely wets its own solid, held just below the fusion point (refer to Chapter 3; Schiaffino and Sonin 1997b). This hypothesis, while not proven generally and conclusively, seems reasonable because, except for the difference in phase, which may admittedly affect the surface energies, the fluid would be thermodynamically similar to the solid. Since the fluid and solid material very near the moving molten contact line are both approximately at the fusion point (see Chapter 2), we expect that $\theta_m = \theta_s$. Drawing a parallel to the isothermal case, even if $\theta_m$ slightly exceeds $\theta_s$, the effect on the velocity-angle relationship will be negligible during most of the spreading process. This will be discussed more fully in Chapter 6.

4.2.3 Numerical Solutions and the Parametric Study of the Velocity-Angle Relationship

Hoffman's law and the near-arrest law are useful for predicting the limiting behavior of the molten dynamic contact line governing equations, but the required assumptions are restrictive. When these assumptions are not satisfied, it is necessary to solve for the velocity-angle relationship using a numerical calculation. This section presents the results of a series of numerical solutions which explore the sensitivities of the dimensionless velocity-angle relationship.
\[ \theta_a = f \left( \text{Ca}; \theta_s, \theta_m, \frac{\lambda}{h_m}, \frac{H}{h_m}, Hq_a \right). \] 

(4.36)

For all numerical integrations we use a Runge-Kutta-Fehlberg method (4th and 5th order equations; see The Math Works, 1995, p. 509-510).

We begin the analysis by solving the governing equation for the outer region,

\[ \sin \theta \frac{\partial \theta}{\partial h} = 4Ca \left( \frac{\sin \theta - \sin \theta_a}{h - \theta_a} \right) \frac{\sin \theta}{\theta - \sin \theta} + q_a, \] 

(4.37)

beginning at the observation length scale where \( h=H \), \( \theta=\theta_a \), and radius of curvature=\( 1/q_a \), and proceeding to the edge of the inner region where \( r=h/\sin \theta=\lambda \). At this transition point we record the curvature \( q_\lambda \) and switch to the inner region equation,

\[ \frac{\partial \theta}{\partial h} = 4Ca \left( \frac{\sin \theta}{h} - \frac{1}{\lambda} \right) \frac{1}{\theta - \theta_a} \frac{1}{\sin \left( 2\left( \theta - \theta_a \right) \right)} + \frac{q_\lambda}{\sin \theta}, \] 

(4.38)

which applies down to the molecular cut-off scale, where \( h=h_m \) and \( \theta=\theta_m \). We implement an iterative algorithm that allows us to vary \( Ca \) until the calculated value of \( \theta_m \) matches the pre-specified value within a specified tolerance (usually \( \pm 0.5^\circ \)). Table 4.1 lists the cases considered in the parametric study, and the calculated numerical results for the velocity-angle relationships for each case appear in Appendix B. The selected values of the parameters reflect the range of expected conditions for the wax on solid wax and water on ice deposition experiments described in Chapter 4. Case B is adopted as a benchmark for comparison of the various calculations.

<table>
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<th>Case</th>
<th>( \theta_s ) (deg)</th>
<th>( \theta_m ) (deg)</th>
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<th>( H/h_m )</th>
<th>( Hq_a )</th>
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<td>( 10^5 )</td>
<td>( 2 \times 10^1 )</td>
</tr>
</tbody>
</table>

Table 4.1 Values of the parameters for each case considered in the numerical study of the governing equations for the piecewise model of the molten dynamic contact line. Case B is considered a reference case for comparison purposes.
In Cases A through D the solidification angle \( \theta \), is varied from 20° to 50°. Based upon the prominence of \( \theta \) in the near-arrest law (4.34), we expect this parameter to critically impact the \( \theta \) vs. \( Ca \) relationship for the molten dynamic contact line. We show this relationship, as well as the \( \theta \)-\( \theta \) vs. \( Ca \) relationship, for Cases A through D in Figures 4.7 and 4.8. In Figure 4.8 the Hoffman-Tanner-Voinov law (Equations (4.1) and (4.2) with \( H/h_m=10^5 \) and \( \theta _m=0^\circ \)) and the near-arrest law (Equations (4.34) and (4.35) with \( \lambda/\h_m=10^2 \) and \( \theta _s=20^\circ \) and 50° for Cases A and D, respectively) are shown alongside the numerical results. Hoffman's law provides surprisingly good agreement with the numerical solutions over a wide range of \( Ca \); it errs by no more than 5° for the conditions considered in the Figure. For Case A the near-arrest law is within 5° of the numerically calculated value for \( Ca<2 \cdot 10^{-4} \); for Case D it is within this range when \( Ca<2 \cdot 10^{-3} \). The near-arrest law holds when \( \theta _a-\theta _s<<\theta _s \), but based upon Figure 4.8, it gives reasonable engineering approximations up to the point where \( \theta _a-\theta _s=\theta _s/2 \).

An alternative interpretation of these findings (and others to follow) is that the power law forms of the Hoffman and near-arrest laws are valid, but the coefficients \( \kappa_H \) and \( \kappa_s \) must deviate from their analytically determined values to give exact agreement with the numerical results. Readers interested in this approach may construct appropriate values of \( \kappa_H \) and \( \kappa_s \) by direct calculation from the numerical data presented in Appendix B.
Figure 4.7 Plot of the numerically calculated $\theta_s$ vs. $Ca$ relationship for varying $\theta_s$. Here $\theta_m=\theta_s$, $\lambda/h_m=10^3$, $H/h_m=10^3$, and $H_{\theta_m}=0$. The plot symbols correspond to numerical solutions.

Figure 4.8 Data for Cases A and D rewritten as $\theta_s-\theta_s$ vs. $Ca$ relationship. The solid lines correspond to the near-arrest law (4.35) with $\theta_m=\theta_s$. $\kappa_s$ is evaluated using (4.36) with $\lambda/h_m=10^3$, and $\theta_s=20^\circ$ and $50^\circ$ for Cases A and D, respectively. The dashed line is Hoffman's law (4.1) with $\theta_m=0^\circ$ and $\kappa_H$ evaluated using (4.2) with $H/h_m=10^3$. 

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Next we compare Cases E, F, and G with the reference Case B to assess the effect of the $\theta_m$ parameter on the numerically determined $\theta_a$ vs. $Ca$ relationship. Figure 4.9 shows that the value of $\theta_m$ affects the $Ca \to 0$ asymptotic limit of the $\theta_a$ vs. $Ca$ relationship. This is as expected, since by definition $\theta_a \to \theta_m$ as $Ca \to 0$. Comparing Cases B and E suggests that the effect of $\theta_m$ on the $\theta_a$ vs. $Ca$ relationship for $\theta_m \sim \theta_a$ is confined to very small $Ca$. The Figure also suggests that the numerical solutions converge toward a universal solution (given approximately by the Hoffman law) when $\theta_a >> \theta_m$. In Figure 4.10 the results from Cases B and G are presented in $\theta_a$-$\theta_t$ vs. $Ca$ form. Appropriate forms of the near-arrest law (shown as solid lines) provide a very small $Ca$ asymptotic limit for the numerical solutions.

Figure 4.11 illustrates the effect of $\lambda/h_m$ on the velocity-angle relationship. To interpret this Figure, it is helpful to recall that the increase in the free surface angle from $\theta_m$ at the contact line to $\theta_a$ is caused by the pressure gradient induced by viscous resistance. This resistance is strongest in the inner region where $r<\lambda$ and $\theta \sim \theta_m$, so smaller $\lambda/h_m$ leads to larger $Ca$ for a given $\theta_a$, and larger $\lambda/h_m$ results in smaller $Ca$ for a given $\theta_a$. The $\theta_a$-$\theta_t$ vs. $Ca$ plot for varying $\lambda/h_m$ appears in Figure 4.12. The Figure shows that the near-arrest law is more accurate for the larger values of $\lambda/h_m$. It is less accurate when the inner region is small compared to the outer region ($\lambda/h_m << H/h_m$) because the assumption that $\theta$=constant in the outer region breaks down.

Figure 4.13 shows the effect of $H/h_m$ on the governing equations. This effect is small because the angle of the free surface changes slowly when far from the contact line. The effect of the $Hq_a$ parameter is illustrated in Figure 4.14, which shows that the dimensionless curvature associated with a far-field pressure $Hq_a$ may significantly affect $Ca$ for a given $\theta_a$. As illustrated by Case P, for sufficiently large $Hq_a$ the contact line must advance with a capillary number greater than some critical value in order to satisfy the imposed constraints. For $Hq_a$ larger than about $2 \times 10^{-1}$ meaningful $\theta_a$ vs. $Ca$ solutions could not be found. The inclusion of this parameter in the model may facilitate the analysis of drops of markedly different size scales than those considered in this work.
Figure 4.9 Plot of the numerically calculated $\theta_s$ vs. $Ca$ relationship for varying $\theta_m$. Here $\theta_s=30^\circ$, $\lambda_h=10^3$, $H/h_m=10^5$, and $H_{m}=0$. The plot symbols correspond to numerical solutions.

Figure 4.10 The data for Cases B and C rewritten as $\theta_a-\theta_s$ vs. $Ca$ relationship. The solid lines correspond to the near-arrest law (4.35) for $\theta_f=30^\circ$ and $\psi$ evaluated using (4.36) with $\lambda_h=10^3$. The dashed lines correspond to Hoffman's law (4.1) with $\theta_m=30^\circ$ and $60^\circ$ for Cases B and G, respectively. $\psi$ is evaluated using (4.2) with $H/h_m=10^5$. 

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Figure 4.11 Plot of the numerically calculated $\theta_a$ vs. $Ca$ relationship for varying $\lambda/\mu_m$. Here $\theta_m=30^\circ$, $H/\mu_m=10^1$, and $Hq_o=0$. The plot symbols correspond to numerical solutions.

Figure 4.12 Data for Cases H and J rewritten as a $\theta_a-\theta_s$ vs. $Ca$ relationship. The solid lines correspond to the near-arrest law (4.35) with $\theta_m=\theta_s$. $\kappa_i$ is evaluated using (4.36) with $\theta_s=30^\circ$, and $\lambda/\mu_m=10^1$ and $10^4$ for Cases H and J, respectively. The dashed line is Hoffman's law (4.1) with $\theta_m=0$ and $\kappa_H$ evaluated using (4.2) with $H/\mu_m=10^3$. 

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Figure 4.13 Plot of the numerically calculated $\theta_\alpha$ vs. $Ca$ relationship for varying $H/h_m$. Here $\theta_m=\theta_c=30^\circ$, $\lambda/h_m=10^2$, and $Hq_a=0$. The plot symbols correspond to numerical solutions.

Figure 4.14 Plot of the numerically calculated $\theta_\alpha$ vs. $Ca$ relationship for varying $Hq_a$. Here $\theta_m=\theta_c=30^\circ$, $\lambda/h_m=10^2$, and $H/h_m=10^3$. The plot symbols correspond to numerical solutions.
4.3 Summary of the Theoretical Analysis

In this Chapter we developed a relatively simple model of the molten contact line that enables numerical calculation of the velocity-angle relationship in the form

$$\theta_a = f(Ca; \theta_s, \theta_m, \frac{\lambda}{h_m}, \frac{H}{h_m}, Hq_a).$$  \hfill (4.39)

In the limiting case $\theta_a \gg \theta_s$, this relationship approaches the Hoffman-Tanner-Voinov law,

$$Ca = \kappa_H \left( \theta_a^3 - \theta_m^3 \right)$$  \hfill (4.40)

where

$$\kappa_H = \frac{1}{9 \ln \left( \frac{H}{h_m} \right)}.$$  \hfill (4.41)

When $\theta_a - \theta_s \ll \theta_s$, the numerical solution asymptotes to the near-arrest law,

$$Ca = \kappa_s \left[ \frac{\left( \theta_a - \theta_s \right)^4 - \left( \theta_m - \theta_s \right)^4}{\sin \theta_s} \right],$$  \hfill (4.42)

where for $\lambda/h_m >> 1$

$$\kappa_s = \frac{1}{12 \left[ \ln \left( \frac{\lambda \sin \theta_s}{h_m} \right) - 1 \right]}.$$  \hfill (4.43)

Broadly speaking, Hoffman's law may be applied to the quasi-steady molten contact line problem when $S$ is small (say $S=0$ to 0.2, for microcrystalline wax) and $Ca$ is moderately small (say $Ca>10^{-4}$ or $10^{-3}$ for wax). The near-arrest law holds just before molten contact line arrest, when $Ca$ is extremely small (say $Ca<10^{-4}$). In general a full numerical solution of the governing equations is required.

The parametric study of the numerical solutions of the governing equations suggests that the velocity-angle relationship for the molten contact line is especially sensitive to $\theta_s$. A 10° increase in $\theta_s$ increases $\theta_a$ by about 10° for a given $Ca$, or decreases $Ca$ by at least an order for a given $\theta_s$. $\theta_m$ controls the $Ca \to 0$ limit of the velocity-angle relationship, but has a weak effect on the relationship when $\theta_a \gg \theta_s$. As suggested by the logarithmic dependence of $\kappa_s$ on $\lambda/h_m$ in (4.43), there is only a weak dependence of the velocity-angle relationship on $\lambda/h_m$. A four-order-of-magnitude increase in
\( \lambda/h_m \) increases \( \theta_a \) by about 10° for a fixed \( Ca \), or decreases \( Ca \) by about a factor of four for a fixed \( \theta_a \). The effect of \( H/h_m \) on the solution is negligible provided \( H/h_m \gg 1 \). The influence of the \( Hq_a \) term is negligible if \( Hq_a < 10^{-2} \). For larger values of \( Hq_a \) the geometry of the near contact line region is significantly altered and the \( Hq_a \) parameter plays a meaningful role in the velocity-angle relationship.
Chapter 5

Molten Drop Deposition Experiments Part II:
Experimental Investigation of Molten Contact Line Dynamics

The advance of a molten dynamic contact line is investigated by using high speed video microscopy techniques to examine the deposition of individual millimeter-scale molten drops on cold, solid targets of the same material. The experimental methods, parameters, and results are presented and discussed in this Chapter, which is organized as follows: §5.1 molten microcrystalline wax drops on horizontal solid wax targets, §5.2 water on horizontal ice targets, and §5.3 molten wax drops on inclined solid wax targets. The measurements include the footprint size (radius $R$ for the axisymmetric horizontal depositions or length $L$ for the inclined depositions) and the apparent contact angle $\theta_e$ as functions of time. For wax drop deposition on horizontal wax targets we also obtain the centerline height $H$ as a function of time. The footprint size data is differentiated to produce the contact line velocity $U$ ($dR/dt$ or $dL/dt$) as a function of time.

The transient data is discussed in the context of the arrest mechanism suggested by Schiaffino and Sonin (1997b and c). The data is consistent with their theoretical framework, but for drop deposition experiments on inclined targets the theory does not fully explain our observations. The quasi-steady theory for the molten dynamic contact line developed in Chapter 4 is applied to the experimental data in Chapter 6.

5.1 Molten Microcrystalline Wax Drops On Horizontal Solid Wax Targets

Small granules of solid microcrystalline wax (Reed 6882) were placed inside a hot aluminum crucible (Figure 5.1). As the material melted it flowed through a small hole in the cone at the bottom of the crucible and accumulated at the tip in the form of a pendant drop. The drop increased rapidly in size until it fell under its own weight toward the solid target below. The entire "melt and dispense" process took about 2 seconds to complete. If the drop did not fall in this allotted time, the flow of molten material to the cone tip was likely obstructed by an air bubble in the crucible and the test was aborted.

The temperature of the crucible was managed using an automatic temperature controller (Omega CN76000 1/16 DIN Auto-Tune), a cartridge heater (delivered 100 W), and a type T thermocouple bonded using thermocouple cement to the surface of the aluminum very near the cone tip. The solid wax target was formed by filling with molten wax a shallow cup (2.5 mm deep and 25
mm diameter) cut into the surface of a 6.3 mm thick aluminum plate. A 10 \( \mu \text{m} \) thick type T thermocouple was positioned approximately 0.5 mm below the free surface of the molten wax, and the wax was allowed to solidify. We assume that this thermocouple obtained a measurement that accurately reflected the target surface temperature. The root-mean-square surface roughness of a target prepared in this manner was of order 1 to 5 \( \mu \text{m} \) (see §3.2).

