Positive Pressure Drop-on-Demand Printhead for Three-Dimensional Printing

by

Blake Wilbur Gleason

B.S., Mechanical Engineering (1998) Harvard University

Submitted to the Department of Mechanical Engineering in Partial Fulfillment of the Requirements for the Degree of Master of Science in Mechanical Engineering

at the

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ABSTRACT

In drop-on-demand printing, wetting out of the binder fluid onto the orifice face typically has been prevented by some combination of the following: coatings on the orifice face, high surface energy fluids, and negative pressure. This non-wetting approach is not practical for low surface energy fluids.

A new positive pressure method of drop-on-demand printing has been developed which eliminates the requirement for a non-wetting system; modifications to the binder fluid properties or to the orifice material to ensure non-wetting are no longer necessary for reliable drop formation. In fact, slight positive pressure (relative to atmosphere) is maintained in the binder fluid at the orifice to achieve *intentional* wetting of a small area around the orifice. The pressure causes the binder meniscus to bulge out from the orifice until it detaches from the orifice edge and wets the orifice face. The binder wetting continues outward from the orifice edge along the plane of the orifice face, and would continue uncontrolled were it not for an additional constraint: the orifice face ends abruptly with a sharp corner to which the meniscus attaches, thus defining the wetting boundary for the binder. With such a boundary in place, the fluid meniscus forms a spherical cap on the orifice face. The thickness of the cap can be varied by adjusting the level of positive pressure.

Benefits of this controlled wetting include successful drop-on-demand printing with low surface energy fluids, including ethanol and chloroform, and also successful drop formation using polymer-loaded binder without the build-up of solid polymer deposits at the orifice. Polyacrylic acid (PAA) and polyetherimide (PEI) have been printed in both aqueous and alcoholic binder fluids using an alumina positive pressure nozzle. Forty micrometer diameter drops can be ejected reliably at five meters per second velocity and one kilohertz frequency.

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Table of Symbols

| Во | Bond number | |
|------------|---|--|
| g | gravitational constant | |
| d | drop diameter | |
| ρ | density of binder fluid | |
| σ | surface tension of binder fluid | |
| F | force | |
| P | pressure in binder fluid at the meniscus | |
| a | orifice inside radius | |
| r | radius of spherical meniscus cap | |
| α | binder fluid contact angle on orifice | |
| R_{face} | radius of orifice face (radius of orifice outside edge) | |
| h_{cap} | thickness of the spherical meniscus cap | |
| V | volume | |
| l | distance traveled by wave before reflection | |
| c | speed of sound | |
| t | time | |
| В | Bulk modulus | |
| f | frequency | |
| m | mass of drop | |

1. Introduction

1.1. Problem and Motivation

1.1.1. Drop-on-Demand

In Drop-on-Demand printing, one drop at a time is ejected from a printhead when commanded by the printing machine. This ability to eject single drops at arbitrary time intervals allows great flexibility in many different printing systems. For example, in a particular 3DP™ (three-dimensional printing) process, parts can be printed with a vector outline and a raster fill using the same printhead and printing system.

Unfortunately, standard Drop-on-Demand printheads cannot form drops reliably and consistently with two main categories of binder fluids that are important for certain 3DPTM material systems. The standard printheads cannot satisfactorily print either low surface energy fluids (such as solvents) or fluids with dissolved solids (such as polymers used in common binders).

1.1.2. Solvent Printing

Many material systems useful for 3DPTM involve a solvent binder such as alcohols and chloroform. These solvents have low surface energy, which allows them to wet most orifice materials easily. For comparison, the following table shows the surface tension values for common solvent binders compared to that of water.

| Fluid | Surface Tension (dynes/cm) |
|-------------|----------------------------|
| Water | 70 |
| Isopropanol | 22 |
| Ethanol | 22 |
| Methanol | 22 |
| Chloroform | 27 |

Figure 1. Comparison of binder surface tensions. Common solvents have relatively low surface tension and are likely to wet out on any orifice face.

The standard 3DPTM orifice is made from a ceramic (ruby) and has a large, flat orifice face. With this type of orifice, negative pressure in the printhead usually keeps the binder from wetting out onto the orifice face. In fact, Drop-on-Demand printheads in general use this negative pressure method to keep the orifice face from being wet. However, low surface energy fluids always wet the surface eventually when drops are being ejected. Without any boundary for the wetting, an amorphous puddle of binder creeps out from the orifice, as shown in Figure 2. The depth and circumference of the puddle vary unpredictably as drops are ejected, causing disturbance to the drops and rendering them relatively useless for any printing application that depends on their uniformity.

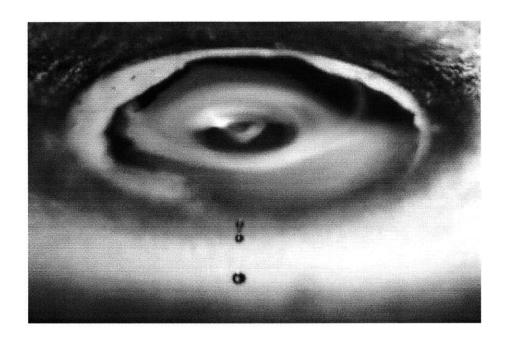


Figure 2. Amorphous puddle. Ethanol (surface tension 22 dynes per centimeter) wetting the face of a standard negative pressure 40 micrometer ruby orifice as drops are ejected. The unpredictable wetting boundary is shown.

1.1.3. Polymer Printing

Another important category of binders used in 3DPTM systems contain dissolved polymers such as polyacrylic acid (PAA) and polyetherimide (PEI). Further complications result when polymer is introduced to binders because the polymer can be deposited near the orifice as the binder evaporates. These deposits adversely affect drop formation, either by changing the wetting condition at the orifice, or by causing asymmetrical drop breakoff, or by clogging the orifice partially or completely. Solid polymer deposits are shown are shown below in Figure 3.

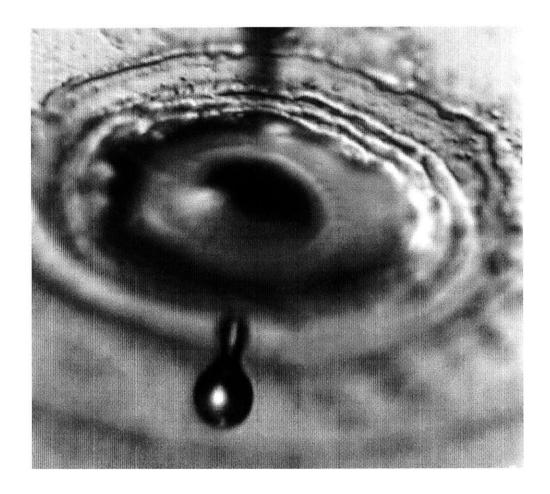


Figure 3. PAA buildup. Drop ejection with PAA binder on a standard negative pressure 40 micrometer ruby orifice builds up PAA rings around the orifice, and drop breakoff changes dramatically. Eventually, drops stop forming altogether.

Clearly, satisfactory printing with these solvent and polymer-loaded binders is not possible with the standard Drop-on-Demand printhead due to uncontrolled wetting and solid deposition.

1.2. Solution – Current Work

In response to the needs outlined above for reliable printing with solvent and polymer-loaded binders, a printhead compatible with these binders has been developed. This positive pressure Drop-on-Demand printhead will be the main topic of the present paper.

This printhead works basically as follows: by using a custom orifice geometry designed to allow wetting on the orifice face only to a well-defined radius, consistent drops can be formed because the wetting condition is consistent. Further, the wetting condition is maintained by applying a *positive* pressure to the binder fluid at the orifice, to force wetting to occur in a predictable manner.

Therefore, the main feature of a "positive pressure" Drop-on-Demand printhead is that it controls the wetting condition of the binder fluid at the orifice where drops are ejected. In particular, the binder fluid is intentionally caused to wet the face of the orifice, but only to a predetermined boundary. This controlled wetting achieves a uniform, predictable fluid cap through which drops can be ejected. Benefits of this controlled wetting include the possibility of Drop-on-Demand drop formation with low surface energy fluids, and also the possibility to form drops with a polymer-loaded binder without building up solid polymer deposits at the orifice.

The positive pressure concept is shown in Figure 4, in which binder fluid is shown wetting one variety of positive pressure orifice face. The intentional wetting is obtained by imposing a slight positive pressure (relative to atmosphere) on the binder fluid inside the printhead. This pressure causes the binder meniscus to bulge out from the orifice until it detaches from the orifice edge and wets the orifice face. The binder wetting continues outward from the orifice edge along the plane of the orifice face, and

would continue forever were it not for an additional constraint. The orifice face ends abruptly with a sharp edge to which the meniscus attaches, thus defining the wetting boundary for the binder.

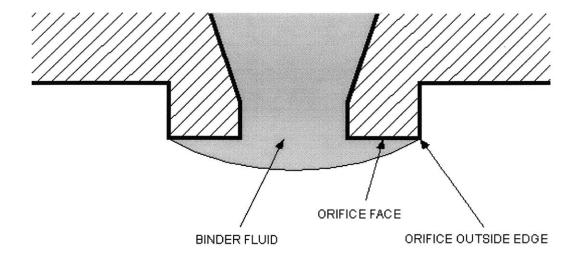


Figure 4. Positive pressure concept. Binder fluid is forced to wet a small area of the orifice face by positive pressure. Wetting is constrained by the orifice outside edge.

2. The Geometry and Fabrication of Positive Pressure Nozzles

The necessary features of the nozzle orifice are the following: that it sufficiently constrain and define the drop size, and for the positive pressure mode of printing, that it provide the proper wetting conditions for at least one particular binder material system. It must also interface with the rest of the nozzle and printhead in such a way as to allow uninterrupted internal fluid path, easy of assembly and disassembly, ease of cleaning, long-term mechanical robustness, and resistance to any solvents used in binder solutions.

2.1. Range of orifice sizes

In particular, the orifice diameter is the parameter that most strongly defines the size of any drop produced. Other parameters have some effect on the drop size, but the orifice diameter determines the available operating range. In most cases, drop diameter is approximately equal to orifice diameter, for the range of orifice diameters in which surface tension is the dominant force. The present work does not address very large orifices or drops in which gravity, for example, plays an important role in drop formation. For a particular binder fluid, this upper limit on orifice and drop size is related to the Bond number, which should be much less than unity for the present discussion to be relevant.

$$Bo = \frac{g(\rho_{binder} - \rho_{air})d^2}{\sigma} \cong \frac{g\rho d^2}{\sigma}$$
 (Equation 1)

The Bond number, which directly compares the gravitational force to the surface tension force, indicates that for a typical binder fluid, drop and orifice size should be less than one millimeter. For a lower limit on drop and orifice size, relevant factors include

resolution of orifice fabrication methods and maximum expected binder particle size.

Diameters down to ten micrometers are certainly possible.

The throat length of the orifice is usually scaled with the orifice diameter, so that the aspect ratio is approximately the same. A short throat length, with aspect ratio of throat length to orifice diameter as much less than 1:1 as fabrication techniques allow, ensures that viscous effects are relatively small. A relatively long (undesirable) throat is shown in Figure 5.

