

# Hole Closure in Langmuir Fluid Monolayers

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May, 2007

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# Abstract

Amphipathic molecules are basically long chains, one end of which likes water (is hydrophilic) and the other end abhors it (is hydrophobic). These molecules tend to sit vertically in a fluid and adhere to each other. This attraction of adjacent molecules causes the molecules to condense into regions, referred to as polymer Langmuir layer domains, which are a single molecule thick and behave like a two-dimensional fluid. This attraction also manifests itself as a *line tension*, analogous to surface tension in a fluid droplet, which causes the regions to become circular as they attempt to minimize the length of their perimeter.

Often the layer will form holes, gaps in the liquid monolayer which contain a much smaller density of molecules. In the presence of humidity, the holes are observed to close up, pulled together by the line tension as well as condensation of the hole molecules at the boundary. Previous researchers have computed the fluid velocity for the process when the hole is assumed to be a vacuum. I, however, propose to replace this model with a gas, adding condensation of gas from the hole into the liquid domain of the monolayer to the line tension force. The hope is to obtain a mathematical model that better corresponds to the physical problem than current models do.



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# Chapter 1

## Introduction to Langmuir Layers

### 1.1 Formation

Langmuir layers form when an *amphipathic* molecule is introduced into an aqueous environment. Amphipathic molecules are characterized by their dual structure: one end is polar, and thus hydrophilic, and the other will be non-polar, hydrophobic. Adding these molecules to an aqueous fluid will result in one end pushing towards the surface (to get out of the water), and the other trying to “stick” to the water. The balance is struck at the surface of the fluid, where the hydrophobic end interfaces with the surface, while the non-polar hydrophilic end keeps pointed outward. The overall effect of having many of these molecules spread over the surface is to have a thin (one monomer in thickness) film layer over the surface of the fluid [3].

Examples of Langmuir layers include soap and water, and fatty layers which form on top of soups and stews. Similar molecular interactions can also be seen in cells, where the cell membrane is formed by a double-thick layer of amphipathic molecules: the hydrophobic ends point inward, while the hydrophilic “heads” point out, interacting with either the cytoplasm or the extracellular space, forming a malleable, yet watertight seal around the cell [3].

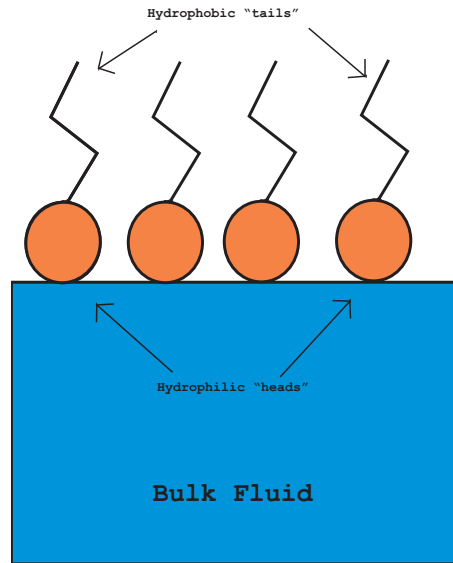


Fig 1: Amphipathic molecules sitting atop a bulk fluid. The brown "heads" represent the polar end, interfacing with the surface, and the kinky "tails" represent the non-polar end, repelled from the water at the surface

### 1.2 Phases

Due to their structure, if there are less than enough molecules to fully cover the surface of the fluid (as is often the case), then the layer will stay one monomer thick, as the molecules' structure keeps them from orienting on top of each other, and will generally stay confined to the surface of the fluid. Because of this, the layers themselves can be approximated as two-dimensional. Despite their dimensionality, they can still exhibit phases similar to those exhibited by three-dimensional media. Phases are generally classified by dividing the area by the total number of molecules on the surface, to obtain a measure of how closely packed together the molecules are. These phases can be classified similarly to those in a standard media: as gas, solid, or liquid.

The gas phase occurs when the area per molecule of the monolayer is fairly high, so the molecules rarely interact. Though they are "stuck" to the bulk fluid, they are still capable of moving freely along the surface, diffusing around in a way similar to a gas. The liquid (sometimes referred to as *expanded*) phase is more tightly-packed, with more interactions between individual molecules, but there is still room for the molecules to slide around

and past each other (much like a three-dimensional liquid). In the solid (*condensed*) phase, the molecules are much closer together, and do not move individually. Fig. 2 shows the types of configurations which occur in the three phases:

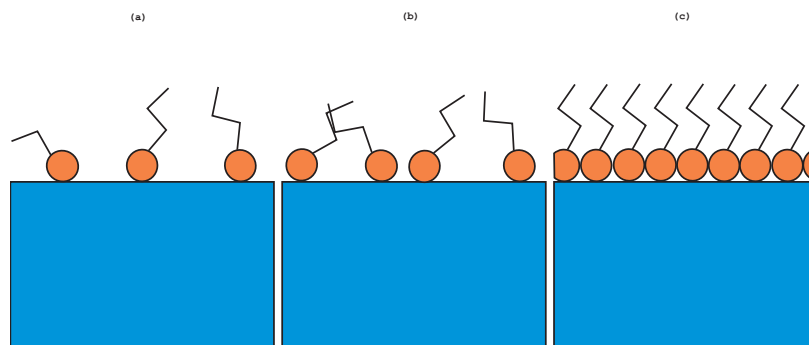


Fig. 2: (a) The gas phase, little interaction between molecules. (b) The liquid phase, some interaction, still room to move. (c) Solid phase, little room to move, tightly packed molecules.

Due to the complicated nature of monolayers, the condensed (solid) phases of the monolayers are not as cut and dry as they may sound. Much like the crystalline structures exhibited by many three-dimensional solids, different substances will exhibit different two-dimensional structures when formed into a monolayer. As in their three-dimensional counterparts, the different structural orientations correspond to difference in physical properties, such as viscosity, compressibility, molecule orientation, etc. The phases occur similarly to how they do in standard substances, i.e. a phase diagram can be drawn to show when the monolayer will be in a given phase, including the various condensed phases which may arise. The difference is that instead of having pressure and temperature axes, the pressure axis is replaced by *surface pressure*, in units of concentration per unit length, which is calculated as the difference between the surface pressure of the bulk liquid and the new surface pressure with the monolayer present [3]. Fig 3 shows two types of condensed phases which are formed by two different substances at the same temperature (22° C):

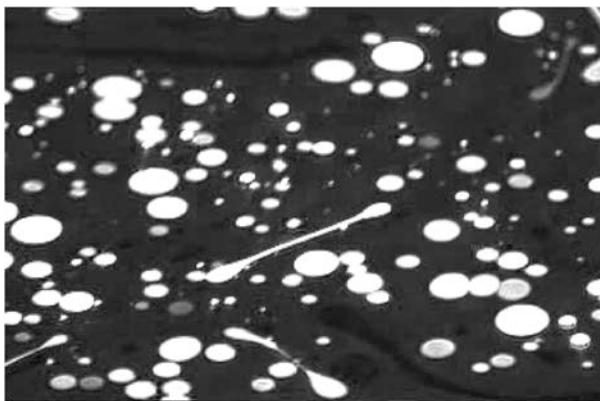


Fig. 3: Different condensed phases formed by octylcyanobiphenyl, Brewster Angle Microscopy photos (by Lu Zou) from Prof. Elizabeth Mann's laboratory at Kent State University.

### 1.3 Holes

Figure 3 demonstrates an interesting phenomenon: formation of domains of differing phase. Surely if there are different phases which can occur in any given monolayer, then it would make sense that certain areas may be able to exhibit one phase, while another area an altogether different phase. Certain polymers, when unable to completely condense over the entire surface, are more inclined to concentrate into several domains, rather than one big semi-condensed or possibly liquid phase (this is primarily due to *line tension*, which will be discussed in more detail later. Additionally, one could imagine a monolayer in an almost completely expanded (liquid) phase, yet small, gaseous "holes" form in various parts, creating a "Swiss cheese" effect in the monolayer. The holes would not be vacuums, of course, just like air bubbles in liquids still contain gas, but would be domains in which the monolayer is gaseous, rather than liquid.

