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Contact angle hysteresis and the energy principle

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CONTACT ANGLE HYSTERESIS
AND
THE ENERGY PRINCIPLE

by

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Contact Angle Hysteresis

and

The Energy Principle

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ABSTRACT

Experimental evidence suggests that contact angle hysteresis is related, in some cases, to surface roughness or heterogeneity on a microscopic scale. This work investigates the effect of periodic roughness or heterogeneity on quasi-static motion of a liquid/vapor/solid contact line. We determine the static stable equilibrium configuration(s) of the liquid/vapor interface in a system by minimizing the sum of the Helmholtz free energy and gravitational potential energy (or the total energy) of the system. This is the energy principle.

Our model presumes that both the surface of the solid and the liquid/vapor interface can be generated by drawing normals through a curve in a vertical plane. The solid is dipped into a liquid reservoir. A uniform gravitational field is present. The Young's Law contact angle varies
along the curve in the vertical generating plane corresponding to the surface of the solid. Only a single contact line is allowed. This model is a much more general treatment of these problems than found in the literature. Application of the energy principle results in a family of possible liquid/vapor interfacial configurations.

The capillary length of the liquid/vapor pair is the determining length scale of the model. If the wavelength of surface roughness or heterogeneity is much smaller than the capillary length, then hysteresis of the apparent contact angle occurs. (The apparent contact angle is measured as though the surface of the solid is a vertical plane.)

The effect of relaxing the single contact line assumption is studied when the solid boundary surface is a sawtooth. Here, the general framework of the model breaks down. However, this case is treatable using a more specific theory. In certain cases, trapped droplets or bubbles are formed which are stable in a limited technical sense, and which suppress apparent contact angle hysteresis. Then the apparent contact angle may approach either 180° or 0° as the wavelength of the boundary surface approaches zero.
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TO MY FATHER.
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CHAPTER I
INTRODUCTION

1.1 WETTING AND CONTACT ANGLES

Liquid on a solid surface may cover the solid surface completely. An example of this is oil on waxed paper (11). In other cases, the liquid will form drops on the solid. Water on a smooth wax surface and mercury on a glass surface both form droplets at equilibrium (22). This is called intermediate wetting. We can imagine the case where a liquid is completely excluded from the surface of the solid; the above example of mercury on glass is close to this case.

Figure 1.1 shows a liquid vapor interface which contacts the surface of a solid for the intermediate wetting case. Figure 1.1 is a side view. Point P is a cross section of the contact line between all three phases. At P, the tangent to the solid forms an angle $\theta$ with the tangent of the liquid/vapor interface, measured through the liquid. $\theta$ is the contact angle at the point P. The contact angle is always measured through the denser phase by convention. The
contact angle is a measure of how well the liquid wets the surface of the solid. As \( \theta \) approaches zero, the liquid wets the solid more and more. As \( \theta \) approaches 180\(^\circ\), the liquid is excluded from the solid more and more. In the cases above, from contact angle data, mercury is almost entirely excluded from a glass surface (22).

The degree of wetting is important in several industrial applications. In the manufacture of photographic film, coatings are layered on to a solid medium such as plastic. Spreading agents (surfactants) are added to the photographic emulsion (bottom layer) to control surface tension, thus insuring complete wetting of the solid support. They may also be added to some of the upper coatings to insure complete wetting of the previous coating (1). The froth flotation process is used to separate pure minerals such as copper and lead from the waste material of their ores. The ore is crushed to a particle size of about 208 micrometers, and placed in a vat of water or brine. Air is sparged through the vat. The idea is that mineral particles will attach to the water/air surfaces of the bubbles and float to the top. The particles are then skimmed off the top. In practice, frothing agents are added to the water to encourage the process. These additives cause the water to be excluded from the surfaces of the particle by the air as
Figure 1.1: DEFINITION OF CONTACT ANGLE
much as possible. The contact angle is a parameter of prime importance in froth flotation research (2).

1.2 CONTACT ANGLE HYSTERESIS

Consider a droplet on the surface of a solid whose volume can be increased or decreased by flow through a perforation in the solid. Figures 1.2 illustrates an idealized experiment in which the contact line moves through volume changes of the drop. The contact line moves with zero displacement velocity, and the drops can be considered equilibrated at all times. The drop volume is small enough at all times so that the drop shape is a spherical cap, the contact line is circular, and the contact angle $\Theta$ is constant along the contact line. The figures show what is observed for most liquid/vapor/solid systems (25,11).

In Figure 1.2a, liquid is fed into the drop. The contact line advances along the solid surface. The contact angle all along the contact line is $\Theta_a$, where the subscript a stands for advancing. If the liquid flow is reversed, the contact line will stick as the volume of the drop decreases and the contact angle decreases, until the contact angle remains $\Theta_r$ for receding. This is shown in Figure 1.2b. Then the contact line recedes, and the contact angle equals
Figure 1.2a: CONTACT ANGLE HYSTERESIS; ADVANCING
Figure 1.2b: CONTACT ANGLE HYSTERESIS; STATIC
Figure 1.2c: CONTACT ANGLE HYSTERESIS; RECEIVING
Note that for a static contact line, the contact angle can be anywhere between $\Theta_r$ and $\Theta_a$. $\Theta_a$ is always greater than $\Theta_r$, and the difference can be quite substantial.

In practice, $\Theta_a$ and $\Theta_r$ are measured by extrapolating dynamic contact angles to zero velocity. The review by Dussan V (25) describes different experimental methods for measuring contact angles. For a given experimental method, there is a critical contact line velocity below which measurement of the dynamic contact angles becomes impossible. The reason is due to a stick-slip motion of the contact line below this critical velocity. Stick-slip motion also occurs if the surface of the solid has not been cleaned thoroughly (25).

I.3 ORGANIZATION OF THESIS

The goal of this thesis research was to suggest a mechanism for the occurrence of contact angle hysteresis, using a tractable model of a moving but quasi-static liquid/vapor interface contacting the surface of a solid. The results are consistent with previous work. The theory developed here is more general than in the current literature.
Chapter two discusses the interfacial tension force, and the use of the energy principle in determining static stable equilibrium. The classical analysis of intermediate wetting is presented. This analysis fails to predict contact angle hysteresis for quasi-static drops and the range of equilibrium contact angles for static drops. That analysis assumes an idealized surface of the solid. Improvements on the classical analysis are then discussed, showing how this work fits into and extends previous work.

In Chapter three we present a model of a quasi-static liquid/vapor interface moving along a solid surface with a single contact line. The energy principle is applied to this model, and a family of static stable equilibrium liquid/vapor interfaces are derived. It is shown that all static stable interfaces for this model must come from this family. Formulae are derived for the computation of how a quasi-static interface moves along a smooth surface. The case where the solid has corners is then worked out. The treatment of heterogeneous surfaces is also discussed.

Chapter four covers case studies of two types. The first type is where the solid is homogeneous, but its surface is rough. Smooth but heterogeneous surfaces are the
second type. Contact angle hysteresis is predicted for certain types of surface profiles of the solid. These predictions are consistent with the remarks in I.2 above and extend previous theoretical work.

The single contact line assumption is removed in Chapter five. The consequences of this relaxation are demonstrated for solid surface profiles which are sawtooth waves. These results are consistent with observation.

Chapter six contains the conclusions and possible extensions of this thesis work.
CHAPTER II
BACKGROUND AND PREVIOUS WORK

II.1 STATIC STABLE EQUILIBRIUM AND THE ENERGY PRINCIPLE

At static equilibrium, the forces acting on the object in question are in balance, so that the both the velocity and acceleration of the object are zero. Liquid/vapor interfaces which satisfy the Laplace capillarity equation are static equilibrium interfaces. However, static equilibrium is not the same as static stable equilibrium. A pen standing on its point is at equilibrium, but is obviously not stable to perturbation. Examples involving capillary bridges where there are two solutions to the Laplace equation, one stable and one not, are well known; see for example the review by Dyson (6).

There are two approaches to determining the stability of an object at static equilibrium. The dynamical approach involves specifying the dynamical equations for the object in question and solving them. Unfortunately, the dynamics of the moving contact line are still not well understood and
only simple problems in capillary hydrostatics have been analyzed successfully with this approach (6).

The other approach used is known as the energy principle. The system in question is taken to be at constant temperature and constant volume. The sum of the Helmholtz free energy and the gravitational potential energy of such a system is minimized at static stable equilibrium, according to a theorem of classical thermodynamics (23). A static stable configuration will (locally) minimize the total energy over the set of all physically possible configurations.

Presumably, the two approaches should be equivalent, and they have been shown to be so in a limited number of cases (6, 21). There is no proof that they are equivalent in general, but no counter examples either. Support for the energy principle comes from the derivation of correct equilibrium conditions, such as Laplace's equation and contact angle boundary conditions, from requiring that the first variation of the total energy vanish (See 6, 21, and this work, III.3 and III.5 below).

The energy principle is not limited to use in capillary hydrostatics. In a chemical reaction at constant
temperature and pressure, the energy principle states that the Gibbs free energy is minimized at stable equilibrium. This analysis is commonly used in the study of chemical reaction equilibrium (3).

The total energy of the model studied in this work is the sum of two contributions. One is the gravitational potential energy of the bulk phases (see III.2 below). The other contribution is from the Helmholtz free energy of liquid/vapor, liquid/solid, and vapor/solid interfaces. The latter is the subject of the next section.

II.2 INTERFACIAL TENSIONS AND THE HELMHOLTZ FREE ENERGY

A liquid and its vapor will have an interfacial region between them. As shown in Figure 2.1a, the interfacial region is of finite thickness, and is made up of both phases. From Young (4) and Gibbs (5) onwards, this interfacial region has been modelled as a boundary of infinitesimal thickness between the two phases, as shown in Figure 2.1b. This boundary acts like a stretched membrane, with a force per unit length acting on the surface of the interface itself. Figure 2.2a shows an imaginary dividing line segment AB made in the interface. The length of AB is $\delta l$. The material $A'$, on one side of AB, exerts a pull on the material $B'$, on the
Figure 2.1: REAL LIQUID/VAPOR INTERFACE AND MODEL
other side, and vice versa, so the surface is in tension. The pulls are of equal magnitude $\sigma_{lv} A$, and are directed in the surface and normal to the line segment AB. $\sigma_{lv}$ is the proportionality constant commonly known as the surface tension. Its units are usually dyne/cm. The subscripts stand for liquid/vapor (see below). If another imaginary dividing line segment is drawn in the surface, the force pairs acting across it are the same as for AB. The surface tension is thus isotropic (6).

Another way to look at the surface tension is as an energy per unit area of the interface. To increase the surface area of a liquid/vapor interface with tension $\sigma_{lv}$ by $dA$ requires reversible work equal to $\sigma_{lv} dA$ to be done. Suppose that this interface is in a system which is kept at constant temperature, and the volume of the liquid and vapor phases are held constant. Then the reversible work $\sigma_{lv} dA$ done on the system by the surroundings increases the Helmholtz free energy of the system by the same amount.

Consider a drop of liquid in a reservoir of another liquid with no gravitational field present, as in Figure 2.3. Both phases are taken to be incompressible, and the temperature is held constant. The stable static
Figure 2.2: SURFACE TENSION
configuration of the drop will minimize the Helmholtz free energy of the system over all possible drop configurations. The position of the drop does not matter, there being no gravity field present. The shape of the drop must minimize its surface area given the total volume of the liquid as a constraint. The drop formed is thus perfectly spherical.

When a solid is also present, there are two other interfaces to consider. Referring back to the drop in Figure 1.1a, the solid/liquid and solid/vapor interfaces are also present. They also have an energy per unit area associated with them. Figure 2.4 shows the side view of a solid plate dipped into a reservoir of liquid. P is the sectional of the contact line. The liquid/vapor surface tension pulls on the contact line away from the surface of the plate. If there were no tensions associated with the other two interfaces, the contact line would be pulled off the plate's surface. The proportionality constant for these two interfaces are called the solid/liquid and solid/vapor interfacial tensions; in notation \( \sigma_{sl} \) and \( \sigma_{sv} \). (Sometimes the symbol \( \gamma \) is used instead of \( \sigma \); \( \gamma_{lv} \), etc.) These tensions balance the vertical force components along the contact line. A force must also balance the horizontal force components. This cannot be an interfacial tension, since it cannot be tangent
Figure 2.3: SPHERICAL DROP OF LIQUID IN A RESERVOIR
Figure 2.4: INTERFACIAL TENSIONS
to the surface of the solid. This force is adhesive, and resists the tendency of the surface tension to pull the contact line off the surface of a solid. It is analogous to the force a solid exerts on an object resting on it in a gravitational field. This force pushes up on the object with a magnitude equal to the gravitational force pulling the object downwards (11).

The liquid/vapor surface or interfacial tension can be easily measured. The solid/vapor and solid/liquid tensions are very hard to measure. It turns out that the application of the energy principle to the contact angle problem does not require an explicit value for the latter two interfacial tensions. A classical model using the energy principle is discussed in the next section.

II.3 CLASSICAL ANALYSIS OF THE CONTACT ANGLE PROBLEM

The energy principle can now be applied to the intermediate wetting case. Figure 2.5 shows a droplet resting on the surface of a planar, homogeneous solid. No gravitational field is present, so the droplet shape is a spherical cap. The system is kept at constant temperature, and the liquid is incompressible. Thus it is the Helmholtz free energy of the system which is minimized at static stable
Figure 2.5: SPHERICAL CAP DROP
equilibrium. The only change in the Helmholtz free energy can come from changing the interfacial areas. The relation E in this case is the sum of the interfacial energies in equation [11], which assumes that all interfacial tensions are constant:

\[ E = A_{lv}\sigma_{lv} + A_{sl}\sigma_{sl} + A_{sv}\sigma_{sv} \]  

[1]

The minimum of E depends on the ratio k given in equation [2]:

\[ k = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \]  

[2]

There are three cases. If \( k \leq -1 \), then the liquid is completely excluded by the vapor at static stable equilibrium, as in the case of mercury on glass in air. If \( k \geq 1 \), the liquid completely wets the surface of the solid, as in the gasoline/iron/air case mentioned above. If \(-1 < k < 1\), then the only configuration of the liquid/vapor interface which could minimize E has a contact angle of \( \Theta_e \) with the surface of the solid, where \( \Theta_e \) is defined in equation [3]:

\[ \cos(\Theta_e) = k \]  

[3]

This result comes from considering the first derivative of E with respect to contact angle. Thus [3] is a necessary
condition only. Equation [3] is commonly known as Young's Law. As shown by Tyuptsov (24), introducing a gravity field into this analysis changes the configuration of the liquid/vapor interface, but not the contact angle, which may minimize $E$. This is contradictory with the observation of contact angle hysteresis for quasi-static drops and the range of contact angles for stable static drops.

II.4 PREVIOUS WORK

Several explanations have been proposed for the failure of the above analysis (11). The surface may be contaminated by patches of impurities. Glass surfaces are notorious for this (11); it has been shown experimentally that the removal of these patches can make contact angle hysteresis of water on glass disappear. Good and Neumann (8) discuss how a patchy surface can give rise to hysteresis. Their analysis uses the energy principle to investigate heterogeneous surfaces consisting of homogenous horizontal or vertical strips. They qualitatively argue from these results that a patchy surface should give rise to hysteresis.