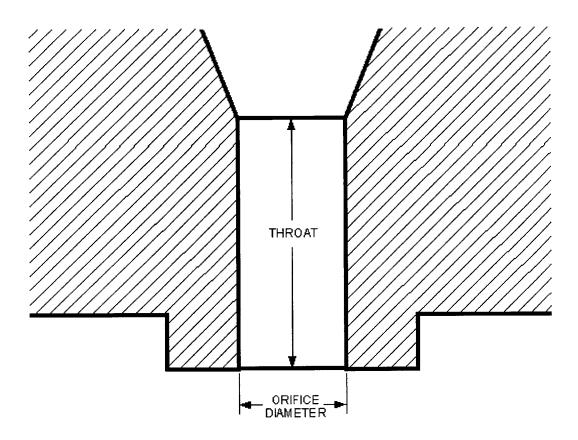


Figure 5. Long throat. The throat is much longer than the orifice diameter. Viscous drag on the binder fluid as it moves through the throat will adversely affect drop formation.

2.2. Range of orifice outside edge sizes

The most important function of the positive pressure orifice is to define the wetting condition of the binder meniscus. As described above, it is desirable to have a thin cap of fluid on the face of the orifice. The thickness of the fluid cap for a given fluid is determined by both the positive pressure (discussed below) and the orifice geometry. For a given orifice diameter, there are a range of orifice face sizes that will work to properly constrain wetting. Clearly, a lower bound on the outside edge diameter is given by the orifice diameter itself, as shown in Figure 6. The outside orifice edge is shown only slightly larger than the orifice diameter. Available fabrication techniques determine the actual minimum orifice face size.

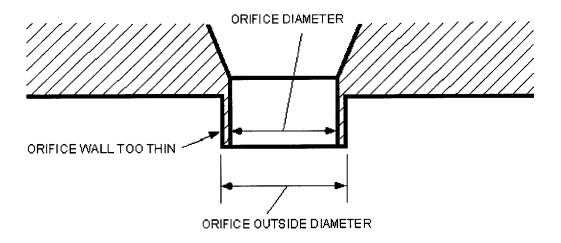


Figure 6. Minimum edge thickness. For a 40 micrometer orifice diameter, the outside orifice edge diameter must be enough larger than 40 micrometers to ensure robustness and existence of a useful orifice face.

However, there are also fluid dynamic concerns that dictate the minimum outside edge diameter. In general, if the outside edge is too close to the orifice, disturbances

from drop ejection will detach the meniscus from the outside edge, and, in many cases, cause fluid to run over the edge, causing uncontrolled wetting and persistent "weeping." Additionally, with very small orifice outside edge diameter, the volume of fluid wetted onto the orifice face will be much smaller than a drop volume, and each drop ejection will change the wetting condition substantially. As a rule of thumb, the minimum outside edge diameter should be at least fifty percent larger than the orifice diameter.

On the other extreme, the orifice outside diameter should not be larger than necessary. The absolute maximum is given by the same criteria as for the orifice itself: surface tension must dominate. Again, the maximum size for typical fluids would then be approximately one millimeter. However, several detrimental effects occur before the gravitational limit. A small orifice and a large outside edge make a large land (orifice face), as shown in a photograph in Figure 7. A large land means that a limited range of positive pressures can be used (described below). Further, for a thin fluid cap, complete wetting of a large land is not always guaranteed. There may be dry spots, or the fluid cap may not extend all the way to the orifice edge, resulting in a poorly defined boundary and unreliable drop forming conditions. Finally, a large outside edge diameter will allow relatively low frequency surface waves to interrupt drop formation at drop formation rates well below the upper limits imposed by the rest of the system (as discussed below in Surface Waves, page 49).

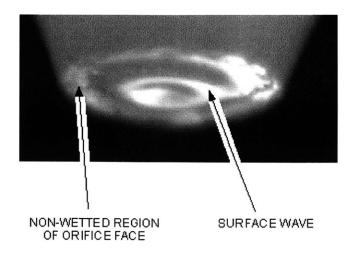


Figure 7. Surface wave on orifice face. Dry spots are visible as well.

This large land limitation reduces the maximum flow rate available from the printhead. In other words, for a large land, several of the benefits of positive pressure drop formation are lost.

Because of the dependence of optimal outside edge diameter on orifice diameter, it makes sense to consider the ratio of these diameters as well as their absolute values. This ratio also defines the relationship between the volume of fluid ejected in each drop to the volume of the fluid cap for a given positive pressure. When there is less volume in the cap than in the drop, it is possible for the drop formation process to completely dry the orifice face during the drop forming cycle. A complete exchange of cap fluid is then possible every cycle.

This exchange and washing of the orifice face helps in some cases and hurts in others. A continuously refreshing cap maintains the intended binder chemistry in the cap if, for example, the binder has a dissolved polymer. Without continuous refreshing, solvent evaporation from the cap increases polymer concentration in the cap beyond desired values. In fact, for any mixture of fluids in which one is more volatile than the

other, the relative concentrations will also change over time without continuous cap refreshing.

On the other hand, complete drying of the orifice face may contribute to buildup of polymer deposits near the orifice. Each time the face is allowed to dry, a thin film of solids may be deposited, again defeating one of the benefits of the positive pressure printhead.

2.3. Range of outside edge angles

The final defining feature of the positive pressure orifice geometry is the angle of the outside edge. Again, various tradeoffs allow for a range of appropriate angles. For the exterior angle of the outside edge, the minimum outside edge angle required to define any edge is just over 180 degrees, and the maximum theoretical angle is just less than 360 degrees. Figure 8 shows a minimum outside edge angle that is too small to be an effective wetting boundary.

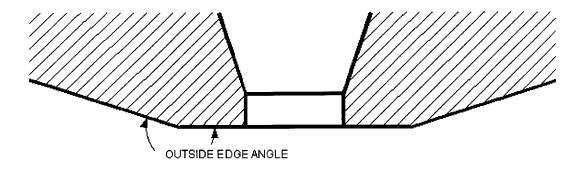


Figure 8. Minimum outside edge angle. This minimum angle is not a particularly effective boundary for binder fluid wetting.

Clearly, durability and fabrication considerations limit the maximum angle to well less than 360 degrees, but angles greater than 270 degrees should be possible (as for example, by the undercutting action of some etching techniques). This maximum outside edge angle, with substantial undercut, is shown in Figure 9.

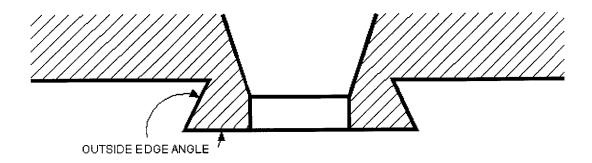


Figure 9. Very large outside edge angle. The larger the outside edge angle, the better the boundary against wetting, as long as the sharpness can be maintained.

The purpose of the outside edge is to provide a well-defined boundary for the orifice face beyond which the binder fluid will not wet. Both the angle of the outside edge and the quality of the edge (sharpness) are important. A higher angle will present a better barrier to wetting over the edge, because the angle will be that much greater than the wetting angle of the binder fluid.

However, a higher angle will be more difficult to fabricate and maintain with a sharp edge. In many brittle materials, a sharper edge at a higher angle leads to higher likelihood of chipping, both in manufacture and in handling. Typical edge angle is around 270 degrees for a boss orifice nozzle (Figure 10A), and typical edge angle is around 255 degrees for a cone-tip nozzle (Figure 10B).

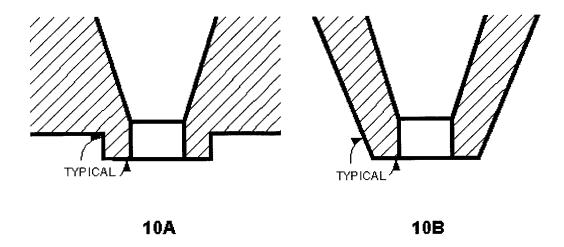


Figure 10. Boss-tip nozzle versus cone-tip nozzle. Typical outside edge angles are 270 degrees for the boss nozzle and approximately 255 degrees for the cone nozzle.

In any case, the outside edge of the orifice will always have a finite radius, which also affects the quality of the wetting barrier. A smaller radius will provide a better boundary for the meniscus, but will be harder to fabricate and maintain. As shown in Figure 11, the radius on the outside edge should usually be significantly smaller than the radius of the spherical cap formed by the binder fluid meniscus during printhead operation.

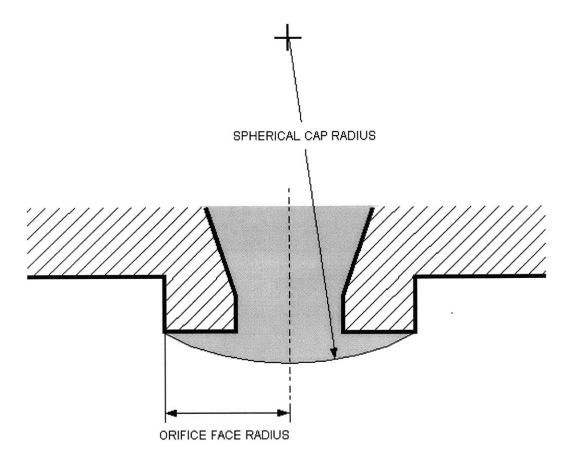


Figure 11. Comparison of orifice face radius to spherical cap radius.

Figure 12a shows an enormous binder meniscus successfully constrained by a sharp outside orifice edge on a cone-type nozzle. This spherical cap demonstrates the well-defined wetting boundary, but is much larger than a typical operating cap, shown in Figure 12b.

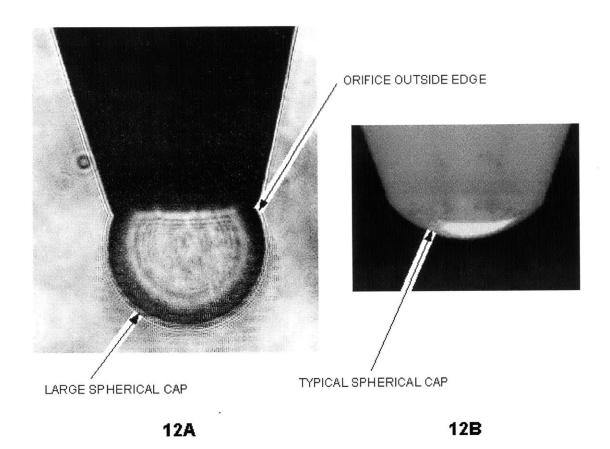


Figure 12A and 12B. Demonstration of bounded spherical caps. Figure 12A shows a very large spherical cap, with approximately 10 inches of positive pressure. Figure 12B shows a more typical cap (although still large, for the sake of visibility) with five inches of positive pressure. The alumina orifice face is 90 micrometers in diameter in both cases.