During an experiment the target assembly was placed on a large aluminum hot plate (1 cm x 9 cm x 21 cm), which was heated by flexible resistive heaters (which delivered about 80 W). The ultra-flat thermocouple was used to provide feedback to a second Omega temperature controller connected to the hot plate heaters. Thermally conductive paste (GC Electronics Type Z9 Heat Sink Compound) was applied to ensure good thermal contact between metal surfaces. At the time of drop deposition the crucible tip temperature \( T_o \) and target temperature \( T_t \) were recorded.

The deposition events were photographed from a shallow angle (3 to 7° above the plane of the target surface) with a Kodak EktaPro EM-1012 high speed digital video motion analyzer outfitted with a microscope objective lens. The EM-1012 captures 8-bit gray scale, 239x192 pixel resolution, full frame digital images at user selectable frame rates of 50, 125, 250, 500, or 1,000 frames per second (abbreviated fps). Frame rates up to 12,000 fps may be achieved using a split screen feature. Depending on the selected frame rate and screen size, the exposure time may range
Figure 5.2 Image acquisition hardware layout for molten drop deposition experiments.

from 1/50 s to 1/12,000 s. At full frame size and 1,000 fps acquisition rate, the image system's memory stores up to a maximum of approximately 2.5 s of video.

A fiber optic illuminator provided sufficient light to acquire full frame video at 1,000 fps (1 ms between frames) and 1/1,000 s exposure time. The video recordings were archived onto Super-
VHS video tape, and select frames were re-digitized at high resolution using a PC equipped with image analysis hardware and software (Figure 5.2). The software facilitated the measurement of drop footprint diameter 2\( \cdot R \), the centerline height \( H \), and the apparent contact angle \( \theta_a \). The contact line spreading velocity \( U=\frac{dR}{dt} \) was determined by differentiating the radius data. A 2\(^{nd}\) order polynomial was best fit by minimization of least squares to five adjacent \( R(t) \) points, and the polynomial's derivative was evaluated at the third (the center) point. Marching this "spline technique" through the data, five points at a time, produced the \( U(t) \) information.

A typical low \( S \) wax drop deposition experiment is pictured in Figure 5.3. The drop falls from the crucible, and stretches a ligament of molten material until it snaps free. As the main drop begins its descent toward the target, the ligament coalesces into a 0.29 mm diameter satellite drop. The presence and consistent size of the satellite drop in all of these experiments is testament to the repeatability of the drop formation and snap-off process. After impact the main drop spreads radially outward over the surface, its apparent contact angle and spreading velocity decreasing as time passes. The centerline height decreases as well, the highest point vanishing briefly when the drop assumes a donut-like shape at about 15 ms after impact. The drop recoils from this donut shape, and continues to oscillate as the contact line creeps outward over the surface. The oscillations eventually damp out, and at approximately 1.2 s after impact the molten contact line arrests. Since the time scale for complete drop solidification is very large compared to the arrest time, the bulk of the drop is still near its original temperature when contact line arrest occurs. Drops deposited onto colder targets arrest more quickly and with steeper apparent contact angles than the case depicted in the Figure.

5.1.1 Wax on Solid Horizontal Wax: Characterizing the Deposition Conditions

Wax drop deposition experiments spanning a range of \( S=0.03 \) to 0.7 were examined: full transient measurements are presented for three of these experiments (\( S=0.14 \), 0.33, and 0.65).

For the three experiments examined in detail, the drop sizes were nearly identical. For simplicity, in the analysis we use an average value of the radius \( a \) for the three drops considered. The average is obtained as follows: 1. measure the major (vertical) and minor (horizontal) radii of the elongated wax drop (assumed to be an ellipsoid) just before detachment from the ligament, 2. estimate the radius \( a \) of the spherical drop with volume equivalent to the ellipsoid according to

\[
a = \left( \frac{r_{\text{vert}}^2 \cdot r_{\text{hor}}^2}{3} \right)^{1/3},
\]

and 3. average the results over the three drops. Calculations show that the drop radius is \( a=1.92 \pm 0.055 \) mm (the error is determined using a \( t \)-test, and represents a 95% confidence interval).
Figure 5.3 Select video frames showing the deposition of a molten wax drop ($S=0.14$, $\beta=2.61$).
Table 5.1 Summary statistics and parameters for the presented wax drop deposition experiments on a horizontal solid wax surface.

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<th>$\beta$</th>
<th>$r_{non}$</th>
<th>$r_{vert}$ (mm)</th>
<th>$Bo$</th>
<th>$Z$</th>
<th>$We$</th>
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<td>1.88, 1.98</td>
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<tr>
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<td>1.13</td>
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<td>0.4</td>
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<tr>
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<td>1.81, 2.15</td>
<td>1.13</td>
<td>0.088</td>
<td>2.41±0.58</td>
<td>0.7</td>
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</table>

Using this value of $a$, the material properties of Appendix A, and various experimental measurements, the summary statistics shown in Table 5.1 are calculated. The values of $S$ and $\beta$ are calculated from the measured temperature values for each experiment, and the errors are based on a conservative estimate of ±2°C accuracy. $Bo$ and $Z$ are calculated directly from their definitions, presented in Chapter 2. With $Bo$~1 the deposited drop will be slightly “flattened” due to gravitational effects. Since the apparent contact angle measurements are made on a small scale ($H$~100 μm) we expect the resulting error in the angle measurements to be negligible compared to the measurement error.

The exact time of drop impact and the value of $We$ at impact are calculated by tracking the approach of the lowest point of the molten drop to the target surface in the video images. We formulate the position versus time curve for this point by directly measuring the video images of the falling drop, and extrapolate the curve to estimate the impact time and velocity (and the error associated with these quantities). The impact time is used to establish a $t=0$ reference for the transient data ($R$, $U$, $\theta_a$, and $H$), and the impact velocity $V$ is used to calculate $We$. Very small $We$ experiments are not possible using this technique because the cone tip may not be positioned arbitrarily close to the target for two reasons: 1. the heated cone will thermally disturb the target; and 2. the wax drop needs approximately two diameters of free fall distance for the neck to thin to the point of breaking. For each of the first few experiments the distance from cone tip to target surface was gradually reduced until the desired snap-off behavior was attained. For the $S=0.65$ case the drop snaps free of the neck and falls over a short distance before impact with the target. For the $S=0.14$ and 0.33 cases the drop snaps free of the ligament between 4 and 6 ms after contact with the target.

Under the influence of surface tension and inertial forces a non-spherical drop will oscillate with a period $t_{osc}$ until viscous forces damp out the oscillation. For this reason we also estimate the maximum possible change in $We$ that may occur due to drop oscillation during the deposition, and denote the result as $We_{osc}$. The calculation of $We_{osc}$ assumes that the maximum possible oscillation velocity is of order $V_{osc}=(r_{vert}-r_{hor})/(t_{osc}/2)$, where $r_{vert}$ and $r_{hor}$ are the radii of the ellipsoid used in
(5.1). An order-of-magnitude estimate of $\tau_{osc}$ is obtained using the results of Lamb (1945), who gives the period of oscillation of a near-spherical, inviscid drop as

$$\tau_{osc} = 2\pi \sqrt{\frac{\rho a^3}{8\sigma}}.$$  \hspace{1cm} (5.2)

For the studied wax drops $\tau_{osc} \sim 33$ ms, and for the cases considered in Table 5.1, $V_{osc}$ is as high as 18% of the free fall velocity.

Since the effective Weber number is of order unity, the experiments fall along the $We$ boundary of the capillarity-driven regime described by Schiaffino and Sonin (see 1997a). As such, impact forces will play a small but non-negligible role in determining the spreading history for these drops. We are principally interested in the near-arrest conditions, however, and these should not depend critically upon the early stage spreading dynamics.

For the wax drops deposited from the pendant drop dispenser, the characteristic inertial spreading time scale $\tau_i = \tau_{osc} \sim (\rho a^3/\sigma)^{1/2}$ is approximately 15 ms, and the associated characteristic spreading velocity $U_i \sim (\sigma/\rho a)^{1/2}$ is approximately 13 cm/s.

5.1.2 Wax on Solid Horizontal Wax: Summary of Arrest Conditions

The values of $R'/a$ and $\theta_a^*$ were obtained for each horizontal target wax drop deposition experiment completed. The results are plotted against $S$ in Figures 5.4 and 5.5. The trends agree qualitatively with those observed by Schiaffino and Sonin (1997a), who suggested a one-third power law fit for $R'/a$ data for mercury and water drops. Considering the dynamic nature of our experiments, the new arrest angle data agrees well with their $\theta_a^* = 85S^{1/2}$ correlation.
Figure 5.4 $R^*/a$ vs. $S$ for millimeter scale wax drop deposition on horizontal targets. Schiaffino and Sonin used one-third power law fits for correlating their drop deposition data for mercury and water.

Figure 5.5 $\theta_2^*$ vs. $S$ for millimeter scale wax drop deposition on horizontal targets. Schiaffino and Sonin's data and power law correlation are shown for reference.
5.1.3 Wax on Solid Horizontal Wax: Discussion of Transient Variables

Plots of $R/a$, $U$, $\theta_a$, and $H/a$ vs. $t$ for $S=0.14$, 0.33, and 0.65 appear in Figure 5.6. For clarity the data is shown on a case-by-case basis in Figures 5.7 through 5.9. Several features of these results deserve comment. First, we consider the characteristic time scales. For $S=0.14$ and $S=0.33$ the $R/a$ vs. $t$ curves pass "shoulders" when $t\sim\tau_\ell\sim15$ ms. The shoulders correspond to the beginning of recoil of the drop from the target surface, and their presence indicates that the forces associated with inertia are diminishing in importance compared to the viscous and capillary forces acting near the contact line. The $\theta_a$ vs. $t$ plots for these two cases show that oscillations of the apparent contact angle persist until $t\sim40$ ms. This time scale corresponds, perhaps coincidentally, with Lamb's result (1945) for the decay time $\tau_d$ of oscillations of a near-spherical drop. He finds for integral mode numbers $n=(2, 3, 4, \ldots)$ and $\tau_d<\tau_{osc}$ that

$$
\tau_d = \frac{1}{(n-1)(2n+1)} \frac{\rho a^2}{\mu},
$$

so $\tau_d\sim33$ ms for $n=2$ (see also Schiaffino and Sonin, 1997a). The $S=0.65$ drop arrests abruptly when $t<\tau_c$, and its apparent contact angle oscillates until $t\sim50$ ms.
Figure 5.6a Comparison of the wax drop deposition data presented in Figures 5.7 to 5.9. The time measurements are referenced to the impact time, and are correct within ±0.3 ms. Thermal conditions are shown in the plot legends. Plot continued on next page.
Figure 5.6b  Continued from previous page.
Figure 5.7a Experimental measurements of $R/a$, $U$, $\theta_n$, and $H/a$ vs. $t$ for a wax drop deposited on a horizontal wax surface. The thermal conditions are given by $S=0.14$ and $\beta=2.61$. Plot continued on next page.
Figure 5.7b  Continued from previous page.
Figure 5.8a  Experimental measurements of $R/a$, $U$, $\theta_n$, and $H/a$ v. $t$ for a wax drop deposited on a horizontal wax surface. The thermal conditions are given by $S=0.33$ and $\beta=1.03$. Plot continued on next page.
Figure 5.8b  Continued from previous page.
Figure 5.9a Experimental measurements of $R/a$, $U$, $\theta_0$, and $H/a$ v. $t$ for a wax drop deposited on a horizontal wax surface. The thermal conditions are given by $S=0.65$ and $\beta=0.57$. Plot continued on next page.
Figure 5.9b  Continued from previous page.
Next consider the slight upward shift in the \( R/a \) data (for \( t<2\cdot10^3 \) s) for \( S=0.65 \) compared with \( S=0.14 \) and 0.33. This shift is a consequence of inertial effects: the higher impact \( We \) for the \( S=0.65 \) case causes \( R \) to grow more quickly during the first few moments of impact. The shift in \( R/a \) vs. \( t \) was observed by Schiaffino and Sonin (1997a) in experiments with mercury drops deposited on frozen mercury, and with water drops deposited on ice. Their results suggest that the arrested drop geometry shows a small dependence on \( We \).

The \( H/a \) data mimic the \( \theta_a \) data except near \( t\sim10 \) ms, where data is "missing" because the donut-like shape of the drop obscures the centerline from view. It is interesting to evaluate the effect of \( Bo>1 \) (a requirement for the pendant drop to fall) using the \( H/a \) data. For a perfectly hemispherical drop geometric considerations require that the hemispherical drop height \( H_{\text{hemi}} \) is

\[
H_{\text{hemi}} = \frac{R(1-\cos\theta_a)}{\sin\theta_a},
\]  

(5.4)

but the measured values of \( H \) (when the drop oscillations die out) are 13 to 21% below \( H_{\text{hemi}} \) due to gravitational "flattening" of the center of the drop. Gravitational distortion will affect the apparent contact angle, but since the angle measurements were made on a very small length scale (<100 \( \mu \)m) the error introduced is negligibly small compared to the measurement error (estimated at \( \pm10^\circ \) just after impact, reducing to \( \pm2^\circ \) during the slowest stages of spreading for all drops measured).

Examining the subtleties of the data provides further insight into the dynamics of molten drop spreading and arrest. Looking first at the \( S=0.14 \) case, the molten contact line continues to spread radially outward (albeit slowly) during recoil and subsequent drop oscillations. For \( \tau<\tau \), the molten contact line velocity decreases gradually as the apparent contact angle and centerline height fall. Final arrest occurs about 1.2 s after impact when the apparent contact angle reaches \( \theta_a^*=28.5^\circ \), which is the smallest angle attained during the entire spreading process.

In the \( S=0.33 \) case the contact line halts momentarily when \( t\sim27 \) ms, which corresponds to the point of maximum drop recoil (refer to the \( \theta_a \) vs. \( t \) and \( H/a \) vs. \( t \) curves in Figure 5.8). At this moment the apparent contact angle reaches its minimum value of \( \theta_a=49.5^\circ \). Subsequent oscillations cause the molten contact line's motion to restart when \( t\sim40 \) ms and \( \theta_a\sim70^\circ \). Creeping motion continues until final arrest occurs at \( t\sim0.8 \) s and \( \theta_a^*=54.0^\circ \).

This "halt-and-restart" mechanism may be explained in light of Schiaffino and Sonin's picture of the molten contact line. From their work we expect that the apparent contact angle \( \theta_a \) of an advancing molten contact line exceeds the solidification angle \( \theta_s \) (which, they argue, is approximately equal to \( \theta_a^* \)). Given the measured values of \( \theta_a \), it is consistent to suggest that recoil forces pull the liquid near the molten contact line backward and cause the contact line to recede over the thin (order of 1 \( \mu \)m thick, say) solidification front. Referring to Figure 5.10, this retreat causes \( \theta_a \) to fall to even shallower angles on observation length scales.
Figure 5.10 Schematic of a possible mechanism explaining the observation that $\theta_a$ falls below $\theta_a^*$ during post-arrest, recoil induced drop oscillations. Drawing not to scale.

We hypothesize that "restart" occurs because the oscillation induced increase in $\theta_a$ causes an increase in the flow of thermal energy from the bulk of the molten drop to the near contact line region. The heat flux from the liquid remelts a portion of this region and reestablishes the motion of the molten contact line along the plane of the target surface. This mechanism is possible only if there is sufficient superheat in the molten liquid to remelt the target, that is, if $\beta>1$ ($\beta=1.12$ for the present case). After restart the molten contact line for the $S=0.33$ case proceeds unimpeded until final arrest, because oscillations have sufficiently decayed so that $\theta_a$ never falls to less than $\theta_a^*$ during the remainder of the spreading process.