Another explanation is that contact angle hysteresis occurs because of small length scale surface roughness.
Some theoretical work has been done on this point. Good and Neumann (8) considered a solid plate dipped into a reservoir of liquid. The surface of the plate is a sawtooth with vertically aligned vertices. The contact point is allowed to move up or down along the sawtooth. They calculated the total energy versus the position of the contact point. In general, they found several minima of the total energy. Johnson and Dettre (9) looked at a spherical cap drops advancing or receding on a sine wave of revolution (the so-called "record groove" surface). Unlike Good and Neumann (8), they did not use the energy principle but restricted drop configurations to those that satisfied equation [3] (Young's Law) above. Thus they could not analyze the stability of the drop configurations. In both papers, the most interesting results were for small wavelength sawtooth or sine wave surface profiles. In these cases, the surface of the solid would appear to be planar. Both papers calculated the apparent contact angle $\Theta_{\text{app}}$, measured as though the surface of the solid were truly planar. Neumann and Good (8) found several stable values of $\Theta_{\text{app}}$ corresponding to the minima of the total energy. Johnson and Dettre (9) found hysteresis of $\Theta_{\text{app}}$. Huh and Mason (10) considered the same problem as Johnson and Dettre, without the Young's Law restriction. They found that for small wavelength sine
waves. The contact line would jump over a portion of the sine wave as it moved; Figure 2.6 is a replication of their Figure 3 illustrating this. The dotted lines are equilibrium positions, but not stable positions in general, of the contact line. Only the lines going through A (the initial configuration) and A' (the final configuration) are stable static equilibrium configurations of the liquid vapor interface. Again, they found hysteresis of $\Theta_{app}$. They then attempted to analyze more general problems, strictly enforcing the Laplace capillarity equation and doing a first order perturbation calculation. Because of the Laplace equation constraint, however, only one equilibrium position is possible for a given drop volume. Contact angle hysteresis is impossible in such a model. They also could not duplicate their previous results using the "record groove" surface (25).

Yet another explanation of hysteresis is that the solid interfacial tensions will change due to adsorption on the surface of the solid. Miller (11) gives an example from Zisman et. al. (13) where adsorption is a reasonable explanation for the experimental results obtained.
Fig. 3. Schematic diagram of the nonequilibrium jump from A to A' (Fig. 1) of the contact line between the equilibrium configurations of the liquid drop. For explanation see text.

Figure 2.6
The model presented in this work treats the first two theories in a general framework, which is restricted to involve cylindrical surfaces (These are not in general circular cylinders; see III.1). We also assume enough viscous damping so that the contact line can latch onto a new stable position from an initial, unstable one. Heterogeneous surfaces can be treated as well. The E functional and the configurations of the liquid/vapor interfaces are rigorously derived. The jumping mechanism mentioned by Huh and Mason (10) is explained in terms of the curvature of the surface of the solid along a contact line in relation to the capillary length $\sqrt{\gamma / \kappa}$, where $\kappa$ is defined in equation (8c) in III.2 below. This in turn explains why these contact jumps can be seen for small length scale roughness, but not for large length scale roughness. Hysteresis due to heterogeneity can be explained in terms of the curvature of a contact angle function, which is an expression of the surface composition. More details are given in the next chapter, which describes the model used and the application of the energy principle to this model.
CHAPTER III
MODEL DESCRIPTION AND MINIMIZATION PROBLEM

III.1 PHYSICAL SYSTEM

Consider an arbitrary curve $C_B$ in a vertical plane $P_\perp$. $C_B$ may be piecewise smooth or have corners. The normals of the plane which intersect $C_B$ form a surface $S_B$ which is a cylinder. (The right circular cylinder is the most familiar example, where $C_B$ is a circle.) This surface will be the surface of the solid in our model. The solid dips into an infinite reservoir of liquid, so that both the vapor phase (on top) and the liquid phase (on bottom) make contact with the surface of the solid. The contact line is assumed to be coincident with one of the ruling lines of $S_B$, and is thus horizontal. The liquid-vapor interface is also assumed to be cylindrical, and its cross section in a plane parallel to $P_\perp$ is a smooth plane curve $C_{LV}$. $C_{LV}$ is restricted to have only one intersection point with $C_B$ (this restriction is removed in Chapter Five). $C_{LV}$ is assumed to flatten out far away from its one contact point with $C_B$. The system is bounded by two parallel planes a distance $W$ apart which are
parallel to \( P_A \). A heat reservoir surrounding the system keeps it at constant temperature.

Figure 3.1 is the cross section through \( P_A \) of such a system. The coordinate system is chosen so that \( y \to 0 \) as \( x \to -\infty \) on \( C_{LV} \). In Figure 3.1, \( C_B \) is a smooth curve and passes through the origin. In general, \( C_B \) can have corners, and does not have to pass through the origin. These restrictions are convenient for now but will be removed later in this chapter. \( C_B \) is defined by the functions \( X(s) \) for the abscissa and \( Y(s) \) for the ordinate of the Cartesian axes \( X,Y \) shown in Figure 3.1. \( X(s) \) and \( Y(s) \) are smooth functions (later extended to piecewise smooth functions) of the arc-length \( s \), with \( s = 0 \) at the origin. \( C_B \) is parameterized by equation [4]:

\[
C_B: X(s), Y(s) \quad s_a \leq s \leq s_b
\]

Positive travel along \( C_B \) leaves the solid to the right in Figure 3.1, and \( s \) increases along the direction of positive travel indicated by the arrowheads on \( C_B \). \( P \) is the sectional of the three phase contact line with coordinates \( X(s_1), Y(s_1) \), where \( s_a \leq s_1 \leq s_b \). If \( s < s_1 \), then \( X(s), Y(s) \) lies below \( P \) on the liquid-solid interface and if \( s > s_1 \), \( X(s), Y(s) \) lies above \( P \) on the vapor-solid interface. For a given
Figure 3.1: CROSS SECTION OF MODEL SYSTEM IN A VERTICAL PLANE P_x.
point \( Q \) on \( C_B \), we can define an angle \( \psi \) corresponding to it as shown in the Figure. Let the ray \( QH \) be directed from \( Q \) in the sense of the positive abscissa, and the ray \( QR \) be tangent to \( C_B \) at \( Q \) and directed in the sense of positive travel along \( C_B \). The counterclockwise angular displacement of \( QH \) required to make it coincide with \( QR \) is \( \psi \). We define \( \psi \) so that it lies in the half open interval \([0, 2\pi)\). \( \psi \) is a continuous function of \( s \) except when the ray \( QR \) becomes coincident with the ray \( QH \), where jumps of \( \pm 2\pi \) may occur even though \( C_B \) is smooth. Later we allow \( C_B \) to be piecewise smooth; \( \psi(s) \) will then jump at the corners of \( C_B \).

The sectional \( C_{LV} \) of the liquid-vapor interface is described by the functions \( x(t) \) for the abscissa and \( y(t) \) for the ordinate of the cartesian axes in Figure 3.1. The functions \( x(t) \) and \( y(t) \) are always assumed to be smooth. As \( t \to -\infty \), \( x(t) \to \infty \) and \( y(t) \to 0 \). \( C_{LV} \) is represented by equation [5]:

\[
C_{LV}: x(t), y(t) \quad -\infty < t \leq t_1
\]

[5]

and the coordinates of \( P \) are \( x(t_1), y(t_1) \). At a given point on \( C_{LV} \), as shown in Figure 3.1, the angle \( \phi \) is analogous to the angle \( \psi \) defined for the point \( Q \) on \( C_B \). The ray for the tangent to \( C_{LV} \) is directed in the sense of increasing \( t \).
The tension of the liquid-vapor interface, $\sigma_{lv}$, is presumed to be constant. However, the solid-liquid tension $\sigma_{sl}$ and the solid-vapor tension $\sigma_{sv}$ can vary as functions of $s$. No variation is allowed along the rulings of the solid surface. The values of the tensions are constrained by equation [6]:

$$-1< k < 1$$ [6]

where $k$ is defined in equation [22] in chapter two. The contact angle function $\theta_e$ along $C_B$ is defined by equation [7]:

$$\cos(\theta_e(s)) = k \quad 0 < \theta_e(s) < \pi$$ [7]

(compare with equation [3]). $\theta_e(s)$ is a known function in the model. Heterogeneous surfaces of a solid are treated by specifying the function $\theta_e(s)$. Here, $\theta_e(s)$ is taken to be smooth; in chapter four the theory is extended to include $\theta_e$'s which are step functions.

III.2 ENERGY PRINCIPLE

From Schwartz and Garoff (14), Eick, Good, and Neumann (12), and Dyson (6) the energy principle can be written for this system immediately. The configuration of the liquid-vapor interface whose sectional is $C_{LV}$ will be stable
towards small cylindrical perturbations if and only if the functional $\sigma_{tv}$ is minimized. $E$ is given by equations \[ \text{[8]} \]:

\begin{align*}
E &= I + J - K \\
I &= \int_{t=-\infty}^{t=t_1} F(x,y,\dot{x},\dot{y}) \, dt \quad \text{[8a]} \\
x &= x(t), y = y(t); \dot{x} = dx/dt; \dot{y} = dy/dt \quad \text{[8b]} \\
F &= (\dot{x}^2 + \dot{y}^2)^{1/2} + (\kappa y^2 - 1) \dot{x}; \kappa = (\rho_L - \rho_F g/2\sigma_{tv}) \quad \text{[8c]} \\
J &= \int_{s=0}^{s=s_1} (1-\kappa y^2)(dX/ds) \, ds \quad \text{[8d]} \\
K &= \int_{s=0}^{s=s_1} \cos(\theta_e(s)) \, ds \quad \text{[8e]} \\
\end{align*}

and the one contact point constraint is equations \[ \text{[9]} \]:

\begin{align*}
x(t_1) &= X(s_1) \quad \text{[9a]} \\
y(t_1) &= Y(s_1) \quad \text{[9b]} \\
\end{align*}

With our choice of origin (see above):

\begin{align*}
X(0) &= Y(0) = 0 \quad \text{[10]} \\
\end{align*}

The set of configurations over which $E$ is minimized are smooth plane curves $x(t), y(t)$ for which as $t \to -\infty, x(t) \to -\infty$ and $y(t) \to 0$; each curve intersects one and only one point on the boundary curve $C_B$. No loops are allowed, and the integral \[ \text{[8a]} \] must be defined and be convergent. Other, more
technical restrictions on the set of configurations over which \( E \) is minimized are discussed below.

It is instructive to explain the physical meaning of equations [8]. Suppose that a planar liquid vapor interface contacts the surface of the solid along the line whose sectional is the origin in Figure 3.1. Then \( C_{LV} \) is a horizontal line which intersects \( C_B \) at the origin. The quantity \( \sigma_{lv} \) represents the total reversible work needed to move the contact line to the new position represented by \( P \). There are three contributions to the reversible work. First, the surface area of the liquid-vapor interface is increased. The increase in surface area is the integral over \( t \) of equation [11]:

\[
(x^2 + y^2)^{1/2} - x
\]

Second, the areas of the liquid-solid and vapor-solid interfaces change as the contact point is moved. Equation [8e] is the weighted sum of the change in these interfacial areas. The weights depend on the values of the interfacial tensions. These two contributions together multiplied by \( \sigma_{lv} \) equal the change in the Helmholtz surface free energy. Finally, bulk liquid and vapor are displaced in moving the configuration of \( C_{LV} \) from \( y=0 \) to \( x(t), y(t) \). The remaining
terms times $\sigma_{lv}$ equal the change in gravitational potential energy. We say that $\sigma_{lv} WE$ is the change in the total energy when the liquid-vapor interface is displaced from a planar configuration to one whose sectional is $x(t), y(t)$.

The parameter $\kappa$ in equations [8] has dimensions of length$^{-2}$. It is a ratio of gravitational forces over interfacial tension forces. The quantity $\sqrt{1/\kappa}$ is known as the capillary length of the liquid-vapor pair. This length scale is an important factor in the behavior of the model, as we shall see in Chapter four.

III.3 SOLUTION-NECESSARY CONDITION

Suppose that $E$ has a minimizer $x^*(t), y^*(t)$ that meets $C_B$ at a point $p$. Then certainly $x^*(t), y^*(t)$ must minimize $E$ over all configurations of $C_{LV}$ which go through $p$. Over all curves which go through $p$, the integrals $J$ and $K$ are constant. Thus $x^*(t), y^*(t)$ must minimize the integral $I$ over these curves. They must solve the fixed endpoint problem of variational calculus.

From the theory of variational calculus given in Bliss (15) and Bolza (16), the minimizer(s) of $I$ must satisfy
Weierstrass's form of the Euler- Lagrange equation, which is equation [12]:

\[ T = F_{xy} - F_{yx} + F_1(\dot{x}y - xy) = 0 \quad [12] \]

\[ F_1 = \frac{F_{xx} + F_{yy}}{x^2 + y^2} \quad [12a] \]

where \( \ddot{x} \) and \( \ddot{y} \) are the second derivatives of \( x \) and \( y \) with respect to \( t \). This equation treats the integrand of \( I \), the \( F \) given in equation [8c], as a function of the four independent variables \( x, y, \dot{x}, \dot{y} \) in equation [8b]. Thus partial derivatives of \( F \) can be taken with respect to any combination of the four variables. Plugging [8c] into [12] results in [13]:

\[ T = \frac{1}{r} - 2\dot{x}y = 0 \quad [13] \]

where \( 1/r \) is the curvature, i.e.

\[ \frac{1}{r} = (\dot{x}y - \ddot{y}x) / (\dot{x}^2 + \dot{y}^2)^{3/2} \quad [14] \]

Note that equation [14] is the Laplace equation of capillary hydrostatics. Integrating once with respect to \( t \), equation [14] becomes equation [15]:
\[ Z = \frac{\dot{x}}{(\dot{x}^2 + \dot{y}^2)^{1/2}} + ky^2 - 1 = \text{const.} \quad [15] \]

To satisfy the boundary condition that \( C_{LV} \) flattens to a horizontal as \( x \to -\infty \), the constant in equation [15] must equal zero. We conclude that the minimizing \( C_{LV}(s) \) must satisfy equation [16]:

\[ \cos(\phi) = \frac{\dot{x}}{(\dot{x}^2 + \dot{y}^2)^{1/2}} = 1 - ky^2 \quad [16] \]

The first equality is another definition of \( \phi \) (see Figure 3.1). Equation [16] may be integrated again to get \( x(t), y(t) \). Some solutions of [16] do not satisfy [13]; these are singular solutions. They cannot be minimizers since \( T \) does not equal zero. These solutions are:

\[ x = -t + \text{const.} \quad ; \quad y = \pm \sqrt{2/k} \quad [17] \]

In this case \( T \) equals \( \pm \sqrt{8k} \).

A subset of the regular solutions can be written in terms of "dimensionless" variables \( u \) and \( v \), where

\[ u = x\sqrt{k/2} \quad , \quad v = y\sqrt{2/k} \quad [18] \]

These relevant solutions are:

\[ u = \sqrt{1-v^2} - 0.5 \arccosech(|v|) + B \quad [19] \]
$0 < |v| \leq 1$ \hspace{1cm} [19a]

where $B$ is the integration constant.