2.4. Orifice materials

As described above, most positive pressure printhead nozzles are made with somewhat demanding geometric tolerances on a relatively small scale. For this and several other reasons, the material choices for these nozzles are limited. The nozzle material should be quite hard, so as to be resistant to wear from handling and fluid flow. However, it must not be so brittle that chipping results from the fabrication process or from regular handling. The nozzle material should be dimensionally stable over time and

operating conditions, including the flow of binder fluids. A material that swells due to contact with any binder solutions will clearly not be dimensionally stable.

Other interactions between nozzle material and binder fluids are equally important. Any nozzle material that is not resistant to binder solvents will have a short useful lifetime. For example, composites bonded with epoxy will fail when printing chloroform, because the binder will gradually dissolve the nozzle. Corrosion and resulting wear of cobalt in tungsten carbide nozzles severely limit the useful life of these nozzles with water-based binder fluids. Figure 13 shows an end view of a tungsten carbide cobalt nozzle with severe corrosion. The orifice diameter and outside edge diameter are shown. Only a small section of the bright, polished orifice face remains.

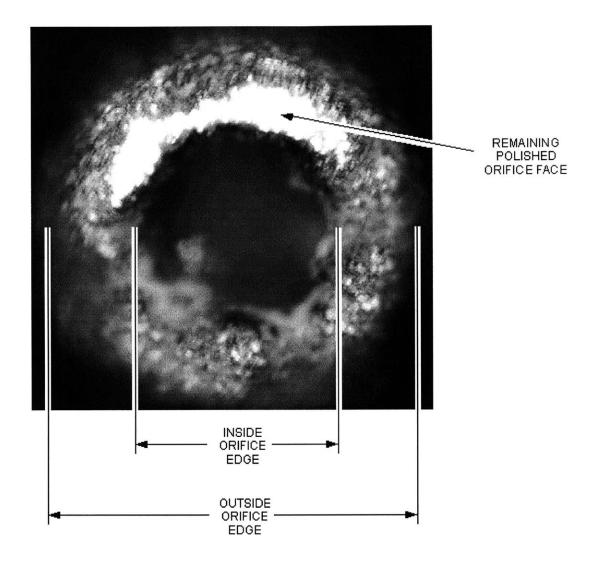


Figure 13. Corroded tungsten carbide cobalt nozzle. Only a small section of the original polished orifice face remains uncorroded.

Further, the nozzle material will determine the wetting angle of the meniscus at the orifice for each binder solution. Materials that are less wetted (higher contact angle) by the intended binder solution allow a larger spherical cap to form before weeping occurs but have a larger minimum cap size to maintain a fully wetted orifice face. On the other hand, more wettable materials, which have a lower contact angle, are also good

nozzle candidates because they allow a very small spherical cap to entirely wet the orifice face.

Candidate materials then include ceramics such as alumina, ceramic-metal composites such as tungsten carbide cobalt, and several other hard metals. While alumina is electrically insulating and tungsten carbide cobalt is electrically conductive, printhead design can easily accommodate both cases. Heat conductivity should not factor into material selection. Engineering polymers such as Delrin (acetal) have proved too soft for the fragile nozzle tip, but they could be molded. Additionally, many polymer materials swell in water, thus changing shape over time while operating.

2.5. Fabrication requirements

Besides the tight geometric tolerances called for at the orifice end of a positive pressure nozzle, a few other fabrication requirements make the production of these nozzles somewhat difficult. The orifice face itself should be smooth; otherwise, unpredictable and asymmetric wetting conditions on the orifice face will cause off-axis drop ejection. In order to achieve this necessary surface finish, polishing of the orifice face must be accomplished while maintaining a sharp outside edge. Additionally, any polishing must be carried out to a precise depth in order to achieve consistent and desirable throat depths.

As a final requirement, provision must be made for attachment of the nozzle to the rest of the printhead assembly. The interface should be durable, secure, airtight, and consistent, leaving a minimum of edges and corners to which air bubbles might attach.

2.5.1 Vendor

Gaiser Tool Company (Ventura, CA) makes standard and custom wire bond and vacuum pickup tools. Custom tungsten carbide cobalt and alumina tools from this vendor can be used successfully as Drop-on-Demand nozzles, although alumina is preferred because tungsten carbide cobalt can be corroded rapidly by common binder fluids. Please see Appendix B for details of the best-to-date custom tool for the positive pressure Drop-on-Demand printhead.

3. The Function of Positive Pressure Drop-on-Demand Printheads

3.1. Positive pressure

The basic premise of the positive pressure Drop-on-Demand printhead is that the orifice face be completely wet by the binder fluid both when the printhead is generating drops and when it is idle. This intentional wetting is achieved by maintaining a small and constant positive pressure (relative to atmosphere) in the binder fluid at the orifice.

If the meniscus is upstream of the orifice exit (in the "throat"), surface tension and positive pressure will drive the meniscus towards the orifice exit regardless of the magnitude of the positive pressure.

Once the meniscus reaches the orifice exit, it attaches to the edge of the orifice. At this point, the magnitude of the positive pressure becomes important. In an equilibrium state, this positive pressure, supplied by the upstream fluid supply system, is balanced at the binder-air interface by Laplace pressure. For positive pressure, the meniscus bulges out from the orifice in a spherical cap. The balance of positive pressure and surface tension determines the radius of the spherical cap. For a hemisphere, the force from the positive pressure and the force from the surface tension are given by

$$F_{pressure} = F_{surface}$$
 (Equation 2)

$$P\pi a^2 = 2\pi a\sigma \tag{Equation 3}$$

$$P = \frac{2\sigma}{a}$$
 (Equation 4)

where a is the hemisphere radius. This Laplace relation holds for any spherical cap meniscus, so the pressure necessary to produce a cap of a given radius r, called the Laplace pressure, is

$$p_{Laplace} = \frac{2\sigma}{r}$$
 (Equation 5)

As positive pressure increases, the meniscus bulges out farther as its radius decreases until either the binder fluid wets out onto the orifice face or the meniscus becomes hemispherical, with the same radius as the orifice itself. The latter case is only possible for fluids that have a contact angle of greater than ninety degrees with the solid orifice material (non-wetting). Otherwise, wetting out will occur as soon as the binder fluid meniscus bulges out enough that it reaches its natural contact angle.

For non-wetting systems, wetting of the orifice face must be forced, usually by using a combination of static positive pressure and pulsed pressure waves, of the kind used to eject drops. However, reduction of surface tension of the binder allows it to wet the orifice face without forcing. Similarly, an increase in the surface energy of the orifice face, either by changing materials or by surface treatment, can transform the system from non-wetting to wetting. The surface treatment could be, for example, mechanical roughening, or chemical, as in coating or etching.

Regardless of the method of wetting the orifice face, the equilibrium meniscus locates itself at the outside edge of the orifice, forming a spherical cap covering the entire orifice face. The thickness of the cap can be varied by adjusting the level of positive pressure in the fluid at the orifice. As the thickness of the cap increases, the angle between the tangent plane to the meniscus at the orifice outside edge and the plane of the orifice face increases. This internal angle is shown in Figure 14.

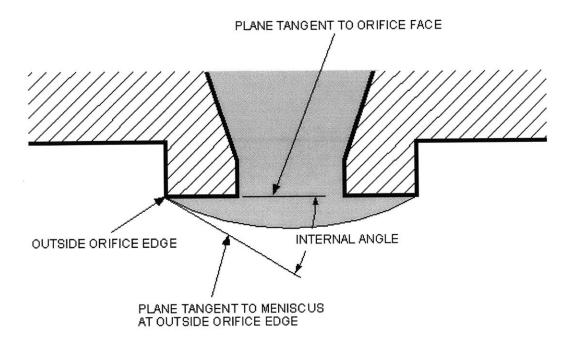


Figure 14. Internal fluid angle. This is the angle formed by the meniscus where it meets the outside orifice edge. This angle must be maintained greater than the contact angle for the system in order to have complete wetting of the orifice face.

As long as this internal angle of the fluid at the orifice edge remains above the contact angle for the system, the cap is self-sustaining. The positive pressure required to create a cap with this contact angle relative to the orifice face is the minimum pressure to maintain the completely wetted orifice face.

The other extreme is shown in Figure 15: when the spherical cap is expanded to the point where the angle between the tangent to the fluid surface at the attachment point and the plane of the outside orifice wall reaches the critical contact angle, the fluid will begin to wet over the orifice outside edge. This condition is approximately 90 degrees beyond the minimum wetting angle described and shown above in Figure 14. This fluid

"weeping" constitutes a failure in most cases, as the purpose of that edge is to provide a well-defined boundary for the fluid.

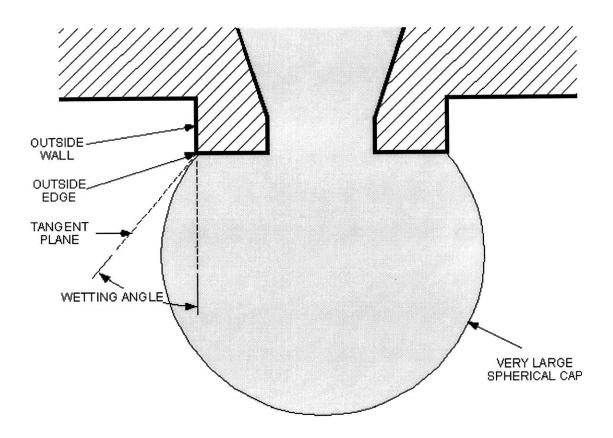


Figure 15. Maximum cap size before weeping. If the spherical cap was any larger, the wetting angle shown would reach the system contact angle and the fluid would wet the outside wall, a condition called "weeping."

The minimum positive pressure to maintain a cap is determined by the binder solution contact angle with the orifice face and the size of the orifice face.

$$P_{\min} = \frac{2\sigma}{R_{face}} \sin(\alpha_{contact})$$
 [Derivation in Appendix C] (Equation 6)

The maximum positive pressure allowed before weeping occurs depends to some extent on the quality of the outside edge; both the finite radius of the edge and the certainty of small chips or other flaws limit the maximum spherical cap size. Usually, the maximum allowable pressure is that required for a hemispherical cap:

$$P_{\text{max}} = \frac{2\sigma}{R_{face}}$$
 (Equation 7)

Even though a larger spherical cap is possible, the hemisphere represents the highest pressure (smallest radius) condition.

Between these extremes, the orifice is completely wet by a spherical cap. The maximum thickness of the cap (at the center) can be set by varying the positive pressure. Assuming a spherical cap governed by the Laplace pressure condition and using geometric relations, the thickness of the cap, shown in Figure 16, can be found to depend on the surface tension, the positive pressure, and the orifice face radius as follows.

$$h_{cap} = \frac{2\sigma}{P} - \sqrt{\frac{4\sigma^2}{P^2} - R_{face}^2}$$
 [Derivation in Appendix D] (Equation 8)

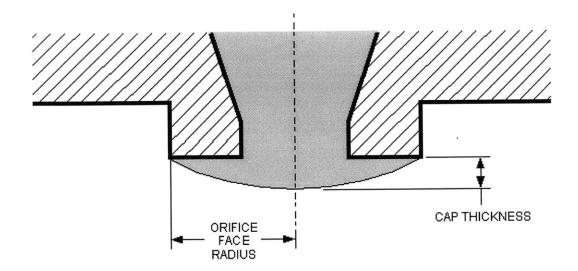


Figure 16. Spherical cap thickness. The cap thickness should be significantly less than the orifice face radius. If the two are equal, the spherical cap is a hemisphere.