Now that the holes have been established, what forces are at work inside them? What is keeping them open, driving them to expand or contract? The forces inside are going to be similar to those that would be expected in any gas. The first would be condensation. The "gas" molecules are very similar to gas molecules in a three-dimensional environment, and generally diffuse randomly throughout their domain. However, if a liquid boundary is surrounding the gaseous domain, the gas molecules would "condense" onto the liquid boundary in a fairly random way, much like a

3-D gas may. Similarly to this is the liquid on the boundary's ability to vaporize. Any liquid has associated with it a certain vapor pressure, and confining it to two dimensions does little to change this fact. It stands to reason that the liquid layer would then experience some amount of vaporization, either on a large or small scale. In addition to these is the pressure of the gas inside pushing outward on the boundary of the hole. If one were to blow a bubble, simply out of air and any kid's bubble solution, they could then push (lightly) on it, and feel resistance pushing back. This is due (in part) to the pressure of the gas inside the bubble. The same is true for the hole (simply a 2-D bubble), the pressure of the gas inside would be pushing outward on the boundary. The final force is the most complicated, yet turns out to be the most important, of the four. Going back to three-dimensions, imagine a water droplet sitting on a table. The reason the droplet maintains its shape and doesn't just break up into a bunch of little molecules covering (as best they can) area of the table is because of the surface tension of the water. Like most things in 3-D materials, surface tension (energy per unit area) has an analogue in 2-D as well: line tension. Line tension is the force exerted on the interface between the gas and liquid phases of monolayers, and is energy per unit length, instead of area. Much like surface tension, which is the primary cause for water and other liquids forming droplets to try and minimize surface area and thus energy, it generally drives the 2-D domains into more energetically favorable states, hence the domains that formed in Figure 3. Below is a figure demonstrating the four forces mentioned, and how they would affect a circular hole in a monolayer:

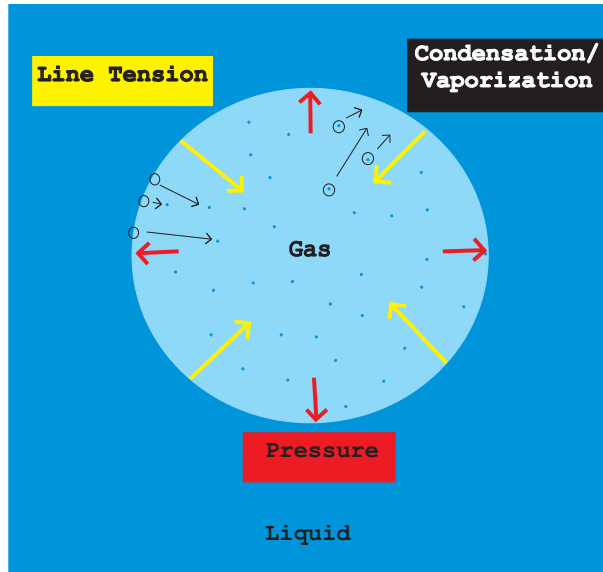


Fig 4: A circular “bubble” inside a monolayer, with the four primary forces driving its shape: condensation, evaporation, vapor pressure, and line tension

What ends up happening actually depends on whether or not the hole is in the presence of ambient humidity. “Ambient” referring to the air or gas above the monolayer and fluid. If the air above is “dry,” free of humidity, then stable holes will actually form and stay open in the monolayer. But in the presence of humidity, the holes close. This is due mainly to evaporation. If the air is dry, then water from underneath the layer will evaporate from the exposed surface in the hole domain. The loss of molecules at the surface of the fluid causes water to come from deeper in the fluid to replace it, essentially creating a velocity field of fluid being advected up towards the hole. This, in turn, cancels the velocity field created by the line tension closing the hole, and the hole will stabilize. If the air is humid, however, evaporation does not occur (or is severely diminished), and the hole will close as normally [1].

The problem at hand naturally arises from the fact that the holes close: how quickly do they close? Is it a slow crawl to equilibrium, or is it rapid? Do the hole close in finite, or infinite time? That is exactly the problem being studied, how to model the gas inside the hole, and the liquid outside, to accurately reflect the physical forces at work inside the hole, and attempt to model its closure.

## 1.4 Previous Model and Work

Previous work was done by Bernoff, Mann, et al. It was done under several different assumptions, and given actual experimental treatment. The model was put together assuming, first, that the hole was not a gas, but instead a vacuum. This implies that there is no condensation/vaporization, nor is there any vapor pressure from the gas inside. The only force which drives the closure of the hole is the line tension. In addition, the underlying bulk fluid was modelled under Stokesian assumptions. As the line tension drives the closure of the hole, the monolayer, still bound to the surface of the fluid, “drags” the fluid along with it, which in turn induces a velocity field. The model has been used to determine how the area of the hole changes over time, a relationship determined to be linear. The model was used to predict hole area versus time under experimental conditions, and plotted against real data:

## 8 Introduction to Langmuir Layers

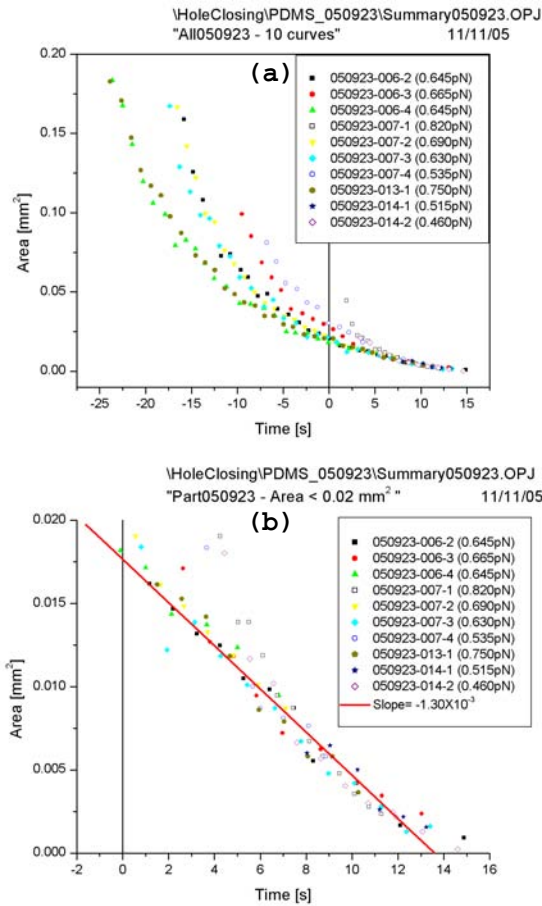


Fig 5: (a) Plot over all time of area of hole versus time (b) Magnification of (a) from  $t = 0$ , with model prediction as the red line. Figures by Elizabeth Mann and Lu Zou from Kent State University, reproduced with permission.

Experimentally the model works well as the area of the hole gets closer to 0; that is it works well for small holes. The primary reason behind this being that as the hole gets smaller, the line tension becomes the dominant force (the same occurs in surface tension of small droplets). Because of this, the holes not only become circular (the strong line tension “drives” the hole to a lower energy state), but also follow the vacuum model more closely, as the other forces take a back seat to the line tension. However when the holes were larger, the rates of closure were observed to be sublinear (notice in Figure 5a, the curve dips downward as time decreases). It was clear

that the vacuum assumption was not capturing enough of the physics, and the problem needed to be remodelled under more physically accurate assumptions. The current problem at hand is to formulate a more complete model of the hole, and attempt to solve the model for the hole behavior, and see if it better fits the data obtained in experiments.