Profiles for $B = 1, 1.5$, and $2$ are shown in Figure 3.2 together with their envelopes

$u = \pm 1$ \hspace{1cm} [20]

which are equivalent to the singular solutions in equation [17]. Each point of the envelope is tangent to a member of the set of curves [19].

For $B = 1.5$, as $y$ increases from $0$ to $1$, the curve comes in from $u = -\infty$ and passes through the points $A, B, D$, and then terminates at $E$. The maximum of $u$ is at $D$. The broken curve connecting $E$ to $G, H, J$, and then $u = \infty$ is a reflection of the curve $B = 1.5$ through the vertical line that goes through the tangent to the curve at the envelope. For any value of $B$, these reflection curves can be generated. They constitute the rest of the regular solutions of [16] not included in [19].

The limit of [19] as $B \to \infty$ is any part of the $u$ axis:

$u = 0 \ ; \ u \geq \alpha$ \hspace{1cm} [21]

where $\alpha$ is any fixed number. This corresponds to a planar
Figure 3.2

REGULAR SOLUTIONS OF EQUATION [13]
liquid-vapor interface. The curve \( v = 0 \) satisfies [16] and [13].

Princen (27) expresses the regular solutions of [13] in parametric form. There are other possible algebraic representations of the regular solutions of [13] as well. The representation in equations [19, 19a] is simple and well suited to our purposes below.

III.4 SOLUTION-SUFFICIENCY

It is easily shown that the family of curves [19] (one member for each value of \( B \)) form a simple cover of the open strip

\[ |v| < 1 \]  

[22]
i.e. one and only one member of the family passes through a given point in the region [22]. Let this family be denoted by \( \tilde{F} \). Then \( \tilde{F} \) comprises a field of extremals (see Bliss (15)) over [22].

Let \( e(x_1, y_1) \) be the segment of the member of \( \tilde{F} \) which connects the points \(( -\infty, 0) \) and \(( x_1, y_1) \), where \(( x_1, y_1) \) is in the interval [22]. It satisfies [13], which is a static equilibrium condition. However, we have not shown that e
minimizes I (i.e. that the liquid-vapor interface to which e is a sectional is a stable equilibrium interface). We can in fact prove that e is a minimizer of I in this case, by comparing $I_e$ (the value of I corresponding to e) with $I_C$, the value of I corresponding to a comparison curve segment C which ends at $(x_1, y_1)$ and lies entirely in the region [22].

Figure 3.3 depicts the proof. Using equations [8a], [8b], and [16], the integral $I_e$ may be written as

$$I_e = \int_{t=-\infty}^{t=t_1} (\sec \phi - \cos \phi) \dot{x} \, dt \quad [23]$$

which can be transformed easily into an integral in $y$ ($dy = \dot{y} \, dt$):

$$I_e = \int_{y=0}^{y=y_1} (\sin \phi) \, dy \quad [24]$$

$I_C$ can also be rewritten, using the angle $\zeta$ defined in Figure 3.3:

$$I_C = \int_{t=-\infty}^{t=t_1} (\sec \zeta - (1 - ky_C^2)) \dot{x}_C \, dt \quad [25]$$

Since C lies entirely in region [22], it has an extremal going through any of its points (such as P in Figure 3.3). The slope of that extremal is the same as the slope of the curve segment e($x_1, y_1$) at the same value of $y$, since the cosine of $\phi$ depends on $y$ alone (equation [16]). Thus
Figure 3.3: SUFFICIENCY PROOF; FIXED ENDPOINT
\[ \cos(\phi) = (1 - ky_C^2) \]  \[ \text{[26]} \]

Transforming \[ \text{[25]} \] to an integral along \( \tilde{s} \), the arclength of \( C \), and substituting \[ \text{[26]} \], we get

\[ I_C = \int_{s=-\infty}^{s=1} (1 - \cos \phi \cos \zeta) \, ds \]  \[ \text{[27]} \]

The integral \( I_e \) may also be expressed as a line integral along the curve \( C \), using the transformation

\[ dy = \tilde{s} \sin \zeta \]  \[ \text{[28]} \]

Putting it all together;

\[ I_C - I_e = \int_{s=-\infty}^{s=1} (1 - \cos \phi \cos \zeta - \sin \phi \sin \zeta) \, ds \]  \[ \text{[29]} \]

Thus,

\[ I_C - I_e = \int_{s=-\infty}^{s=1} (1 - \cos(\phi - \zeta)) \, ds \geq 0 \]  \[ \text{[30]} \]

where equality holds only if \( \phi - \zeta = 2n\pi \), where \( n \) is an integer. Since one point \( (x_1, y_1) \) is the same for both, this implies that \( C \) must be the unique extremal segment \( e(x_1, y_1) \) in order to minimize \( I \).

This proof applies only if \( (x_1, y_1) \) lies in the region \[ \text{[22]} \]. If \( y_1 = |\sqrt{2/k}| \), then the corresponding extremal does not minimize \( I \). We prove this when \( y_1 = \sqrt{2/k} \); the other case is symmetric. Suppose that the extremal through \( A, B, D, \)
and \( E \) in Figure 3.2 does minimize \( I \). Equation [31] represents this extremal which we call \( e \);

\[
e; \quad (x(t), y(t), -\infty \leq t \leq t_1) \tag{31}
\]

Let \( C_1 \) be the extremal through the points abde, \( C_2 \) be the line eE, and \( C^+ \) the union of \( C_1 \) and \( C_2 \). Then

\[
C_1; \quad (x(t)+\nu, y(t)), -\infty \leq t \leq t_1 \tag{32}
\]

\[
C_2; \quad (x(t_1)+\nu-t, \sqrt{2/\kappa}), 0 \leq t \leq \nu \tag{33}
\]

where \( \nu \) is the length of the line eE. Substituting [31], [32], and [33] into the formula for \( I \) [8a-b], we get that \( I_e = I_{C_1} \) and \( I_{C_2} = 0 \). Thus \( I_e = I_{C^+} \). But since \( C^+ \) includes a singular solution of [16], \( I \) is not minimized by \( C^+ \). But this means that \( I_e \) is not a minimum! We conclude that \( e(x_1, \sqrt{2/\kappa}) \) is not a minimizer of \( I \). This also implies that extending \( e \) along the curve GHJ could not lead to a minimizing extremal. This is why we reject that set of trajectories from inclusion in \( \tilde{F} \).
III.5 VARIABLE ENDPOINTS; SMOOTH $C_B$ CASE

We have seen that $E$ cannot be minimized unless the endpoint $(x_1, y_1)$ lies in $[22]$ and $C_{LV}$ is the extremal segment $e(x_1, y_1)$. We assume below that $C_{LV}$ is $e(x_1, y_1)$. Suppose that these conditions hold and we fix $s_1$, the upper limit of the integrals $J$ and $K$ in $[8d, e]$, on a fixed $C_B$. Then the member of $\tilde{F}$ which intersects $C_B$ at $X(s_1), Y(s_1)$ minimizes $I$. Since $J$ and $K$ are fixed, the same member $e$ of $\tilde{F}$ minimizes $E$ for the given value $s_1$.

To compute the minimum (or minima) of $E$ as a function of $s_1$, it seems that all we need to do is insert into the integral $I$ the corresponding member $e(X(s_1), Y(s_1))$ of $\tilde{F}$. There are two technical difficulties, however. First, the point $(X(s_1), Y(s_1))$ must be the only intersection of the segment $e(X(s_1), Y(s_1))$ with $C_B$. Second, we require that there exists an $\epsilon' > 0$ small enough so that for all $|\epsilon| < \epsilon'$, the extremal segment $e(X(s_1 + \epsilon), Y(s_1 + \epsilon))$ also has only one contact point with $C_B$. The first requirement is the assumption we have been making all along. The second requirement is discussed in V.1 below. It holds for any smooth section of $C_B$ where the contact angle is neither 0 nor $\pi$. If $s_1$ corresponds to a corner of $C_B$, the second requirement says
that the continuation of \( e(X(s_1), Y(s_1)) \) must penetrate the solid; this point is discussed further in IV.3.1.4 below. The integral resulting from inserting the segment \( e(X(s_1), Y(s_1)) \) into \( I \), written as \( I_e \), is easily transformed to an integral along \( C_B \):

\[
I_e = \int_{s=0}^{s=s_1} \sin \phi \sin \Psi \, ds \tag{34}
\]

(recall \( \Psi \) and \( \phi \) from Figure 3.1). The integral \( J_e \) can also be transformed:

\[
J_e = \int_{s=0}^{s=s_1} \cos \phi \cos \Psi \, ds \tag{35}
\]

Combining (34), (35), (8), (8e), and a standard trigonometric identity, we get a simple formula for \( E_e \):

\[
E_e = \int_{s=0}^{s=s_1} f(s) \, ds + \text{const.} \tag{36}
\]

where

\[
f(s) = \cos(\Theta) - \cos(\Theta_e) \tag{37}
\]

\[
\Theta = \Psi - \phi - 2n\pi \tag{38}
\]

where \( n \) is chosen to be 0 or 1 so that \( \Theta \) is the contact angle measured through the liquid (denser) phase. \( \Theta \) is in the interval \([0, \pi]\) for any pair \( \phi \) and \( \Psi \) which correspond to a realizable physical system. If, for example, \( \phi = -\pi/3 \) and \( \Psi = 11\pi/6 \), then \( n = 1 \) gives \( \Theta = \pi/6 \). However, for an unrealizable
system such as $\phi = \pi/6$ and $\Psi = 0$, neither $n=0$ or $n=1$ puts $\Theta$ in the correct range.) The constant accounts for $C_B$ which do not go through the origin.

Equation [36] has a thermodynamic interpretation, which is consistent with our remarks about the quantity $\sigma_{lv}^{\text{WE}}$ in section two of this chapter. If the contact line is fixed at $s^*$ by some agency which can vary $s^*$, then $\sigma_{lv}^{\text{WE}}(s^*)$ is the force required (in the direction of increasing $s$) to hold the contact line in place. Thus $\sigma_{lv}^{\text{WE}}$ is the reversible work required to move the contact line from $s=0$ to $s=s_1$. This corresponds to the increase in total energy (Helmholtz surface free energy plus gravitational potential energy) of the system in moving the contact line reversibly (i.e., with zero displacement velocity).

Finally, for smooth $C_B$, we can derive the conditions for minimizing $E$ with respect to $s_1$ simply by taking derivatives of [36]. In this case, the relations [39] and [40] imply local minimization of $E$ at $s=s_1$:

$$\cos(\Theta) = \cos(\Theta_e) \quad ; \quad s=s_1 \quad [39]$$

$$\frac{d}{ds}(\cos(\Theta) - \cos(\Theta_e)) < 0 \quad ; \quad s=s_1 \quad [40]$$
Conversely, minimization of $E$ at $s=s_1$ implies [39] and [40] with $<$ weakened to $\leq$. Since $\Theta$ and $\Theta_e$ both lie in the interval $[0,\pi]$, [39] and [40] can be rewritten as [41] and [42] respectively:

\[ \Theta = \Theta_e ; \quad s=s_1 \]  
\[ \frac{d\Theta}{ds} - \frac{d\Theta_e}{ds} \leq 0 ; \quad s=s_1 \]  

In the next section, minimization conditions are derived for the case of $C_B$ with corners.

III.6 VARIABLE ENDPOINTS; $C_B$ WITH CORNERS

If $C_B$ has a corner, then a jump will occur in $f(s)$. Suppose that this jump occurs at $s=s_1$. We require that the limits of $f(s)$ from below, $f_-(s)$, and from above, $f_+(s)$, to be well defined. We also require that $f'(s)$ be continuous near $s_1$ with well defined limits $f_-'(s)$ and $f_+'(s)$. In this case, consider how $E$ changes when the contact point is moved from $s_1$ to $s_1+z$; we equate this to $\Delta E$. $\Delta E$ can be estimated to second order in $z$:

\[ \Delta E = zf_+(s_1) + (1/2)z^2f_+'(s_1) ; \quad z \geq 0 \]  
\[ \Delta E = zf_-(s_1) + (1/2)z^2f_-'(s_1) ; \quad z \leq 0 \]
This quadratic model enables us to determine the first order behavior of $E$ when $z$ is equal to zero, at $s=s_1$. This allows us to determine contact line stability at $s=s_1$. The nine possible cases are illustrated in Figure 3.4. In case C, where $f_+'>0$ and $f_->0$, a minimum of $E$ at $s_1$ is guaranteed. In cases A, D, G, H, and I, $E$ is not minimized and the contact line is unstable in the directions indicated by the arrows. In case B, $f_+'(s_1)>0$ guarantees a minimum, as does $f_-'(s_1)>0$ in case F. Finally, in case E $f$ is continuous, and $f_+'(s_1)>0$ and $f_-'(s_1)>0$ imply minimization. If $f'$ is also continuous, then the relations [41] and [42] imply local minimization.

Having derived the conditions guaranteeing minimization of $E$, we can now apply them to model quasi-static displacement of a liquid-vapor interface along the boundary of a solid surface. This is the topic of the next chapter.
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$\alpha = \arctan f_+ \quad \beta = \arctan f_-$

Figure 3.4: FIRST ORDER BEHAVIOR OF $\Delta E$ AT A CORNER OF $C_B$
Chapter IV
SINGLE CONTACT LINE CASES

IV.1 QUASI-STATIC MODEL

In III.1 above, $C_B$ was the boundary of a solid dipped into a constant temperature liquid reservoir. The theory developed above is equally applicable if $C_B$ is the profile of the left-hand side of a solid whose left and right hand sides are both cylindrical, with the ruling lines on each side parallel. Figure 3.1 is then the left side vertical cross section of this system.

Liquid-vapor interfaces advancing and receding on the surface of a solid can be modelled by such a system. Suppose that Figure 3.1 represents a stable initial configuration. That is, $C_{LV}$ satisfies equations [41] and [42]. Now we let $C_B$ be displaced vertically upwards a distance $\epsilon$. The coordinates of $P$ before displacement are $X(s_1), Y(s_1)$ in the coordinate system fixed relative to the liquid level at $x=\infty$ in Figure 3.1. The new coordinates of $P$ in this same system are:

51
P; \( X(s_1), Y(s_1) + \varepsilon \) \hspace{1cm} [45]

(The material coordinates of P are still \( X(s_1), Y(s_1) \)). If the contact point moves on \( C_B \), it will move down \( C_B \); it recedes. (For an advancing interface, change \( \varepsilon \) to \(-\varepsilon \).) Let us focus on the receding case. Define a function \( E \) as follows:

\[
E(s_1, \varepsilon) = \min_{C_{LV}} E(s_1, \varepsilon, C_{LV}) \hspace{1cm} [46a]
\]

Suppose it is possible to construct the function \( s_1(\varepsilon) \) as in [46b]:

\[
s_1(\varepsilon) = \text{Solution of } \min_{s_1} E(s_1, \varepsilon); 0<\varepsilon<\delta \hspace{1cm} [46b]
\]

where \( \delta \) is small enough so that one and only one solution of the minimization problem in [46] exists. Then the value of \( s_1(\varepsilon) \) is taken as the arclength coordinate of the new intersection point of \( C_B \) and \( C_{LV} \). Note that the set \( E \) is minimized over is open. For the cases below, it is easy to show that the construction of \( s_1(\varepsilon) \) is always possible.