This cap thickness affects drop formation in several ways. The ratio of cap volume to drop volume is a dimensionless parameter that gives the relative importance of the fluid cap in the jetting process. The drop diameter usually scales with the orifice diameter, so the volume ratio may be small because the outside orifice edge is only slightly larger than the orifice itself, or because the positive pressure is only slightly above the minimum required for wetting. In either case, such a minimal cap most likely will be completely removed each time a drop is formed. This dimensionless volume ratio parameter is given by

$$V_{ratio} = \frac{V_{cap}}{V_{drop}} \approx \frac{\left(\pi R h^2 - \frac{\pi h^3}{3}\right)}{\left(\frac{4}{3}\pi a^3\right)} = \frac{3}{4} \frac{h^2}{a^2} \left(R - \frac{h}{3}\right)$$
 [Derivation in Appendix E] (Equation 9)

For lower surface tension binder solutions, a lower applied positive pressure is necessary to generate a given spherical cap volume. The ideal positive pressure is usually the minimum amount necessary for complete wetting of the orifice face, plus enough of a margin to ensure complete wetting even for some variation of other parameters. If the orifice face is large enough that surface waves are an issue, a thinner fluid cap (lower pressure) will reduce the wave effect because the waves will damp out faster.

Other effects of the size of the spherical cap can be seen in the following figures. First, some control over drop size can be accomplished by varying the amount of positive pressure. Increased pressure leads to increased size of the fluid cap, which in turn allows more fluid to be ejected in each drop, as shown in Figures 17 and 18. Larger drops cause larger overall flow rate (for the same drop frequency).

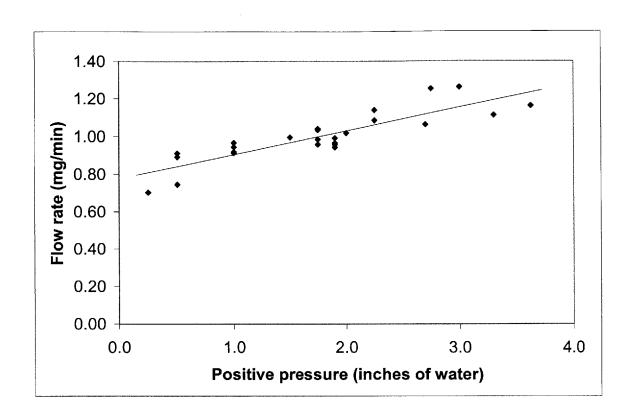


Figure 17. Flow rate variation with pressure for ethanol. Measurements were taken and proved to be relatively stable over a 24 hour period. Flow rate of 1 milligram per minute corresponds to a drop diameter of approximately 32 micrometers for this drop frequency of 1000 Hertz.

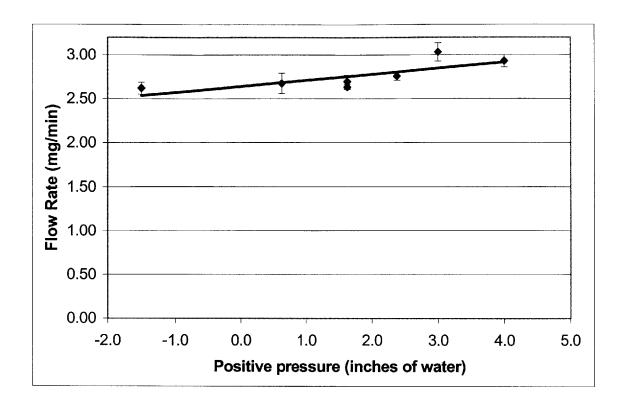


Figure 18. Flow rate variation with pressure for PEI in water. Flow rate of 2.75 milligrams per minute corresponds to a drop diameter of approximately 44 micrometers. Error bars show the uncertainty in measurements due to resolution of the balance.

On the other hand, an increase in the size of the spherical cap, as provided by an increase in positive pressure, also acts to slow down the ejected drop above a certain point. This effect can be beneficial when satellites are present, because they will often merge more readily with the main drop when the main drop is slower. In Figure 19 below, this control over satellites with pressure is demonstrated. At a particular operating point of peak-to-peak voltage and level of positive pressure, very little velocity is sacrificed, but satellites are removed. Any further increase in pressure beyond this point will bring a continuous decrease in drop velocity.

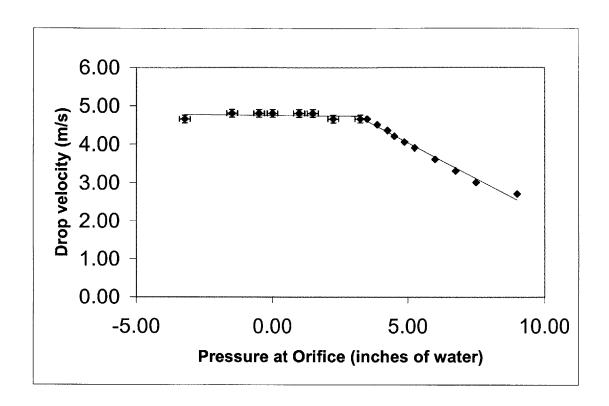


Figure 19. Satellite control with pressure. Data points with extra lines indicate the presence of satellites. The fluid is water.

3.2. Waveform and Short Reflections

Another important set of parameters in the operation of the positive pressure printhead determines the quality of drop formation: the waveform applied to the piezo-electric actuator. Up to this point, the discussion has focused on the static equilibrium state of the fluid at the orifice. Drop formation is dynamic, of course, and requires a sudden change in pressure at the orifice. This sudden pressure change can be accomplished by a piezo-electric element upstream of the orifice. A sudden change in shape of the piezo element creates a pressure wave that travels through the binder fluid to the orifice, where, under the right conditions, a drop can be ejected.

The motion of the piezo is related to the change in electric field across its electrodes, which is generated by the drop-ejection waveform applied to the electrodes. For the purposes of this discussion, a positive change in the applied voltage creates a positive pressure change in the binder fluid, and vice versa. For example, a sufficiently large positive waveform step should generate a large enough pressure wave in the binder to eject a drop from the orifice.

Any applied pressure wave will, of course, be added to or subtracted from the quiescent positive pressure supplied farther upstream. However, only the rapid change in pressure associated with the waveform applied to the piezo makes a difference for drop ejection; the quiescent level only matters in that it determines the meniscus condition before drop ejection occurs.

Further, the induced pressure waves travel in both directions from the piezo; they reflect from the orifice, the supply side of the printhead body, and any other abrupt changes in the fluid path. These reflections can be used to amplify the pressure change by sending a reinforcing wave at the right time so that it adds with a reflected wave (see Wallace, for example). A typical drop-ejecting pulse can be generated in this way by first sending a negative pressure wave, which reflects as a positive wave, and then reinforcing this positive wave with another positive wave. The time between sending the negative wave and sending the reinforcing positive wave is given by the time it takes the negative fluid wave to travel to the point of reflection and back. This method amounts to first expanding the piezo (negative pressure wave), holding, then contracting (positive wave). A typical waveform that achieves these piezo geometry changes is shown in Figure 20. Indicated are the parts of the waveform that correspond to the initial

expansion, the expansion hold time, the drop-producing contraction, the contraction hold time, and the final expansion back to the quiescent state. Also indicated is the total peak-to-peak voltage.

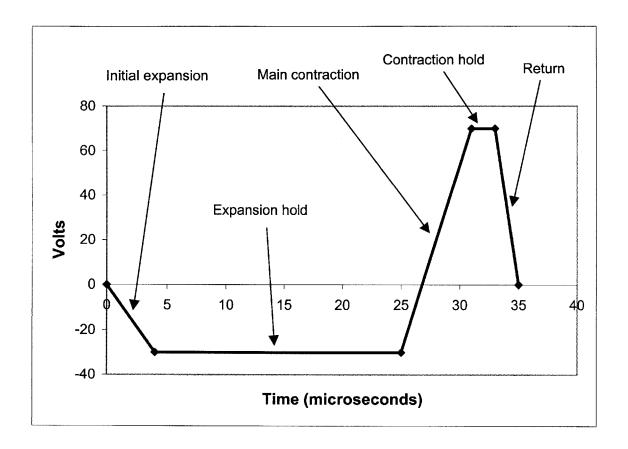


Figure 20. Typical waveform. The five main sections are highlighted.

Depending on the printhead geometry and the binder fluid, the expansion hold time can be adjusted to give maximal wave reinforcement and overall printhead efficiency. The hold time should be approximately

$$t_{\text{exp}\,ansion} = \frac{2l}{c}$$
 (Wallace) (Equation 10)

where the relevant length is the distance from the actuator to the reflecting end, and the relevant wave velocity is the speed of sound in the binder fluid, given by the square root of the bulk modulus over the density of the fluid:

$$c_{sound} = \sqrt{\frac{B}{\rho}}$$
 (Equation 11)

This reinforcement from the short reflection can be quite evident as expansion hold time is varied, as shown in Figure 21, which shows a strong maximum in printhead efficiency (as measured by drop velocity) at the predicted value of the expansion hold time.

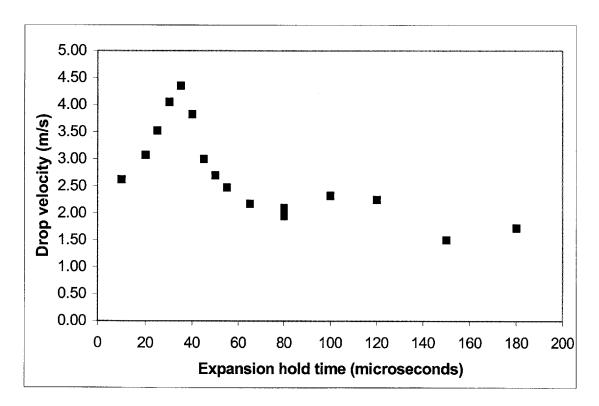


Figure 21. Importance of the expansion hold time. The large peak at 35 microseconds indicates a significant reinforcement of the expansion pulse for that value. These data were taken with PAA in water with 2 inches of positive pressure using a typical 40 micrometer orifice, 90 micrometer orifice outside edge diameter nozzle.

In Drop-on-Demand printing, it is almost always desirable to eject a single drop without creating additional droplets (satellites). To this end, the length of the ejected fluid column should be kept as short as possible. Longer fluid columns are more likely to break up into several drops, although the final form of an ejected column also depends on the relative velocity of the front and back of the column. That is, if the rear of the column has a higher velocity than the front, it will overtake and merge with the front before breaking up into two or more drops.

3.2.1 Control over velocity with waveform

By far the most important parameter of the waveform applied to the piezo is the total peak-to-peak voltage. Once the other parameters are optimized, the total energy put into the piezo determines how much energy (in the form of pressure waves) is transferred to the fluid and eventually to the ejected drop (size and velocity). Velocity can be directly controlled by varying the peak-to-peak voltage. The relationship is linear over a broad range of drop velocities, as shown in Figures 22 and 23.