## Chapter 2

# Method of Attack

### 2.1 Advection-Diffusion Equations

Clearly the first question to answer is: how does one model the gas inside the hole? To answer this question, one must first answer this: what is going on, physically, in the hole? First, the velocity field of the underlying fluid is known. When this problem was initially noted and studied, the rather difficult task of deciphering what happens to the bulk fluid as the hole closes was computed. Because the molecules, though free to move, are still bound to the fluid, they are still governed by its velocity field, which makes up a considerable amount of their movement. But, as mentioned, the molecules are still free to move, and, like any gas, will diffuse throughout the hole, as any three-dimensional gas would. These two movements, put together, lead naturally to Advection-Diffusion equations.

The Advection-Diffusion equation comes up quite often in fluid mechanics, and is often used to model the behavior of fluids or gases which not only move due to some underlying velocity field, but are also going to freely diffuse throughout whatever space they are confined to. If studying the concentration of a gas in a bubble (as will be done in this problem), denote it  $C$ , and the Advection-Diffusion equation would be the following:

$$C_t + \nabla \cdot [VC] = D\Delta C, \quad (2.1)$$

where  $V$  is the associated velocity field of the gas [4].

## 2.2 Applying Advection-Diffusion to Hole Closure

To solve this particular problem, we knew we could not simply start from the problem (as it was yet to be defined) and try to do a search for the solution, but instead had to start with smaller, simpler problems, and work our way up towards what we eventually hoped would be the actual problem, clearly defined. To do so, we started with some simplifying assumptions (some to be put back later, others done to conform to the actual physical situation we are dealing with), then attempted to solve the problem for certain velocity fields. The major assumptions were as follows:

- Confine the problem to one dimension, denoted  $z$ . This meant that a “hole” was simply a domain in  $z$  ( $z \in [0, 1]$ , for example), which was governed by equation (2.1), and everything outside the domain could be assumed to be liquid, with constant concentration (typically denoted  $C_\infty$ ).
- Set  $V(z)$ . Because the problem was physically motivated, and the underlying fluid velocity field was already studied, we could know what  $V$  would look like. In general we set it have a  $\sqrt{z}$  singularity at the boundary (typically denoted  $z^*$ ), because the real velocity field has similar behavior at the boundary.
- Set  $D = 0$ . Eliminating diffusion stemmed from the fact that the “gas” molecules in the monolayer are bound to the bulk fluid underneath. Because the interaction is so strong, the molecules cannot diffuse around as freely as a three-dimensional gas. And in the presence of the bulk velocity field, the contribution to the movement of the gas from the velocity field is much greater than that from diffusion, making this a valid assumption.
- Assume  $C(z, 0) = C_0$ , where  $C_0$  is some constant. When the hole is initially opened, we just assumed that the gas was more or less evenly distributed throughout the hole, so the initial concentration would be constant.

Given these assumptions, the partial differential equation becomes much simpler:

$$C_t + [VC]_z = 0 \tag{2.2}$$

$$C(z, 0) = C_0 \quad (2.3)$$

To fully capture the physical behavior, we attempted to solve this problem over several different domains with several different velocity fields.

## 2.3 Example Calculations

To illustrate the point of how the calculations were done, using several velocity fields, an example with a typical velocity field is computed below. In the case below, the “hole” or gaseous domain was designated as  $z \in (-\infty, 1)$ , with a velocity field defined in the gas domain, and the evolution of concentration based on (2.2) in that domain. The example uses the method of characteristics, as outlined by Bleecker and Csordas [2], where curves of constant concentration are found, and a change of variables is used to derive a PDE in one variable, instead of two.

### 2.3.1 A Sample Calculation

Based on the work from [1], we know what form the velocity field  $V(z)$  should have, most importantly a square-root singularity at the origin  $z = 0$ . With that in mind, we defined

$$V(z) = \sqrt{1 - z}, \quad (2.4)$$

which meets that requirement. Substituting the above velocity field(2.4) into (2.2) yields the following:

$$C_t + (\sqrt{1 - z})C_z = \left(\frac{1}{2\sqrt{1 - z}}\right)C, \quad (2.5)$$

$$C(z, 0) = C_0. \quad (2.6)$$

To find curves where  $C$  is constant,  $\frac{dC}{dt} = C_t + \frac{dz}{dt}C_z = 0$  must be true. Clearly from the differential equation,  $\frac{dz}{dt} = \sqrt{1 - z}$ . This is a seperable, first order ordinary differential equation, which yields:

$$-2\sqrt{1 - z} + \xi = t,$$

where  $\xi$  is the integration constant gained from solving the general ODE. Solving for  $\xi$  yields the following:

$$\xi(z, t) = t + 2\sqrt{1 - z}, \quad (2.7)$$

which indicates a change of variables. Set  $\tau = t$  to get a system in  $\tau$  and  $\xi$ . Note that

$$\begin{aligned}\xi_t &= 1, & \tau_t &= 1, \\ \xi_z &= -\frac{1}{\sqrt{1-z}}, & \tau_z &= 0.\end{aligned}$$

Using these derivatives, and the chain rule, calculate  $C_t$  and  $C_z$  in terms of  $C_\tau$  and  $C_\xi$ :

$$\begin{aligned}C_t &= \frac{\partial C}{\partial \tau} \frac{\partial \tau}{\partial t} + \frac{\partial C}{\partial \xi} \frac{\partial \xi}{\partial t} = C_\tau + C_\xi, \\ C_z &= \frac{\partial C}{\partial \tau} \frac{\partial \tau}{\partial z} + \frac{\partial C}{\partial \xi} \frac{\partial \xi}{\partial z} = -\frac{1}{\sqrt{1-z}} C_\xi,\end{aligned}$$

which I can then substitute into the original differential equation, (2.5):

$$\begin{aligned}C_t + (\sqrt{1-z})C_z &= C_\tau + C_\xi + (\sqrt{1-z})\left(-\frac{1}{\sqrt{1-z}}\right)C_\xi, \\ &= C_\tau + C_\xi - C_\xi = C_\tau = \frac{1}{2\sqrt{1-z}}C.\end{aligned}$$

The partial differential equation in  $z$  and  $t$  has become an ordinary differential equation in  $\tau$ . Solving (2.7) for  $z$ , and substituting it into this last equation (note  $t = \tau$ ) yields

$$C_\tau = \frac{1}{\xi - \tau}C.$$

Solving gives an expression for  $C(\xi, \tau)$ ,

$$C(\xi, \tau) = A(\xi) \frac{1}{\xi - \tau}, \tag{2.8}$$

where  $A$  is some general function of  $\xi$ . Using (2.7) we find:

$$C(z, t) = A(t + 2\sqrt{1-z}) \frac{1}{2\sqrt{1-z}}. \tag{2.9}$$

To solve for the exact solution, apply the initial condition, (2.6) to obtain the following:

$$C(z, 0) = A(2\sqrt{1-z}) \frac{1}{2\sqrt{1-z}} = C_0.$$

And if we define  $w = 2\sqrt{1-z}$ ;

$$A(w)\frac{1}{w} = C_0 \rightarrow A(w) = C_0 w$$

So the final, exact solution of the PDE is:

$$\begin{aligned} C(z, t) &= (t + 2\sqrt{1-z})C_0 \frac{1}{2\sqrt{1-z}} \\ &= \left[ \frac{t}{2\sqrt{1-z}} + 1 \right] C_0. \end{aligned} \quad (2.10)$$

To get a sense of what this looks like, below are graphs of the characteristics on the  $z-t$  plane, and a three-dimensional graph of the  $C(z, t)$  as well:

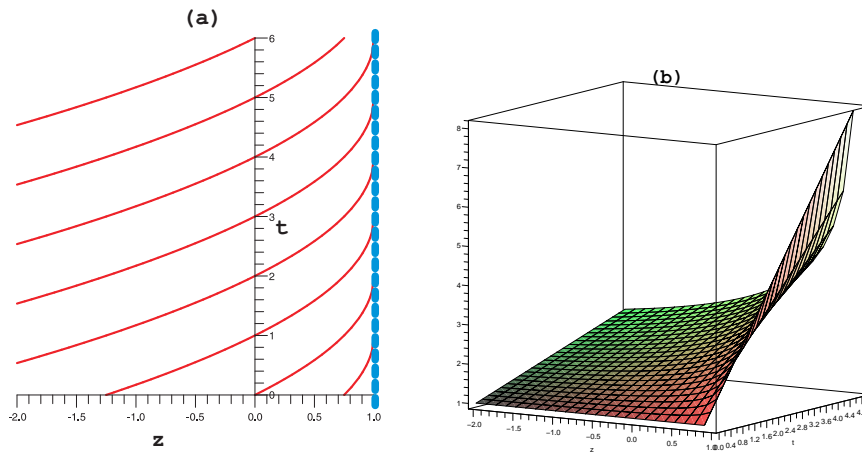


Fig 6: (a) The characteristics of equation (2.5) on the  $z-t$  plane. (b) A plot of the concentration versus time and space, with  $C_0 = 1$ .

Notice that in Figure 6a the characteristics hit the boundary at  $z = 1$  in finite time. This implies that the concentration will build up at the boundary, hence the singularity in Figure 6b at the boundary. Because the molecules are being advected to the right, the concentration will increase at the boundary over time. But the velocity at the boundary is 0, so the molecules have to stop once they hit the boundary, which leads to the buildup.

The problem we are attempting to solve, however, is not how the concentration changes over time, but how the boundary is moving in. In this case, a moving boundary was not explicitly built into the model, but it is still possible to determine how rapidly the boundary is "moving in." First, assume that the liquid phase outside of the hole has a constant concentration. Because the liquid is not as prone to diffusion as a gas, this is a perfectly fair assumption. Now, concentration is in units of moles/volume, but since this polymer is a single substance, this can easily be converted to mass/volume (much like density) with a constant multiplication. Thus if the concentration is known, one could figure out the rate that the outside domain is gaining volume, or growing (which is equivalent to the rate at which the hole is "shrinking," or closing), simply by knowing the rate at which mass is leaving the hole. Thus the idea of measuring the mass-flux of the gas at the boundary enters the picture. Mass flux (denoted  $\mathcal{F}$ ), can be expressed, quite simply, as

$$\mathcal{F}(z, t) = V(z)C(z, t). \quad (2.11)$$

The equation appears, initially, to be somewhat unwieldy, despite its simplicity. The goal is to measure  $\mathcal{F}$  at the boundary, but  $\mathcal{F}$  is the product of, in this case, two functions which have singularities at the boundary. Clearly there would be something inherently non-physical about calculating a mass-flux at the boundary that is singular. However, this problem is, in fact, physically motivated, albeit with some assumptions made, and the velocity field was chosen knowing that the real velocity field of these holes at the boundary has a singularity. It makes sense, then, that the flux should not, in fact, be singular at the boundary, if the problem is in fact modelled correctly under valid physical assumptions. Though we do not yet have an analytic proof of whether or not this is true in general, it can be shown to be true for this particular velocity field. Using equation (2.10) and the equation for  $V(z)$ , and substituting those into (2.11) yields:

$$\mathcal{F}(z, t) = \sqrt{1-z} \left( t + 2\sqrt{1-z} \right) C_0 \frac{1}{2\sqrt{1-z}} = \left( t + 2\sqrt{1-z} \right) C_0.$$

To find the mass-flux at the boundary, simply set  $z = 1$ :

$$\mathcal{F}(1, t) = C_0 t$$

Which is clearly not singular. The flux is, in fact, linear with time, so as time increases the amount mass leaving the hole would be increasing at a rate proportional to the initial concentration in the hole when it was first opened.

## 2.4 Flux and Conservation

After having solved the 1-D problem over a variety of different domains and velocity fields, it became apparent that, though the functions would change, the calculations were remarkably similar. The one thing we were always interested in was the mass flux,  $CV$ , and what it looked like on the boundary of the hole domain. To see how much similarity there really was, we went through a general formulation of the type of problem we had been working with, and discovered an interesting conservation law. To see how it comes about, consider the advection-diffusion equation we were working with, equation (2.2). Then consider the equation for the material derivative  $\frac{DC}{Dt}$ , i.e. the change in concentration along a particle path, which by definition is the same curve as  $\xi(z, t)$ , the characteristics:

$$\frac{DC}{Dt} = C_t + \mathbf{V} \cdot \nabla C \quad (2.12)$$

or, in the case of one-dimension:

$$\frac{DC}{Dt} = C_t + VC_z. \quad (2.13)$$

This is remarkably close to equation (2.2), except for the factor of  $-CV_z$ , so we have:

$$\begin{aligned} \frac{DC}{Dt} &= C_t + VC_z = -CV_z, \\ \frac{1}{C} \frac{DC}{Dt} &= -V_z, \\ \frac{D}{Dt}(\ln(C)) &= -V_z. \end{aligned}$$

We can integrate both sides in time, from  $t_0$  to  $t$ :

$$\int_{t_0}^t \frac{D}{Dt}(\ln(C)) dt = \int_{t_0}^t -V_z dt$$

then make a substitution to put the integral in terms of  $z$ . Since this is along a particle path, then the limits change from  $t_0$  to  $z(t_0) = z_0$ , and from  $t$  to  $z(t) = z$ :

$$= - \int_{z_0}^z V_z \frac{dz}{dt} = - \int_{z_0}^z \frac{V_z}{V} dz$$

because  $\frac{dz}{dt}$  is  $V$ , by definition

$$= - \int_{z_0}^z \frac{\partial}{\partial z}(\ln V) dz = - \ln(V)|_{z_0}^z = \ln \left( \frac{V(z_0)}{V(z)} \right)$$

but this was derived from  $\int_{t_0}^t \frac{D}{Dt}(\ln(C)) dt$ , so I can write:

$$\ln\left(\frac{V(z_0)}{V(z)}\right) = \int_{t_0}^t \frac{D}{Dt}(\ln(C)) dt = \ln(C)|_{t_0}^t = \ln\left(\frac{C}{C_0}\right)$$

all along a particle path. Exponentiating both sides and rewriting yields:

$$CV = C_0V_0. \quad (2.14)$$

Which is a powerful conservation law regarding mass-flux. What it says is that along a particle path (characteristic), the mass flux at the initial point and time of the path is the same at some arbitrary point and time later. This is useful because it meant we did not have to calculate the flux at the boundary, we just had to know the initial flux at the beginning of the path. Since (2.14) was so important, and several assumptions were made on the way to its discovery, an alternate formulation was derived to decide under what conditions mass-flux was conserved. Since it seemed to hold along particle paths, it seemed natural to look again at the material derivative. Instead of looking at  $\frac{DC}{Dt}$ , as before, consider instead  $\frac{D(CV)}{Dt}$ , the change in mass-flux along a particle path. If it truly is conserved, this quantity should be 0,

$$\begin{aligned} \frac{D(CV)}{Dt} &= \frac{\partial}{\partial t}(CV) + V \frac{\partial}{\partial z}(CV), \\ &= C_t V + CV_t + V^2 C_z + V V_z C, \\ &= V(C_t + V C_z + V_z C) + CV_t, \\ &= V\left(C_t \frac{\partial}{\partial z}(CV)\right) + CV_t. \end{aligned}$$

Notice the quantity in the parenthesis is the original differential equation, (2.2), so it must be 0:

$$CV_t = \frac{D(CV)}{Dt}. \quad (2.15)$$

So along a particle path mass flux is only conserved when  $C = 0$ , clearly, or when  $V_t = 0$ , the velocity field is constant in time. This explains why it was true in the problems we were doing, as the velocity depended only on space. This assumption also showed up implicitly during the first derivation of (2.14), as we used the fact that  $V$  was a function of only  $z$  during the calculations. Not only had we discovered a useful conservation law, but we had determined exactly when it would hold true.