For the colder target with $S=0.65$, arrest occurs "on-the-fly"; the $R/a$ curve first reaches its maximum when $t\sim17$ ms and $\theta_a=77^\circ$, and at this moment $\theta_a$ is decreasing at about $7^\circ$/ms and $H/a$ is rising under the influence of the inertial forces of recoil. During subsequent oscillations $\theta_a$ reaches extrema of $54.5^\circ$ (at $t\sim21$ ms) and $82.5^\circ$ (at $t\sim30$ ms), but contact line motion never resumes. For discussion purposes we take the arrest angle for this experiment to be $\theta_a^*=75.0^\circ$ (the value of the apparent contact angle after oscillations decay) because of the high uncertainty associated with the $\theta_a=77^\circ$ measurement mentioned above. The 'halt-and-restart" discussion from the $S=0.33$ case applies to the observed dynamics for the $S=0.65$ case. However, in this case molten contact line motion never resumes during post-arrest oscillations, presumably because oscillation induced thermal transport into the solidified contact line region is insufficient to cause remelting ($\beta=0.57$).
5.2 Water Drops On Horizontal Ice Targets

Millimeter scale water drops were dispensed from a microsyringe (Hamilton model #84855; 25 nL maximum capacity, 90° needle bevel) onto a solid ice surface. The spreading and arrest process was photographed using the high speed video microscopy system of Figure 5.2.

The ice surface temperature was controlled as shown in Figure 5.11. The temperature of the target was automatically controlled using an Omega temperature controller, two 100 W cartridge heaters, and a type T thermocouple embedded in the ice 2±1 mm below the deposition surface. The target was chilled by a solid aluminum bar whose end was submerged in a vacuum flask filled with liquid nitrogen. Target temperatures of \( T_i = -25^\circ \text{C} \) to 0°C were easily maintained. The syringe was maintained at room temperature (\( T_a = 20 \) to 25°C) and was positioned above the cold target just before the experiment commenced.

In order to improve optical access, the experiment was conducted in open air. This allowed ambient humidity to freeze and accumulate on the surface in the form of tiny ice dendrites. When these dendrites became visible in our microscope's field of view (when they reached roughly 10 to 50 μm tall), the target was cleared by placing a 2 mm thick aluminum plate initially at room temperature against the ice surface. The plate melted the dendrites and the surface of the target and was removed. The surface resolidified and reestablished itself at the set point temperature much faster than new dendrites grew. This cleaning procedure was effective for \( T_i > -25^\circ \text{C} \), but for significantly colder temperatures dendrites formed so quickly that clean targets could not be maintained for long. Drops deposited on ice targets covered with "large" dendrites (say a few hundred μm tall) swallowed the structures during spreading, often leading to an irregularly shaped drop footprint.
Figure 5.11 Schematic of the water drop deposition experimental apparatus.

Select video frames for a water drop deposition experiment for $S=0.32$ are shown in Figure 5.12. The most striking difference between this sequence and the wax drop deposition pictured in Figure 5.3 is that the water drop's contact line spreads aggressively outward forming a "bell" of liquid, while the wax drop spreads without ever forming such a highly distorted free surface. These differences in the spreading dynamics of the drop are attributable to the different values of $We$ and $Z$ for the wax and water tests (see Schiaffino and Sonin, 1997a).
Figure 5.12 Select video frames showing the deposition of a water drop on ice ($S=0.32$, $\beta=0.9$). The tip of the syringe is visible at the top of the pictures.
5.2.1 Water on Horizontal Ice: Characterizing the Deposition Conditions

Water drop deposition experiments spanning a range of $S=0.05$ to 0.32 were performed, and full dynamic measurements for $S=0.09$, 0.20, and 0.32 were obtained. For the three experiments measured in detail, the average water drop radius is $a=1.44\pm0.057$ mm (the error represents a 95% confidence interval; see §5.1.1). This value was used in constructing the summary statistics of Table 5.2.

The reported error on $S$ assumes that the surface temperature of the ice may deviate by up to $\pm4^\circ$C from the true value. This value was selected by combining the conservative $\pm2^\circ$C error estimate used for the wax drops with an additional $\pm2^\circ$C error, which approximately accounts for possible differences between the ice surface temperature and the embedded thermocouple temperature. The value of $\beta$ assumes that the drop temperature equals that of the syringe, estimated to be constant at $T_s$. $Bo$ and $Z$ are calculated directly from their definitions given in Chapter 2.

The $We$ values are based upon estimates of the free fall velocity of the drop made by comparing frames of video just before drop impact. The calculated $We$ values are an order of magnitude smaller for the water drops compared to the wax drops for two reasons: 1. the water drop impact velocities are typically one-half as large as those of the wax drops, and 2. the surface tension of water is about three times larger than that of wax. For small $Z$ and $We<0.2$ the spreading dynamics and arrest conditions are insensitive to $We$ (Schiavino and Sonin, 1997a), so highly refined calculations of $We$ were deemed unnecessary. The oscillation velocities $V_{osc}$ (see §5.1.1) for the water drops range from 14% to 61% of the estimated free fall velocities. Since the corresponding $We_{osc}$ is never larger than approximately $\pm0.04$, the effect is considered negligible and is not reported in the Table.

For the water drop deposition events the characteristic inertial spreading time scale $t_s=(\rho a^3/\sigma)^{1/2}$ is approximately 6 ms, and the associated spreading velocity $U_s=(\sigma/\rho a)^{1/2}$ is about 23 cm/s.

<table>
<thead>
<tr>
<th>$S$</th>
<th>$\beta$</th>
<th>$r_{harm}$</th>
<th>$r_{vert}$ (mm)</th>
<th>$Bo$</th>
<th>$Z$</th>
<th>$We$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.09\pm0.05$</td>
<td>$\sim3.2$</td>
<td>1.46, 1.38</td>
<td>$0.28\pm0.01$</td>
<td>($5.2\pm0.06)\cdot10^{-3}$</td>
<td>$\sim0.07$</td>
<td></td>
</tr>
<tr>
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<td>$\sim1.4$</td>
<td>1.37, 1.68</td>
<td>$0.28$</td>
<td>$5.2\cdot10^{-3}$</td>
<td>$\sim0.08$</td>
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<td>$0.32$</td>
<td>$\sim0.9$</td>
<td>1.48, 1.32</td>
<td>$0.28$</td>
<td>$5.2\cdot10^{-3}$</td>
<td>$\sim0.1$</td>
<td></td>
</tr>
</tbody>
</table>
5.2.2 Water on Horizontal Ice: Summary of Arrest Conditions

The values of $R'/a$ and $\theta_a$ were obtained for each horizontal target water drop deposition experiment conducted. The results are plotted against $S$ in Figures 5.13 and 5.14. The trends agree well with those observed by Schiaffino (1996). The scatter is primarily attributable to the errors in the measurement of $S$, but the presence of dendrites on the surface may contribute to error in the results.

![Graph](image)

Figure 5.13 $R'/a$ vs. $S$ for millimeter scale water drop deposition on horizontal ice targets. The power law best fits Schiaffino's data.
Figure 5.14 $\theta_\circ^*$ vs. $S$ for millimeter scale water drop deposition on horizontal ice targets. Schiaffino's data and power law are transformed from the $R/a$ data of Figure 5.13 to $\theta_\circ^*$ data by assuming that the drops are perfect hemispheres (see Equation (3.2)).

5.2.3 Water on Horizontal Ice: Discussion of Transient Variables

$R/a$, $U$, and $\theta_\circ$ vs. $t$ for $S=0.09$, 0.20, and 0.32 appear in Figure 5.15. For clarity the data is shown on a case-by-case basis in Figures 5.16 to 5.18. Many features of these plots qualitatively resemble those of the corresponding wax drop deposition plots. For instance, the $R/a$ curve for $S=0.09$ passes smoothly over a "shoulder" near $t\sim15$ ms. This point manifests itself as a "hiccup" in the $U$ vs. $t$ curve, which is especially evident in the $S=0.20$ and 0.32 data. For the $S=0.09$ case the molten contact line hesitates until $t\sim80$ ms before it advances toward the final arrest angle of $\theta_\circ^*=23^\circ$. The hesitation occurs while $\theta_\circ$ falls toward $\theta_\circ\sim23^\circ$ due to recoil dynamics, and persists until the molten contact line restarts its motion in earnest when $\theta_\circ\sim27^\circ$ near $t\sim100$ ms. Final arrest occurs when $t\sim300$ ms.

In the $S=0.20$ case arrest occurs while $\theta_\circ$ falls from $44^\circ$ to $22^\circ$ between $t\sim18$ and 22 ms ($d\theta_\circ/dt\sim 6^\circ/ms$). Because of the rapid shape change, it is difficult to measure the exact value of $\theta_\circ$ at the moment of arrest, but we expect that it approximately matches the post-oscillation apparent contact angle $\theta_\circ^*=27^\circ$. The post-arrest oscillations of the drop cause $\theta_\circ$ to vary from $24^\circ$ to $33^\circ$, but molten contact line motion never restarts.
The $S=0.32$ case behaves similarly; molten contact line arrest occurs while $\theta_a$ falls from $50^\circ$ to $35^\circ$ between $t \sim 14$ and $16$ ms ($d\theta_a/dt \sim 8^\circ/\text{ms}$). We estimate the arrest angle from the post-oscillation apparent contact angle, which gives $\theta_a^* = 39^\circ$. Post-arrest oscillations of the drop cause $\theta_a$ to climb to as high as $41^\circ$, but contact line motion does not restart.

The water drops are characterized by a lower viscous damping than the wax drops ($a^2/\nu$ is about 7 times larger for the water compared to the wax drops). The effect of drop oscillations on $\theta_a$ becomes insignificant after about $t \sim 70$ ms, which is only slightly larger than the 50 ms oscillation decay time observed for the wax drops.
Figure 5.15 Comparison of the water drop deposition data presented in Figures 5.14 to 5.16. The time measurements are referenced to the impact time, and are correct within ±0.6 ms. Thermal conditions are shown in the plot legends.
Figure 5.16 Experimental measurements of $R/a$, $U$, and $\theta_*$ vs. $t$ for a water drop deposited on a horizontal ice surface. The thermal conditions for the left column are $S=0.09$ and $\beta=3.2$. 

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Figure 5.17 Experimental measurements of $R/a$, $U$, and $\theta_0$ vs. $t$ for a water drop deposited on a horizontal ice surface. The thermal conditions for the left column are $S=0.20$ and $\beta=1.4$. 

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Figure 5.18 Experimental measurements of $R/a$, $U$, and $\theta_e$ vs. $t$ for a water drop deposited on a horizontal ice surface. The thermal conditions for the left column are $S=0.32$ and $\beta=0.9$. 
5.3 Molten Microcrystalline Wax Drops On Inclined Solid Wax Targets

The wax drop deposition experiments described in §5.1 were repeated with solid wax targets inclined from the horizontal at angles $\gamma = 28^\circ$ and $68^\circ$. In these experiments the molten drop ran down the target surface much like a molten wax drop slides down the side of a dripping candle. The downhill contact line is defined as the advancing one, and the uphill contact line as the receding one. However, the word "recede" must be used with caution because a molten contact line generally does not de-wet a cold target without leaving behind a solidified layer.

Selected frames of video showing the $\gamma = 28^\circ$, $S = 0.20$ deposition appear in Figure 5.19. Impact on the sloped target causes the drop to spread and oscillate asymmetrically, with skewness in the direction of the target gradient. Although not clearly visible in the Figure, the receding contact line arrests a few milliseconds after impact and remains stationary throughout the remainder of the spreading process. The molten fluid above the receding contact line gradually drains toward the advancing contact line during the remainder of the spreading process. Note that the advancing apparent contact angle changes only slightly for $t > 100$ ms until arrest occurs when $t \approx 1800$ ms.

It is helpful to begin the discussion of these experiments by introducing several key results from Hocking's (1990) paper on the flow of viscous fluid sheets down an incline (see also Sadhal, et al, 1997 for a brief overview of rivulet flows; Dussan and Chow, 1985). Hocking uses a lubrication analysis and allows for velocity-slip very close to the solid wall in his examination of the shape evolution of a fluid sheet advancing down an inclined plane. Transforming his results to our nomenclature, he shows that the dimensionless length $L/a$ of a two-dimensional fluid sheet (assume that the fluid is infinitely wide and has cross-sectional area $a^2$) obeys

$$\frac{L}{a} = \left( \frac{9}{4} \frac{\rho g a \sin \gamma}{\mu} \right)^{1/3} t^{1/3},$$

where $\gamma$ is the inclination of the plane above the horizontal, $t$ is the total time of spreading, and all other parameters are previously defined. Differentiating (5.5) gives the spreading velocity,

$$U = \frac{dL}{dt} = \left( \frac{1}{12} \frac{\rho g a^2 \sin \gamma}{\mu} \right)^{1/3} t^{-2/3}.$$  \hspace{1cm} (5.6)

The spreading of a two-dimensional sheet differs considerably from our molten drop spreading problem, so (5.5) and (5.6) are only of limited use in this analysis.
Figure 5.19  Select video frames showing the deposition of a molten wax drop (S=0.20, β=3.42, γ=28°).
5.3.1 Wax on Solid Inclined Wax: Characterizing the Deposition Conditions

Wax drop deposition experiments spanning the range $S=0.1$ to $0.5$ were completed for $\gamma=28^\circ$ and $68^\circ$. The spreading dynamics for five of these experiments were analyzed, and important deposition parameters are shown in Table 5.3. The values of $Bo$ and $Z$ are assumed to match those presented in Table 5.1, since the pendant drop method produces very repeatably sized drops. $We$ was difficult to measure accurately because the "uphill" side of the drop impacts the target before the "downhill" side. By the time the downhill side does contact the surface its velocity is influenced significantly by the forces associated with impact. Since the free fall distance along the centerline is approximately constant for the horizontal and inclined target depositions, $We$ is assumed to be of the same order for both sets of experiments.

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$S$</th>
<th>$\beta$</th>
<th>$Bo$</th>
<th>$Z$</th>
<th>$We$</th>
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<td>$28^\circ$</td>
<td>0.20</td>
<td>3.42</td>
<td>1.13</td>
<td>0.088</td>
<td>$-1$ to $5$</td>
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<td>1.13</td>
<td>0.088</td>
<td>$-1$ to $5$</td>
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<tr>
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<td>0.94</td>
<td>1.13</td>
<td>0.088</td>
<td>$-1$ to $5$</td>
</tr>
<tr>
<td>$68^\circ$</td>
<td>0.12</td>
<td>2.24</td>
<td>1.13</td>
<td>0.088</td>
<td>$-1$ to $5$</td>
</tr>
<tr>
<td>$68^\circ$</td>
<td>0.43</td>
<td>0.64</td>
<td>1.13</td>
<td>0.088</td>
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</tr>
</tbody>
</table>

5.3.2 Wax on Solid Inclined Wax: Summary of Arrest Conditions

The values of $L/a$ at arrest, $L'/a$, appears in Figure 5.20 for all of the inclined plate deposition experiments. The similarity between the two data sets for $\gamma=28^\circ$ (one with $\beta=1.5$ to $5.3$ and one with $\beta=0.6$ to $1.9$) shows that $L'/a$ is largely insensitive to $\beta$, which agrees with the findings of Schiaffino and Sonin (1997a) for horizontal deposition experiments. The solid line in the plot is the $R'/a=1.2S^{1/3}$ correlation for wax drop deposition on a horizontal target (see Figure 5.4). The $\gamma=28^\circ$ data falls slightly below the correlation because on the inclined target the drop spreading is restricted by the rapid arrest of the uphill contact angle. The $\gamma=68^\circ$ data resembles the $\gamma=28^\circ$ data in form, but $L'/a$ is about three times as large for the steeper target inclination angle.

In Figure 5.21 the data for the (post-solidification) arrest angles are shown for each of the inclined target experiments. The solid line corresponds to Schiaffino and Sonin's $\theta_a^*=85S^{1/2}$ empirical correlation. The open plot symbols (above the solid line) denote the downhill contact angle, and the solid symbols (below the solid line) denote the uphill contact line. The data suggest that $\theta_a^*$ depends also on $\beta$ and $\gamma$, and show that the arrest angles may differ appreciably from the
values predicted by the $\theta^*_{\text{a}} = 85S^{1/2}$ correlation. The small $\beta$ effect is especially perplexing since Figure 5.20 suggests that $L^*/a$ is largely independent of $\beta$ for $\gamma = 28^\circ$.