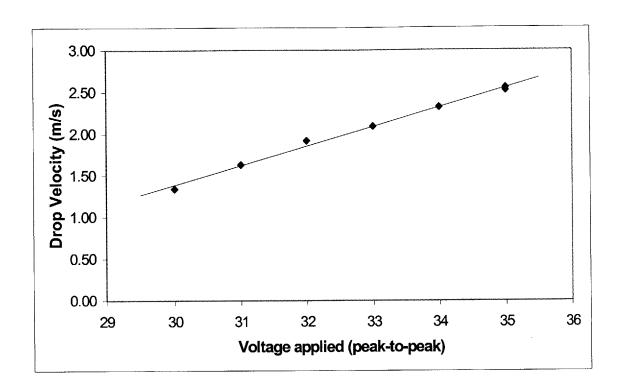


Figure 22. Drop velocity variation with voltage for ethanol. The linear relation is typical for all fluids and all operating conditions. Pressure is 1 inch of water, and the nozzle is the standard alumina 40 micrometer orifice, 90 micrometer outside edge diameter.

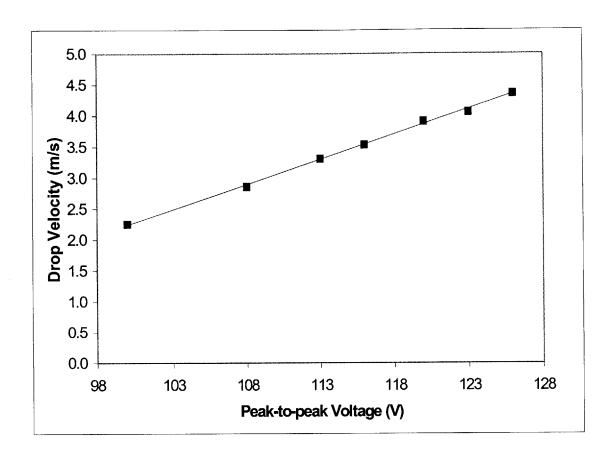


Figure 23. Drop velocity variation with voltage for PEI in water. Once again, the linear relationship is typical. This printhead used the standard 40 micrometer orifice and 90 micrometer orifice outside edge diameter, and pressure level was 1.25 inches of water.

3.2.2 Control over drop size (flow rate) with waveform

For all Drop-on-Demand printheads observed, the drop diameter has scaled exactly with the orifice diameter. Indeed, drop diameter is usually the same as the orifice diameter, within about 25 percent. Even though the drop size is almost completely determined by the orifice size, and to some extent the level of positive pressure, it can be varied within a narrow range by adjusting waveform parameters. Certainly the drop size varies with the peak-to-peak voltage, although not as strongly as the velocity. An

increased voltage generates a larger drop, as shown in Figure 24 below. The transition times (pressure pulse lengths) vary the drop size as far as they vary the ejected fluid column length.

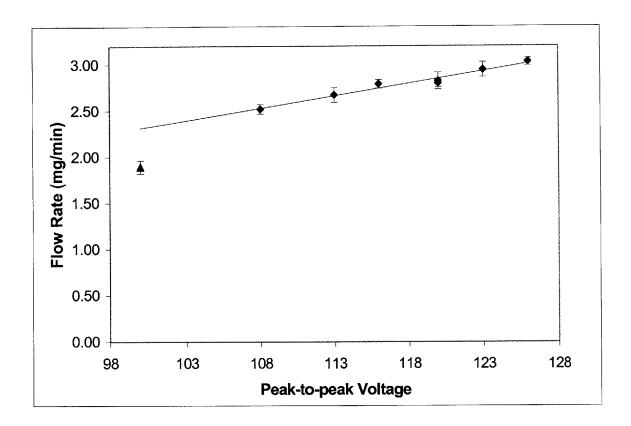


Figure 24. Flow rate variation with voltage. The linear relationship here is less pronounced than with velocity. Error bars are calculated based on the resolution of the balance used for measuring the mass of fluid printed in a measured time period. Standard alumina nozzle.

3.3. Drop frequency and Long Reflections

In the following discussion of reflections, it is important to distinguish between the four distinct types of reflection: long, short, fast and slow. "Long" and "short" reflections refer to the distance (and time) traveled before reflection. Long reflections generally are relevant to drop formation subsequent to the drop which caused the pressure wave which is being reflected, while short reflections are relevant to the immediate drop, as discussed above in the Waveform section. "Fast" and "slow" reflections refer to wave speed in whatever medium is carrying the wave. For example, in the printhead, there are two simultaneous waves: the fast one traveling through the stainless steel at 5000 meters per second, and the slow one traveling in the binder fluid (1500 meters per second for aqueous binders, 1100-1200 meters per second for alcohols). In the supply tubing, there are also two simultaneous waves, but they are reversed: the fast wave is the wave traveling in the fluid, while the slow wave travels in the polymer tubing (500-1000 meters per second).

A true Drop-on-Demand printhead ejects a drop whenever the appropriate waveform is sent to the actuator (piezo, for example). Each drop should be independent of the drops produced before and after it, and each should have the same properties regardless of the time elapsed between drops.

In practice, several forces combine to limit the frequency at which drops can be produced in this Drop-on-Demand mode. Clearly the upper limit has been passed if the drop waveforms overlap each other. This overlap limit, given by the reciprocal of the period of the drop-ejection waveform, is rarely reached.

$$f_{overlap} = \frac{1}{t_{waveform}}$$
 (Equation 12)

3.3.1 Resonant features

Instead, other effects limit the true Drop-on-Demand range to much lower drop ejection frequencies. In fact, drop generation at a frequency near any resonant frequency of the system will result in a distorted Drop-on-Demand. Such resonant features include meniscus oscillations, mechanical vibration of the printhead, and internal fluid reflections from the various fluid path interfaces. These reflections and resonances are at relatively long distances and relatively long time scales, and have the greatest effect not on the present drop ejection, but on subsequent drops. These "long" reflections are therefore distinct from the "short" reflections discussed in the "Waveform and Short Reflections" section, above, which have an immediate effect on the current drop.

Meniscus oscillation

When a drop is ejected, the breakoff event leaves the remaining meniscus in a high-energy state. As the meniscus returns to its lowest-energy quiescent state, it undergoes a damped oscillation along the way. Attempts to eject another drop before the meniscus has returned to quiescence will result in various levels of altered performance, depending on where in the oscillation cycle the next drop ejection pulse comes. The frequency of these meniscus oscillations is related to the surface tension, density, and length scale (orifice radius), and the level of damping is determined by the fluid viscosity. For a restoring force provided by surface tension in the meniscus and inertial forces acting on the volume of fluid in a hemisphere

$$f_{meniscus} = \frac{1}{2\pi} \sqrt{\frac{2\sigma}{\frac{1}{2}m_{drop}}} = \frac{1}{2\pi} \sqrt{\frac{3\sigma}{\pi \rho a^3}}$$
 [Derivation in Appendix E] (Equation 13)

Meniscus oscillations for three different nozzle diameters have been observed directly. These observations agree well with predicted values, as shown in Figure 25.

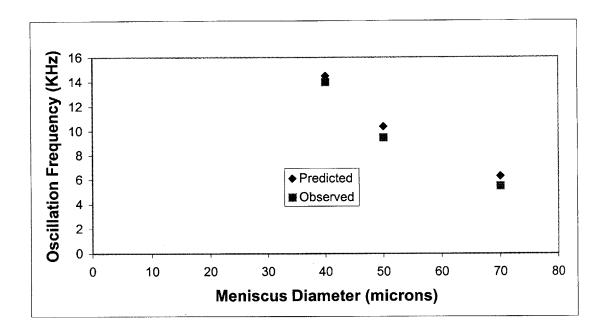


Figure 25. Meniscus oscillations. The frequency of meniscus oscillations has been predicted and measured for three different orifice diameters using a negative pressure (-4 inches of water) ruby orifice and water binder fluid. With water, the negative pressure works to prevent wetting onto the orifice face, so that the meniscus boundary is always the inside edge of the orifice.

Surface waves

For larger orifice faces in which the aspect ratio of outside orifice edge diameter to orifice diameter is much greater than one (approximately five or more), the meniscus has a more complicated motion. Rather than triggering a simple in-and-out oscillation,

drop ejection causes a series of surface waves on the much larger meniscus. These waves travel out from the center of the meniscus, where the drop breakoff occurs, and then reflect from the edge of the fluid cap back towards the center. These waves take longer to damp out than the rapid oscillations associated with a smaller meniscus, and thus limit the upper drop formation frequency more severely, especially for a thick fluid cap, which sustains surface waves longer. The following sequence shows a moderate sized orifice face sustaining a small surface wave for the entire period between drop ejections.

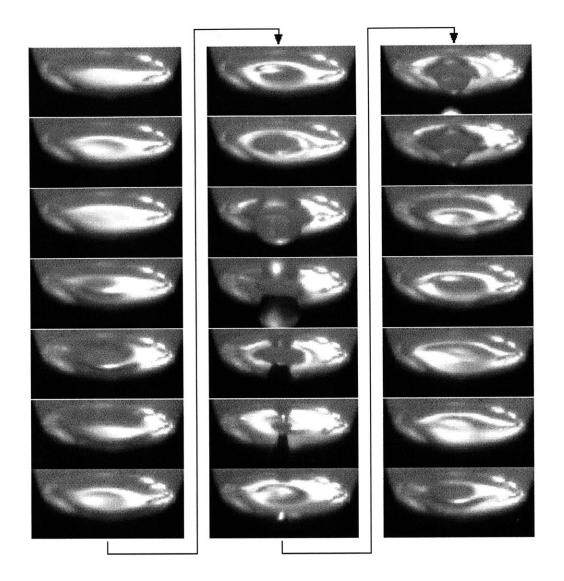


Figure 26. Surface waves in water at 3.25 inches of positive pressure. At just over 3 kilohertz drop frequency, this series of images represents almost the entire period between drops. The time between frames is 10 microseconds. The first frame is at a 0 microsecond delay from the initiation of the waveform pulse, and the oscillations there are from the previous drop ejection. Halfway through the sequence, the present drop is ejected, starting a new wave. These waves are rather small because the orifice face is only slightly larger than desirable: 200 micrometers diameter.

Printhead body reflections

Depending on the particular printhead construction, mechanical resonances of the pressure wave actuator housing may be on a scale that interferes with drop formation. Usually, these mechanical vibrations are at a higher frequency, and damp out faster, than drop ejection frequencies. However, they are occasionally relevant on the individual drop-formation waveform ("short") scale. Typical wave speed in the stainless steel printhead body is 5000 meters per second, which means that a wave travels the length of the printhead (approximately 25 millimeters) in 5 microseconds, which is much shorter than either the 40 microsecond waveform or the 1000 microsecond typical time between drop ejections.