Unfortunately, this clearly creates a problem if the velocity field should depend on time. The issue presents itself, in this problem, when considering the moving boundary. If mass is being advected out of the boundary, and into the liquid domain, then clearly the domain would be moving inwards with time. The velocity field, while dependent on  $z$ , is also only valid inside the gas domain, therefore if the spatial dimension of the gas domain changes in time, the velocity will also change with time. This indicates that, in a realistic interpretation of the problem,  $V_i$  would not be 0, it would change over time, and although (2.15) is still a useful way to calculate mass-flux, the quantity is no longer conserved along particle paths. Thus a reformulation of the problem was necessary, in order to incorporate the inward moving boundary,  $z = R(t)$ .



## Chapter 3

# Incorporating a Moving Boundary

While the identity from equation (2.14) was somewhat exciting, its value dropped significantly when the real problem at hand was contemplated. Even if the velocity field does not explicitly depend on time, if the boundary is coming inwards, then the domain over which the velocity is valid is also changing over time, thus  $V$  will depend implicitly on time. To fully formulate the problem, we had to consider that mass-flux out of the boundary would cause the boundary to change with time, namely to move inward. In addition, we knew that at the boundary, mass moving out the hole does not just “move out,” per se, but condenses on the boundary as liquid. This adds an additional term to the model which must be incorporated and/or dealt with to fully capture the dynamics.

### 3.1 1-Dimensional Case

Consider a 1-dimensional “hole”, as before, starting with some initial concentration  $C(z, 0) = C_0$  and initial radius  $R(0) = R_0$ . It would still be governed by the Advection-Diffusion equation, but no longer on some static interval in  $z$ , the interval would be shrinking. Without loss of generality, (since we could apply a linear change of variables to center the hole anywhere we want), we chose the interval  $z \in (0, R(t))$ . So the first equation governing the behavior is simply

$$C_t + [VC]_z = 0, \quad 0 < z < R(t). \quad (3.1)$$

Where  $V = V(z, R(t)) = V(\frac{z}{R})$ , since  $V$  still only really depends explicitly on the domain, but contracts as  $R$  contracts, making it implicitly dependent on time. Basically  $V = V(\frac{z}{R})$  because  $V$  is constant in time in a reference frame that is moving with  $R$ . Further, because the actual nature of  $V$  in the real problem is known, we can say the following about  $V$ :

$$V(\alpha) (1 - \alpha)^{\frac{1}{2}}, \quad (3.2)$$

as  $\alpha$  increases to 1, meaning that  $V$  has to have a square-root singularity at the boundary (as  $z \rightarrow R$ ). However,  $C$  is no longer the primary function of interest in the problem anymore, as the entire motivation for modelling  $C$  was to get at the boundary,  $R(t)$ , via the mass-flux  $CV$ . Since the method of solving is known (characteristics), we can instead write

$$\frac{dz}{dt} = V \left( \frac{z}{R(t)} \right), \quad (3.3)$$

$$z(0) = z_0, \quad (3.4)$$

which is an ordinary differential equation defining the set of curves which concentration travels on (the particle paths in the gas).

To describe the motion of the boundary,  $R(t)$ , we still use flux. Knowing that the flux out of the boundary is proportional to the growth of the boundary, we have

$$\frac{dR}{dt} C_\infty = -\mathcal{F}|_{z=R}$$

where  $C_\infty$  is the constant concentration of the liquid outside the hole. Substituting  $\mathcal{F} = CV$ , and rearranging yields the following ODE for the motion of  $R(t)$ :

$$\frac{dR}{dt} = -\frac{CV|_{z=R}}{C_\infty}, \quad (3.5)$$

$$R(0) = R_0, \quad (3.6)$$

which is an ordinary differential equation defining one curve, the motion of  $R(t)$ , namely the way the hole closes, which is the entire motivation behind the problem in the first place. These two coupled differential equations with two initial conditions gives a complete model of the one-dimensional problem under the physical assumptions made, and the solution should, hopefully, aid in finding a solution of the actual problem.

### 3.2 Axisymmetric Case

Once the problem defined by equations (3.3)-(3.6) has been solved, either analytically or numerically, the desire is then to move on to a two-dimensional, axisymmetric case. Basically rotate the domain of  $z \in (0, R(t))$  around to put it into polar coordinates, so that  $z$  becomes  $r$ , and the domain transforms to  $r \in (0, R(t))$ , where  $R$  is still the radius of the now circular hole. The primary difference here will be the velocity field used, as it will no longer be so theoretical or approximate to the real velocity field.

Consider the 2-dimensional, circular hole, in polar coordinates. The hole is confined in the domain of  $0 < r < R(t)$ , with a velocity field  $V(r, R(t)) = V(\frac{r}{R})$ . The reason for this particular velocity field is, again, derived from the actual model of the Stoksian subfluid that was calculated. In this iteration of the problem, however, we we actually be using the exact velocity field, rather than an approximation. To lay the groundwork for the velocity field, first let  $A(t)$  be the area of the circular gas hole, then define  $q(t)$  such that  $A_t = -2\pi q(t)$ . Then the velocity field over the entire domain (inside and outside of the hole) is:

$$V(r, t) = -q(t) \cdot \begin{cases} \frac{1}{r} \left[ 1 - \sqrt{1 - \left(\frac{r}{R}\right)^2} \right] & r < R(t) \\ \frac{1}{r} & r > R(t). \end{cases} \quad (3.7)$$

With this, and the advection-diffusion equation (in polar coordinates, now), we can write down the complete problem for a two-dimensional, round hole, with axisymmetric velocity field:

$$C_t + \frac{1}{r} \frac{\partial}{\partial r} (rVC) = 0 \quad (3.8)$$

where  $V$  is as defined in equation (3.7). Further, to define the evolution of  $R(t)$  is the flux condition:

$$C_\infty \frac{dR}{dt} = [C_\infty - C|_{z=R}] V|_{z=R} \quad (3.9)$$

where  $C_\infty$  is the constant concentration of the liquid phase outside of the hole. We can then use these assumptions about flux, and how which factors affect the movement of the radius  $R(t)$  to set up and solve a more specific axisymmetric problem in the following chapter.