There are two possibilities in the receding case for \( s_1(\varepsilon) \). In Case I;

\[
s_1(\varepsilon) = s_1(0) \hspace{1cm} [47]
\]
so that the minimum of E does not move with ε. Here, the contact line will stick to its initial position. In Case II;

\[ s_1(ε) < s_1(0) \]  

[48]

so that the minimum of E moves continuously with ε. Here, the contact line slips downward as \( C_B \) is displaced. If \( C_B \) is a vertical line with the function \( θ_e \) constant, then

\[ s_1(ε) = s_1(0) - ε \]  

[49]

The advancing case is similar. Note again that one and only one contact line is allowed, for either initial interfaces or ones resulting from \( C_B \) displacement.

IV.2 NOTES

There are two general classes of models considered below. The first is where \( θ_e \) is a constant; the second is where \( C_B \) is a vertical line. The first class models boundary surfaces which are homogeneous but not planar. The second class models surfaces of solids which are planar but heterogeneous. We separate these cases for two reasons. First, the calculations involved are easier. Second, it is important to distinguish between the different effects of roughness and of heterogeneity, because in the former case
the apparent contact angle cannot be the Young's Law angle; see Cain et. al. (26).

Recall from above the capillary length $\kappa$ defined in equation [8c]. Suppose that $C_B$ is periodic with wavelength $L$. Then the behavior of the advancing or receding contact line depends on how $L$ compares with $\kappa$. The same is true for the wavelength of a periodic $\Theta_e$ function. From the literature (see II.4) we could expect that when $L \ll \kappa$, then hysteresis of the apparent contact angle occurs. This is in fact the case, as shall be made clear below.

As mentioned in II.4 above, we assume enough viscous damping is present so that the contact line can latch onto a stable position from an initial, unstable one.

IV.3 APPLICATIONS

IV.3.1 Class I: $\Theta_e = \mu$, a constant
IV.3.1.1 \( C_B \) a directed straight line segment -

\( C_B \) makes an angle \( \Psi \) with the positive x axis, as defined in III.1 above. The direction of increasing \( s \) goes from liquid to vapor along \( C_B \), and the solid is to the right. See Figures 4.1a,b. From equation [38]:

\[
\frac{d\Theta}{ds} = - \frac{d\Phi}{ds} = - \frac{d\Phi}{dy} \frac{dy}{ds} = - \frac{d\Phi}{dy} \sin(\Psi) \tag{50}
\]

and combining with [18] and [16]:

\[
\frac{d\Theta}{ds} = - \frac{2\sqrt{k}}{\sqrt{1-v^2}} \sin(\Psi) \tag{51}
\]

Thus, [42] is satisfied for \( \Psi \) in the interval \((0,\pi)\) and violated for \( \Psi \) in \((\pi,2\pi)\), regardless of the value of \( \mu \). Some stable and unstable cases are illustrated in Figures 4.1c to g.

This result is consistent with Eick, Good, and Neumann (12) who treat the cases \( \Psi=\pi/4 \) and \( \Psi=\pi/2 \). They derive some complex formulae for \( E(\Theta) \), and study many individual cases where they specify \( \Theta_e \). In all of these cases, they find a true minimum at \( \Theta = \Theta_e \).
Figure 4.1a: A DIRECTED LINE SEGMENT WITH $\Psi < \pi$
Figure 4.1b  A DIRECTED LINE SEGMENT WITH $\psi > \pi$
\[ \psi = \pi/6 \]

STABLE

Figure 4.1c
\[ \psi = \pi/3 \]

STABLE

Figure 4.1d
\[ \Psi = \frac{5\pi}{6} \]

STABLE

Figure 4.1e
$\psi = 7\pi/6$

UNSTABLE

Figure 4.1f
\[ \Psi = \frac{11\pi}{6} \]

UNSTABLE

Figure 4.1g
For \( \Psi \) equal to 0 and to \( \pi \), the quantity in equation [42] is equal to zero. This corresponds to indifferent equilibrium (see II.1). Horizontal translation of the liquid-vapor interface requires no work to be done on the system. The class of solid boundary surfaces where this is true are discussed in the next section.

IV.3.1.2 \( C_B \): a boundary which includes a transversal segment. -

Suppose that for \( C_B \) in the interval \( s_L \leq s \leq s_U \), equation [52] holds:

\[
f(s) = \cos \Theta - \cos \mu = 0 \quad ; \quad s_L \leq s \leq s_U
\]

Then this segment of \( C_B \) is a transversal, in accordance with standard terminology in the calculus of variations (16). We denote a transversal segment as \( \tilde{C}_B \).

Using formulae [16] and [38], we can obtain the governing differential equations for transversal curves. The angle of the tangent to \( \tilde{C}_B \) with the positive x axis is always equal to \( \mu + \phi \). Thus:

\[
\frac{du}{dl} = \cos(\mu+\phi) = (\cos \mu)(1-2v^2) - 2(\sin \mu)v\sqrt{1-v^2} \quad [53a]
\]
\[
\frac{dv}{dl} = \sin(\mu + \phi) = (\sin \mu)(1-2v^2) - 2(\cos \mu)v\sqrt{1-v^2} \tag{53b}
\]

are the governing equations, with \(l\) a dimensionless arc length along \(\tilde{C}_B\).

Figure 4.2, 4.3, and 4.4 show transversal curves for \(\mu=\pi/4, \pi/2, \) and \(3\pi/4\) respectively, together with some members of \(\tilde{F}\). They were generated using the classical fourth order Runge-Kutta method for numerical integration. Just as \(\tilde{F}\) is generated by horizontal translation of a single member, so all transversal curves for a given \(\mu\) can be generated by horizontal translation of a single \(\tilde{C}_B\).

The \(\tilde{C}_B\) for \(\mu=\pi/4\) in Figure 4.2 has two horizontal asymptotes which separate the curve, at \(v = -0.3826\ldots\) and \(v = 0.9238\ldots\). The former corresponds to \((\mu + \phi) \to 0\); the latter when the sum approaches \(\pi\). These asymptotes are also solutions of [53] and are the cases of \(\tilde{\xi}=0\) or \(\pi\) discussed in the previous section. The \(\tilde{C}_B\) in Figures 4.3 and 4.4, or for any value of \(\mu\) in the interval \((0,\pi)\), show similar characteristics.

Equation [52] implies that \(E\) remains constant over \(\tilde{C}_B\). This is the indifferent equilibrium case; it takes no
Figure 4.2: TRANSVERSALS WITH $\mu = 1/4$
Figure 4.3: TRANSVERSALS WITH $\mu = \pi/2$
Figure 4.4: TRANSVERSALS WITH $\mu = 3\pi/4$
external work to displace the contact line along \( \tilde{C}_B \). Suppose that we take the semi-infinite part of \( \tilde{C}_B \) labelled AB in Figure 4.2, where B is the point (\(-\infty, -0.9238\ldots\)), and separate it from the rest of \( \tilde{C}_B \). Then we let AB drop a small distance. Then \( \theta \) is slightly larger than \( \mu \) everywhere on AB. Thus, \( f(s) \) is less than zero for all \( s \), and \( E \) is a monotonically decreasing function of \( s \) on AB. Therefore, the contact point at P will travel endlessly towards B on AB. Again, all \( \tilde{C}_B \) with \( \mu \in (0, \pi) \), such as in Figures 4.3 and 4.4, exhibit analogous behavior.

The \( \tilde{C}_B \) curves can be used to evaluate the stability conditions [41] and [42]. Figure 4.5 illustrates an example. P is the point P in Figure 4.2 with \( \mu = \pi/4 \). To meet condition [41], the contact angle of \( C_{LV} \) must be equal to \( \mu \). Since \( C_{LV} \) has a contact angle of \( \mu \) with \( \tilde{C}_B \), the transversal and the solid boundary must be tangent at the point P. Condition [41] and [42] together require that the curvature of \( C_B \) must be less than the curvature of \( \tilde{C}_B \) at the point P (see Appendix A for details). Therefore, [42] implies that the transversal must not penetrate the solid boundary in the neighborhood of P. Figure 4.5a is a stable case. Figures 4.5b and 4.5c are cases of one sided penetration. Figure 4.5d shows a case of two sided penetration. The arrows in
FIGURE 4.5
STABLE CASE

FIGURE 4.5a
UNSTABLE CASE

FIGURE 4.5b
UNSTABLE CASE

FIGURE 4.5c
UNSTABLE CASE

FIGURE 4.5d
Figures 4.5b,c, and d show the directions in which a small contact line perturbation will grow. This property of $\tilde{C}_B$ is useful in computing the behavior of our model, as shown in the next section.

IV.3.1.3 $C_B$ a cosine wave -

Here $C_B$ is defined by the equation

$$X = -A \cos \lambda (Y - Y_0)$$  \[54\]

where $A$ and $\lambda$ are parameters. In the dimensionless variables

$$U = X \sqrt{\kappa / 2} , \quad V = Y \sqrt{\kappa / 2} , \quad V_0 = Y_0 \sqrt{\kappa / 2} ,$$

$$\alpha = \lambda \sqrt{\kappa / 2} , \quad \beta = \lambda \sqrt{2 / \kappa}$$  \[55\]

[54] becomes

$$U = -\alpha \cos \beta (V - V_0)$$  \[56\]

The formula for $\Psi$ is

$$\cot \Psi = \alpha \beta \sin \beta (V - V_0)$$  \[57\]

Table One lists the cases we consider in this section. The value of $\mu$ is taken as $\pi/2$ in all cases.
In all cases, increasing the value of $V_0$ is equivalent to upward displacement of $C_B$, thus modelling the receding behavior of the liquid-vapor interface. We start with $V_0$ equals zero, so that $C_{LV}$ is the curve $y=0$. In cases 1 and 2 of Table One, the intersection of $C_{LV}$ and $C_B$ slides down $C_B$, but rises with respect to the fixed coordinate system, as $V_0$ is increased. As $V_0$ continues to increase, the coordinates $X_1, Y_1$ of the intersection point oscillate as the contact line slides down the surface of the solid. This is Case I behavior discussed in section IV.1 above (after equation [46]). For any displacement of $V_0$ in these two cases, the $C_{LV}$ which satisfies [41] also satisfies [42]. This may be seen in Figure 4.2, where case 1 of Table One is drawn as the broken line $C_{B1}$. By sliding $C_{B1}$ upwards and to the left, with no rotation, such that it always stays tangent to $\tilde{C}_B$, we see that $\tilde{C}_B$ never penetrates $C_{B1}$.

Case 3 of Table One is quite different. It is illustrated by the broken curve $C_{B3}$ in Figure 4.3. As we slide $C_{B3}$ down, $\tilde{C}_B$ does not penetrate until the point $A$ is the tangency point. If, starting at $V_0$ equals zero, $C_{B3}$ is displaced upwards, the intersection point slides down $C_{B3}$ until it reaches $A$. If $V_0$ increases no further, the intersection point will spontaneously 'jump' from $A$ to $B$.
TABLE ONE

<table>
<thead>
<tr>
<th>CASE</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>0.02</td>
<td>50</td>
</tr>
</tbody>
</table>

$\mu = \pi/2$ in all cases
(the first point that satisfies both [41] and [42] as we decrease s on $C_{B3}$). If $V_0$ is increased again, the intersection point will slide down $C_{B3}$ again until $V = V_A + 2\pi/\beta$, where another 'jump' occurs. $V_A$ is the value of $V_0$ when $A$ is the intersection point. The contact line jumps are obviously irreversible processes.

We compare cases 2, 4, and 5 of Table One, which all have

$$\alpha\beta = 1$$

Thus $\Psi$ varies between $\pi/4$ and $3\pi/4$. The behavior of the apparent contact angle $\Theta_{app}$ concerns us here (recall the discussion in II.4 above). This is the contact angle if $C_B$ is taken as a vertical line through the intersection of $C_B$ and $C_{LV}$. It is computed by the equation

$$\Theta_{app} = \pi/2 - \phi$$

With [58] and $\mu=\pi/2$, the apparent contact angle will always be in the closed interval $[\pi/4, 3\pi/4]$. In Figure 4.6, $\Theta_{app}$ is plotted against $V_0$ for cases 2, 4, and 5 of Table One. The computations were done using the properties of the transversal curves described in the previous section.
Figure 4.6: PLATE DISPLACEMENT VS. APPARENT CONTACT ANGLE FOR CASES IN TABLE ONE WHERE $\alpha$=1. A=CASE 2, B=CASE 4, AND C=CASE 5
Curve A corresponds to case 2 discussed above. Curve A oscillates smoothly with $V_0$ between 45° and 135°. Curve B plots the behavior of case 4. Contact line instabilities appear as jumps in the apparent contact angle $\Theta_{\text{app}}$ varies between 83° and 135° during advancement, with the jumps occurring close to 135°. $\Theta_{\text{app}}$ varies between 96° and 45° for a receding contact line, with jumps occurring near 45°. In case 5, established advancing or recession takes place over ranges of $\Theta_{\text{app}}$ of about 13°, with 135° and 45° as the limits. For water against air, this corresponds to a wavelength $(2\pi/\lambda)$ of about 1mm. Once again, the jumps take place just below 135° and just above 45°. As $\beta \to \infty$, the ranges of $\Theta_{\text{app}}$ for advancing and recession approach zero, and the jumps take place still just below 135° and just above 45°. Note that this is hysteresis of the apparent contact angle for a quasi-static liquid-vapor interface! (As $\beta \to \infty$, the energy barriers between minima vanish, and a "roller coaster" effect is inevitable for finite viscous damping).

Figure 4.7 depicts the mechanism of contact line advancement for case 5. The initial contact point is the lowest point of the wave where it has a vertical tangent. Downward solid displacement is simulated by moving the contact point
COSINE WAVE: UNSTABLE POINT: PLATE DOWN
AMPLITUDE=.02 , WAVENUMBER=50

X=UNSTABLE POINT
*=JUMP POINT

Figure 4.7:
AN ILLUSTRATION OF CONTACT LINE JUMPS
upwards along the wave. The tangent to each configuration to $C_{LV}$ is the outward facing normal of the wave (pointing towards $-\infty$ on the U axis). Just after the inflection point of the wave, the contact line becomes unstable, and moves to a new position corresponding to the "jump point" in the Figure. The curvature of the wave is zero at the inflection point, but increases rapidly afterwards because $\beta$ is large. As $\beta \to \infty$, the unstable point moves closer to the inflection point. The jump point also moves closer to the inflection point in the direction of increasing $s$. Thus the variation in advancing angles becomes smaller, and the jump occurs just after $\Theta_{app}$ has reached maximum at $135^\circ$ at the inflection point.