Another series of printhead reflections may be important on the "long" scale: subharmonics of the end-to-end fluid pressure wave reflections. These subharmonics might arise because one end of the printhead inverts the pressure wave, and the other end reflects it without inverting. Therefore, a positive pressure wave initiated in the middle of the printhead, at the piezo, must travel four lengths of the printhead before a positive reflection of it returns in the same direction to the point where it started (and where the next wave will be initiated for the next drop). If both ends of the printhead were inverting, or if both ends were non-inverting, the wave would only need to travel two printhead lengths before a positive reflection of it returned in the same direction as the initial wave. Therefore, the four-length wave has double the distance to travel and half the resonant frequency compared to the two-length wave.

The idea that one end of the printhead might be inverting and the other end noninverting was investigated with a special printhead outfitted with several very small piezo elements, in addition to the usual large actuating element. These smaller piezo pieces were monitored for any traveling waves which might disturb them enough to generate an electrical signal. Thus, the main piezo would send waves, and the small piezos would receive them. Although the fast waves traveling through the stainless steel itself tended to mask other waves, the polarity of reflected waves seemed to indicate that the upstream end of the printhead, where the supply tube attaches, is inverting, while the nozzle end is non-inverting.

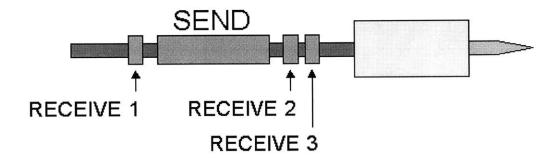


Figure 27. Send/receive piezo assembly. Receivers on both sides of the send piezo (8 millimeter length) indicate how far a wave has traveled by indicating the delay time after the send pulse occurs. Receivers (1 millimeter length) 2 and 3 are close to each other and indicate the *direction* a wave is traveling.

Upstream reflections

A final system resonance includes all fluid reflections from farther upstream in the binder supply path. These long upstream reflections appear to have the most effect on subsequent drop formation. The pressure wave generated by the actuator (piezo, for example) travels both upstream and downstream. The downstream wave ejects a drop (usually after one short reflection). Most of the upstream wave is wasted, but reflections of that wave will certainly reappear in the active region of the printhead after a delay. The length of the delay is determined by the distance the wave travels before encountering supply tube connections or other abrupt fluid path transitions. The reflection that travels the farthest without damping out before returning to the printhead will be most likely to interfere with the next drop formation sequence. That reflection will limit effective drop formation to frequencies less than the implied reflection frequency.

$$f_{drops} < f_{reflection} = \frac{2l_{reflection}}{c_s}$$
 (Equation 14)

Once drop ejection frequencies approach any of these resonant frequencies, uniformity of drops cannot be assured, even for small changes in drop frequency, and the printhead will no longer be operating in true Drop-on-Demand mode. For example, drop velocity will vary substantially with frequency when operating outside the true Drop-on-Demand range, as shown in Figure 28. In true Drop-on-Demand range, the ejection of each drop is independent of the drops before and after it, so the drop velocity remains constant over a wide range of drop frequencies. When drop frequency is increased to a range above the true Drop-on-Demand range, a variety of resonance features of the system begin to cause drop ejections to affect each other in constructive and destructive modes that are highly frequency dependent.

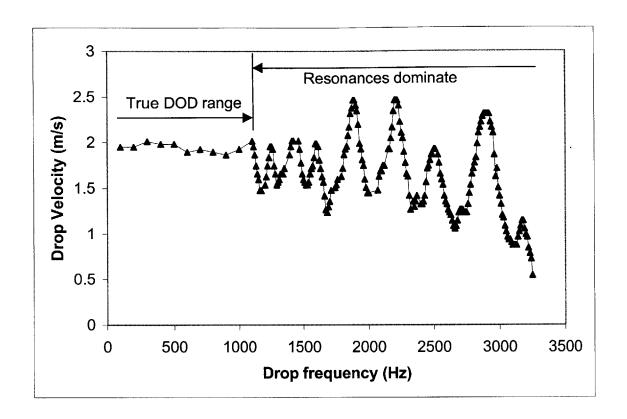


Figure 28. Typical drop velocity variation with drop frequency. Only the flat section of the curve, up to about 1000 Hertz, is true Drop-on-Demand range. When printing at higher frequencies, each drop depends on the previous drop to such an extent that the independence of drops needed for Drop-on-Demand is no longer present. This is low-velocity solvent printing (ethanol) with a standard size tungsten carbide cobalt nozzle.

Supply Tubing

Fluid pressure wave reflections from the interface between the printhead and the supply tubing are important on the individual drop formation time scale (short), because they return into the printhead very soon after the initial pressure wave is generated. Longer time scale reflections from the interface between the supply tubing and the reservoir are important because certain drop ejection frequencies allow the reflected wave

from one drop to affect the next drop. Similarly, slower peristaltic waves traveling through the supply tubing can return to the printhead and affect subsequent drop formation.

As a demonstration of this effect, note the substantial difference in frequency response between a typical length of supply tubing (approximately 80 millimeters) and an extremely long length of supply tubing (2000 millimeters) in Figure 30. The dramatic drop velocity dependence on drop frequency for the typical length supply tubing shows the importance of these reflected waves. The frequency dependence almost entirely disappears when using the long supply tube, which eventually damps waves before they reflect back to the printhead.

A variety of experiments have been carried out to determine the effects of the supply tube on drop formation. With the exception of silicone, all tube materials (including Tygon, EVA, and Teflon) seem to behave identically. Silicone supply tubing may provide a sub-par initial (short) reflection from the interface between the printhead and the tube, resulting in troublesome drop formation. Low velocity and a spray of satellites result.

Besides material choice, two other supply tube variables have been explored: length and inside diameter.

Inside diameter has a clear effect on individual drop formation. Using the same material (Teflon), a small inside diameter of 0.18 millimeters was compared to a large inside diameter of 0.71 millimeters over multiple trials. In all cases, the smaller inside diameter caused higher velocity drops, presumably because of a stronger (short) reflection from the interface where the tubing connects to the printhead.

However, the smaller inside diameter tubing caused more rapid variation in drop velocity with increasing drop frequency, as shown in the following figure. Because this smaller inside diameter tubing has a much thicker wall, the slow wave traveling in the tubing is much faster (the tube wall is stiffer). The explanation, then, is that the reflections return to the printhead faster in the thicker wall (smaller inside diameter) Teflon tubing.

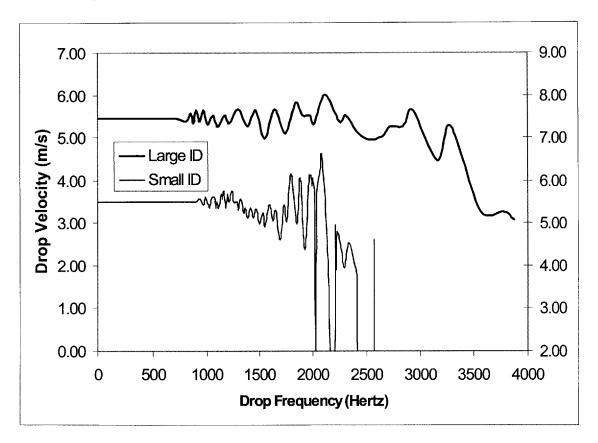


Figure 29. Large and small ID 80 mm length Teflon tubing compared. The much more rapid velocity variation with frequency of the small inside diameter tubing is apparent. The small inside diameter tubing graph is translated downward (secondary axis) for clarity, but has the same scale. Both versions have low-frequency (DOD) velocity of 5.5 meters per second. The fluid is water and the nozzle is standard alumina. Positive pressure is 5 inches of water.

Finally, the following hypothesis was tested: these long reflections from the reservoir end of the supply tubing might be damped out if the tube itself was extremely long. A 2000 millimeter (2 meter) length of supply tubing was compared to the typical 80 millimeter length. Diameter and material were the same. The following figure shows the results, which indicate that the long reflection in the long tube indeed damps out before returning to the printhead to interfere with subsequent drops.

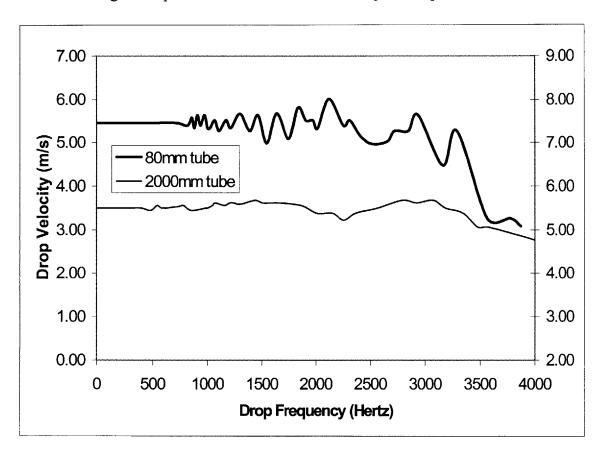


Figure 30. Long and short supply tubes compared. Both are large ID (0.71 mm) Teflon. Clearly the long tube (2000mm) sharply reduces the velocity variation with drop frequency. Again, the long tube graph is translated downward (secondary axis) for clarity, but has the same scale. Again, both versions have low-frequency velocity of 5.5 meters per second. The fluid is water and the nozzle is standard alumina. Positive pressure is 5 inches of water.

In fact, true Drop-on-Demand drop frequencies up to approximately three times greater (3 kilohertz versus 1 kilohertz) are possible with the long supply tube. Later experiments showed that a minimum supply tube length required for this high drop frequency range is approximately 500 millimeters.

Please see the Future Work section of the Conclusions chapter for more information about other experiments to be done on this topic.

3.4. Minimum drop formation frequency (maximum idle time)

On the other extreme, low frequency drop formation should be possible with only one limitation: evaporation of binder fluid at the orifice. For binders with polymers or other dissolved solids, evaporation of the solvent will quickly change the concentration of solids at the orifice. To the extent that this change in concentration affects the fluid properties (viscosity and surface tension) of the binder, drop formation will suffer. In addition, any polymer skin or precipitates that develop will hinder drop formation. Solid deposits around the edge of the orifice affect the wetting characteristics of the orifice so that drop ejection capability degrades. The use of humectants to decrease the evaporation of solvent may increase the maximum idling time between drops.

Normally, the lower limit of drop frequency is far lower than desired printing frequency. However, this lower limit does set the maximum printhead idling time, which may be on the order of ten to one hundred seconds.

4. Printhead Construction

One successful implementation of the positive pressure Drop-on-Demand printhead is as shown in Figure 31. The printhead consists of a stainless steel tube actuated by a cylindrical piezoelectric ceramic. The alumina nozzle attaches to the stainless steel tube by means of a tight-fitting Delrin coupling. Flexible binder supply tubing is fixed to the upstream end (thin-wall section) of the stainless steel tube.