## Chapter 4

# The Axisymmetric Problem

### 4.1 Two-Dimensional, No Condensation

The concentration in a circular hole is still governed by the Advection-Diffusion equation (2.2), but as before, diffusion is ignored. In addition, we assumed radial symmetry,  $\partial_\theta = 0$ . Thus  $C_\theta = 0$ , which implies  $C = C(r, t)$ . This yields the axisymmetric advection equation:

$$C_t + \frac{1}{r} \partial_r (rVC) = 0. \quad (4.1)$$

But, unlike that previous problem, the radial boundary,  $r = R(t)$  is moving inward. To simplify the movement of  $R$ , we ignore condensation for the moment, which means the movement of boundary is due entirely to line tension. This yields the following differential equation for  $R$ :

$$\frac{dR}{dt} = -\frac{q}{R} \quad (4.2)$$

$$R(0) = R_0, \quad (4.3)$$

where  $q$  is a constant related to the strength of the line tension. Equation (4.2) can be easily solved to obtain

$$R(t) = \sqrt{R_0^2 - 2qt}. \quad (4.4)$$

To model the behavior in the hole, we changed variables into a coordinate system that moved with  $R(t)$ :

$$\rho = \frac{r}{R(t)} \quad \tau = t, \quad (4.5)$$

Transforming the partial derivatives  $\frac{\partial}{\partial t}$  and  $\frac{\partial}{\partial r}$  via the chain rule:

$$\frac{\partial}{\partial t} = \frac{\partial \tau}{\partial t} \frac{\partial}{\partial \tau} + \frac{\partial \rho}{\partial t} \frac{\partial}{\partial \rho} = \frac{\partial}{\partial \tau} + \left( -\frac{rR_t}{R^2} \right) \frac{\partial}{\partial \rho},$$

$$\frac{\partial}{\partial r} = \frac{\partial \tau}{\partial r} \frac{\partial}{\partial \tau} + \frac{\partial \rho}{\partial r} \frac{\partial}{\partial \rho} = \left( \frac{1}{R} \right) \frac{\partial}{\partial \rho}$$

This can then be substituted into equation (4.1) and simplified:

$$\begin{aligned} C_\tau + C_\rho \left( -\frac{r}{R} \frac{R_t}{R^2} \right) + \frac{1}{\rho R^2} \frac{\partial}{\partial \rho} (-qf(\rho)C) &= \\ C_\tau - \left( \frac{\rho R_\tau}{R} \right) C_\rho + \frac{1}{\rho R^2} (-qf_\rho C - qf C_\rho) &= \\ C_\tau + \left[ \frac{\rho q}{R^2} - \frac{qf}{\rho R^2} \right] C_\rho - \left( \frac{qf_\rho}{\rho R^2} \right) C &= 0 \end{aligned} \quad (4.6)$$

This equation can, like previous problems, be solved via characteristics. Letting  $f(\rho) = 1 - \sqrt{1 - \rho^2}$ , we obtained

$$\frac{d\rho}{d\tau} = \frac{\rho q}{R^2} - \frac{qf}{\rho R^2} = \frac{\rho^2 q - qf}{\rho R^2}$$

for the equation of the characteristics. Which implies:

$$d\rho \left( \frac{\rho}{\rho^2 - f} \right) = d\tau \left( \frac{q}{R^2} \right).$$

Then, substituting in the expressions for  $R$  and  $f$ :

$$d\rho \left( \frac{\rho}{\rho^2 - 1 + \sqrt{1 - \rho^2}} \right) = d\tau \left( \frac{q}{R_0^2 - 2q\tau} \right)$$

Solving the respective DE's yields:

$$\log(f) = -\frac{1}{2} \log(R^2) + \log(\zeta)$$

where  $\zeta$  is a constant of integration. Solving for  $\zeta$ , and defining characteristic time coordinate  $s$ , the characteristics are:

$$\zeta = f(\rho)R \quad s = \tau \quad (4.7)$$

Changing variables from  $(\rho, \tau)$  to  $(\xi, s)$ :

$$\frac{\partial C}{\partial \tau} = \frac{\partial C}{\partial s} \frac{\partial s}{\partial \tau} + \frac{\partial C}{\partial \xi} \frac{\partial \xi}{\partial \tau} = C_s - \left(\frac{qf}{R}\right)C_\xi$$

$$\frac{\partial C}{\partial \rho} = \frac{\partial C}{\partial s} \frac{\partial s}{\partial \rho} + \frac{\partial C}{\partial \xi} \frac{\partial \xi}{\partial \rho} = (Rf_\rho)C_\xi$$

Substituting into equation (4.6):

$$C_s + \left(\frac{qf}{R}\right)C_\xi + \left[\frac{\rho q}{R^2} - \frac{qf}{\rho R^2}\right] [Rf_\rho] C_\xi - \frac{qf_\rho}{\rho R^2} C = 0$$

which simplifies down to:

$$C_s = \frac{q}{R^2 \sqrt{1-\rho^2}} C$$

Substituting in expressions for  $s$  and  $\xi$ , and solving the DE, yields:

$$C(\rho, \tau) = \frac{D\left(R(1 - \sqrt{1-\rho^2})\right)}{R\sqrt{1-\rho^2}}, \quad (4.8)$$

where  $D$  is an arbitrary function.

Using the initial condition  $C(\rho, 0) = C_0$  yields to the exact solution:

$$C(\rho, \tau) = C_0 \left[ 1 + \frac{\frac{R_0}{R} - 1}{\sqrt{1-\rho^2}} \right] \quad (4.9)$$

One can also solve for the total mass inside the hole  $M(\tau)$  with:

$$M(\tau) = 2\pi \int_0^{R(t)} C(r, t) r dr = 2\pi \int_0^1 C(\rho, \tau) \rho R^2 d\rho,$$

which ultimately yields:

$$M(\tau) = \pi R_0^2 C_0 \left[ 1 - \left(1 - \frac{R}{R_0}\right)^2 \right], \quad (4.10)$$

With mass-flux

$$M'(\tau) = -2\pi q R_0^2 C_0 \left[ \frac{1}{R} - \frac{1}{R_0} \right]. \quad (4.11)$$

### 4.1.1 Plots

The following are plots of the various functions of interest, to give a more concrete idea of what the system physically looks like. They were done setting  $C_0 = 1$ ,  $q = \frac{1}{2}$ , and  $R_0 = 1$ .

#### Concentration

The following is a plot of  $C(\rho, \tau)$ , using equation (4.9):

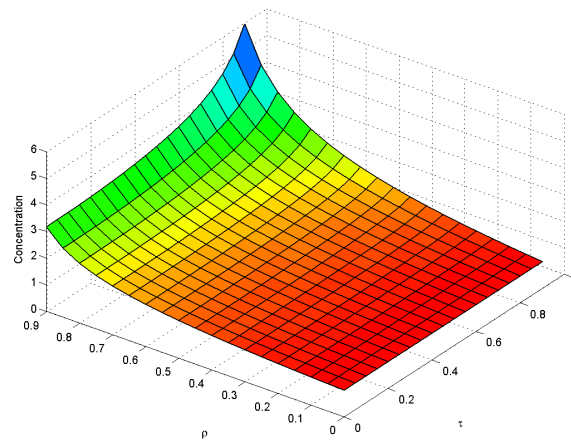


Fig. 7: Concentration as a function of  $\rho$  and  $\tau$ . Note the overall increase in concentration as  $\tau$  increases to the closing time,  $\tau_*$ .

Notice the singularity immediately forming at  $\rho = 1$ , and a “wave” of concentration moving inward. The concentration has gone uniformly to 0 by the closing time,  $\tau_* = 1$  (found simply by setting equation (4.4) to 0 and solving for  $\tau$ ).

#### Characteristics

To find suitable characteristics, we want  $\xi = \rho_0$ , i.e.  $\rho$  at initial time  $\tau = 0$ . Setting that and solving for  $\rho(\tau)$ , the following equation was derived:

$$\rho(\tau) = \sqrt{1 - \left[ 1 - \frac{R_0}{R} \left( 1 - \sqrt{1 - \rho_0^2} \right) \right]},$$

where  $R(\tau)$  is as defined in equation (4.4). Plotting for a variety of  $\rho_0$ 's yields:

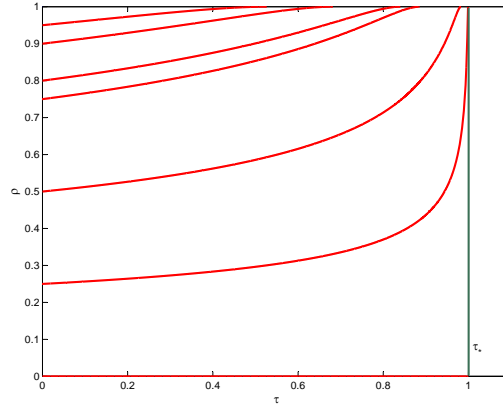


Fig. 8: Characteristics of equation (4.6) for various starting points  $\rho(0) = \rho_0$ .