Huh and Mason (10), as discussed in II.4 above, observed a similar mechanism of contact line instabilities for a drop advancing along the "record groove" surface of Johnson and Dettre (9). The above results are consistent with the formulae of Shuttleworth and Bailey (17) in the limit.
IV.3.1.4 \( C_B \) a sawtooth with vertically aligned vertices

The equation

\[ \Psi = \Psi_A ; n\lambda < (n+1)\lambda ; n \text{ even} \quad [60a] \]

\[ \Psi = \Psi_B ; n\lambda < (n+1)\lambda ; n \text{ odd} \quad [60b] \]

defines \( C_B \) as a sawtooth with vertically aligned vertices with a wavelength of \( 2\lambda \). We define \( \alpha \) so that

\[ \Psi_A = \pi/2 - \alpha ; \Psi_B = \pi/2 + \alpha ; 0 < \alpha < \pi/2 \quad [61] \]

In Figure 4.8, \( \alpha \) is 30° and \( \mu \) is 75°. The Figure is a vertical section of a stable equilibrium system, with the contact point \( P \) on an interior of one of the sawtooth ramps. \( P \) is known to be stable from the theory of the planar solid boundary in IV.3.1.1 above. \( P \) can reversibly advance or recede along the ramp \( B \) away from the vertices (these are discussed below).

It is clear in Figure 4.8 that the interface will never run into an \( A \) ramp while \( P \) lies on a \( B \) ramp. The equivalent condition of excluding such a run-in is the restriction

\[ \mu \lambda 2\alpha \quad [62] \]

The equivalent of excluding a run into a \( B \) ramp while \( P \) lies
Figure 4.8: A SAWTOOTH WITH VERTICALLY ALIGNED VERTICES
on the A ramp is

$$\mu \leq (\pi - 2\alpha)$$  \[63\]

We require [62] and [63] to be satisfied so that only one contact line is possible. The combination of [62] and [63] is

$$2\alpha \leq \mu \leq \pi - 2\alpha$$  \[64\]

If \(\alpha > \pi/4\), then no value of \(\mu\) satisfies [64]. For \(\alpha \leq \pi/4\), the range of allowed contact angles shrinks from \([0, \pi]\) for \(\alpha = 0\) (a planar boundary) to the single value \(\mu = \pi/2\) for \(\alpha = \pi/4\). Cases which violate [64] are discussed in Chapter V of this thesis.

We now discuss the behavior of the vertices of \(C_B\) as intersections with \(C_{LV'}\). Figure 4.8a is a blow-up of Figure 4.8 at a vertex pointing towards the liquid-vapor side (labelled D in both Figures). The dotted lines A'D and B'D are extensions of the A and B ramps. We exclude members of \(\tilde{F}\) whose tangents lie outside the cone A'DB', such as UT, due to the restriction in III.5, just above equation [34]. These curves would be excluded anyway, since if the value of \(\mu\) allows the existence of a neighbor (such as one with the
tangent T) which is in stable equilibrium, then μ does not satisfy the non run-in condition [64].

Consider the stability of a configuration whose tangent lies in the cone A'DB', such as the tangent DF in Figure 4.8a. We can define a contact angle with respect to the A ramp θ_a and a contact angle with respect to the B ramp θ_b. The relationship between them is

$$\theta_b = \theta_a + 2\alpha$$  \hspace{1cm} [65]

which can be combined with the definition of f(s) in equation [37] and its one sided variants f_+ and f_- defined just above equation [43] in III.6 to get

$$f_+ = \cos \theta_a - \cos \mu$$ \hspace{1cm} [66a]

$$f_- = \cos \theta_b - \cos \mu$$ \hspace{1cm} [66b]

From Figure 3.4C, stability is guaranteed if f_+ is positive and f_- is negative. This is true if

$$(\mu - 2\alpha) < \theta_a < \mu \text{ i.e. } \mu < \theta_b < (\mu + 2\alpha)$$ \hspace{1cm} [67]

(Note that because of the restriction in III.5, θ_a and θ_b always have values between 0 and π). If [67] is satisfied, the configuration is stable. The vertex D is called a defect vertex.
Figure 4.8a: CONTACT LINE STABILITY AT A DEFECT VERTEX D
The vertices labelled 0 in Figure 4.8 are called overlap vertices. Suppose the tangents to \( C_{LV} \) making the equilibrium contact angle with the ramp above and below 0 were shown in Figure 4.8. Then these tangents would overlap; hence the name overlap vertex. We show here that a contact line attached at 0 is always unstable. By the same analysis as above

\[
\begin{align*}
    f_+ &= \cos \Theta_b - \cos \mu \\
    f_- &= \cos \Theta_a - \cos \mu
\end{align*}
\]

[68a] [68b]

For \( \Theta_a \) in the interval of [67],

\[
    f_- > 0 \quad \text{and} \quad f_+ < 0 \quad ; \quad (\mu - 2\alpha) < \Theta_a < \mu
\]

[69]

which means that for \( C_{LV} \) curves whose tangents are in the angular overlap region [69], \( \Delta E \) is at a rooftop maximum shown in Figure 3.4G. For \( \Theta_a \) outside [69] but still in the interval \([0, \pi - 2\alpha]\) it is easy to check that \( \Delta E \) is of the form in Figure 3.4A, D, H, or I. This proves our contention.

Next, we apply the above results to our quasi-static interface model. Suppose the initial configuration is that of Figure 4.8, which is stable. \( C_B \) is slowly lowered, and \( P \) slides up the B ramp until it meets the defect vertex D. At this point \( \Theta_B \) is equal to \( \mu \), and the configuration is
stable. \( \Delta E \) corresponds to Figure 3.4F. As \( C_B \) continues to be lowered, the contact point sticks to D since the condition \([67]\) is satisfied. Finally, \( \theta_a \) attains the value of \( \mu \), and then \( P \) slips up the A ramp as \( C_B \) is lowered further. When \( P \) meets the overlap vertex 0, the configuration is unstable, and \( P ' \)jumps' irreversibly upwards to the next point which satisfies \([41]\) and \([42]\), or to the next defect vertex, whichever is closer to 0.

Where \( P \) jumps to depends on how the wavelength \( \lambda \) compares with the capillary length \( \kappa \) defined in equation \([8c]\) in III.2. If \( \lambda \geq \kappa \), then \( P \) ends up on the B ramp just above 0. If \( \lambda \) is an order of magnitude or so less than \( \kappa \), then \( P \) will jump to the D vertex just above 0. If \( \lambda \ll \kappa \), then \( P \) ends up on D and the new contact angle \( \theta_a \) will be very close to \( \mu \). In this case, as \( C_B \) advances, the apparent contact angle is equal to \( \mu + \alpha \). The receding case behaves in a similar fashion, with \( \theta_{app} \) equal to \( \mu - \alpha \). Once again, hysteresis of \( \theta_{app} \) occurs.

For extremely fine sawtooth surfaces, our quasi-static model will breakdown. The energy barriers between minima will be too low for reasonably strong viscous damping to allow the contact point to latch on the next locally
minimizing point of $C_B$, and the roller coaster effect mentioned in IV.3.1.3 will occur.

The work of Schwartz and Garoff (14) suggest that non-cylindrical variations will further reduce the energy barriers separating local minima. They did not show, however, that the energy minima of the cylindrical theory presented here were lowered by allowing non-cylindrical variations.

The theory derived in this case is consistent with the theory of the smooth case (in IV.3.1.3) if the corners are rounded. The defect vertices correspond to Figure 4.5a, while the overlap vertices correspond to Figure 4.5d.

The conditions [67] are consistent with the more general conditions attributed by Oliver, Huh, and Mason (19) to Gibbs (5). However, Gibbs's conditions are different and wrong unless modified; see Dyson (18).
IV.3.2 **Class II.** $C_B$ a vertical line, $\Theta_e$ variable.

In these cases, $\Theta = \Theta_{app}$ as defined by equation [38] and [59] respectively. The solid is a plate with a planar boundary surface on each side.

**IV.3.2.1** $\Theta_e$ a sine wave.

This case is defined by the equation

$$\Theta_e = \frac{\pi}{4}(2+\sin\lambda(Y-Y_0))$$  \[70\]

where $Y_0$ is the displacement of $C_B$ from an initial position with $Y_0=0$. $Y_0$ is positive for upward displacement (receding interface) and negative for downward displacement (advancing interface). The equation [70] has the property that $\Theta_e$ is in the closed interval $[\pi/4, 3\pi/4]$. It was chosen so that the results could be compared with previous cases.

Introducing the dimensionless variables of equation [55] in IV.3.1.3, we write [70] as

$$\Theta_e(V, V_0, \beta) = \frac{\pi}{4}(2+\sin\beta(V-V_0))$$  \[71\]

Using [16] from III.3, [38] from III.5, and noting that $\Psi$ equals $\pi/2$ everywhere, $\sin\Theta$ in dimensionless variables is
\[
\sin \theta = 1 - 2v^2; \quad |v| \leq 1
\]

the restriction on \(v\) coming from the fact that the surface of the solid is planar. Taking the \(\arcsin\) function as going from the interval \([0,1]\) to the range of angles \([0, \pi/2]\), equation \([72]\) can be solved for \(\theta\):

\[
\arcsin(1-2v^2); \quad v > 0
\]

\[
\theta = \pi - \arcsin(1-2v^2); \quad v < 0
\]

Equation \([41]\) (equilibrium) for this case (equating \([71]\) and \([73]\)) can result in multiple solutions. Thus the added condition for stability \([42]\) must be tested on all solutions of \([41]\). To analyze the nature of the solutions graphically, it is convenient to define the variable \(\Delta\) as

\[
\Delta = V - V_0
\]

For a given \(\beta\), we plot \(\theta_e\) versus \(\Delta\), and \(\theta\) versus \(\Delta\). The \(\theta\) curve "moves" across the graph left to right as \(V_0\) is decreased. The solutions to \([41]\) are the intersections.

In Figure 4.9, the case of \(\beta = 1\) is shown for \(V_0\) increasing from \(-\pi\) to \(\pi\). There is only one solution for any
value of $V_0$, and by applying [42] all of these solutions are stable. Physically, this indicates that as the plate is slowly raised the liquid-vapor interface attaches at the appropriate contact angle, and no hysteresis is observed. This process is fully reversible.

The case where $\beta = 5$ is different. Figure 4.10 shows this case. At $V_0$ equals zero, there is a unique intersection corresponding to a contact angle of 90°. As $V_0$ is decreased, the stable equilibrium case is represented by the point moving up the sine curve towards P. Once it reaches P, it no longer represents stable equilibrium. If $V_0$ is held here (at -.752...), the contact line moves irreversibly until the situation represented by Q obtains. Q is a stable equilibrium case. This can be seen by noting that the curve for $\Theta_\varepsilon$ between P and Q lies beneath $\Theta$. Thus the first derivative of E, $f(s)$ in equation [37] (see III.5), is negative in this whole region. For cases with three intersections, such as $V_0$ between -.502... and -.752..., the middle solution is unstable and represents a local maximum of E. Contact line recession could be modeled by increasing $V_0$ from $V_0 = 2\pi/\beta$. The stable intersections would move from P to Q to the point S, where a jump occurs to T.
Figure 4.9: CASE WITH $\beta=1$ IN EQUATION [71]
Figure 4.10: CASE WITH $\beta=5$ IN EQUATION [7.1]
As $\beta \to \infty$, the family of $\theta$ curves become almost flat in relation to the rapidly oscillating $\theta_e$ curve. Advancement will result in jumps from just beyond the crest of the $\theta_e$ curve to just before the next crest to the right. Recession gives rise to jumps just after the troughs of $\theta_e$ and reattaches just before the next trough to the left. This results in an advancing contact angle of $135^\circ$ and a receding contact angle of $45^\circ$. At extremely large $\beta$, as before, viscous damping is no longer effective in quenching contact line oscillations.

IV.3.2.2 $\theta_e$ a step function -

This case is defined by

\[ \theta_e = \theta_a ; \ n \lambda < (Y-Y_0) < (n+1)\lambda ; \ |n| \text{ even or zero} \] \hspace{1cm} [75a]

\[ \theta_e = \theta_b ; \ n \lambda < (Y-Y_0) < (n+1)\lambda ; \ |n| \text{ odd} \] \hspace{1cm} [75b]

\[ \theta_a < \theta_b \] \hspace{1cm} [75c]

where $\lambda$ is the half wavelength of the square wave. We refer to the lines on the boundary surface which separate the constant $\theta_e$ strips as cracks. Here we apply the general theory, generating the actual E curve and showing how the minima behave.
Writing $[75a,b]$ in dimensionless form gives

$$\theta_e = \theta_a; \quad nL \ll(V-V_0) \ll(n+1)L; \quad |n| \text{ even or zero} \quad [76a]$$

$$\theta_e = \theta_b; \quad nL \ll(V-V_0) \ll(n+1)L; \quad |n| \text{ odd} \quad [76b]$$

where

$$V_0 = V_0 \sqrt{k/2}; \quad L = \lambda \sqrt{k/2} \quad [77]$$

To illustrate, we study below the particular case

$$\theta_a = 45°; \quad \theta_b = 135°, \quad L = 0.5 \quad [78]$$

The $\theta_e$ function [78] is graphed in Figure 4.11a.

Figure 4.11b depicts the the curve $C_B$ with $V_0 = 0$ together with some selected line segments from a family of line segments all of whose elements meet $C_B$ at the equil-ibrium contact angle. Figures 4.11c and d are the same with $V_0$ equal to .5 and to .6276... respectively. Any equili-brium liquid-vapor curve not meeting the plate at a crack would have to have a tangent at the contact point parallel to the family of line segments. In Figure 4.11b, two cases are possible, but in Figure 4.11c, no $C_{LV}$ can meet $C_B$ off a crack without violating this condition. Thus it is important to determine the stability of interfaces which have cracks as contact lines.
Figure 4.11: (a) GRAPH OF THE CONTACT ANGLE FUNCTION IN EQUATIONS [76a], [76b], and [78b]. (b) POSSIBLE CONFIGURATIONS OF $C_{LV}$ WHEN $V_0=0.0$. (c) $V_0=0.5$. (d) $V_0=0.6276...$
There are two types of cracks, labelled 0 and D in Figure 4.11b-d. The 0 cracks are overlap cracks, because the family of line segments overlap around 0. The D cracks are called defect cracks because the tangent segments form a defect at D (Compare with IV.3.2.1).

The 0 cracks are always unstable as contact lines. If $\Theta _{0_b}$, then from [37] $f_{-}$<0 which corresponds to Figures 3.4G, H, and I and guarantees instability in the direction of decreasing s. If $\Theta _{0_a}$, then $f_{+}$<0, Figures 3.4A, D, and G apply. Instability is in the direction of increasing s. If $\Theta _{0_a}$< $\Theta _{0_b}$, then $f_{-}$>0 and $f_{+}$<0, and E is at a rooftop maximum (Figure 3.4G).

Defect cracks are stable contact lines if $\Theta _{0_a}$<$\Theta _{0_b}$. Here $f_{+}$>0, $f_{-}$<0, and this corresponds to a minimum in E (Figure 3.4C). For $V_0$=.5 (Figure 4.11c) $C_{LV}$ must meet at a crack for stable equilibrium.

We can confirm the above results and gain further information by calculating the total energy as a function of $\nu$ and $V_0$ using equations [36], [37], [76a,b], and

$$\cos \Theta = 2\nu \sqrt{1-\nu^2}$$  [79]
derived from [16] and [38] with $\Psi = \pi/2$. Figures 4.12 and 4.13 show the results of these calculations. Each total energy curve corresponds to a particular value of $v_0$. The values of $v_0$ are given in Table Two. The curves are labelled at the corners and at the endpoints $v = \pm 1/\sqrt{2}$. That is, curve 1 connects the points A B C D E. Further, $E^* = E\sqrt{2/\pi}$. Curve 1 shows $E^*$ as a function of $v$ for $v_0 = 0$. Clearly, the minimum of curve 1 occurs at $v=0$. Thus the equilibrium interface for the plate configuration shown in Figure 4.11(c) is flat and contacts the plate at the defect boundary $v=0$.