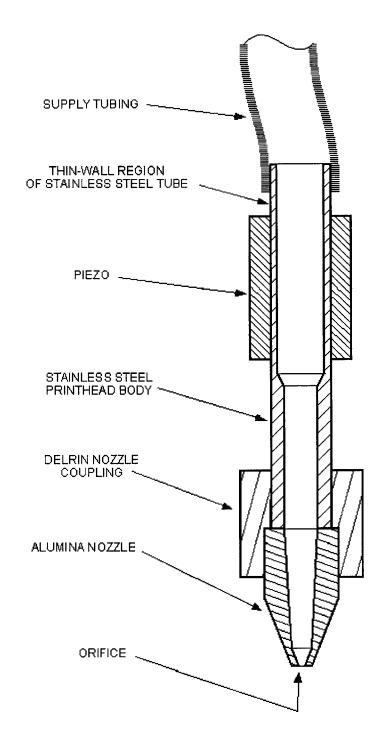
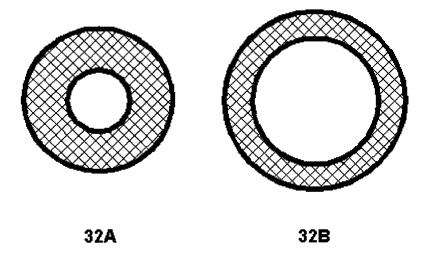


Figure 31. The drawing is schematic. Large features are to scale, but smaller features (the change in inside diameter of the stainless steel tube, and the orifice end of the nozzle) have been exaggerated for clarity.

4.1. Description of printhead elements

4.1.1 Cylindrical piezo

The cylindrical piezoelectric ceramic is the printhead actuator. As shown (exaggerated) in Figure 32, when a voltage is applied across its electrodes, the piezo contracts (32A) or expands (32B), depending on the polarity of the applied voltage. In particular, the inside diameter of the piezo grows or shrinks. Since the piezo is tightly coupled (soldered) to the stainless steel tube, which holds the binder fluid, every contraction or expansion of the piezo pushes or pulls on the stainless steel tube, which in turn causes a pressure wave in the fluid.



Figures 32A and 32B. Piezo contracted and expanded. In general, both inside and outside diameters change.

Geometry

The geometry of the cylindrical piezo determines how effective it will be in transferring power to the binder fluid. A typical piezo is shown in Figure 33. For a given inside diameter, the radial displacement of the inside piezo surface decreases with increasing outside diameter. Thus, relatively thin-walled piezo devices affect greater volume change in the printhead. Both the radial displacement and the axial displacement are proportional to the voltage applied across the piezo electrodes. Each piezo material has different strain constants for directions parallel and perpendicular to the electrodes. For PZT5H, the perpendicular strain constant is almost three times greater in magnitude than the parallel strain constant. It is possible to choose an outside diameter such that application of voltage to the piezo results in a displacement of the inside surface only (the outside surface of the cylinder remains at constant diameter). However, such a constraint is not necessary for the current device, which has a 0.030 inch inside diameter and a 0.050 inch outside diameter.

In addition, the volume change in the printhead will be greater for longer piezo devices. However, the piezo should not be so long that the time it takes a pressure wave to propagate the length of the piezo is longer than the time scale of drop ejection. An 8 millimeter piezo length corresponds to a wave propagation time in water of approximately 5 microseconds, which is slightly less than typical drop ejection time.

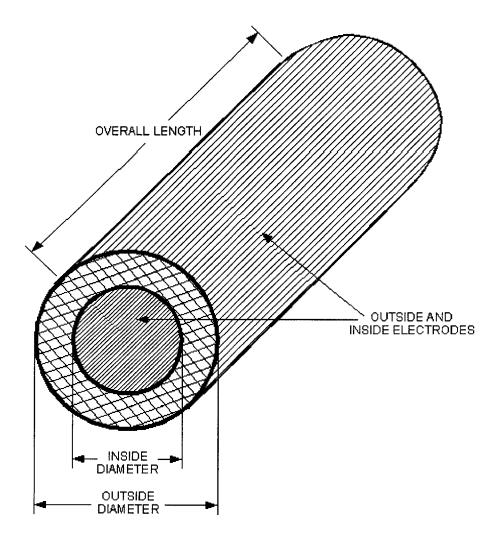


Figure 33. Typical piezo. Material is PZT5H, outside diameter is 0.050 inches, inside diameter is 0.030 inches, and length is 8 millimeters. Electrodes are electroless nickel.

Material

Piezo materials range dramatically in their properties. PZT5H from Morgan Matroc, Inc., is one of the high sensitivity piezoelectric ceramics. It has an extremely

high piezoelectric constant, which means it generates a high amount of strain for a given electric field.

Both the inside and outside electrodes of the piezo cylinder are electroless nickel. This material allows easy soldering. Neither the electrodes nor the ceramic itself need be compatible with binder solvents, as the binder fluid is entirely contained inside the stainless steel tube.

Polarization

This type of piezo can be poled in air at 425 volts for 270 seconds. Usually, the inside electrode is positive. To avoid excessive stress on the piezo during poling, the piezo should not be poled while installed on the stainless steel tube because there is a volume change during the poling process. Instead, it should be poled before installation, free of external stress.

PZT5H has a very low Curie temperature of 195 degrees Celsius, so care should be taken to keep the piezo temperature low after it has been poled. If the piezo temperature rises too much during soldering or in operation, it will be partially of completely de-poled. Similarly, care should be taken not to exceed approximately 250 volts (peak-to-peak, for 0.030 inch inside diameter, 0.050 inch outside diameter) across the piezo electrodes, to avoid de-poling.

4.1.2 Thin-wall stainless steel tube

The printhead body itself is made of a stainless steel tube formed to have a thin wall section where the piezo is attached. The thin wall allows the piezo to more easily expand and contract the tube. One end of the stainless steel printhead body attaches to the binder supply tube, and the other end accepts the nozzle containing the orifice.

Geometry

The current printhead implementation uses a piezo with a 0.030 inch inside diameter, as mentioned above. The desired outside diameter of the stainless steel tube should match well with the piezo, while leaving a very slight gap for the solder that will later ensure a good connection.

Thus, 22XX gauge hypodermic tubing can be used. With a starting inside diameter of 0.024 inches and a starting outside diameter of 0.028 inches, this gauge is well-suited for a printhead body. It is available from several vendors, including Vita Needle Company (Needham, MA). The tubing is fully hard 304 stainless steel, TIG welded and drawn.

The tubing can be further formed from one end to produce a thin-wall section with inside diameter of 0.026 inches and an outside diameter of 0.029 inches, leaving a 0.0015-inch wall thickness and an approximately 0.0005 inch gap between the flared tube and the inside of the piezo. One method of forming involves inserting the tube inside a thick-wall brass tube with inside diameter 0.029 inches. Using the point contact achieved by rotating a 0.026 inch diameter drill bit *in reverse* into the end of the stainless steel tube, the stainless steel is pushed out to the inside wall of the brass as the drill enters, and

it subsequently flows outside the drill (but inside the brass) towards the open end of the brass. The stainless thus assumes the required 0.026 inch inside diameter (set by the drill size) and 0.029 inch outside diameter (set by the brass tube).

After forming, the stainless steel tube is ready for assembly into the printhead. The thin-wall section provides lower stiffness where the piezo is attached, and the original thicker wall section allows greater strength for the nozzle to attach. Since the nozzle may be removed and replaced often, this higher strength area is important.

The forming method of shaping the tube allows very good surface finish on both the inside and outside of the printhead body.

4.1.3 Low melting temperature, no shrink solder

For attaching the piezo to the printhead body, A non-standard solder is necessary for two reasons. First, to avoid pre-stressing the piezo, the solder must have close to zero shrinkage open solidification. Second, it must have a very low melting point so as to stay well below the piezo Curie temperature (195 degrees Celsius). By poling the piezo only before assembly, it is possible to avoid the excess stress that would result from poling with the piezo soldered to the stainless steel tube.

A solder available from the Indium Corporation of America (Utica, NY), number 136, is 49 percent bismuth, 21 percent indium, 18 percent lead, and 12 percent tin. It has close to zero dimension change upon solidification and a very low melting point of 58 degrees Celsius.

4.1.4 Nozzle coupling

Finally, the nozzle containing the orifice must be connected to the printhead body. The nozzle is a 0.375 inch alumina cone-type (see Figure 16), with 90 micrometer orifice outside edge diameter and 40 micrometer orifice diameter. The main body of the nozzle has outside diameter of 0.0625 inches. To couple the alumina nozzle to the stainless steel printhead body, a Delrin sleeve is used. The nozzle has an interference fit with the Delrin sleeve, and the Delrin sleeve is sized for a press fit over the end of the stainless steel tube. See Figure 31 for the final assembly.

Delrin is used because it is dimensionally stable, has high solvent resistance, and provides a good press fit for repeatable nozzle installation. The coupling is designed to minimize small spaces where air bubbles could be trapped. It also avoids large internal diameter changes, to minimize excess fluid reflections in the printhead.

5. Support Systems and Operation

The positive pressure Drop-on-Demand printhead has little use without a support system. This system provides the fluid to be printed, the positive pressure necessary for printing as well as high pressure purging, a suitable waveform for the piezo, and inspection apparatus useful for troubleshooting and fine-tuning printhead operation.

5.1. Fluid System

The fluid system must supply suitably prepared binder fluid to the printhead. In the printhead described above, the upstream end of the stainless steel tube has a flexible polymeric tube as its supply line. The other (upper) end of the flexible tube attaches to the binder fluid reservoir, which is always mounted directly above the printhead, on the same (vertical) axis. This inline reservoir minimizes destructive pressure pulses that would otherwise be caused by net fluid acceleration in the supply line during intended printhead movements, or any other machine movements or vibrations that result in printhead acceleration in the printing (X-Y) plane.

The reservoir has one bottom outlet for binder supply to the printhead, and four top inlets. Each has an associated valve so that only one is open at a time. One is for binder fluid refill of the reservoir. This inlet line has an integral filter (5 micrometer sintered stainless steel) which removes any last particles from the binder before it enters the reservoir and printhead. The other inlets are for pressure control. One is for the high-pressure air line used when purging binder at a high flow rate through the printhead, as during startup. One is a vent to atmosphere, which allows the high-pressure air left in the reservoir after purging to vent when opened, leaving the reservoir air at atmospheric pressure. The final inlet allows the application of a variable pressure air line to the

reservoir. This variable pressure source determines the operating pressure in the reservoir during drop formation and therefore allows fine control over the operating pressure at the orifice, as explained below.

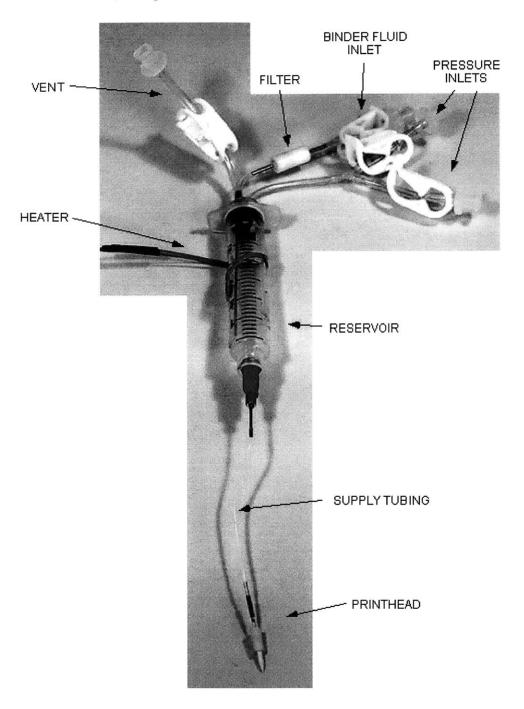


Figure 34. Binder supply reservoir. All inlets are shown, as well as the reservoir heater, the supply tubing, and the printhead.