Every characteristic curve hits the boundary at  $\rho = 1$  at different times, but all have hit by time  $\tau_*$ .

### Mass and Mass-Flux

Below are plots of the Mass (left) and Mass-Flux(right) as functions of time  $\tau$ :

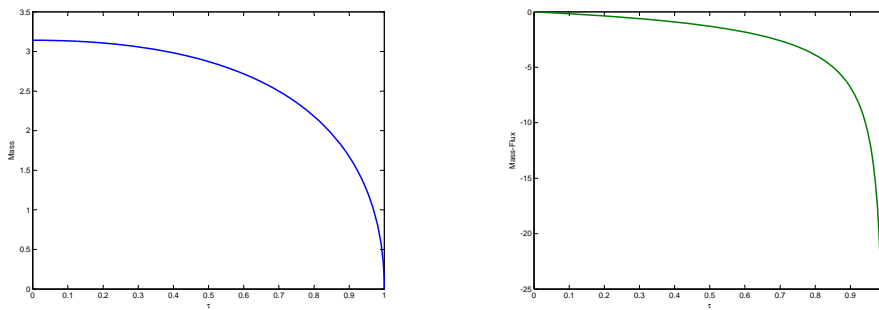


Fig. 9: Left: Mass as a function of time, Right: Mass-flux as a function of time.

Notice on the left that the mass has reached exactly 0 at closing time  $\tau_* = 1$ , and that on the right the mass-flux starts at 0, and has reached  $-\infty$  by the closing time.

### 4.1.2 Area

Since the data from the original experiments are taken as Area versus Time, we decided to use our data to calculate  $A(t)$ , the area, or at least approximate it. Taking calculations from [1], we know that

$$A_t = -2\pi q(t),$$

but  $q$  was taken to be constant, so this would merely give the linear relationship determined earlier. However, we can, use an alternate formulation of  $q$ . We know that, in a full scale model, area would be affected by two things: matter pulled in from the far edges due to line tension, and condensation. Even though we left condensation out of this solution, we can retroactively put it back in to  $q(t)$ , and see if we don't get some useful information about  $A(t)$  from doing so. So, based on condensation, the formula for  $q$  becomes:

$$q(t) = q_\infty + \frac{M_t}{2\pi C_\infty},$$

where  $q_\infty$  is simply the constant  $q$  due to line tension used before, and  $C_\infty$  is the constant concentration of the liquid phase outside the hole. This means that

$$A_t = -2\pi q_\infty - \frac{M_t}{C_\infty}.$$

This equation can be explicitly integrated with respect to  $t$  to obtain the following equation for area as function of time:

$$A(t) = - \left[ 2\pi q_\infty t + \frac{1}{C_\infty} (M(t) - M(0)) \right] + A_0, \quad (4.12)$$

where  $A(0)$  is the initial hole area (directly obtained from  $R_0$ ), and  $M(0)$  is the initial mass of the hole (obtained by substituting  $t = 0$  into equation (4.10)). Plotting equation (4.12):

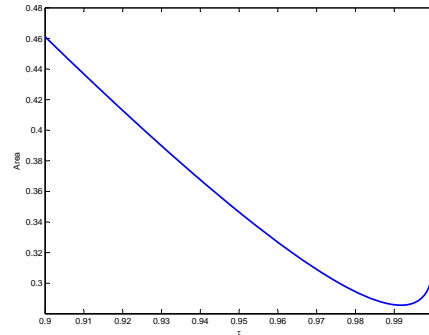
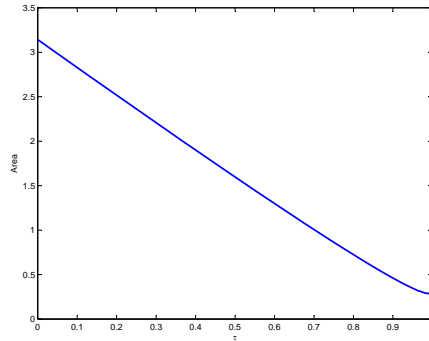


Fig. 10: Left: area of hole versus time, Right: Close-up of non-linearity for area versus time plot.

The first plot is in a time interval of  $[0, t_*]$ , and is generally linear until the hole has become small, and the nonlinearity becomes stronger. The second is a closeup of the nonlinearity, which forms, in this case, around  $t = 0.9$ , quite close to the closing time  $t_* = 1$ . This is a key result of our work, as the experimental data obtained in [1] is data of the area of the hole versus time. Unfortunately, as Figure 5 showed, the area relationship starts non-linear, then becomes linear as the hole becomes smaller, the opposite of our area plot. This seems to indicate that our analytical approach was lacking in some respect.

### 4.1.3 Concentration with General IC

Because it will become useful later, and the result is relatively simple to obtain, we calculated the concentration  $C(\rho, \tau)$  for an arbitrary initial condition  $C(\rho, 0) = \gamma(\rho)$ . By simply plugging into equation (4.8), it's easy to obtain the following:

$$C(\rho, \tau) = \frac{\gamma(\rho) \left( \frac{R_0}{R} - 1 + \sqrt{1 - \rho^2} \right)}{\sqrt{1 - \rho^2}}. \quad (4.13)$$

## 4.2 Two Dimensional, With Condensation

After seeing how our calculation of area differed not only with experimental results, but also with the original model, it became obvious that at least one of our simplifying assumptions had been overly simplistic. Looking more deeply into how the area of the hole changes, in a physical sense, we see that:

$$\frac{d}{dt}(\text{Area}) = - [\{\text{Mass flux from } \infty\} + \{\text{condensation at the edge}\}],$$

so the assumption that condensation can be ignored is clearly invalid, and it would have to be inserted back into the problem. Ignoring condensation initially allowed us to write equation (reference), the simple differential equation involving  $R(t)$ . The change is caused in  $q$ , where it is no longer a constant, but a function  $Q(t)$  which involves the constant flux from infinity

due to line tension pulling mass in, and the mass flux from inside the hole which condenses at the edge:

$$Q(t) = q_\infty + \frac{M_t}{2\pi C_\infty}. \quad (4.14)$$

Where  $M_t$  is just the mass flux out of the hole, and  $C_\infty$  is the constant concentration of the liquid phase outside of the hole. Thus equation (4.2) changes to

$$\frac{dR}{dt} = -\frac{Q(t)}{R(t)}. \quad (4.15)$$

Again, this can be substituted into equation (4.1) to obtain the following differential equation for the concentration:

$$C_\tau + \frac{1}{R^2} \left[ Q\rho - \frac{q_\infty f}{\rho} \right] C_\rho = \frac{q_\infty f \rho}{\rho R^2} C. \quad (4.16)$$

To eliminate  $R$  from the equation, we defined a new variable  $T$ , such that:

$$T_\tau = \frac{1}{R^2}, \quad (4.17)$$

so now

$$C_\tau = C_T (T_\tau) = C_T \left( \frac{1}{R^2} \right).$$

Thus equation (4.16) becomes

$$C_T + \left[ Q\rho - \frac{q_\infty f}{\rho} \right] C_\rho = \frac{q_\infty f \rho}{\rho} C. \quad (4.18)$$

This can no longer be solved explicitly using characteristics, but we can still write the characteristic equation, namely

$$\frac{\partial \rho}{\partial T} = Q\rho - \frac{q_\infty f}{\rho}. \quad (4.19)$$

Assuming that we have a  $\rho(\xi, T)$  which solves the above equation, then equation (4.18) becomes

$$C_T = \frac{q_\infty f \rho}{\rho} C. \quad (4.20)$$

The final unsolved function is that of the mass,  $M$ , but it can be obtained by simply integrating  $C$ :

$$M(\tau) = R^2 \int_0^1 \rho C \, d\rho \quad (4.21)$$

as before. Putting these together, we get a system of five equations for five functions of interest:

$$\begin{aligned} C_T &= \frac{q_\infty f_\rho}{\rho}, \\ \frac{d\rho}{dT} &= Q\rho - \frac{q_\infty f}{\rho}, \\ T_\tau &= \frac{1}{R^2}, \\ Q(t) &= q_\infty + \frac{M_t}{2\pi C_\infty}, \\ M(\tau) &= R^2 \int_0^1 \rho C d\rho. \end{aligned}$$

Unfortunately, we were unable to solve the system defined by equations (4.14), (4.17), (4.19), (4.20), and (4.21) analytically, and as time in the research period began to grow short, a more numerical approach was necessary to solve the problem.