![Figure 5.20 $L^*/a$ vs. $S$ for wax drop deposition on an inclined wax target.](image)

Figure 5.21 $\theta^*_{\text{a}}$ vs. $S$ for wax drop deposition on an inclined wax target. The hollow data points denote advancing arrest angles, the solid points denote receding arrest angles.
5.3.3 Wax on Solid Inclined Wax: Discussion of Transient Variables

Plots of $L/a$, $U$, and $\theta_o$ vs. $t$ for the inclined deposition experiments appear in Figures 5.22 and 5.23. We begin by comparing the $L/a$ data to the $R/a$ data of the horizontal wax deposition experiments (refer back to Figure 5.6a). The curves show significant differences: the "shoulder" characteristic to the horizontal deposition experiments is only vaguely evident in the $\gamma=28^\circ$ curves, and the "creeping motion" during the late stages of low $S$ horizontal spreading appears in the inclined depositon experiments when $S$ is as large as 0.6. These differences occur because deposition of a drop on an incline favors the advance of the molten contact line in the downhill direction. Hocking's results (5.5) and (5.6) do not strictly apply to this problem, but they are included in the Figures to show that the molten drop deposition data agree in basic form with classic rivulet theory.

A striking distinction from the horizontal target experiments is evident in the $U$ vs. $t$ data. The Figures show that the advancing molten contact line undergoes "stick-slip" motion when $S$ is sufficiently small and $\gamma$ is sufficiently large. The $S=0.12$, $\gamma=68^\circ$ case (see Figure 5.23) exhibits this behavior definitively, and we estimate from this $U(t)$ data that the characteristic period for this stick-slip motion is $\tau_{ss}=0.2$ s.
Figure 5.22 Experimental measurements of $L/a$, $U$, and $\theta_s$ vs. $t$ for wax drops deposited on a wax surface with $\gamma=28^\circ$. The time measurements are referenced to the impact time, and thermal conditions are shown in the plot legends. To highlight the "stick-slip" behavior the $U$ vs. $t$ plot is shown on a linear scale.
Figure 5.23 Experimental measurements of $L/a$, $U$, and $\theta$, vs. $t$ for wax drops deposited on a wax surface with $\gamma=68^\circ$. The time measurements are referenced to the impact time, and thermal conditions are shown in the plot legends. To highlight the "stick-slip" behavior the $U$ vs. $t$ plot is shown on a linear scale.
The angle measurements $\theta_a(t)$ for the $\gamma=28^\circ$ cases appear to be affected by the inclination of the target. They tend to "bottom-out" near $\theta_a=60^\circ$ when $t$ ranges between about 70 and 300 ms, and fall very gradually for larger times. The zoom lens used to photograph the $\gamma=68^\circ$ experiments did not provide sufficient magnification to allow us to resolve the fine details of $\theta_a$ evolution during stick-slip motion.

The stick-slip phenomenon is reminiscent of the hysteresis observed during the post-arrest oscillations of a wax drop on a horizontal target. We hypothesized that (if $\beta$ is sufficiently large) contact line motion can restart after arrest if, due to system scale dynamics, $\theta_a$ becomes large enough compared to $\theta$, to allow for remelting of the arrested contact line region. For the $S=0.12$, $\beta=2.24$ drop advancing down the $\gamma=68^\circ$ incline, gravitational forces maintain $\theta_a$ at about $60^\circ$ for $t>1$ s. Based upon the data of Figure 5.5 we expect the contact line should arrest when $\theta_a^*=85S^{1/2}\approx30^\circ$, but the downhill contact line actually arrests when $\theta_a^*=59^\circ$, a factor of two larger than the expected value (see Figure 5.24). This implies that the arrest angle is affected by factors other than $S$, perhaps including $\beta$, $\gamma$, and convection processes within the "bulb" at the bottom of the drop.

While we do not offer a model that explains all of these phenomena, we do offer a scaling analysis that lends further insight into the importance of $\beta$ as a driver of stick-slip motion. We simplify the problem by assuming that at $t=0$ an unspecified mechanism causes $\theta_s$ to instantaneously climb to $\theta_a$, which causes the liquid near the molten contact line to solidify up to a distance $r=\delta_a$ from the contact line and $U$ to fall to zero ("stick" occurs). The scale of the distance $\delta_a$ may be estimated using a simple, one-dimensional model that describes the remelting of the solidified material.

Refering to Figure 5.25, the heat flux singularity is circumvented by assuming that the fusion interface makes a right angle with the free surface. At $t=0$, the contact line was advancing at a speed $U$, so the $T_f$ thermal layers penetrated a distance of order $\alpha U$ into both the fluid and the solid. These distances grow like $(\alpha t)^{1/2}$ starting when stick occurs at $t=0$, so the heat fluxes from the liquid to the fusion interface ($q_l$) and from the fusion interface to the solid ($q_s$) are of order

$$q_l \sim \frac{-k(T_o - T_f)}{\sqrt{\alpha + (\alpha U)^2}}$$  \hspace{1cm} (5.7)$$

and

$$q_s \sim -\frac{k(T_f - T_i)}{\sqrt{\alpha + (\alpha U)^2}}.$$  \hspace{1cm} (5.8)$$
Figure 5.24 The side view of the $\gamma=68^\circ$, $S=0.12$ drop after complete solidification. $\theta_c=59^\circ$ for the drop.
The energy balance across the fusion interface is then

\[ q_2 - q_1 = -\rho L \frac{d\delta}{dt}. \]  

(5.9)

Substituting (5.7) and (5.8) into (5.9) gives a differential equation for \( \delta(t) \). Taking \( \delta(t=0)=\delta_0 \) and \( \delta(t=\tau_s)=0 \) allows us to estimate the length scale \( \delta_o \) that is melted in a specified time \( \tau_s \), and we find that

\[ \delta_o = 2S(\beta - 1) \left[ \sqrt{\alpha \tau_s + (\alpha/U)^2} - \alpha/U \right]. \]  

(5.10)

For the \( S=0.12, \beta=2.24, \gamma=68^\circ \) case, \( U\sim 10^{-3} \) m/s just before "stick", and for microcrystalline wax \( \alpha=3.6 \cdot 10^{-8} \) m²/s (the average of liquid and solid wax thermal diffusivities; see Appendix A). Using (5.10) we find that a distance of about \( \delta_o \sim 10 \) µm is melted in \( \tau_s=\tau_s/2\sim 10^{-1} \) s. This simple calculation suggests that the solidified region that may be responsible for stick-slip motion is of thickness order \( \alpha/U \) (\( \alpha/U \sim 36 \) µm), which is \( 10^1 \) to \( 10^2 \) times larger than the expected inner region cut-off length scale \( \lambda \).
5.3.4 Wax on Solid Inclined Wax: Profilometry Study of $\gamma=68^\circ$, $S=0.12$ Case

To learn more about the arrest geometry of solidified drops on inlines, we examined the solidified $S=0.12$, $\gamma=68^\circ$ drop using a surface profilometer (Tencor model P10, maximum vertical deflection of 300 $\mu$m). The instrument allows the user to precisely map the surface topography of a sample using a diamond tipped stylus. It provides the surface topography data, as well as myriad statistics including surface roughness, maximum/minimum roughness height, etc.

The stylus was scanned transversely across the tail of the drop, and the cross-sections at various distances away from the receding contact line appear in Figure 5.26 (refer back to Figure 5.24). The profilometer was unable to measure the cross-sections of the

![Graph showing surface profile measurements](image)

<table>
<thead>
<tr>
<th>$x$ (mm)</th>
<th>Average $\theta_a$ on side of drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>16.7$^\circ$</td>
</tr>
<tr>
<td>3.1</td>
<td>16.9$^\circ$</td>
</tr>
<tr>
<td>7.1</td>
<td>22.0$^\circ$</td>
</tr>
<tr>
<td>11.1</td>
<td>32.2$^\circ$</td>
</tr>
<tr>
<td>15.1</td>
<td>39.6$^\circ$</td>
</tr>
<tr>
<td>19.1</td>
<td>44.2$^\circ$</td>
</tr>
</tbody>
</table>

**Figure 5.26** Cross sections of the tail of the $\gamma=68^\circ$, $S=0.12$ drop obtained with the profilometer. The receding contact line is at $x=0$. Data points are separated by 1 $\mu$m; there are 8,000 points on each of the curves in the Figure. The table shows the average of the left and right contact angles measured from the profilometry data of the figure. The angles were computed by fitting a straight line through the $h(y)$ data for $h \varepsilon [2 \mu m, 10\mu m]$. Data with $h < 2 \mu m$ were discarded because surface roughness reached heights up to 2 $\mu$m above the plane of the target surface.
"bulb" at the bottom of the drop because the height of the bulb far exceeded the maximum vertical deflection of the stylus.

Consider the evolution of the shape of the cross-sections shown in Figure 5.26. For $x>15$ mm the tail takes on a peculiar shape: it has steep angles at its edges, plateaus briefly toward the center of the cross-section, and rises into a distinct hump in the center. This profile results because throughout the drop spreading process molten fluid drains toward the bulb under the action of gravitational forces. Even after the perimeter of the drop has solidified, the molten fluid continues to drain slowly down the center of the drop, thereby building the centerline hump. The cross-sectional profiles indicate that the flow field that occurs during the spreading process is fully threedimensional.

The Table accompanying the Figure shows that the magnitudes of the transverse post-solidification contact angles increase with the distance $x$ from the arrested uphill contact angle. The values are consistent with our observation that the advancing contact angle arrest when $\theta_a^*=59^\circ$, but they do not explain why the bead arrests when the measured arrest angle is so much larger than the expected arrest angle.

5.4 Summary of Experiments Part II

This Chapter presents and discusses the results of empirical investigations of the spreading dynamics of millimeter scale molten drops. It considered wax drops deposited on horizontal solid wax targets, water drops deposited on ice targets, and wax drops deposited on inclined solid wax targets. From the experiments we obtain transient measures of the drop footprint radius $R$, the spreading velocity $U$, the apparent contact angle $\theta_o$, and (for wax on horizontal wax) the centerline height $H$. The measurements may be used to form an empirical velocity-angle relationship for each experiment.

The transient measurements were discussed in the context of the picture of the molten contact line suggested by Schiaffino and Sonin, and their model is found to be generally consistent with the observed spreading dynamics. However, their model does not explain our measurements of the downhill arrest angles for molten wax drops deposited on inclines. The angles are typically larger than those predicted using Schiaffino and Sonin's horizontal wax drop deposition correlation, and show dependence on the parameters other than $S$, namely $\beta$ and possibly $\gamma$. The "stick-slip" behavior characteristic to low $S$ drop deposition on a steep incline may be explained by the solidification of the region of thickness order $\alpha/U$ away from the molten contact line. The data presented in this Chapter is used in Chapter 6 to assess the validity of our theory for molten contact line advance (see Chapter 4).
Chapter 6

Comparison of the Theoretical and Experimental Velocity-Angle Relationship

The theoretical analysis of the advancing molten contact line suggests that Hoffman's law (4.40) is approximately valid when $\theta_o >> \theta_n$, and the near-arrest law (4.42) is approximately valid when $\theta_o - \theta_n << \theta_n$. These limits are shown graphically in the regime map, Figure 4.6. Outside of these limits a full numerical solution is required, and the model suggests it has the dimensionless form given by (4.39).

This Chapter compares the theoretical results of Chapter 4 to the empirical results of Chapter 5. Three sets of experiments are considered: §6.1 microcrystalline wax on horizontal solid wax, §6.2 water on horizontal ice, and §6.3 microcrystalline wax on a solid wax incline. For each of the experiments we attempt to match the measured velocity-angle relationship using the theoretical model of the advancing molten contact line. Considering the simplicity of the theoretical model, it provides surprisingly good agreement with the experimental data. The stick-slip motion described in Chapter 5, however, leads to velocity-angle histories and arrest conditions that are not well predicted using existing theory.

This Chapter also assesses the applicability of two criteria for complete molten contact line arrest ($Ca=0$): 1. the molten liquid reaches a small but non-zero "equilibrium" contact angle $\theta_c = \theta_m - \theta_n$ relative to the solidification front, and 2. the Peclet number $Pe_R$ based on the drop footprint size $R$ approaches unity, signaling the end of quasi-steady thermal conditions.

6.1 Microcrystalline Wax on Horizontal Solid Wax

As described in §5.1, we performed detailed analysis of the spreading dynamics of three molten wax drops on sub-cooled horizontal wax targets. The drops studied had a radius of approximately $a=1.92$ mm, and impacted the target with $We=1$ to 2.5. The solid wax targets were characterized by $S=0.14$, 0.33, and 0.65. In terms of Schiavino and Sonin's (1997a) analysis of the similarity laws of drop spreading, these experiments fall on the border between the impact-driven and the capillarity-driven regimes, and near the border between the inviscid and highly viscous limits.

We calculate the velocity-angle relationship for each of the spreading experiments from the $\theta_o$ and $U$ vs. $t$ data presented in §5.1.3. When calculating the capillary number $Ca=\mu U/\sigma$ we evaluate the absolute viscosity $\mu$ and the surface tension $\sigma$ at 95°C, just above the wax fusion temperature $T_f$. 
(the fluid very near the molten contact line is close to $T=T_f$, as explained in Chapter 2). Relevant values of the properties appear in Appendix A.

6.1.1 Wax on Horizontal Solid Wax: $S=0.14$

First, we examine the wax drop deposition for which $S=0.14$ and $\beta=2.61$. The $R(t)$ and $\theta_\alpha(t)$ data (refer to Figure 5.7a and 5.7b) suggest that the drop's inertia becomes unimportant after two events occur: 1. the $R/a$ curve passes its "shoulder" at $t\sim 25$ ms, and 2. the oscillations in $\theta_\alpha$ die out near $t\sim 40$ ms. For $t>40$ ms the drop creeps radially outward until arrest occurs at $t\sim 1.3$ s. The drop arrests at an angle of $\theta_\alpha^*=28.5^\circ$, which agrees well with the $33^\circ$ value predicted using Schiaffino and Sonin's (1997b) $\theta_\alpha^*=85S^{1/2}$ empirical correlation for microcrystalline wax.

Consider the application of the near-arrest law (4.42) to the data. We do not know a priori the values of $\theta_i$ and $\lambda h_m$, but Schiaffino and Sonin's work suggests that $\theta_i=\theta_\alpha^*$ and $\lambda=10^{-7}$ m. Researchers of the isothermal dynamic contact line problem (e.g. Boender, Chesters, van der Zanden, and Voinov) agree that the molecular cut-off length $h_m$ is of order $10^{-9}$ m, so we begin by assuming $\theta_i=29^\circ$ and $\lambda h_m=10^3$. §4.2.3 shows that for these parameters the near-arrest law provides good agreement with the numerical solution up to $\theta_\alpha=\theta_i=29^\circ$, so we estimate that for $\theta_i=29^\circ$ the near-arrest law should apply to data for which $\theta_\alpha<45^\circ$. A best fit of the data with $\theta_\alpha<45^\circ$ suggests that $\theta_i=23^\circ$, which is considerably smaller than original guess of $\theta_i=29^\circ$, so we further restrict the analysis to data with $\theta_\alpha<34^\circ$. Applying the near-arrest law to this smaller data set (highlighted using solid plot symbols) produces the results shown in Figure 6.1.

The curve fits are parameterized as follows: i) $\theta_i=28.5^\circ$ and $\lambda h_m=10^2$, ii) $\theta_i=21.2^\circ$ and $\lambda h_m=10^2$, and iii) $\theta_i=28.5^\circ$ and $\lambda h_m=6$. For all of the curves $\theta_m=\theta_i$, which is acceptable since we are simply trying to learn about the expected magnitudes of $\theta_i$ and $\lambda h_m$. Curve i) corresponds to the case for which Schiaffino and Sonin's arrest hypothesis ($\theta_\alpha^*=\theta_i$) and their solidification front cut-off length calculations ($\lambda h_m=10^2$) both hold. Curve ii) relaxes the arrest hypothesis, but maintains the value of the cut-off length, and curve iii) enforces the arrest hypothesis, but relaxes the restriction on the magnitude of the cut-off length. Values of $\kappa$ are calculated using (4.43).