Note that there is considerable overlap among the total energy curves in Figures 4.12 and 4.13. The $\cos\Theta$ term in Equation [37] depends only on $y$, and thus its contribution to the integral does not vary with $y_0$. $\cos\Theta_e$ varies with $y_0$, or $v_0$ in dimensionless variables (see [55] and [77]). However, if two $v_0$'s are within $L$ of each other then there is a range of $v$ over which the $\cos\Theta_e$ terms are the same. Thus the values of $E$ for two different $v_0$'s are equal over that interval. Note also that these curves have corners due to the discontinuities in the equilibrium contact angle given by equation [69]. In particular, Curve 1 has a corner at its minimum.
Figure 4.12: TOTAL ENERGY VERSUS V COORDINATE OF CONTACT LINE
Figure 4.13: TOTAL ENERGY VERSUS V COORDINATE OF CONTACT LINE
The value of $v$, $\bar{v}$, which minimizes $E$ depends on the parameter $v_0$, although over some intervals of $v_0$ $\bar{v}$ is a constant. Figures 4.12 and 4.13 depict $E^*$ as a function of $v$ over the range of $v_0$ between .5 and 1.5. Let us start with a flat interface contacting the plate which is at $v_0 = .5$ as in Figure 4.11(c), and pull the plate upward. As indicated by Curve 1 in Figure 4.12, the starting interface is in stable equilibrium.

Curve 2 in Figure 4.12 shows the graph of $E^*$ after a net plate displacement of $0.1276...$ dimensionless units (see [59]). The minimum has moved the same amount, from $v = 0$ to $v = 0.1276...$. Thus at equilibrium the contact line is still the defect boundary and the interface makes a contact angle of 75.34 degrees with the plate, which is calculated using [79]. Since the contact line moves up the same distance the plate does, we say the contact line sticks to the plate. Sticking is expected in this case because the interface still cannot assume a neighboring configuration with a Young's Law angle on any constant contact angle strip. The same is true for the interface whose $E$ function is curve three in Figure 4.12. Curve 3 is the graph of $E^*$ after a net plate displacement of $0.2551...$ dimensionless units. Clearly the equilibrium interface will have a value of
for its parameter \( v \), which gives a contact angle of 60.44 degrees. In curve 4 of Figure 4.12, which corresponds to a net plate displacement of .3827 dimensionless units, a minimum occurs at \( v = .3827 \), at a contact angle of \( \Theta_a \) (45 degrees). Up to this point, the equilibrium contact line was stuck on the boundary and has been dragged up as \( v_0 \) increases. (Curve 4 has a one-sided first derivative which is continuous from the left at its minimum.) As \( v_0 \) continues to increase, the contact line starts to move down the same distance as the plate moves up. We say the contact line now slips along the plate. Now, \( \bar{v} \) does not move along with plate displacement but stays the same at .3827. (Further, the \( E \) curves now have a continuous first derivative from both the right and the left at their minima.) The contact line is now on a \( \Theta_a \) strip, so the contact angle satisfies Young's Law. Curve 5 of Figure 4.12, for which \( v_0 = 1 \), has a relative minimum at \( v = .3827 \). Thus the contact line slips down the plate, always on a \( \Theta_a \) strip, in accordance with Young's Law.

Figure 4.13 illustrates total energy curves for further upward plate displacement. Curves 6 and 7 have relative minima at \( v = .3827 \) just like Curve 5 of Figure 4.12. They also have absolute minima at \( v = -.3827 \) and -.2551
respectively, but these minima are separated by the energy barriers shown in the figure. The contact line continues to slip on the \( \theta_a \) strip with the Young's Law angle as the plate is displaced. Curve 8 has a corner at \( v = 0.3827 \). With this value of \( v \), the contact line would lodge directly in a crack with \( \theta_a \) on top and \( \theta_b \) on the bottom, with a contact angle of \( \theta_a = 45^\circ \). It appears that the slightest perturbation would knock \( v \) down to the minimum at \( v = -0.1173 \ldots \), given the steep descent in \( E \) to the left ending at \( v = -0.1173 \). In this new configuration, the contact line to the plate is on a defect crack which is 2L down from the initial defect crack, and \( C_{LV} \) meets the plate with a contact angle of 103.47 degrees. The new contact line will stick to the plate with further upward plate displacement. Finally, we come full circle to Curve 1 in Figure 4.13, which is equivalent to Curve 1 in Figure 4.12 because of the periodicity of \( \theta_e \). Thus \( v = 0 \) once again gives the minimum of \( E_A \), and the interface is once again flat and stuck to the plate at a defect crack. The total net plate displacement for the above cycle is 1.0 dimensionless units. If the plate is displaced further upwards, this pattern will repeat itself periodically, with a period of 1.0 dimensionless units for \( v_0 \). The contact angle variation for one period of this movement is shown in Figure 4.14.
Figure 4.14
Without detailed analysis let us describe the results of downward plate displacement from the same original plate configuration in Figure 4.11(c). As \( v_0 \) decreases from .5 to .1173..., the contact line sticks to the plate while the contact angle increases to 135°. Then, as \( v_0 \) continues to decrease, the contact line slips along the plate maintaining this contact angle until \( v_0 = -.3827 \). At this point, the contact line jumps upwards and then sticks to the plate at a defect crack with a contact angle of 76.53°. As \( v_0 \) decreases to -.5 and the contact angle increases to 90°. This is one complete period of contact angle variation.

As \( L \to 0 \), the upward displacement angle (receding) approaches a constant of \( \Theta_a \), and the downward (advancing) angle a value of \( \Theta_b \). This happens because the contact point travels on only one type of constant contact angle strip (\( \Theta_a \) for upward displacement, \( \Theta_b \) for downward) as the plate is displaced. Since L is small, the contact angle change is very small during "jumps" over the strips upon which the contact line can never reside (e.g. \( \Theta_b \) strips for upward displacement). The result is analogous to the case with \( \beta \to \infty \) in equation [64] for case 2.1 above. Further, for \( L \) small enough, and for a curve \( C_{1v} \) of the family \( \tilde{F} \) with a contact point \( p \) and a contact angle in the interval \([\Theta_a, \Theta_b]\), there
will be another curve of $\tilde{F}$ arbitrarily close to $C_{1v}$ which will meet $C_s$ at a (stable) defect boundary point.

Neumann and Good (8) plotted the total energy of the above problem for fixed $Y_0$ and varying $Y$. They determined values of $Y$ corresponding to local energy minima, but since they didn't move the plate, they were unable to depict the motion of the contact line upon it. Our results are consistent with their findings, and we can derive their basic equations from ours.

IV.4 SUMMARY OF RESULTS

We have demonstrated that the behavior of the apparent contact angle depends on how the capillary length $\sqrt{1/k}$ (see equation [8c]) compares with the length scale of boundary surface roughness or heterogeneity (for periodic $C_B$ or $\Theta_e$, the length scale is simply the wavelength). If the length scale is equal to or greater than the capillary length, no hysteresis occurs. If the length scale is much smaller than the capillary length, then hysteresis of the apparent contact angle occurs for quasi-static interfaces. (If the length scale is extremely fine, our model may break down due to the "roller coaster" effect discussed above). Hysteresis involves contact line 'jumps' as the interface advances or
recedes and reaches points of unstable equilibrium. At defect vertices or cracks, the apparent contact angle can take on a range of values between the receding and the advancing apparent contact angle.

In the next chapter, we consider the case in IV.3.1.4 with the one contact line assumption removed.
# TABLE TWO
PLATE DISPLACEMENTS CORRESPONDING
TO THE TOTAL ENERGY CURVES IN FIGURES 4.12 AND 4.13.

<table>
<thead>
<tr>
<th>CURVE NUMBER</th>
<th>DISPLACEMENT ($v_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (4.12)</td>
<td>0.5000</td>
</tr>
<tr>
<td>2 (4.12)</td>
<td>0.6276</td>
</tr>
<tr>
<td>3 (4.12)</td>
<td>0.7551</td>
</tr>
<tr>
<td>4 (4.12)</td>
<td>0.8827</td>
</tr>
<tr>
<td>5 (4.12,13)</td>
<td>1.0000</td>
</tr>
<tr>
<td>6 (4.13)</td>
<td>1.1276</td>
</tr>
<tr>
<td>7 (4.13)</td>
<td>1.2551</td>
</tr>
<tr>
<td>8 (4.13)</td>
<td>1.3827</td>
</tr>
<tr>
<td>1 (4.13)</td>
<td>1.5000</td>
</tr>
</tbody>
</table>
CHAPTER V
MULTIPLE CONTACT LINE CASE

This chapter discusses the relaxation of the one contact line assumption for the case in IV.3.1.4, $C_B$ a sawtooth with vertically aligned vertices.

V.1 WEAK AND STRONG VARIATIONS

Figure 5.1 is an enlargement of the cross section of $C_B$ in the vertical plane $P_\lambda$ near a defect point $D$. The curve $e_D$ is the member of $\tilde{F}$ which meets $C_B$ at $D$. The contact angle $\Theta_b$ of $e_D$ with the ramp $DB$ is less than $2\alpha$. Thus the tangent to $e_D$ at $D$ is outside of the cone $A'DB'$ (compare with Figure 4.8a). This is a violation of the restriction imposed in sections III.5 and IV.3.1.4 above. Let $s=s_1$ at $D$. The coordinates of $D$ are $X(s_1), Y(s_1)$. We pick a pair of values of $s$, $s_L$ and $s_U$, so that the value of $s_1$ is greater than $s_L$ and less than $s_U$. Because the tangent of $e_D$ lies outside the cone $A'DB$, there exists the values of $s$, $s_2$ and $s_3$, so that
\[ s_L < s_2 < s_1 < s_3 < s_U \]  \[ \text{[81]} \]
and
\[ e(X(s_2), Y(s_2)) \text{ is a subset of } e(X(s_3), Y(s_3)) \]  \[ \text{[82]} \]
as shown in Figure 5.1. The extremal \( e(X(s_3), Y(s_3)) \) penetrates the solid boundary \( C_B \). Clearly, it does not correspond to a physical liquid/vapor interface.

This is an important point in determining whether \( e_D \) represents a stable static equilibrium liquid/vapor interface. If \( e_D \) is stable, then certainly \( E(e_D) \) is less than or equal to \( E(C_S) \), where \( C_S \) meets \( C_B \) at \( G \) on the AD ramp (see Figure 5.2), and \( G \) has the coordinates \( X(s_3), Y(s_3) \). The extremal \( e(X(s_3), Y(s_3)) \) is the only member of \( \tilde{F} \) which goes through \( G \), since \( \tilde{F} \) is a simple cover. It is not the cross section in the plane \( P_x \) of a possible liquid/vapor interface. At this time we cannot compare \( E(e_D) \) to the value of \( E \) for any curve which has its only contact point with \( C_B \) on the ramp AD and which corresponds to a physical liquid/vapor interface (such as \( C_S \)). The theory developed to this point cannot determine whether, in fact, \( E(e_D) < E(C_S) \).

Below we will use the notions of weak variations and strong variations. Let \( e_x \) be a member of \( \tilde{F} \). \( e_x \) can be represented by
Figure 5.2
PROOF THAT $e_D$ IS STABLE TO STRONG VARIATION
Figure 5.2a
$e_x : x(y)$ \[83\]

just as in equations [19] and [19a], but using $x$ and $y$ instead of $u$ and $v$. From Bolza (16), a variation of $e_x$, $C_x$, can be written as

$$C_x : x(y) + \Delta x(y, \varepsilon)$$ \[84\]

where $\varepsilon$ is a parameter and the limit of $\Delta x$ vanishes as $\varepsilon$ approaches zero. If it is also true that

$$\lim_{\varepsilon \to 0} \Delta x(y, \varepsilon) = 0$$ \[85\]

where subscript $y$ denotes partial derivative, then $C_x$ is a weak variation of $e_x$. Otherwise, $C_x$ is a strong variation of $e_x$ (16).

Suppose that the integration constant $B$ (in equation [19]) for the extremal segment $e_D$ has the value $B_D$. Then the member of $\tilde{F}$ with $B = B_D + \varepsilon$ is a weak variation of $e_D$. The minimizer of the total energy over the set of all weak variations must be in $\tilde{F}$ (if it exists). If $E(e_D) \leq E(e_x)$ for any extremal $e_x$, then $e_D$ is the local minimizer of $E$ over all weak variations of $e_D$, and we say that $e_D$ is stable with respect to weak variation. If $e_D$ minimizes $E$ over the set of strong variations, we say that $e_D$ is stable with respect to strong variation. If $e_D$ is stable with respect to strong
variation, then it must be stable to weak variation, since weak variations are a subset of strong ones.

If the tangent of $e_D$ was in the cone $A'DB'$, then from previous theory $e_D$ would be stable with respect to strong variation. In the case of Figure 5.1, the tangent to $e_D$ is not in this cone. A weak variation of $e_D$ could not have a contact point with the ramp $AD$ and not penetrate $C_B$ for all $\varepsilon > 0$, since the first derivative at each point of the weak variation must approach the first derivative of $e_D$. For some $\varepsilon$ small enough, the weak variation will either not intersect the ramp $AD$ or will penetrate $C_B$. The curve $C_S$ in Figure 5.2 is intended to represent an example, for some $\varepsilon$, of a variation which intersects the solid at and only at the point $G$ of $AD$. $G$ depends on $\varepsilon$, and tends to $D$ as $\varepsilon \to 0$. It follows that this cannot be a weak variation of $e_D$, but must be in fact a strong variation.

Up to now we have not defined precisely over what type of neighborhood we have been minimizing $E$. The theory we have applied so far (from Bolza (16)) implies that the member of $F$ (if any) which satisfies the sufficient conditions [41] and [42] (in III.5 above) minimizes $E$ over the set of its strong variations for some value of $\varepsilon > 0$. Below,
we distinguish between minimization over the set of strong and/or the set of weak variations of an extremal.