### 4.3 Stroboscopic Approximation

Because condensation is clearly so important, but neither of our previous analytical efforts of modelling the behavior, we have decided that the best next step at this point is to use the solution obtained from the original, condensation-free model, Equation (4.6), and perform a *stroboscopic approximation*. The idea is simple: Use equation (4.13) for  $C$  to approximate the behavior for a small time  $\Delta t$ , yielding a function of one variable ( $\rho$ ) for the concentration  $\tilde{C}(\rho, \Delta t)$ , and constant for the radius  $\tilde{R}(\Delta t)$ . Then use the mass-flux, also from the original calculation (equation (4.11)), to calculate how much mass has left the hole. Based on the value of  $C_\infty$ , we then could calculate a correction for the radius, giving a new radius  $R(\Delta t)$ . Then we would just simply rescale  $C$  to reflect the new radius, and use that new  $C(\rho, \Delta t)$  as  $\gamma(\rho)$  in equation (4.13), and repeat until we had gotten up to the closing time  $t_*$ . The procedure would go as follows:

First, calculate  $C(\rho, \Delta t)$  for some small interval  $\Delta t$ , in this case  $\Delta t = 0.1$ :

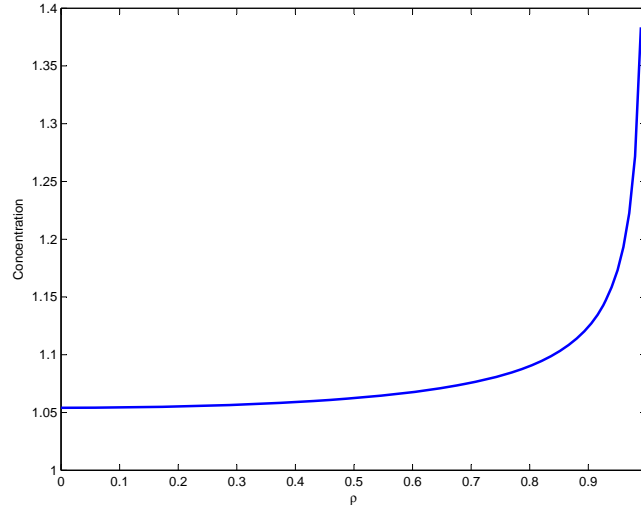


Fig. 11: Plot of  $C(\rho, \Delta t)$  obtained from equation (4.9), substituting in  $\tau = 0.1$  to obtain a function of one variable  $C(\rho)$ . The first step of the stroboscopic approximation is solving (4.9) for a short period  $\Delta t$  to obtain such a function. Figures 11-13 use same parameter values as plots in Section 4.1.1.

Follow by using the mass-flux and mass-balance to calculate how much mass has condensed, and calculate a new radius ( $R_{n+1}$ ) from the previous radius( $\tilde{R}_{n+1}$ ):

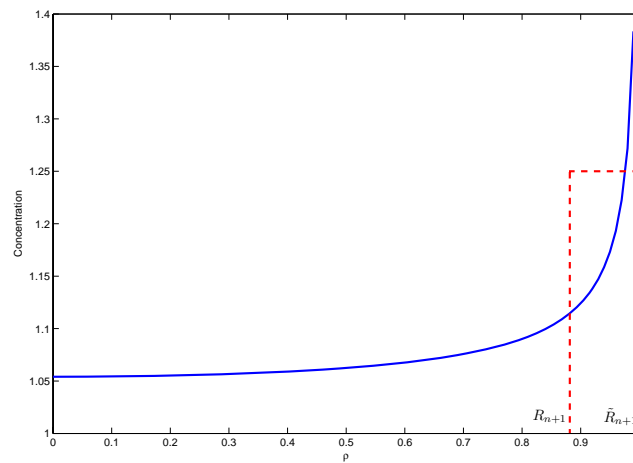


Fig. 12: Calculate the new radius  $R_{n+1}$  based on mass-flux out the hole.

Finally, truncate  $C$  to reflect the new radius:

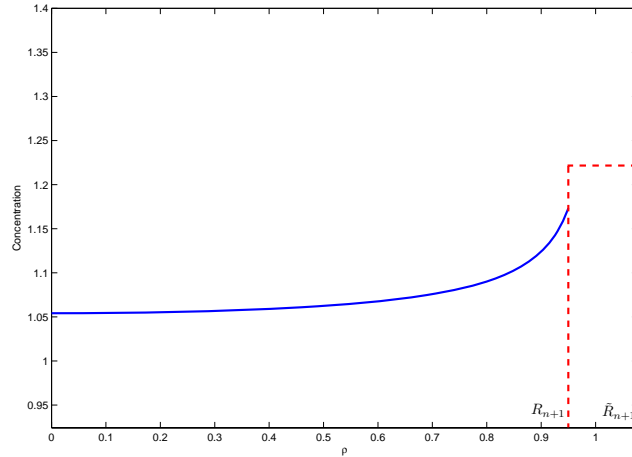


Fig. 13: Truncate and rescale the function  $\tilde{C}_{n+1}$  to obtain a function of  $\rho$   $C_{n+1}(\rho)$ , which becomes the new initial condition for (4.13).

You can now use the rescaled concentration as the initial condition for equation (4.13), take another time step  $\Delta t$  forward, and repeat until you have reached the closing time  $t_*$ .

Unfortunately, time constraints prohibited us from coding and running this approximation ourselves, and it is instead left as a possible future direction to follow-up on in future research on this particular problem.



# Conclusion

I, personally, had hoped that by the end of the year I would have a decent model for the closure of the hole which could be compared to experimental data, to see if our simplifying assumptions were valid or not, etc. Unfortunately, due to the constraints of time, we were unable to actually formulate a specific model to compare to the data. What we ended up doing was proving the importance and invalidity of two previous assumptions: that condensation could be ignored, and that diffusion could be ignored. These set up a framework for future researchers (much like what Alexander et. al. did for me) who wish to work on this problem. And while I myself may not be able to carry out the stroboscopic approximation, that too may provide useful information about the relationship between the area of the hole and time as it closes. Despite the lack of any concrete, decent solutions for this problem, I still feel that we went a long way into understanding many of the physical and mathematical complexities and subtleties within it, and made future research on Langmuir layers just a little bit easier.



# Bibliography

- [1] James C. Alexander, Andrew J. Bernoff, Elizabeth K. Mann, J. Adin Mann Jr., and Lu Zou. Hole dynamics in polymer langmuir films. *Physics of Fluids*, 18(6), 2006.
- [2] David Bleeker and George Csordas. *Basic Partial Differential Equations*. International Press of Boston, 1997.
- [3] Stephen H. Davis. *Theory of Solidification*. Cambridge University Press, 2001.
- [4] J.M. Ottino. *The Kinematics of Mixing: Stretching, Chaos, and Transport*. Cambridge University Press, 1989.
- [5] Michael C. Petty. *Langmuir Blodgett Films: An Introduction*. Cambridge University Press, 1996.