Figure 6.1 suggests that if we accept $\theta_\alpha^*=\theta_i$, then $\lambda h_m$ must be several orders of magnitude smaller than expected to provide an acceptable near-arrest asymptotic solution. If we instead accept that $\lambda h_m=10^3$, then $\theta_\alpha^*$ must slightly exceeds $\theta_i$ (by about $10^\circ$) to ensure good agreement with the data. Based upon the discussion in Schiaffino and Sonin (1997c), there is much more liberty to vary $\theta_i$ by a few degrees than to vary $\lambda$ by several orders of magnitude. Our model therefore suggests that at molten contact line arrest $\theta_\alpha^*$ slightly exceeds $\theta_i$, and for this data $\lambda h_m=10^2$ and $\theta_i=20^\circ$ based upon the fit of the near-arrest law to the solid plot symbols in Figure 6.1.

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Figure 6.1 The near-arrest law is used to explore the asymptotic behavior of the empirical data obtained for wax drop deposition on a horizontal wax surface characterized by $S=0.14$, $\beta=2.61$. The solid plot symbols correspond to data points for which inertial forces have decayed sufficiently and $\theta_\alpha<34^\circ$.

Figure 6.2 shows that the approximate numerical solution for $\theta_m=\theta_z=19^\circ$, $\lambda/h_m=10^2$, $H/h_m=10^2$, and $Hq_\alpha=0$ (extrapolated from the $\theta_m=\theta_z=20^\circ$, $\lambda/h_m=10^2$, $H/h_m=10^3$, and $Hq_\alpha=0$ case of §4.2.3) agrees with the viscous-dominated data ($Ca$ less than about $3\cdot10^{-3}$). The $H/h_m$ parameter was chosen as $10^5$ because we estimate that $H\approx10^{-4}$ m. To an order-of-magnitude $q_\alpha=(P_{\alpha}-P_\infty)/\sigma$ is equal to the radius of curvature of the drop in the plane of the video images. By direct measurement $q_\alpha=10^1$ m$^{-1}$ during the final stages of spreading, so in dimensionless terms $Hq_\alpha=10^{-3}$. Figure 4.14 shows that when $Hq_\alpha$ is smaller than $10^{-2}$ the effect of the $Hq_\alpha$ term on the velocity-angle relationship is negligible, so for simplicity we take $Hq_\alpha=0$ in the numerical solutions.
Figure 6.2 A linearly extrapolated numerical solution is fitted to the empirical data for the wax drop deposition characterized by $S=0.14$, $\beta=2.61$. The numerical solution, which asymptotes to the near-arrest law as $Ca\to0$, has $\theta_m^*=\theta_s=19^\circ$, $\lambda/h_m=10^2$, $H/h_m=10^4$, and $Hq_o=0$.

The numerical solution and near-arrest law shown in Figure 6.2 do not give the proper limiting behavior as $Ca\to0$. In this limit they approach $\theta_m^*=\theta_s=19^\circ$, which is smaller than the measured value of the arrest angle $\theta_o^*=28.5^\circ$. We investigate two possible alterations to the model to remedy this shortcoming: 1. inclusion of an "equilibrium" angle $\theta_c=\theta_m-\theta_s$ to allow for the possibility that $\theta_m^*>\theta_s$, and 2. introduction of a critical capillary number $Ca^*$ below which the assumption of quasi-steady thermal conditions becomes invalid.

By permitting $\theta_m$ to exceed $\theta_s$, we allow for the possibility that there exists an equilibrium contact angle $\theta_c=\theta_m-\theta_s$ for a liquid on its own solidification front, both held at the fusion temperature $T_f$. The empirical data (including that of Schiaffino and Sonin) does not conclusively support or refute the possibility that a small equilibrium contact angle exists in this limit. Experiments in which the drop, target, and environment temperatures are held precisely at $T_f$ should be conducted to explore this limit.

We construct the velocity-angle relationship for $\theta_m^*>\theta_s$ by extrapolating from the numerical solutions presented in §4.2.3. The results appear in Figure 6.3, along with the numerical fit already
Figure 6.3 The extrapolated numerical solution for which $\theta_m = \theta_0 = 28.5^\circ$ is shown alongside the numerical solution of Figure 6.2. All other parameters are the same as in Figure 6.2. The value of $Ca^* (Ca$ when $Pe_R = 1)$ is about $5 \times 10^{-6}$.

shown in Figure 6.2. The new solution asymptotes to $\theta_m = 28.5^\circ$, and nearly identically matches the $\theta_m = \theta_0$ solution for $Ca > 10^{-4}$.

The second alteration listed above involves the introduction of a critical capillary number $Ca^*$, which is defined such that when $Ca \rightarrow Ca^*$ the thermal solution near the molten contact line shifts from quasi-steady to fully transient. In practice, we assume that $Ca$ falls abruptly to zero when $Ca = Ca^*$. An estimate of $Ca^*$ may be obtained from a scaling analysis of the energy equation for the solid material under the molten liquid (see Schiaffino and Sonin 1997c). They showed that the transient energy equation collapses to the quasi-steady form

$$\frac{U \partial T}{\partial x} = \alpha \nabla^2 T$$

(6.1)

on length scales $x/R << 1$ and $x/R << Pe_R^{-1/2}$ ($x$ is the horizontal distance from the contact line measured along the target surface and $Pe_R = UR/\alpha$ is a Peclet number for the spreading drop). The solution of the energy equation therefore undergoes a fundamental transformation on length scales $x \sim \alpha/U$ when $Pe_R \rightarrow 1$, and we hypothesize that quasi-steady molten contact line motion ceases in this limit.

The critical capillary number $Ca^*$ may be easily calculated by recognizing that

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\[ Ca = \frac{\alpha}{\sigma a/\mu} \frac{Pe_R}{R/a}, \]  

(6.2)

so

\[ Ca^* = \frac{\alpha}{\sigma a/\mu} \frac{1}{R/a} = \frac{Z^2}{Pr} \frac{1}{R/a}, \]  

(6.3)

where \( Pr \) is the Prandtl number for the fluid. \( Ca^* \) is indicated in Figure 6.3 by the vertical line labelled \( Pe_R=1 \), and it provides a reasonable estimate for the magnitude of the last measured \( Ca \) before arrest. The \( Pe_R=1 \) criterion serves as a supplemental arrest hypothesis for molten contact lines moving in a quasi-steady manner; arrest occurs when \( \theta_a \) falls to \( \theta_i \) (or \( \theta_m \) if there exists an equilibrium angle for a liquid on its own solid, both held at \( T_f \)) due to system scale dynamics, or when \( Pe_R \) reaches order unity during inertia-free, viscous-dominated molten contact line advance.

### 6.1.2 Wax on Horizontal Solid Wax: \( S=0.33 \)

Next consider the wax drop deposition for which \( S=0.33 \) and \( \beta=1.03 \). From the discussion of §5.1.3, the drop arrests at an angle \( \theta_a^*=54.0^\circ \) (see also Figures 5.8a and 5.8b). This arrest angle agrees satisfactorily with the \( 50^\circ \) angle predicted by Schiaffino and Sonin's \( \theta_a^*=85.5^{1/2} \) empirical correlation. Arrest occurs on a time scale of the order of the characteristic spreading time, so the majority of the \( Ca>0 \) spreading data is strongly influenced by inertial forces. Curve fits of the nearest-arrest law to the inertia-free data with \( \theta_a; \theta_s<\theta_i/2 \) (for \( \theta_i=44^\circ \)) appear in Figure 6.4. The data used in the curve fitting process in highlighted using solid plot symbols.

The curve fits in the Figure are for: i) \( \lambda/h_m=10^2 \) and \( \theta_a^*=\theta_i=54.0^\circ \), ii) \( \lambda/h_m=10^2 \) and \( \theta_s=43.6^\circ \), and iii) \( \lambda/h_m=15 \) and \( \theta_a^*=\theta_i=54.0^\circ \). In i) Schiaffino and Sonin's arrest hypothesis \( \theta_a^*=\theta_i \) and cut-off length calculations \( (\lambda/h_m=10^3) \) both hold. In ii) \( \lambda/h_m \) is held fixed and \( \theta_i \) is free to vary, and in iii) \( \lambda/h_m \) is free to vary and \( \theta_i \) is held fixed. We surmise that curve ii) provides the most convincing fit of the data, given the arguments presented in §6.1.1, and conclude that \( \theta_i \) must again be about \( 10^\circ \) below the arrest angle \( \theta_a^* \) to obtain a convincing fit of the data.

The fact that our model requires a non-zero difference between \( \theta_a^* \) and \( \theta_i \) represents a very important conclusion. It suggests, as described above, that there exists a non-zero equilibrium angle \( \theta_i \) for a molten liquid on its own solid, both held at \( T_f \). It also implies that Schiaffino and Sonin's arrest hypothesis

\[ \theta_a^* = \theta_s, \]  

(6.4)

may be more generally written as
\[
\theta^* = \theta_s + \theta_e = \theta_m,
\]  
(6.5)

where the equilibrium angle \( \theta_e \) is a physical property of the material system under consideration (see also Schiaffino and Sonin, 1997a, for a discussion regarding additional dimensionless parameters needed to describe the interfacial conditions at the contact line). With \( \theta_e = 10^\circ \) for microcrystalline wax, the correlation \( \theta^* = 85S^{1/2} \) and the arrest hypothesis (6.4) should be replaced by the equations

\[
\theta^* = \theta_m = 85S^{1/2}
\]  
(6.6)

and

\[
\theta_s = \theta_m - \theta_e = \theta_m - 10^\circ.
\]  
(6.7)

As one final point, this result suggests that at molten contact line arrest there exists a small "wedge" of molten liquid (with maximum thickness of order \( \lambda \theta_e = 20 \) nm for wax) between the solidification
front and the liquid's free surface. If this wedge actually exists, it may prove important in
determining the mechanism that bounds the heat flux at the molten contact line.

Returning to the $S=0.33$ data of Figure 6.4, we interpolate between the numerical solutions of
§4.2.3 to find the approximate velocity-angle relationship for $\theta_m=\theta_s=44^\circ$ ($\lambda/h_m=10^2$, $H/h_m=10^3$, $Hq_a=0$). The result appears in Figure 6.5, along with the corresponding form of the near-arrest law.
In Figure 6.6 we compare the numerical solution shown in Figure 6.5 to the numerical solution for
which $\theta_m=\theta_a^* = 54.0^\circ$ and $\theta_s=44^\circ$ (linearly extrapolated from the available numerical results). Indicated in the Figure is the critical capillary number $Ca^*$, which is within a factor of 2 of the smallest non-zero $Ca$ measured.
Figure 6.5 The numerical solution is fitted to the empirical data for the wax drop deposition (S=0.33, β=1.03). Other parameters not listed in the plot are $H/h_m=10^3$ and $H_{q_o}=0$.

Figure 6.6 The extrapolated numerical solution for which $\theta_m=\theta_s=54.0^\circ$ is shown alongside the numerical solution of Figure 6.5. All other parameters are the same as in Figure 6.5. The value of $Ca^*$ (Ca when $Pe_R=1$) is about $7\times10^{-6}$.
6.1.3 Wax on Horizontal Solid Wax: $S=0.65$

Consider the wax drop deposition case for which $S=0.65$ and $\beta=0.57$. As explained in §5.1.3 (see also Figures 5.9a and 5.9b) the drop comes to rest when its apparent contact angle is 75.0°, which agrees satisfactorily with the 69° angle predicted by Schiaffino and Sonin's $\theta^*=85S^{1/2}$ empirical correlation. Arrest occurs abruptly when $Ca\approx10^{-3}$, but contact angle oscillations continue for 30 to 40 ms after arrest. Because molten contact line arrest occurs on a time scale slightly shorter than the characteristic spreading time scale, we are unable to obtain any inertia-free spreading data. For the reader's information Figure 6.7 shows that an approximate numerical solution for $\theta_m=\theta_s=55°$ gives the correct velocity-angle trend.

Since no data is available for $0<Ca<10^{-3}$, we have no reason to explore solutions with $\theta_m>\theta_s$, which only differ from the $\theta_m=\theta_s$ solution at small $Ca$. For this experiment $Ca^*=8\cdot10^{-6}$ according to (6.3), but we measure capillary numbers no smaller than $10^{-3}$ before arrest occurs. This is consistent with our notion that the $Pe_R=1$ criterion serves as a supplemental arrest condition during quasi-steady advance of the molten contact line. The $S=0.65$ drop arrests before quasi-steady motion is realized because, according to the theory, system scale dynamics cause $\theta_s$ to fall to $\theta_t$ (or $\theta_m$).

![Graph showing experimental measurements of $\theta_s$ vs. $Ca$ for a wax drop deposited on a horizontal wax surface. The thermal conditions are given by $S=0.65$ and $\beta=0.57$. Other parameters not listed in the plot are $h/h_m=10^2$ and $Hq_m=0$.](image)

Figure 6.7 Experimental measurements of $\theta_s$ vs. $Ca$ for a wax drop deposited on a horizontal wax surface. The thermal conditions are given by $S=0.65$ and $\beta=0.57$. Other parameters not listed in the plot are $h/h_m=10^2$ and $Hq_m=0$. 

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6.1.4 Comparison of Hoffman's Law with the Data for Molten Wax Drop Deposition

We also compare the Hoffman-Tamner-Voinov law (4.40) to the empirical wax drop velocity-angle relationships. Figure 6.8 shows that the law provides qualitative agreement with the deposition data for roughly \( C_a > 4 \cdot 10^{-2} \) and \( \theta_a > 90^\circ \). We expect from the regime map (Figure 4.6) that Hoffman's law should approximately hold for quasi-steady molten contact line motion if \( \theta_a \gg \theta_i \) and \( \theta_i \ll 30^\circ \). These geometric conditions are met by much of the data in question, but the data is not quasi-steady. Further study of the effect of inertial forces on molten contact line dynamics will help to determine if the agreement between Hoffman's law and the data of Figure 6.8 is grounded in science or is simply coincidental.

![Graph showing comparison of Hoffman's law with data for molten wax drop deposition.](image)

Figure 6.8 Hoffman's law (4.40) for \( H/h_m = 10^4 \) and \( \theta_m = 0^\circ \) compared to the empirical velocity-angle relationship for wax drops deposited on horizontal wax targets.

6.2 Water Drops on Horizontal Ice Surfaces

§5.2 presents data for experiments in which water drops of radius \( a = 1.44 \) mm were gently \((We < 0.1)\) deposited onto horizontal ice surfaces. Transient data were acquired for deposition on targets characterized by \( S = 0.09, 0.20, \) and \( 0.32 \). In this section we apply the molten contact line model to the empirical data using the techniques employed in §6.1.

The water drop experiments differ from the wax experiments because of their smaller values of \( We \) and \( Z \). Referring to Schiaffino and Sonin (1997a), the water experiments fall definitively in
the inviscid, capillarity-driven spreading regime, while the wax experiments fall near the upper $We$ boundary of that region. This implies that the water drop spreading process is driven by capillarity and resisted by inertia in the bulk of the drop. Viscous forces, of course, are always important in regions sufficiently close to the contact line. In the $S=0.09$ experiment final arrest occurs after oscillations have decayed, so the final stages of drop spreading may be characterized as quasi-steady. For the $S=0.20$ and 0.32 cases oscillations persist for times considerably longer than the arrest time, so the quasi-steady requirements are never satisfied. We nevertheless attempt to apply our theory to each of the water drop experiments in order to explore the robustness of the model.