For a variety of problems for which an extremal meets a solid boundary at a defect corner only, both

\[ \Theta_b \geq \mu \]  \hspace{1cm} \text{[86a]}

and

\[ \Theta_a \leq \mu \]  \hspace{1cm} \text{[86b]}

are necessary for minimization, according to an argument which dates back to Gibbs (5) (see Dyson (18)). The theory of chapter III (developed more fully in IV.3.1.4) can be used to derive these conditions. In cases such as Figure 5.1, where the angle \( \Theta_b \) is less than the angle \( B'D'B \) (which is \( 2\alpha \) in the figure), we can show that if \( e_D \) satisfies [86a], then it is weakly stable. In this case, [86a] implies [86b] (in fact, \( \Theta_a \) must be negative). Equation [86a] is derived by comparing \( e_D \) with members of \( \tilde{F} \) whose contact point with \( C_B \) can be written \( X(s_x), Y(s_x) \) where \( s_x \leq s_1 \). Thus either \( f_\leq 0 \), or \( f_\leq 0 \) and \( f'_\leq 0 \), is sufficient for weak stability. Equation [86b] is derived in a similar fashion when \( \Theta_a \) is greater than the angle \( A'D'B' \).
We assert that if an extremal segment which does not run into $C_B$ but meets it only at a defect point is stable to weak variation, then it is stable to strong variation. Figure 5.2 illustrates our proof. We compare $e_D$ which satisfies (86a) with a strong variation $C_S$. $C_S$ intersects $C_B$ at the point $G$ on ramp $AD$. We extend $C_B$ at $D$ along the curve $DH$. The curve $DH$ is a section of a transversal (recall IV.3.1.2 above) with $\mu=\pi/2$. $DH$ is an extension of the solid boundary curve $C_B$. The extremal $e_H$ makes contact with the solid boundary curve at $H$. Figure 5.2a shows the notation for the values of $s$ and $t$. The arclength $s$ increases from $s=0$ to $s=s_1$ from $B$ to $D$. From $B$ to $H$, $s$ increases from $s_1$ to $s=s_2$. From $H$ back to $D$, $s$ increases to $s=s_2$. Finally, from $D$ to $G$ $s$ increases to $s=s_3$. The parameter $t$ on $C_S$ increases from $-\infty$ to $t=t_1$ at $H$. It then increases to $t=t_2$ from $H$ to $G$. The curve $e_H$ is the extremal through the point $H$.

The projection $DH$ does not change the value of the functional $E$ for $e_D$, since the portion of $C_B$ from $s=0$ to $s=s_1$ is unaffected. The projection $DH$ contributes nothing to the $J$ and $K$ integrals of $E$ for $C_S$ (see equations (8d,e) in III.2). Along $DH$, $\cos\Theta_e=0$, and so $K$ from $s=s_1$ to $s=s_2$ equals zero. The integral $J$ from $D$ to $H$ is canceled out by
the integral \( J \) from \( H \) to \( D \). The integral \( I \) for \( C_S \) is unaffected by the extension, since \( I \) is taken along \( C_S \) itself and not \( C_B \). Thus the extension \( DH \) does not change the value of the \( E \) functional of \( C_S \).

Let \( \tilde{I} \) be equal to the integral \( I \) of \( C_S \), and similarly for \( \tilde{J} \). We can split \( \tilde{I} \) and \( \tilde{J} \) into two parts:

\[
\tilde{I} = I_{S,H} + I_{S,\text{HG}} \quad [87]
\]

\[
\tilde{J} = J_{S,H} + J_{S,\text{HG}} \quad [88]
\]

where \( I_{S,H} \) is over the interval \( (\infty, t_\tau) \), \( I_{S,\text{HG}} \) is over the interval \( (t_\tau, t_3) \), \( J_{S,H} \) is over the interval \( (0, s_\tau) \), and \( J_{S,\text{HG}} \) is over the interval \( (s_\tau, s_3) \). The sum of the integrals \( I \) and \( J \) for \( e_D \) and \( e_H \) are the same, since \( E \) is the same for both and \( K \) vanishes along \( C_B \) as mentioned above.

Let \( H \) be the sum of \( I \) and \( J \), thus

\[
H_{e_H} = H_{e_D} \quad [89]
\]

We note from the sufficiency theory in section III.4 that \( I_{e_H} \) must be less than or equal to \( I_{S,H} \). The \( J \) and \( K \) integrals are equal for \( e_H \) and for the segment of \( C_S \) up to the point \( H \) (same limits of \( s \) along same boundary curve). Thus

\[
I_{S,H} + J_{S,H} \leq H_{e_H} \quad [90]
\]
with equality requiring the curves to be coincident.

The difference in $E$ between $e_D$ and $C_S$ is

$$
\tilde{E} - E_{e_D} = I_{S,H} + I_{S,HG} + J_{S,H} + J_{S,HG} - H_e_D - K_{S,DG}
$$

and combining with [90] gives

$$
\tilde{E} - E_{e_D} \geq I_{S,HG} + J_{S,HG} - K_{S,DG}
$$

The first integral on the right hand side can be written as follows:

$$
I_{S,HG} = L_{S,HG} + M_{S,HG}
$$

where $L_{S,HG}$ is just the arclength of $C_S$ from $H$ to $G$, and

$$
M_{S,HG} = \int_{t=t_3}^{t=t_1} (\kappa_y^2 - 1) \times ds
$$

Adding $M_{S,HG}$ to $J_{S,HG}$ (which of course is taken over the boundary HDG), and multiplying the sum by $W_{1_H}$ corresponds to the work done raising the volume of liquid enclosed by a cylinder of width $W$ (the width being the dimension perpendicular to the plane of Figure 5.2) with cross section HDCH from zero elevation and displacing the same volume of vapor. Thus

$$
M_{S,HG} + J_{S,HG} \geq 0
$$
Combining [92] with [95] gives

$$\tilde{E} - E_{\tilde{e}_D} \geq L_{S,HG} - K_{S,DG}$$  \[96\]

Since $0 < \Theta < \pi$, we have

$$K_{S,DG} < L_{DG}$$  \[97\]

where $L_{DG}$ is the length of DG.

Suppose the angle HDG is greater than $\pi/2$, as it is in Figure 5.2. Then

$$L_{DG} < L_{S,HG}$$  \[98\]

and thus $\tilde{E} > E_{\tilde{e}_D}$ as we set out to prove. If HDG is less than $\pi/2$, then clearly points on AD near D are accessible to members of $\tilde{F}$ which do not penetrate the solid near D, and thus the stability is covered by previous theory. Cases for which the AD ramp is accessible, but the BD ramp is not, may be handled by a similar argument.

The extremal $e_D$ in Figure 5.2 can satisfy [86a] and [86b] (thus corresponding to a stable static equilibrium interface) and at the same time violate the non run in condition equation [64] in IV.3.1.4 above. If we start upward displacement of $C_B$ with the configuration of $C_{LY}$ equal to $e_D$.
in Figure 5.1, then $C_{LV}$ will run into another point on $C_B$ after some recession. We are forced to consider the stability of $C_{LV}$ with more than one contact point on $C_B$. In general, we cannot determine the stability of such a case using the methods above. However, a special case where we have derived useful results is discussed in the next section.

V.2 A SPECIAL CASE

From here onwards we restrict the values of $\mu$ and $\alpha$ to satisfy either of the following relationships:

$$\mu < \alpha$$  \hspace{2cm} \text{[99a]}$

or

$$\mu > (\pi - \alpha)$$  \hspace{2cm} \text{[99b]}

Equations [99] clearly allow for a run in. Consider upward displacement of $C_B$ where $e_D$ in Figure 5.1 is the initial configuration of $C_{LV}$. If [99a] holds, then $C_{LV}$ sticks to $D$ at and beyond the displacement where the tangent to $C_{LV}$ at $D$ is vertical. Figure 5.3 is a cross section through the plane $P_*$ of such a case. The wedge DOD$_l$ is one period of $C_B$. The broken line $L$ is vertical and runs through $D$ and $D_l$. $L$ intersects $C_{LV}$ at $D'$. We can construct a new solid boundary curve $C_B'$ with the wedge DOD' being one period. The
FIGURE 5.3
DROPLET FORMATION DURING UPWARD DISPLACEMENT
point O is halfway between D and D' in the y or v coordinate. \( C'_B \) is a sawtooth with vertically aligned vertices. \( C'_B \) has the property that \( C_{LV} \) runs into D' while sticking to D during upward displacement. This construction is always possible for upward displacement if [99a] holds. A similar construction is always possible for downward displacement if [99b] holds. Note that [99a] and [99b] cannot be true at the same time (because \( \alpha < \pi/2 \)).

Below, we consider the case of upward \( C'_B \) displacement (interface receding) in a system for which [99a] holds.

Figure 5.4 depicts the situation when the run into D' has just occurred. We divide \( C_{LV} \) into the semi-infinite part \( C_{LV,SI} \) with one contact point at D', and the finite part \( C_{LV,F} \), connecting D' and D. The contact angle of \( C_{LV,F} \) at D is \( \gamma_t \); at D' it is \( \gamma_b \). The angles \( \gamma_t \) and \( \gamma_b \) are clearly less than \( \alpha \). The contact angle of \( C_{LV,SI} \) at D' is \( (2\alpha - \gamma_b) \). This is greater than \( \alpha \), and from equation [99a] we know that \( C_{LV,SI} \) is stable to strong variation. Note that \( C_{LV,SI} \) is itself a member of \( \tilde{F} \). We assert that \( C_{LV,F} \) is stable to any weak variations, and to strong variations with the same contact points D and D' as \( C_{LV,F} \).
FIGURE 5.4
CONTACT ANGLES AT D AND D'
First we test $C_{LV,F}$ against strong variations which do not change the endpoints $D$ and $D'$. Figure 5.5a illustrates such a variation $C'_{LV,F}$. Suppose that $E(C'_{LV,F})$ is smaller than $E(C_{LV,F})$. Then the curve that is the union of $C'_{LV,F}$ and $C_{LV,SI}$ should have a smaller value of $E$ than the union of $C_{LV,F}$ and $C_{LV,SI}$. But this latter curve belongs to $F$, and thus by the previous theory minimizes $E$ over the class of curves which join $(-\infty,0)$ to the point $D$, but do not necessarily intersect $D'$. This class obviously includes as a subclass those which do include $D'$. Therefore we have a contradiction.

Next, we test $C_{LV,F}$ against a weak variation where the endpoint $D$ is not changed. The curve $D3$ in Figure 5.5b is such a variation. The curve $DD'$ is $C_{LV,F}$. (A test for stability to strong variation would allow the point 3 be on the ramp $D'0''$, for example). The theory in Bolza (16, pg.138-140, 143) gives conditions which together are sufficient for stability. All except one of the conditions have been shown to hold by previous arguments. The remaining condition requires that the difference in $E$ between $C'_{LV,F}$ and $C_{LV,F}$ be positive to first order. This difference can be written as

$$I_{3D} - I_{D'D} + (J_{3D} - J_{D'D}) - (K_{3D} - K_{D'D})$$

[100a]
where \( I, J, \) and \( K \) are the integrals in the equation for \( E \) (equations [8],[8a-e], III.2) along the paths \( 3D \) and \( D'D' \) (on \( C_{LV,F} \) for \( I, \) on \( C'_B \) for \( J \) and \( K \)). As before, (equations [4] and [5], III.1) we define \( C'_B \) by specifying \( X(s),Y(s) \) and \( C_{LV,F} \) by specifying \( x(t),y(t) \). The first subscript refers to the lower limit of integration, and the second subscript to the upper limit, in equation [100a] and below as well. We start by estimating to first order the quantity

\[
(I_{3D} - I_{D'D'}) - I_{3D'}
\]

[100b]

where \( I_{3D'} \) is the integral \( I \) taken along the path \( 3D' \) on the solid boundary \( C'_B \). Let \( s_D \), and \( s_3 \) be the arclength of \( C'_B \) at points \( D' \) and \( 3 \). Define \( \varepsilon = s_3 - s_{D'} \). Then from Bolza (16) [100b] can be estimated to first order as

\[
\varepsilon [X'(F_X(x,y,X',Y') - F'_X(x,y,\dot{x},\dot{y})) - Y'(F_Y(x,y,X',Y') - F'_Y(x,y,\dot{x},\dot{y}))]\big|_{D'}
\]

[101]

where \( \big|_{D'} \) means that the entire quantity in brackets is evaluated at the point \( D' \). The derivatives with respect to \( s \) are denoted by primes and with respect to \( t \) by dots. Evaluating [101], combining with [16] (in III.3), and using the identity
\[(X',^2+Y',^2)^{1/2} = 1\]  \[\text{[102]}\]

(s is an arclength), we find that \([101]\) is equal to

\[\varepsilon [1 - X' \cos \phi - Y' \sin \phi] |_{\Gamma} \]  \[\text{[103]}\]

Next, we note that from the definition of \([I_{3D}']\), it equals

\[
\int_{S_3}^{S_{D'}} \frac{(kY'^2 - 1)X'}{1+(kY'^2 - 1)} \, ds
\]  \[\text{[104]}\]

Also, the differences in the \(J\) and \(K\) integrals between the curve \(D3\) and the curve \(DD'\) can be combined into one integral each (see \([100a]\));

\[
J_{3D} - J_{D'D} = J_{3D'}
\]  \[\text{[105a]}\]

\[
K_{3D} - K_{D'D} = K_{3D'}
\]  \[\text{[105b]}\]

Combining \([104]\) with \([105a]\) results in

\[
I_{3D'} + J_{3D'} = -\varepsilon
\]  \[\text{[105c]}\]

We note that since \(s\) is an arclength,

\[
X' = \cos \Psi, Y' = \sin \Psi
\]  \[\text{[106]}\]

where \(\Psi\) is as before (see III.1 and Figure 3.1). Finally, we add on the integral \(K\) evaluated from \(s_D\) to \(s_3\), and combine with equation \([38]\) in III.5 (the definition of \(\Theta\) which in this case is equal to \(\gamma_\beta\)), \([106]\), \([105b-c]\), and \([103]\) to get a first order estimate of the difference in \(E\) between
$C_{LV,F}$ (the curve DD') and the curve D3:

$$E_{3D} - E_{D'D} = \varepsilon (\cos \mu - \cos \gamma_{D'}) \quad [107a]$$

If $\gamma_{D'} > \gamma_t$, the quantity in [107a] is positive. This is shown to be true in appendix B. Thus $C_{LV,F}$ is stable to a weak variation which changes one endpoint.

Last, we show that $C_{LV,F}$ is stable to weak variation of both endpoints. Figure 5.5c illustrates this proof. The curve 43 is a one point variation of D3 and a two endpoint variation of $C_{LV,F}$. We let 43 be a member of $\tilde{F}$; then 43 is a weak variation of $C_{LV,F}$. The arc 43 is stable to strong variation from the argument above. Thus the arc 34 minimizes the functional $E$ over the set of all arcs which contact $C_B$ at points 3 and 4 (and only those points). For both $C_{LV,F}$ and 43, the horizontal inclination is depends on $y$ alone. From equation [16], the value of $\phi_D$ is larger than the value $\phi_4$. Thus the contact angle of D4 at point 4, $\theta_4'$, is larger than $\gamma_t$. With the same arguments as above:

$$E_{3D} - E_{34} = \varepsilon (\cos \theta_4 - \cos \mu) \quad [107b]$$

where $\varepsilon = s_D - s_4$ and $\varepsilon > 0$. Thus [107b] is negative. Adding together [107a] and [107b], we see that $E_{34} - E_{D'D}$ is positive. Thus $C_{LV,F}$ is stable to weak variation.
If \( \text{[101b]} \) holds, then a similar argument demonstrates that an arc of \( \tilde{F} \) which connects two adjacent defect vertices is stable to weak variation. This result is pertinent when \( C_B' \) is displaced downwards (i.e. the interface advances).

V.3 CASE STUDY

In this section we assume that any trapped drops of liquid are stable. That is, configurations such as \( C_{LV,F} \) with both endpoints at defect vertices are subject only to variations to which they remain stable (discussed above).