From the $\theta_e$ and $U$ vs. $t$ data presented in §5.2.3 we establish the empirical velocity-angle relationship for each of the spreading experiments. When calculating the capillary number $Ca=\mu U/\sigma$ we evaluate the absolute viscosity $\mu$ and the surface tension $\sigma$ at $2^\circ C$, just above the fusion temperature $T_f$ (the fluid very near the molten contact line is close to $T=T_f$ as explained in Chapter 2). Relevant values of the properties appear in Appendix A. Schiaffino (1996) suggests a cut-off length $\lambda$ for water which is, like that for wax, of the order of $10^{-7}$ m.

6.2.1 Water on Horizontal Ice: $S=0.09$

Consider the water drop deposition for $S=0.09$, $\beta=3.2$, the transient data for which appears in Figure 5.16. The velocity-angle relationship is shown in Figure 6.10, which highlights using solid plot symbols the data for which the drop's inertia is negligibly small and $\theta_e\approx\theta_s/2$ ($\theta_s=19^\circ$). Final arrest occurs when $\theta_e^*\approx23^\circ$. A best fit of the near-arrest law (fit to all solid plot symbols using minimization of least squares), and an appropriate numerical solution ($\theta_m=\theta_s=19^\circ$, $\lambda/\ell_m=10^2$, $H/h_m=10^5$, and $H=q_s=0$) are shown in the Figure. The numerical solution of Figure 6.10 is repeated in Figure 6.11, along with an approximate numerical solution for which $\theta_m=\theta_e^*=23^\circ$ and $\theta_s=19^\circ$. Since the difference $\theta_e-\theta_s=4^\circ$ is small the two numerical solutions are approximately equal except at very small $Ca$. For the $S=0.09$ water drop Equation (6.3) gives $Ca^*\approx8\cdot10^{-7}$, which is about one-seventh of the smallest measured $Ca$. 

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Figure 6.9 The numerical solution is fitted to the empirical data for the water drop deposition ($S=0.09$, $\beta=3.2$). Solid plot symbols correspond to post-inertial data points for which $\theta_a<33^\circ$. Other parameters used in the numerical solution are $H/h_m=10^2$ and $Hq_m=0$.

Figure 6.10 The extrapolated numerical solution for which $\theta_m^*=\theta_a^*=23^\circ$ is shown alongside the numerical solution of Figure 6.9. All other parameters are the same as in Figure 6.9. The value of $Ca^*$ ($Ca$ when $Pe_\alpha=1$) is about $8\cdot10^7$. 

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6.2.2 Water on Horizontal Ice: $S=0.20$

The transient data for the water drop deposition characterized by $S=0.20$ and $\beta=1.4$ appears in Figure 5.17. In this experiment arrest occurs abruptly while $\theta_0$ is falling under the action of inertial forces, and we estimate from the post-oscillation shape of the drop that $\theta_0^*=27^\circ$. The abruptness of arrest is evident in the velocity-angle relationship (Figure 6.11), which jumps to $Ca=0$ after a measurement near $Ca=10^4$. Surprisingly, the simple model gives good agreement with the data using "expected" values of the dimensionless parameters ($\theta_m=\theta_s=25^\circ$, $\lambda/h_m=10^2$, $H/h_m=10^3$, and $H_{q.o}=0$). In Figure 6.12 the numerical solution from Figure 6.11 is repeated, along with the solution for which $\theta_m=\theta_s^*=27^\circ$, $\theta_s=25^\circ$. Since $\theta_e=\theta_m-\theta_s=2^\circ$ is small the two numerical solutions are nearly identical. Equation (6.3) gives $Ca^*\sim1\cdot10^{-6}$, but since this drop arrests before quasi-steady motion is achieved the $Pe_R=1$ criterion not appropriate.

![Figure 6.11](image)

Figure 6.11 The numerical solution is fitted to the empirical data for the water drop deposition ($S=0.20$, $\beta=1.4$). Other parameters not listed in the plot are $H/h_m=10^3$ and $H_{q.o}=0$. 

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6.2.3 Water on Horizontal Ice: $S=0.32$

Figure 6.12 shows the extrapolated numerical solution for which $\theta_m=\theta_a=27^\circ$ is shown alongside the numerical solution of Figure 6.11. All other parameters are the same as in Figure 6.11. The value of $Ca^*$ ($Ca$ when $Pe_\infty=1$) is about $1 \times 10^{-6}$.

Figure 5.18 shows the transient data for a water drop deposited on a target characterized by $S=0.32$ and $\beta=0.9$. Just as in §6.2.2, the molten contact line arrests on a time scale slightly shorter than the characteristic spreading time scale so inertia-free velocity-angle data is unavailable. Nevertheless, Figure 6.13 shows that the model respectably fits the data for "expected" values of the dimensionless parameters ($\theta_m=\theta_s=30^\circ$, $\lambda/h_m=10^2$, $H/h_m=10^4$, and $Hq_s=0$). In Figure 6.14 the numerical solution from Figure 6.13 is repeated, along with the solution for which $\theta_m=\theta_a^*=39^\circ$, $\theta_s=30^\circ$. There is little difference between the two solutions when $Ca>10^4$.

Since the water drop spreading events are highly inertial, it is surprising that such good qualitative agreement between the model and the data is obtained for all three experiments over the entire range of measured $Ca$. The reason for this agreement is unclear at this time. We do not draw any conclusions about the value of $\theta_s$ for the water/ice system since the quasi-steady model is, strictly speaking, inappropriate for these experiments.
Figure 6.13 The numerical solution is fitted to the empirical data for the water drop deposition ($S=0.32$, $\beta=0.9$). Other parameters not listed in the plot are $H/h_m=10^5$ and $Hq_a=0$.

Figure 6.14 The extrapolated numerical solution for which $\theta_m=\theta_s=39^\circ$ is shown alongside the numerical solution of Figure 6.13. All other parameters are the same as in Figure 6.13. The value of $Ca^*$ ($Ca$ when $Pe_m=1$) is about $10^{-6}$. 

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6.2.4 Comparison of Hoffman's Law with Data for Water Drop Deposition

Figure 6.15 shows that Hoffman's law (with $H/h_m=10^5$ and $\theta_m=0^\circ$) does not agree well with the water drop deposition data. This is in marked contrast with Figure 6.8, which shows that the isothermal law qualitatively matches the wax drop empirical data. This disparity may result from the different values of $We$ and $Z$ for these two classes of spreading experiments (for water $We=0.07$ to 0.1 and $Z=5.2 \cdot 10^3$; for wax $We=1.1$ to 2.4 and $Z=8.8 \cdot 10^2$). As suggested in the discussion of Schiaffino and Sonin (1997a) the boundary between inviscid, capillarity-driven deposition (Region II in their paper) and highly viscous, capillarity-driven deposition (Region III) may actually be centered at $Z=10^2$. This would place our wax experiments on the $We$ boundary of Region III, where Hoffman's law generally applies. The water drop experiments still fall inside of Region II, where Hoffman's law is inappropriate.

![Figure 6.15 Hoffman's law (4.1) for $H/h_m=10^5$ and $\theta_m=0^\circ$ compared to the empirical velocity-angle relationship for water drops deposited on horizontal ice.](image)

6.3 Microcrystalline Wax on Inclined Solid Wax

§5.3 presents experimental results describing the deposition of millimeter scale molten wax drops on targets inclined at an angle $\gamma$ above the horizontal. Transient measurements were obtained for deposition on a $\gamma=28^\circ$ target with $S=0.20$, 0.40, and 0.60, and a $\gamma=68^\circ$ target with $S=0.12$ and 0.43. Chapter 5 explains that these drops generally arrest when the downhill (advancing) contact
angle is larger than the value predicted using Schiaffino and Sonin's $\theta^*_S=85S^{1/2}$ correlation. Also, "stick-slip" behavior is evident in the experiments with small $S$ (roughly $S \leq 0.2$). A simple calculation suggests that stick-slip motion involves solidification mechanisms that act on length scales of order $\alpha/U$. This section applies the quasi-steady molten contact line theory to the data, and presents some additional discussion of our observations.

6.3.1 Wax on Inclined Wax: $\gamma=28^\circ$

The empirical velocity-angle data for the $S=0.20, \gamma=28^\circ$ experiment appears in Figure 6.16. The clustering of the data between $Ca=2\cdot10^{-4}$ and $10^{-3}$ results from stick-slip motion, and the downhill contact angle arrests when $\theta^*_a=47^\circ$. The Figure also shows the numerical solution obtained with the model for $\theta_m=38^\circ, \theta_s=28^\circ, \lambda/h_m=10^2$, and $Hq_0=0$. The values of $\theta_m$ and $\theta_s$ were calculated using (6.5) and (6.6) with $\theta_a=10^\circ$. The agreement of the theoretical result with the data for $Ca>4\cdot10^{-4}$ is acceptable, but the data break-off from the theory during the final moments of contact line advance.

![Figure 6.16 The numerical solution compared to the empirical data for the wax drop deposition on an incline ($S=0.20$, $\beta=3.42$, $\gamma=28^\circ$). Other calculation parameters not listed in the plot are $H/h_m=10^3$ and $Hq_0=0$. The value of $Ca^*$ when $Pe_L=1$ is about $3\cdot10^{-6}$, and the value of $Ca^*$ when $Pe_L=1$ is approximately $1\cdot10^{-5}$.](image)
The calculation of the critical capillary number \( Ca^* \) for these experiments should account for the aspect ratio (length to width ratio) of the elongated drop. Since the calculation is only valid to an order of magnitude, we simply present upper and lower bounds on the value of \( Ca^* \); the lower calculated with \( R/a \) replaced by \( L/a \) in (6.3), and the upper with \( R/a \) replaced by unity (i.e. \( R=a \)). Both values are indicated in Figure 6.16, and the capillary number where \( Pe_a=1 \) agrees within an order of magnitude with the final measurement with \( Ca>0 \).

The experimentally determined velocity-angle relationships for the \( S=0.40 \) and \( 0.60 \) cases appear in Figures 6.17 and 6.18. For the \( S=0.40 \) case \( \theta_a^*=57^\circ \), and for the \( S=0.60 \) case \( \theta_a^*=59^\circ \). These values agree reasonably with the \( \theta_a^*=85 S^{1/2} \) correlation (referring to Figure 5.21, some of the advancing arrest angles fall close to the Schiaffino and Sonin correlation for \( S>0.4 \)).

Figure 6.17 shows a numerical solution for which \( \theta_m=85 S^{1/2}=54^\circ, \theta_s=\theta_m-10^\circ=44^\circ, \lambda/h_m=10^2 \), and \( Hq_a=0 \), and Figure 6.18 shows a solution for which \( \theta_m=85 S^{1/2}=56^\circ, \theta_s=\theta_m-10^\circ=46^\circ, \lambda/h_m=10^3 \), and \( Hq_a=0 \). The disparity between the empirical data and the theory is qualitatively similar to that observed for wax drop spreading over horizontal targets with \( S=0.33 \) and \( 0.65 \) (see Figures 6.6 and 6.7). As in the horizontal target cases, we attribute the difference between theory and experiment to the dominance of inertial effects during the early stages of spreading. It is unclear whether the inclination of the target plays a significant role in degrading the fit of theory to experiment. For reference the Figures also indicate the critical capillary numbers based upon \( Pe_L=1 \) (\( Ca^* \sim 4 \cdot 10^{-6} \) for both experiments) and \( Pe_a=1 \) (\( Ca^* \sim 1 \cdot 10^{-6} \)).

![Figure 6.17](image-url)

Figure 6.17 The numerical solution compared to the empirical data for the wax drop deposition on an incline (\( S=0.40, \beta=1.36, \gamma=28^\circ \)). Other calculation parameters not listed in the plot are \( h/h_m=10^3 \) and \( Hq_a=0 \). The value of \( Ca^* \) when \( Pe_L=1 \) is about \( 4 \cdot 10^{-6} \), and the value of \( Ca^* \) when \( Pe_a=1 \) is approximately \( 1 \cdot 10^{-5} \).
Figure 6.18 The numerical solution compared to the empirical data for the wax drop deposition on an incline ($S=0.60$, $\beta=0.94$, $\gamma=28^\circ$). Other calculation parameters not listed in the plot are $H/h_m=10^5$ and $H/q_0=0$. The value of $Ca^*$ when $Pe_m=1$ is about $4\cdot10^{-4}$, and the value of $Ca^*$ when $Pe_m=1$ is approximately $1\cdot10^{-3}$.

6.3.2 Wax on Inclined Wax: $\gamma=68^\circ$

The velocity-angle relationships for the $\gamma=68^\circ$ experiments with $S=0.12$ and $S=0.43$ appear in Figures 6.19 and 6.20. In order to increase the field of view to observe the full length of these drops during spreading, we used a zoom lens with smaller magnification than the microscope objective lens used in our other experiments. As a result we could not resolve any small $\theta_a$ oscillations that might have occurred during stick-slip motion.

Just as in §6.3.1, the numerical solutions shown in Figures 6.19 and 6.20 are based upon parameters calculated using (6.5) and (6.6) with $\theta_v=10^\circ$. For the $S=0.12$ case there is insufficient data with $Ca>10^2$ to confirm whether the theory properly matches the empirical $\theta_v$ versus $Ca$ trend during the early stages of spreading. The data definitively departs from the theoretical curve when $Ca<4\cdot10^{-3}$, and as discussed in §5.3.3, arrest occurs when $\theta_v=59^\circ$, a factor of two larger than our prediction based upon (6.5).

The data for the $S=0.43$ case shown in Figure 6.20 is anomalous as well. As in Figure 6.17 the model appears to underpredict $Ca$ for a given $\theta_v$ during the early stages of spreading. For
Figure 6.19 The numerical solution compared to the empirical data for the wax drop deposition on an incline \((S=0.12, \beta=2.24, \gamma=68^\circ)\). Other calculation parameters not listed in the plot are \(H/h_m=10^3\) and \(Hq_0=0\). The value of \(Ca^*\) when \(Pe_I=1\) is about \(8 \times 10^{-7}\), and the value of \(Ca^*\) when \(Pe_u=1\) is approximately \(1 \times 10^{-5}\).

Figure 6.20 The numerical solution compared to the empirical data for the wax drop deposition on an incline \((S=0.43, \beta=0.64, \gamma=68^\circ)\). Other calculation parameters not listed in the plot are \(H/h_m=10^3\) and \(Hq_0=0\). The value of \(Ca^*\) when \(Pe_I=1\) is about \(2 \times 10^{-6}\), and the value of \(Ca^*\) when \(Pe_u=1\) is approximately \(1 \times 10^{-5}\).
the data does not follow the trend predicted by the theory, and arrest occurs when $\theta_a$ exceeds our prediction of $\theta_a^* = \theta_m = 56^\circ$ by more than 30%.

Figures 6.19 and 6.20 indicate the critical capillary numbers based upon $Pe_L=1$ ($Ca^* \approx 8 \cdot 10^{-7}$ for $S=0.12$ and $Ca^* \approx 2 \cdot 10^{-6}$ for $S=0.43$) and $Pe_a=1$ ($Ca^* \approx 1 \cdot 10^{-5}$). The final non-zero measurements of $Ca$ are approximately $5 \cdot 10^{-4}$ for $S=0.12$ and $3 \cdot 10^{-4}$ for $S=0.43$, which are about one-and-a-half orders of magnitude larger than the upper bound on $Ca^*$.

For drops on the $\gamma=68^\circ$ incline, the theories for molten contact line arrest, namely that arrest occurs when system scale dynamics cause $\theta_a$ to fall to $\theta_i$ (or $\theta_m$ if there exists a non-zero "equilibrium" angle $\theta_e$) or when $Pe_L$ or $Pe_a$ approach unity for quasi-steady molten contact line advance, appear to be lacking. The disparity likely arises because, as evinced by the stick-slip behavior, $\beta$ has a non-negligible effect on the drop spreading history and the arrest conditions. We do not include $\beta$ in our model because calculations (see Chapter 2; Schiaffino and Sonin, 1997c) and previous experiments (see Schiaffino and Sonin, 1997a) suggest that $\beta$ plays only a minor role in determining the arrest conditions.