Consider the case where

\[
\lambda = .08666... \tag{108}
\]

where \( \lambda \) is the dimensionless wavelength of \( C_B' \) (i.e. the separation between adjacent defect of overlap vertices in the \( v \) coordinate). The equilibrium contact angle \( \mu \) and the angle \( \alpha \) are specified so that equation \( \text{[101a]} \) is satisfied and \( \gamma_t \geq \mu \). This allows for a wide range of possible \( C_B' \), as shown in Figure 5.5, where \( \lambda \) is constant but \( \alpha \) changes.

Suppose we start upward displacement with the configuration of \( C_{LV} \) is \( e_D \) when the tangent to \( e_D \) in Figure 5.1 is vertical, as in Figure 5.7a. Thus \( \gamma_t \) is equal to \( \alpha \).
FIGURE 5.6
VARYING $\alpha$ WITH CONSTANT $\lambda$
Since $C_{LV}$ is tangent to the vertical broken line $L$, the apparent contact angle $\Theta_{app}$ of $C_{LV}$ is equal to zero degrees. As $C_B$ is displaced upwards, $L$ intersects $C_{LV}$ at a point $Q$ below $A$, shown in Figure 5.7b. $\Theta_{app}$ is the angle $C_{LV}$ makes with $L$ at $Q$. $\Theta_{app}$ increases to a value of

$$\Theta_{app}^{max} = (\pi/2) - \Phi_D$$

when $C_{LV}$ makes contact with $D'$ in Figure 5.7c. The angle $\Phi_D$ is the horizontal inclination of $C_{LV}$ at $D'$. In this case $\Theta_{app}^{max}$ equals 6.8916... degrees. It is clear from Figure 5.6 that $\Theta_{app}^{max}$ is independent of $\alpha$. The maximum apparent contact angle is only a function of the first derivative of $C_{LV}$ at $D'$. This in turn depends only on the choice of $\lambda$; once $\lambda$ is set, the maximum apparent contact angle is set. With further upward displacement of $C_B$, $C_{LV,SI}$ sticks to $D'$, $C_{LV,F}$ is trapped, and the apparent contact angle decreases to zero as shown in Figure 5.7a. The cycle repeats itself with further displacement. Figure 5.8 shows the behavior of the apparent contact angle over one cycle for the case discussed.

As $\lambda$ approaches zero, the maximum apparent contact angle approaches zero. The minimum apparent contact angle remains equal to zero. For downward displacement where
FIGURE 5.7a
SEQUENCE DURING DOWNWARD DISPLACEMENT OF

\[ C'_B: (a) \quad C_{LV} \text{ TANGENT TO D A VERTICAL LINE} \]
FIGURE 5.7b

$c_{lv}$ intersects $L$ at $Q$
\( \theta_{\text{app}} = (\pi/2 - \phi_{D'}) \)

**FIGURE 5.7c**

*CLV RUNS INTO D'.*
Figure 5.8 APPARENT CONTACT ANGLE VERSUS UPWARD SOLID DISPLACEMENT WITH $\lambda = 0.08666...$
[101b] holds, the maximum apparent contact angle is $180^\circ$, with the minimum apparent contact angle approaching $180^\circ$ as $\lambda \to 0$. Bubbles of vapor are trapped as downward displacement continues.

Now consider what happens when upward displacement of several wavelengths of $C_B$ is followed by downward displacement. Several drops of liquid are trapped, as shown by the solid curve in Figure 5.10 below (the broken curve is discussed below). The liquid/vapor interface has multiple contact lines. We let upward displacement end when $C_{LV}$ has just run into another defect vertex. The section through $P_*$ is shown in Figure 5.9. Starting downward displacement, the question arises as to whether $C_{LV,F}$ will detach from $D'$ immediately or whether the liquid remains trapped. Appendix C shows that the former is favored (i.e., the resulting value of $E$ is less in the former case immediately after downward displacement begins). As downward displacement continues, curve in Figure 5.8 describes the behavior in reverse of the apparent contact angle. Unlike the one contact line case, there is no contact angle hysteresis. A similar argument is true for initial downward displacement followed by upward displacement when [101b] holds, and trapped bubbles of vapor remain. It should be noted that the actual motion of the
liquid/vapor interface is not followed in reverse for this process. During upward displacement, $C_{LV}$ runs into $C_B$ in a smooth fashion. The detachment of $C_{LV}$ from a defect vertex such as $D'$ in Figure 5.9 during downward displacement is spontaneous, since it results in a lowering of the total energy. Thus the detachment is not reversible.

V.4 DISCUSSION

The arguments above suffer from the deficiency that a liquid/vapor interface between two defect vertices has not been shown to be stable to simultaneous variation occurring over several trapped drops. Stable equilibrium. However, an experiment done by Dyson (28) suggests that the trapped drops can be regarded as isolated from interaction while the liquid/vapor surfaces at a defect vertex have a corner with the same convexity as the defect vertex. We conjecture two reasons for this. First, the corners of the surface of a solid with small length scale roughness will be rounded to some extent. Thus the drops of liquid formed during upward displacement will be isolated from each other, rather than connected. Even a strong variation (for $\varepsilon \to 0$) will not be enough to dislodge an isolated liquid drop. Second, even if not isolated, it would take at least a weak variation of the multiple contact line liquid/vapor interface to cause
FIGURE 5.9
UNION OF $C_{LV,F}$ AND $C_{LV,SI}$ AT D AN EXTREMAL
instability. Such a weak variation is pictured as the broken curve in Figure 5.10. At the defect corners, a nonzero force which does not tend to zero with $\varepsilon$ would be required just to dislodge the interface a distance $\varepsilon$. If one considers the examples of weak variations considered previously, invariably the energy varies as $\varepsilon^2$. The force thus varies as $\varepsilon$, and tends to zero as $\varepsilon \rightarrow 0$. 
FIGURE 5.10
SOLID CURVE: MULTIPLE CONTACT LINE INTERFACE
BROKEN CURVE: A WEAK VARIATION OF THE MULTIPLE CONTACT LINE
CHAPTER VI
CONCLUSIONS AND EXTENSIONS

The model of quasi-static liquid-vapor interfaces presented above suggests:

1. Observed contact angle hysteresis may be hysteresis of the apparent contact angle. On the surface of a solid which appears smooth, but is rough on a microscopic scale, the real contact angle may not undergo hysteresis while the apparent contact angle does.

2. Hysteresis of the apparent contact angle occurs when the length scale of boundary surface roughness or heterogeneity is much smaller than the capillary length of the liquid-vapor pair.

3. Apparent contact angle hysteresis occurs via a series of irreversible contact line jumps.

4. Bubbles or drops trapped on the surface of the solid can suppress hysteresis effects.

We suggest the following extensions of this work:

1. A case study of an interface advancing or
receding along a random cylindrical boundary surface.

2. Attempting to apply the above methods to systems with a volume constraint (i.e. a small reservoir of liquid).

3. A study of the stability of cylindrical liquid-vapor interfaces to non-cylindrical variations (see (14)).
APPENDIX A

JUSTIFICATION OF CURVATURE COMPARISON FOR EVALUATING STABILITY

In IV.3.1.2 above, it was stated that the conditions [41] and [42] required that (1) $C_B$ and $\tilde{C}_B$ be tangent at the contact point $P$ and (2) that the curvature of the solid must be less than that of the transversal at $P$. Here these statements are justified.

We begin by writing $C_B$ and $\tilde{C}_B$ in parameterized form. Recall that $\tilde{C}_B$ is defined by the equations [53a,b] above, in terms of a dimensionless arclength $l$. $\tilde{C}_B$ here is restricted to the middle branch between the two asymptotes. (The argument for the other two branches is similar, although they were not used in practice.) $C_B$ can also be parameterized in terms of a dimensionless arclength which will be called $s$. The defining equations are

$$C_B: U(s), V(s); \quad s_L \leq s \leq s_U \quad [A1]$$

$$\tilde{C}_B: \tilde{U}(1), \tilde{V}(1); \quad -\infty < l < \infty \quad [A2]$$
\[ V_L, V^0, V_Y \]

where \( V_L \) and \( V_Y \) are the asymptotic limits of \( \tilde{C}_E \) e.g. 
\( V_L = -0.358 \ldots \), \( V_Y = 0.233 \ldots \) for \( \mu = \pi/4 \).

Since \( l \) and \( s \) are arclengths, the angles of inclination of these curves can be expressed as

\[ \sin \Phi = \frac{dV^0}{ds} \quad \cos \Phi = \frac{dV}{ds} \quad [A3a] \]

\[ \sin(\phi + \mu) = \frac{dV^0}{dl} \quad \cos(\phi + \mu) = \frac{dV}{dl} \quad [A3b] \]

Note that [A3b] is just a restatement of [E3a,b].

Condition [A1] means that \( \phi = \mu \). Recalling equation [E3] in III.E which defines \( \theta \), we note

\[ \Psi = \mu + \theta \quad [A4] \]

Taking the tangent of each side, it is clear that \( C_{E_1} \) and \( C_{E_2} \) are tangent to each other at the contact point \( F \). \( F \) can be solved for in principle by combining [A3a,b] and [A4] to solve for \( s_1 \) and \( l_1 \) such that

\[ F: \quad U(s_1) = U(l_1) \quad \text{and} \quad V(s_1) = V(l_1) \quad [A5] \]
Condition [42], when combined with [A4], yields

\[
\frac{d\psi}{ds} - \frac{d(\psi+\mu)}{ds} < 0 \quad ; s = s_1
\]

From the definition of \( \psi \) (in III.1) it is clear that the leftmost term of [A6] is the curvature of \( C_B \) at the point \( P \). The next term is not as obvious, since \( s \) is arclength along \( C_B \) and not \( \tilde{C}_B \). We need a result from functional analysis (20) that the function \( \tilde{V}(l) \) is invertible in the neighborhood of \( P \) if \( \tilde{dV}/dl \) does not equal zero at \( l_1 \). This condition is certainly satisfied, since we are on a branch of the transversal which is not a horizontal line. Thus we can write

\[
\frac{d(\psi+\mu)}{ds} = \frac{d(\psi+\mu)}{dl} \frac{dl}{ds}
\]

[A7]

where the first term on the right hand side is equal to the curvature of \( \tilde{C}_B \). Now

\[
\frac{dl}{ds} = \frac{dl}{d\tilde{V}} \frac{d\tilde{V}}{dV} \frac{dV}{ds}
\]

[A8]

The middle term on the right hand side is obviously equal to one. Combining [A3a,b] with [A8], we can evaluate \( dl/ds \) at the contact point \( P \):
\frac{dl}{ds} = \frac{\sin \psi}{\sin(\phi + \mu)} \quad [A9]

which [A4] tells us is equal to one! Thus the curvature of the solid must be less than the curvature of the transversal at P.
APPENDIX B

COMPLETION OF PROOF IN SECTION V.3

Figure B1 depicts a vertical line L going through a member of \( \tilde{F} \). L intersects \( e \) at points C and E. The tangents to \( e \) at C and E make acute angles \( \theta_C \) and \( \theta_E \) with L. We wish to show that

\[
\theta_C < \theta_E \tag{B1}\]

The curvature of \( e \) satisfies equation [13] in III.3. This is written in dimensionless variables (equation [18]) as

\[
C = 2\sqrt{2k} \tag{B2}\]

The equation for \( e \) itself is [19] in III.3, duplicated here;

\[
u = \sqrt{1-v^2 - 0.5 \text{ arcsech}(|v|)} + B \tag{B3}\]

The ordinate at A in Figure B1 is \( 1/\sqrt{2} \). The ordinate at 0 is 1. The part A0 of \( e \) may be represented by:

\[A0: q = \phi_1(p) \tag{B4}\]
where \( p \) and \( q \) are coordinates as shown in Figure B1. The origin of the \( pq \) axes is at \( A \), and \( p \) increases in the negative \( u \) direction. In [B4], \( q \) is a monotonically increasing function of \( p \). Combining [B2] and [B4], it is clear that

\[
C_1 = C(\phi_1(p)) \tag{B5}
\]

where \( C_1 \) is the curvature of \( AO \) and is a monotonically increasing function of \( p \).

The part of \( e \) from \( u=\infty \) to \( A \) is reflected about the line \( v=1/\sqrt{2} \) in Figure B2. The curve \( AO \) is also shown, in \( pq \) coordinates. The ordinate \( q \) can be expressed as a function of \( p \) just as for \( AO \) in [B4]:

\[
q = \phi_2(p) \tag{B6}
\]

and \( \phi_2 \) is a monotonically increasing function of \( p \). The curvature may be written as:

\[
C_2 = C(\phi_2(p)) \tag{B7}
\]

From [B2], the function \( C_2(q) \) monotonically decreases with \( q \), and thus [B7] monotonically decreases with \( p \). At \( p=0 \), the functions \( \phi_1 \) and \( \phi_2 \) are equal. Thus

\[
C_2(p) \leq C_1(p) ; 0 \leq p \leq P_0 \tag{B8}
\]
FIGURE B2
where $p_0$ is the value of $p$ at the point 0. Equality in \[B8\] holds only at $p=0$. From \[B8\], equation \[B9\] follows immediately:

$$\phi'_2(p) \geq \phi'_1(p); \quad 0 \leq p \leq p_0 \tag{B9}$$

where the prime denotes a derivative with respect to $p$. Equation \[B1\] follows in turn from \[B9\], which completes the proof.
APPENDIX C

PROOF OF CONTENTION IN V.3

In Figure Cl, $C_B'$ is the cross section of the solid boundary curve through the vertical plane $P_*$ as before. We assume that equation [101a] holds, and that during upward displacement of $C_B'$ an arc of the family $\tilde{F}$ is formed between two adjacent defect vertices D and D'. We begin downward displacement right when $C_{LV}$ runs into D' as shown in Figure 5.9 above. With downward displacement, we compare two possibilities; (1) The curve $C_{LV,F}$ detaches from D' and joins with $C_{LV,SI}$ to from an extremal, and (2) The curve $C_{LV,F}$ remains attached to both defect vertices.

The curve $e_D$ is the extremal segment which ends at D and $e_D'$, at D'. $C_{LV,F}$ is the arc formed from previous upward displacement of $C_B'$. The curve $e_D$ corresponds to possibility (1) above, and the union of the curves $C_{LV,F}$ and $e_D'$, written as $(e_D, UC_{LV,F})$, corresponds to possibility (2) above.
Since $e_D$ and $(e_D, UC_{LV,F})$ both have the same endpoint $D$, we can use the fixed endpoint theory developed in III.3 above to compare their values of the $E$ functional. We need only compare the $I$ integrals, since the endpoint is fixed. We assign $e_D$ to $e$ (extremal) and $(e_D, UC_{LV,F})$ to $C$ (comparison curve) in equation (30). The result is that the integral $I$ of $e_D$ is less than the integral of $(e_D, UC_{LV,F})$ if they do not coincide.

The fixed endpoint theory will not apply to a comparison curve such as shown in Figure C2. The comparison curve is the union of $C_{LV,F}$, the part of $C_B$ between $D'$ and $P$, and the extremal segment $e_P$. However, the contact angle $\theta_P$ of $e_P$ is clearly greater than the angle $2\alpha - \gamma_b$ in Figure 5.4, which in turn is greater than $\mu$. Thus $e_P$ is unstable, and cannot form as a result of downward displacement. We conclude that the extremal $e_D$ will be formed during downward displacement (possibility (1)).
FIGURE C2
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