### 6.4 Summary of the Comparison of Theory with Experiment

This Chapter applies the quasi-steady molten contact line theory developed in Chapter 4 to experimental data that describes the spreading of millimeter-scale molten drops over cold, solid targets. It considers the spreading of microcrystalline wax drops on horizontal wax targets, water drops on ice, and wax drops on targets inclined at: $\gamma=28^\circ$ and $68^\circ$ above the horizontal.

The deposition of wax drops on horizontal wax surfaces is well predicted using the theory, provided the data meets the requirements of quasi-steadiness. For wax drop data that is significantly influenced by the impact or inertial forces, the theory tends to underpredict $Ca$ for a given $\theta_a$. The near-arrest law (4.42) was used to show that $\theta_a^*$ must exceed $\theta_e$ by a small "equilibrium" angle ($\theta_e=10^\circ$ for microcrystalline wax) in order to ensure good agreement between theory and experiment. This leads us to recast Schiaffino and Sonin's (1997b) arrest hypothesis ($\theta_a^* = \theta_e$) and empirical correlation for microcrystalline wax drop deposition ($\theta_a^* = 8 S^{1/2}$) as

$$\theta_a^* = \theta_m = 8 S^{1/2}$$  \hspace{1cm} (6.8)

and

$$\theta_s = \theta_m - \theta_e = \theta_m - 10^\circ.$$  \hspace{1cm} (6.9)

Since careful experiments to investigate the possibility that $\theta_e \neq 0$ have not been completed, we must allow for the possibility that $\theta_e$ is an artifact of our model. We also introduce the concept of a
critical capillary number \( Ca^* \) (the \( Ca \) for which \( Pe_R=1 \)) below which quasi-steady advance of the molten contact line ceases. For quasi-steady spreading \( Ca^* \) gives an order of magnitude estimate for the value of \( Ca \) just before drop arrest. Also, we found that the Hoffman-Tanner-Voinov law (4.40) qualitatively predicts the form of the velocity-angle relationship for the early stages of wax drop spreading, when \( \theta_s \gg \theta_c \).

The water drop experiments fall completely within Schiaffino and Sonin's (1997a) "inviscid, capillarity-driven" spreading regime. The motion of the drops was therefore resisted by inertial forces in the bulk of the drop, and by viscous forces very near the contact line. The quasi-steady requirements are never satisfied by these drops (except during the final stages of spreading in the \( S=0.09 \) experiment), but our simple theory predicts the trends in the velocity-angle relationships surprisingly well. We do not offer an explanation for this agreement. Hoffman's law does not match the empirical data over the measured range of \( Ca \).

Equations (6.8) and (6.9) are used to attempt to fit the theory to the empirical data for wax drop depositions on inclined targets, but the efforts met with only limited success. For \( S=0.20, \gamma=28^\circ \) the theory matched the data until the final stages of stick-slip motion. The \( S=0.40 \) and 0.60 experiments were influenced strongly by inertial forces, so the theory underpredicted \( Ca \) for a given \( \theta_s \). The \( \gamma=68^\circ \) experiments resulted in velocity-angle histories and arrest angles that differed markedly from the empirical correlation (6.8). The disparity may be linked to the role played by \( \beta \) in driving the stick-slip motion of the contact line.
Chapter 7

Concluding Remarks

In this Chapter we summarize the findings of this thesis and present suggestions for future research.

7.1 Summary of Results and Conclusions

This thesis examines the molten contact line problem by investigating the deposition of millimeter-scale molten drops on cold, solid targets. There are two primary areas of experimental study. First, we obtain data describing the arrest conditions ($\theta_a^*$ and $R'/a$) for new material systems not explored by Schiaffino and Sonin. Second, we obtain the velocity-angle relationship for molten drops spreading over sub-cooled solid targets. Even though this relationship is central to the solution of the molten contact line problem, our measurements represent the first of their kind. Motivated by these experiments we develop a simple theoretical model of the molten contact line region that enables us to predict the velocity-angle relationship as a function of system parameters. This is not a first-principles model: the contact line heat flux singularity remains unresolved, and the solidification front is replaced with a "wedge-step" approximation. Despite its approximations the model provides surprisingly good agreement with much of the experimental data.

We experimentally obtain the post-arrest geometry for three types of deposition experiments: 1. solder on oxidized solid solder, 2. octacosane on solid octacosane with varying surface roughness, and 3. octacosane on glass, both clean and coated with several types of self-assembled monolayers (SAMs). These experiments add to the molten drop deposition data of Schiaffino and Sonin, and also provide insight into the importance of target surface chemistry on the molten drop deposition process.

The solder experiments showed that nanometer-scale surface oxidation ($\text{SnO}_2$) has a negligible effect on the $\theta_a^*$ versus $S$ relationship for the solder/solder system for $S=0.02$ to 0.07. Since the interfacial properties are approximately constant for all targets (they all have nanometer-scale oxide layers), our findings imply that the oxide layer does not significantly effect the heat transfer from the molten drop to the targets. Specifically, thermal diffusion through the layer occurs much faster than other relevant transport processes, and the thermal resistance of the layer must be negligibly small.

In the octacosane on solid octacosane experiments we found that $\theta_a^*$ was only weakly dependent on $S$ over the range $S=0.06$ to 0.5. We contrast this to the results for microcrystalline wax, which show that $\theta_a^*$ is a strong function of $S$ over the same range. This behavior may be linked
to the difference in thermal and interfacial properties between octacosane and wax. We examined octacosane drop deposition on both "rough" ($R_{rm}=8$ to 22 $\mu m$ and surface angles primarily in the range $\pm 10^{\circ}$) and "smooth" ($R_{rm}=2$ to 4 $\mu m$ and surface angles primarily in the range $\pm 1.6^{\circ}$). These roughness distributions led to insignificant differences in the drop arrest geometry because the measured arrest angles $\theta_a$ were always much larger than the surface angles ($\theta_a > 60^{\circ}$ for all data obtained).

We also deposited octacosane drops on glass slides coated with several different kinds of SAMs. The structure of the SAM molecules determines the surface energy of the coating, and hence determines the equilibrium angle $\theta_e$ for liquid octacosane on the coated glass (held at $T>T_f$). Our experiments suggested that $\theta_e$ played an important role in the $\theta_a$ versus $S$ relationship up to roughly $S=0.2$. For larger values of $S$ the arrest geometry was nearly independent of $S$.

Taken together, these experiments confirm that the physical chemistry and properties of the target surface (its chemical composition and associated surface energy, surface roughness, etc.) may affect the velocity-angle relationship and arrest conditions of a molten drop under certain conditions. For the homologous problem, in which drop and target are the same material, the surface roughness will affect spreading and arrest unless the angles of the surface are small compared with the arrest angle. For the non-homologous problem the surface of the target may be chemically modified to influence the spreading and arrest behavior of a molten drop via $\theta_e$.

Schiaffino and Sonin hypothesized that during molten drop spreading a solidification front trails the advancing molten contact line. Their attempts to calculate the angle $\theta_s$ of the front just behind the contact line were, however, vexed by the presence of a singularity in the heat flux at the molten contact line. They hypothesized that an unknown mechanism bounds the heat flux and that the angle $\theta_s$ is constant up to a cut-off distance $\lambda$ from the contact line.

With this result in mind, we use a simple "wedge-step" representation of the solidification front when developing our model for the flow field near the advancing molten contact line. In the inner region ($r<\lambda$) we take $\theta_s=\text{constant}$, and in the outer region ($r>\lambda$) we take $\theta_s=0$. Since the viscous stresses are largest in the inner region (viscous stresses scale with $r^{-2}$ in the dynamic contact line problem) the geometry of the outer region has only a minor effect on the problem solution. The model leads to an approximate velocity-angle relationship for the molten dynamic contact line of the form

$$\theta_a = f\left(Ca; \theta_s, \theta_m, \frac{\lambda}{h_m}, \frac{H}{h_m}, Hg_a \right).$$

(7.1)

Numerical solutions of (7.1) for a range of parameters appear in Appendix B, for those who wish to interpolate or extrapolate from our results.
In the limit of small apparent contact angles \(\theta_a \ll 30^{1/2}\) and much smaller solidification angles \(\theta_s \gg \theta_s\), the relationship (7.1) reduces to the Hoffman-Tanner-Voinov law

\[
Ca = \kappa_H \left( \theta_a^3 - \theta_m^3 \right),
\]

where \(\kappa_H\) is a logarithmic function of the dimensionless length scale of observation \(H/\lambda_m\) (see Equation (4.41)). When the liquid wedge between the free surface and the solidification front is much smaller than the solidification angle \(\theta_a - \theta_s \ll \theta_s\), Equation (7.1) reduces to what we call the near-arrest law,

\[
Ca = \kappa_s \frac{\left( \theta_a - \theta_s \right)^4 - \left( \theta_m - \theta_s \right)^4}{\sin \theta_s}.
\]

Here, \(\kappa_s\) is a logarithmic function of the inner region parameters \(\theta_s\) and \(\lambda/\lambda_m\) (see Equation (4.43)). Equation (7.3) suggests that the solidification angle is the most important parameter in determining the velocity-angle relationship and the arrest geometry of a molten contact line. We emphasize that (7.3) is an asymptotic solution to (7.1), and applies only in the final stages of slow, quasi-steady spreading (just before arrest), where the flow is viscosity-dominated.

The advancing molten contact line theory was compared to data obtained for three types of experiments: 1. microcrystalline wax on horizontal solid wax, 2. water on horizontal ice, and 3. wax on inclined solid wax.

For the wax on horizontal wax experiments we found using (7.3) that the angle \(\theta_s\) must fall about 10° below the arrest angle \(\theta_a^*\) in order to match theory with experiment. This implies that there exists a small "equilibrium" contact angle \(\theta_a = \theta_m - \theta_s\) between the molten liquid and its own solid (\(\theta_m\) and \(\theta_s\) are both measured with respect to the target surface). Thus, the arrest correlations of Schiaffino and Sonin may be written more generally as

\[
\theta_a^* = \theta_m = f(S),
\]

where

\[
\theta_m = \theta_s + \theta_e.
\]

Using Schiaffino and Sonin's empirical correlation for molten wax drop deposition, \(\theta_a^* = \theta_m = 855^{1/2}\) and \(\theta_e = 10^\circ\) we obtained good agreement between theory and quasi-steady experimental data for wax drops deposited on horizontal targets. As expected, the quasi-steady model does not match spreading data significantly influenced by the inertia associated with drop impact.

Much to our surprise, with "expected" values of the parameters the model also predicts well the empirical velocity-angle relationships for water drops deposited on ice. In these experiments
inertial forces dominate viscous forces in the bulk of the drop, so our quasi-steady model should not apply. We do not offer an explanation for this agreement.

The wax and water deposition experiments on horizontal targets appear to be consistent with the presence of a solidification front under the advancing molten contact line. In both sets of experiments careful tracking of the evolution of the velocity-angle relationship reveals that contact line advance halts when the apparent contact angle falls to a value consistent with measurements of the final arrest angle. In cases where arrest occurred before inertial forces decayed, we made several important observations. First, we found that the apparent contact angle may fall to values smaller than the final arrest angle, presumably because the forces associated with recoil pulled the contact line backward over the thin (order of 1 µm thick, say) solidification front. Second, we observed that contact line motion may restart during post-arrest oscillations. When \( \theta_a \) oscillates after arrest occurs, restart may result from remelting of the molten contact line region during periods in which \( \theta_a \) increases. A minimum condition for this kind of restart is \( \beta > 1 \).

Wax drops deposited on inclined targets generally arrest with advancing contact angles that are larger than those of drops deposited on horizontal targets (see 7.4). For \( S < 0.2 \) at least, this result may be linked to an observed stick-slip motion of the contact line. For the \( S = 0.12, \gamma = 68^\circ \) experiment we estimate that the characteristic period of stick-slip motion is approximately \( \tau_{ss} \approx 0.2 \text{ s} \). We propose a simple mechanism for near-contact line remelting that suggests that stick-slip motion is driven by \( \beta \) and involves solidification mechanisms acting on a length scale of order \( \alpha / U \). Unfortunately, the heat flux singularity prevents us from predicting the solidification angle \( \theta_s \) or the role of \( \beta \) as a driver of stick-slip motion from first-principles.

The quasi-steady molten contact line theory works well for the majority of the \( S = 0.20, \gamma = 28^\circ \) spreading data, but it does not match the data just before arrest. The other \( \gamma = 28^\circ \) data are significantly affected by inertial forces. The \( \gamma = 68^\circ \) cases are not well predicted using our quasi-steady theory, presumably because inertial forces and stick-slip behavior influence the data.

### 7.2 Suggestions for Future Work

The key to the molten contact line problem lies in the development of a theory that allows for the direct prediction of \( \theta_s \) from first principles. Based upon the experimental data we expect that to the lowest order, \( \theta_s \) will be a function only of \( S \), but under certain conditions \( \beta \) appears to play a significant role in the velocity-angle relationship. We expect that the resolution of the heat flux singularity requires a fundamental modification of the thermal boundary condition along the solidification front very near the molten contact line. In the formulation used by Schiaffino and Sonin, the temperature along the front was fixed at \( T = T_f \) outside of the cut-off length \( \lambda_s \), and the heat
flux was assumed constant for \( r < \lambda \). The proper form of the near-contact-line thermal boundary condition is unclear at this time.

Although our simple quasi-steady model agrees well with much of the data, the dominance of inertia in many experiments disqualified some of the data from comparison with theory. On a small enough length scale, the physics of the contact line depends only on the balance of viscous and surface tension forces, but in practice observations are made on larger length scales where inertia becomes important. Further exploration of the influence of inertial forces on both isothermal and molten contact line dynamics are in order.

We conclude with a final point regarding the molten contact line problem. While the isothermal contact line problem relates the nanoscale \((\sim h_n)\) to the microscale \((\sim H)\), the molten dynamic contact line problem links the nanoscale, the mesoscale \((\sim \lambda \text{ or } \alpha/U)\), and the microscale. The couplings between these scales are poorly understood at best, largely because the mesoscale is controlled by unknown mechanisms that mitigate the heat flux singularity at the contact line. We have shown in this thesis that both the nanoscale (physical chemistry of surfaces) and the mesoscale \((\theta_n, \lambda h_n, \alpha/U)\) play important roles in determining the macroscale behavior of moving molten contact lines. This represents a first attempt to assemble a theory which begins to bridge these scales in a consistent manner.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Thermal diffusivity</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Ratio of liquid superheat to target sub-cooling, $\beta=(T_o-T_f)/(T_r-T_i)$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Dynamic contact angle in Figure 1.5</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Inclination angle above the horizontal</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Angular polar coordinate</td>
</tr>
<tr>
<td>$\kappa_H$</td>
<td>Proportionality coefficient in the Hoffman-Tanner-Voinov law, e.g. Equation (2.2)</td>
</tr>
<tr>
<td>$\kappa_c$</td>
<td>Proportionality coefficient in the near-arrest law, e.g. (4.35)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Cut-off length for inner region. $\lambda=10^{-7}$ m according to Schiaffino and Sonin (1997c)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Absolutely viscosity (Pa·s)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Kinematic viscosity, $\nu=\mu/\rho$ (m$^2$/s)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Surface tension (N/m)</td>
</tr>
<tr>
<td>$\sigma_{sg}$</td>
<td>Interfacial energy of solid/gas interface</td>
</tr>
<tr>
<td>$\sigma_{sl}$</td>
<td>Interfacial energy of solid/liquid interface</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle of the free surface with respect to the horizontal, see Figure 4.3</td>
</tr>
<tr>
<td>$\theta_a$</td>
<td>Apparent contact angle measured at height $H$</td>
</tr>
<tr>
<td>$\theta_c$</td>
<td>Apparent contact angle at molten contact line arrest</td>
</tr>
<tr>
<td>$\theta_e$</td>
<td>Equilibrium contact angle</td>
</tr>
<tr>
<td>$\theta_i$</td>
<td>Angle of the rough surface at data point $i$ in the profilometry study</td>
</tr>
<tr>
<td>$\theta_m$</td>
<td>Molecular contact angle, $\theta$ evaluated at the molecular cut-off $h_m$</td>
</tr>
<tr>
<td>$\theta_s$</td>
<td>Angle of the solidification front just behind the advancing molten contact line</td>
</tr>
<tr>
<td>$\theta_{s, l}$</td>
<td>Local angle of the solidification front, $\theta_{s, l}(x=0)=\theta_s$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Characteristic time scale</td>
</tr>
<tr>
<td>$\tau_d$</td>
<td>Decay time for drop oscillations</td>
</tr>
<tr>
<td>$\tau_i$</td>
<td>Inertial time scale, $\tau_i=(\rho a^2/\sigma)^{1/2}$</td>
</tr>
<tr>
<td>$\tau_f$</td>
<td>Fluid stress tensor</td>
</tr>
<tr>
<td>$\tau_{osc}$</td>
<td>Characteristic oscillation time scale</td>
</tr>
<tr>
<td>$\tau_{sg}$</td>
<td>Fluid shear stress in polar coordinates</td>
</tr>
<tr>
<td>$\tau_{ss}$</td>
<td>Time scale associated with stick-slip motion</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Stream function</td>
</tr>
</tbody>
</table>

$\alpha$ | Drop radius |

$A, B, C, D$ | Undetermined constants in Equation (4.19) |

$B_o$ | Undetermined constants in Equation (2.5) |

$Bo$ | Bond number, $Bo=\rho g a^2/\sigma$ |

$c$ | Specific heat capacity (J/kg·K) |

$Ca$ | Capillary number, $Ca=\mu U/\sigma$ |

$Ca^*$ | Critical capillary number ($Ca$ when $Pe=1$), see Equation (6.3) |

$D/Dt$ | Total derivative operator, $D/Dt=\partial/\partial t+U\cdot\nabla$ |

$f(\cdot)$ | Function |

$fps$ | Frames per second |

$g$ | Gravitational constant, $g=9.8$ m/s$^2$ |

$h_m$ | Molecular cut-off scale, $h_m=10^{-5}$ m in this thesis |

$h$ | Height of the free surface above the plane of the solid |

$H$ | Height of the free surface at which $\theta_c$ is observed |

$H_{hem}$ | Centerline height of an arrested hemispherical drop, see Equation (5.4) |

$L$ | Latent heat (J/kg); length of a drop deposited on an incline |
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta m$</td>
<td>Increase in mass of a sample due to the deposition of drops, see Equation (3.3)</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of drops deposited on sample, see Equation (3.3)</td>
</tr>
<tr>
<td>$q$</td>
<td>Curvature (m$^{-1}$)</td>
</tr>
<tr>
<td>$q_b$</td>
<td>Curvature of the free surface at the boundary of the inner and outer regions</td>
</tr>
<tr>
<td>$q_a$</td>
<td>Curvature of the free surface at height $H$</td>
</tr>
<tr>
<td>$q_l$</td>
<td>Heat flux from the molten liquid to the solidification front</td>
</tr>
<tr>
<td>$q_s$</td>
<td>Heat flux from the solidification front to the solid</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
</tr>
<tr>
<td>$P_w$</td>
<td>Ambient pressure</td>
</tr>
<tr>
<td>$Pe_R$</td>
<td>Peclet number based on dimension $R$, $Pe_R=UR/\alpha$</td>
</tr>
<tr>
<td>$Pr$</td>
<td>Prandtl number, $Pr=v/\alpha$</td>
</tr>
<tr>
<td>$r$</td>
<td>Radial polar coordinate, distance from the contact line into the fluid or solid</td>
</tr>
<tr>
<td>$r_{hor}$</td>
<td>Horizontal radius of a pendant molten wax drop just before snap-off, see Equation (5.1)</td>
</tr>
<tr>
<td>$r_{vert}$</td>
<td>Vertical radius of a pendant molten wax drop just before snap-off, see Equation (5.1)</td>
</tr>
<tr>
<td>$R$</td>
<td>Footprint radius of the deposited drop</td>
</tr>
<tr>
<td>$R^*$</td>
<td>Footprint radius of the deposited drop at arrest</td>
</tr>
<tr>
<td>$R_{rms}$</td>
<td>Root-mean-squared surface roughness, see Equation (3.4)</td>
</tr>
<tr>
<td>$Re_H$</td>
<td>Reynolds number based on dimension $H$, $Re_H=\rho U H / \mu$</td>
</tr>
<tr>
<td>$Re_a$</td>
<td>Reynolds number based on dimension $a$, $Re_a=\rho U a / \mu$</td>
</tr>
<tr>
<td>$S$</td>
<td>Stefan number, $S=c(T_f-T_a)/L$</td>
</tr>
<tr>
<td>$SAM$</td>
<td>Self-assembled monolayer</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_f$</td>
<td>Fusion temperature</td>
</tr>
<tr>
<td>$T_w$</td>
<td>Ambient temperature</td>
</tr>
<tr>
<td>$T_p$</td>
<td>Hot plate surface temperature</td>
</tr>
<tr>
<td>$T_o$</td>
<td>Molten drop temperature</td>
</tr>
<tr>
<td>$T_i$</td>
<td>Target surface temperature</td>
</tr>
<tr>
<td>$U$</td>
<td>Spreading velocity, $U=\partial R/\partial t$ or $\partial L/\partial t$</td>
</tr>
<tr>
<td>$U_i$</td>
<td>Velocity associated with the inertial time scale, $U_i=(\sigma/\rho a)^{1/2}$</td>
</tr>
<tr>
<td>$v_r$</td>
<td>Radial velocity in polar coordinates ($r, \phi$)</td>
</tr>
<tr>
<td>$v_\phi$</td>
<td>Angular velocity in polar coordinates ($r, \phi$)</td>
</tr>
<tr>
<td>$V$</td>
<td>Impact velocity</td>
</tr>
<tr>
<td>$V_{osc}$</td>
<td>Characteristic velocity associated with oscillations of a drop about sphericity</td>
</tr>
<tr>
<td>$We$</td>
<td>Weber number, $We=\rho V^2 a / \sigma$</td>
</tr>
<tr>
<td>$We_{osc}$</td>
<td>Characteristic $We$ associated with oscillations of a drop about sphericity</td>
</tr>
<tr>
<td>$x$</td>
<td>Distance from the contact line along the plane of the target surface</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>Spacing between roughness data points in Equation (3.5)</td>
</tr>
<tr>
<td>$y$</td>
<td>Transverse coordinate for elongated drop profilometry study, see Figure (5.26)</td>
</tr>
<tr>
<td>$y(x)$</td>
<td>Deviation of the rough surface from a straight line, see Equation (3.4)</td>
</tr>
<tr>
<td>$Z$</td>
<td>Ohnesorge number, $Z=\mu(\rho a \sigma)^{1/2}$</td>
</tr>
</tbody>
</table>
References


Cox, R. G. Inertial and viscous effects on dynamic contact angles. *J. Fluid Mech.*, 357, 249-278.


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Schiaffino, Stefano and Ain A. Sonin, 1997c. On the theory for the arrest of an advancing molten contact line on a cold solid of the same material. *Phys. Fluids, 9* (8), 2227-2233.


## Appendix A

### List of Material Properties

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_f$</th>
<th>$k$</th>
<th>$\rho$</th>
<th>$c$</th>
<th>$\alpha$</th>
<th>$L$</th>
<th>$\sigma$</th>
<th>$\mu$</th>
<th>$Pr$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(W/m-K)</td>
<td>(kg/m³)</td>
<td>(J/kg-K)</td>
<td>(m²/s)</td>
<td>(J/kg)</td>
<td>(mN/m)</td>
<td>(Pa·s)</td>
<td></td>
</tr>
<tr>
<td>Solder (60%Sn, 40% Pb) (22.5°C)</td>
<td>183</td>
<td>50</td>
<td>8500</td>
<td>180</td>
<td>3.27·10⁻³</td>
<td>4.60·10⁴</td>
<td>480</td>
<td>2.4·10⁻³</td>
<td>8.6·10⁻³</td>
</tr>
<tr>
<td>Octacosane (70°C)</td>
<td>61.4</td>
<td>0.15</td>
<td>774</td>
<td>2378</td>
<td>7.85·10⁻⁴</td>
<td>1.64·10⁵</td>
<td>26</td>
<td>4.9·10⁻³</td>
<td></td>
</tr>
<tr>
<td>Water (0°C ice)</td>
<td>0</td>
<td>2.22</td>
<td>910</td>
<td>1930</td>
<td>1.26·10⁻⁶</td>
<td>3.3·10⁵</td>
<td>73</td>
<td>1.70·10⁻³</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>(2°C)</td>
<td>0.556</td>
<td>1000</td>
<td>4217</td>
<td>1.32·10⁻⁷</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(95°C)</td>
<td>90</td>
<td>0.073</td>
<td>930</td>
<td>3.9·10⁻⁸</td>
<td>1.9·10⁴ from 30 to 90°C</td>
<td>78</td>
<td>1.70·10⁻³</td>
<td>13</td>
</tr>
<tr>
<td>Air (0°C)</td>
<td>-</td>
<td>0.0251</td>
<td>1.297</td>
<td>1009</td>
<td>1.92·10⁻⁴</td>
<td></td>
<td></td>
<td>1.73·10⁻⁵</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>(90°C)</td>
<td>0.0308</td>
<td>0.975</td>
<td>1007</td>
<td>3.14·10⁻³</td>
<td></td>
<td></td>
<td>2.11·10⁻³</td>
<td>0.69</td>
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<tr>
<td>Aluminum (27°C)</td>
<td>-</td>
<td>237</td>
<td>2702</td>
<td>903</td>
<td>9.71·10⁻⁴</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Glass (27°C)</td>
<td>-</td>
<td>1.38</td>
<td>2200</td>
<td>745</td>
<td>8.42·10⁻⁷</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Appendix B

Results of the Numerical Solutions of the Velocity-Angle Relationship

The governing equations of the piecewise model of the molten dynamic contact line were solved for a range of dimensionless parameters. The cases solved are enumerated in Table B.1, which is repeated here for convenience as Table B.1. The numerical solution of the velocity-angle relationship appears for Cases A through P in Tables B.2 through B.17. For each numerical calculation values of the dimensionless height $h/h_m$, slope $\theta$, and curvature $h_mq_\lambda$ evaluated at the cutoff point $r=\lambda$ are shown.

Table B.1 Values of the parameters for each case considered in the numerical study of the governing equations for the piecewise model of the molten dynamic contact line.

<table>
<thead>
<tr>
<th>Case</th>
<th>$\theta_s$ (deg)</th>
<th>$\theta_m$ (deg)</th>
<th>$\lambda/h_m$</th>
<th>$H/h_m$</th>
<th>$Hq_\lambda$</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>20</td>
<td>20</td>
<td>$10^2$</td>
<td>$10^1$</td>
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<tr>
<td>B</td>
<td>30</td>
<td>30</td>
<td>$10^2$</td>
<td>$10^5$</td>
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<tr>
<td>C</td>
<td>40</td>
<td>40</td>
<td>$10^2$</td>
<td>$10^5$</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>50</td>
<td>50</td>
<td>$10^2$</td>
<td>$10^5$</td>
<td>0</td>
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<tr>
<td>E</td>
<td>30</td>
<td>30</td>
<td>$10^2$</td>
<td>$10^5$</td>
<td>0</td>
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<tr>
<td>F</td>
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<td>50</td>
<td>$10^2$</td>
<td>$10^5$</td>
<td>0</td>
</tr>
<tr>
<td>G</td>
<td>30</td>
<td>60</td>
<td>$10^2$</td>
<td>$10^5$</td>
<td>0</td>
</tr>
<tr>
<td>H</td>
<td>30</td>
<td>30</td>
<td>$10^1$</td>
<td>$10^5$</td>
<td>0</td>
</tr>
<tr>
<td>I</td>
<td>30</td>
<td>30</td>
<td>$10^3$</td>
<td>$10^5$</td>
<td>0</td>
</tr>
<tr>
<td>J</td>
<td>30</td>
<td>30</td>
<td>$10^4$</td>
<td>$10^5$</td>
<td>0</td>
</tr>
<tr>
<td>K</td>
<td>30</td>
<td>30</td>
<td>$10^2$</td>
<td>$10^3$</td>
<td>0</td>
</tr>
<tr>
<td>L</td>
<td>30</td>
<td>30</td>
<td>$10^2$</td>
<td>$10^4$</td>
<td>0</td>
</tr>
<tr>
<td>M</td>
<td>30</td>
<td>30</td>
<td>$10^2$</td>
<td>$5 \cdot 10^5$</td>
<td>0</td>
</tr>
<tr>
<td>N</td>
<td>30</td>
<td>30</td>
<td>$10^2$</td>
<td>$10^5$</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>O</td>
<td>30</td>
<td>30</td>
<td>$10^2$</td>
<td>$10^5$</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>P</td>
<td>30</td>
<td>30</td>
<td>$10^2$</td>
<td>$10^5$</td>
<td>$2 \cdot 10^{-1}$</td>
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Table B.2 Numerical results for Case A.

<table>
<thead>
<tr>
<th>Ref #</th>
<th>$Ca$</th>
<th>$\theta_s$ (deg)</th>
<th>$h/h_m$ @ $r=\lambda$</th>
<th>$\theta$ (deg) @ $r=\lambda$</th>
<th>$h_mq_\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1.433 $\cdot 10^1$</td>
<td>80</td>
<td>9.471 $\cdot 10^2$</td>
<td>71.22</td>
<td>2.889 $\cdot 10^3$</td>
</tr>
<tr>
<td>A2</td>
<td>8.398 $\cdot 10^2$</td>
<td>70</td>
<td>8.943 $\cdot 10^2$</td>
<td>63.36</td>
<td>2.127 $\cdot 10^3$</td>
</tr>
<tr>
<td>A3</td>
<td>4.316 $\cdot 10^2$</td>
<td>60</td>
<td>8.237 $\cdot 10^2$</td>
<td>55.41</td>
<td>1.421 $\cdot 10^3$</td>
</tr>
<tr>
<td>A4</td>
<td>1.814 $\cdot 10^2$</td>
<td>50</td>
<td>7.346 $\cdot 10^2$</td>
<td>47.25</td>
<td>8.160 $\cdot 10^4$</td>
</tr>
<tr>
<td>A5</td>
<td>1.040 $\cdot 10^2$</td>
<td>45</td>
<td>6.829 $\cdot 10^2$</td>
<td>43.06</td>
<td>5.616 $\cdot 10^4$</td>
</tr>
<tr>
<td>A6</td>
<td>5.155 $\cdot 10^3$</td>
<td>40</td>
<td>6.265 $\cdot 10^2$</td>
<td>38.79</td>
<td>3.421 $\cdot 10^4$</td>
</tr>
<tr>
<td>A7</td>
<td>2.041 $\cdot 10^4$</td>
<td>35</td>
<td>5.646 $\cdot 10^2$</td>
<td>34.37</td>
<td>1.720 $\cdot 10^4$</td>
</tr>
<tr>
<td>A8</td>
<td>5.155 $\cdot 10^4$</td>
<td>30</td>
<td>5.000 $\cdot 10^2$</td>
<td>29.78</td>
<td>5.770 $\cdot 10^5$</td>
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Table B.3 Numerical results for Case B.

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<td>B2</td>
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<td>66.80</td>
<td>$9.765 \cdot 10^4$</td>
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Table B.4 Numerical results for Case C.

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<td>$2.117 \cdot 10^4$</td>
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Table B.5 Numerical results for Case D.

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Table B.6 Numerical results for Case E.

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### Table B.7 Numerical results for Case F.

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<td>F3</td>
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### Table B.8 Numerical results for Case G.

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### Table B.9 Numerical results for Case H.

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<th>$\theta (deg) @ r=\lambda$</th>
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### Table B.10 Numerical results for Case I.

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Table B.11 Numerical results for Case J.

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Table B.12 Numerical results for Case K.

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Table B.13 Numerical results for Case L.

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<th>$h/h_m$ @ $r=\lambda$</th>
<th>$\theta$ (deg) @ $r=\lambda$</th>
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Table B.14 Numerical results for Case M.

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