The binder fluid inlet can easily be fed with a syringe. The high-pressure air inlet should have a line attached and supplied with approximately 10 pounds-per-square-inch air. Tight control of this high pressure source is not necessary; it only needs to be high enough to push a continuous stream of binder through the printhead with the nozzle in place. Finally, the variable pressure inlet should be coupled to a pressure source capable of supplying approximately -5 to +5 inches of water pressure to the reservoir.

Usually, the pressure at the orifice due to the height of the binder fluid in the reservoir is greater than the desired orifice pressure, which means that the pressure supplied by the variable pressure source needs to be slightly **negative**, relative to atmosphere, in order to combine to the desired value at the orifice. Since this variable pressure source determines only the pressure in the reservoir *above* the binder fluid, it must be adjusted to take into account the height of the binder fluid above the orifice. One simple and easily adjustable way to provide this variable pressure source is to use a manometer tube with a large reservoir as shown in figure 35. With this method, the pressure at the orifice is given by

$$P_{orifice} = \rho_{binder} g h_{binder} + \rho_{manometer} g h_{manometer}$$
 (Equation 15)

where h_{binder} and $h_{manometer}$ are shown in the figure. For binder fluids with density close to that of water, and using water in the manometer, the pressure at the orifice in inches of water is simply

$$P_{orifice} = h_{binder} + h_{manometer}$$
 [inches of water pressure] (Equation 16)

Adjusting the height of the flexible manometer tube is a simple way to fine-tune the pressure at the orifice.

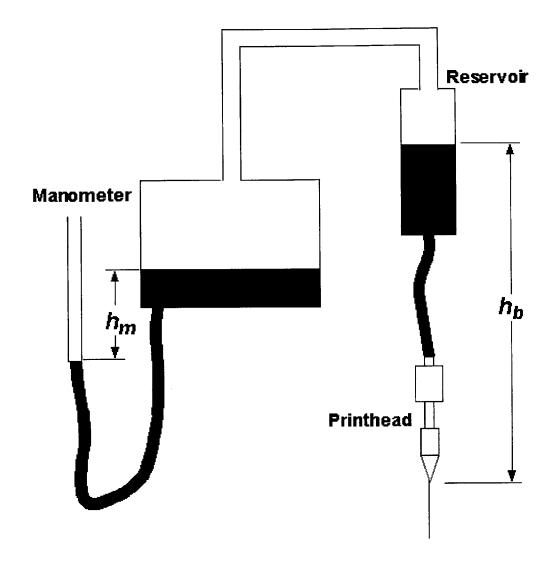


Figure 35. Manometer setup used to control positive pressure. In this example, the desired reservoir pressure is less than atmospheric, so the manometer tube is adjusted so that h_m is negative.

It is also possible to automate the pressure control so that manual adjustment of the manometer tube is not necessary. For example, a level sensor and a vacuum pump can be combined to maintain a specified pressure.

Occasionally, it is possible to run the printhead with pressure at the orifice equal to the pressure due to the height of the binder above the orifice. In this case, the variable

pressure source is not necessary, and the reservoir vent can be left open. Fine control over the pressure at the orifice can be achieved by adjusting the level of binder in the reservoir.

5.2. Heater

The final element of the reservoir is a built-in heater, which is external to the reservoir to avoid contamination of the binder fluid. This heater is used to keep the temperature of the binder fluid in the reservoir a few degrees Celsius above the temperature of the binder fluid in the printhead. Usually, the binder fluid in the printhead is at ambient temperature, so the heater only needs to heat the reservoir a few degrees Celsius above ambient. This heating is undertaken in order to prevent the appearance of air bubbles in the printhead. Of course, with an array of printheads, there is the option of heating the reservoir directly, as shown here, or heating all of the reservoirs with the same heater by heating the reservoir mounting block.

Even a tiny air bubble, with volume on the order of an ejected drop, can absorb much of the pressure change resulting from piezo contraction. If the air bubble absorbs the pressure change, drop ejection will be prevented or severely limited. Therefore, the presence of air bubbles should be avoided during printhead operation. Consider the following typical example: during printhead operation, an air bubble the size of a drop (approximately 35 pL) will absorb enough of the piezo energy to prevent drop formation. For a small temperature change from 20 to 22 degrees Celsius, absorption of air by water decreases from 0.0190 to 0.0183 cubic centimeters of air per cubic centimeter of water. Since the stainless steel body of the printhead contains about 0.0073 cubic centimeters of

fluid, the resulting change in absorption from 138 nL to 133 nL of air in the binder fluid means an extra 5000 picoliters of air may evolve in the printhead. This is equivalent to well over one hundred drop-size air bubbles.

The heater addresses the air bubble problem by slightly raising the temperature of the binder fluid in the reservoir. For many liquids, air absorption decreases with increasing temperature. The equilibrium air concentration in the binder fluid in the reservoir is therefore lower than it would be at ambient temperature. As the fluid travels out of the reservoir, though the supply tubing, and into the printhead, it cools a few degrees to ambient temperature. As it cools, it is able to absorb more air. If there are any remaining air bubbles, the fluid is able to absorb them. In any event, no more air bubbles should be released from the fluid into the printhead, even if ambient temperature varies by one or two degrees.

To demonstrate the magnitude of this effect, figure 36 shows air absorption for water. The effect is strongest when the gradient is highest. Thus, heating the binder fluid slightly above typical room temperature allows a large change in absorption with a minimal change in temperature.

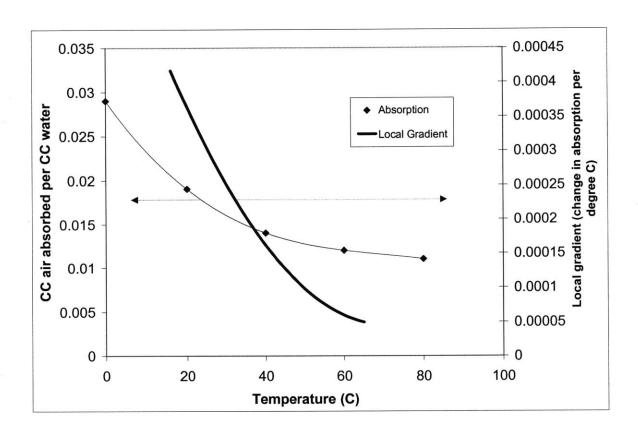


Figure 36. Effect of temperature on air absorption in water. These curves show what a dramatic effect a few degrees temperature change can have on the amount of air water will absorb. The absorption curve shows the absorption of air in water versus temperature. The gradient curve shows how quickly the absorption changes with temperature versus temperature. The gradient is very high near typical room temperature (20 degrees Celsius). Arrows indicate which axis each curve is associated with.

5.3. Supply Tubing

The supply tubing that connects the reservoir to the printhead is another important element in the Drop-on-Demand system. Besides providing the binder fluid path, the tubing also affects wave travel in the system, as discussed in the Waveform and Reflections sections above.

5.4. Startup

The following procedure outlines a typical startup sequence for the positive pressure Drop-on-Demand printhead. First, the binder fluid should be de-gassed under partial vacuum to remove as much air as possible. The controlled reservoir heater can be switched on throughout operation. After loading the fluid into the reservoir through the binder supply inlet, all other inlets should be closed and the high-pressure purge line opened. Optical verification should be made that there is a straight, continuous stream of binder fluid emerging from the nozzle. Application of the drop-ejecting waveform to the piezo should break up the continuous stream into drops quite within about ten drop diameters of the orifice exit. A useful inspection tool is a light emitting diode timed to give a short strobe pulse at a variable delay after the beginning of the piezo waveform. In combination with a high magnification lens, camera and monitor, the strobe pulses effectively "freeze" the drop breakoff for easy inspection.

Initial purging may show the drop breakoff improving over tens of seconds to a few minutes. This improvement occurs as air bubbles are entrained, dissolved and finally carried out of the printhead in the rapid fluid purging activity. When a stable breakoff is obtained, the high-pressure purge line can be closed, and the vent line opened. This action releases the remaining high-pressure air from the top of the reservoir. The vent can then be closed and the low-pressure source line opened. This line determines the quiescent pressure at the orifice. Upon application of the variable pressure source, drops should begin ejecting from the orifice at the frequency set by the electronics.

Using a camera with a high-magnification lens, the sequence of photographs in Figure 37 was obtained by incrementing the delay pulse by 4 microseconds between frames. The sequence shows the initial quiescent state, complete retreat of the meniscus

corresponding to the expansion pulse, the front end of the drop column emerging from the orifice, drop breakoff, recoil of the remaining meniscus, and effective constraint of the recoiled meniscus at the outside orifice edge.

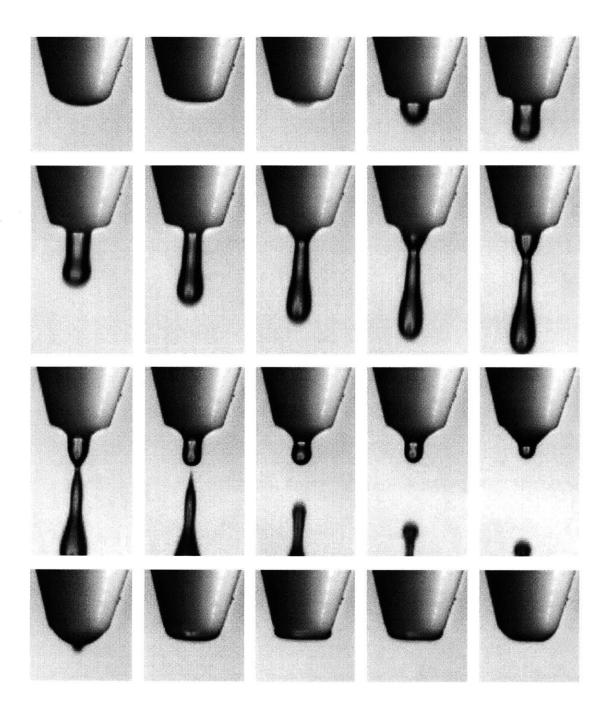
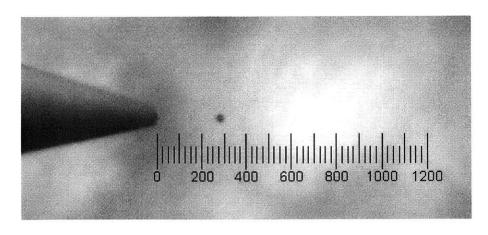


Figure 37. Drop ejection sequence. At 4 microseconds between frames, this sequence shows the first 80 microseconds of a typical drop ejection. Note the meniscus being pulled back by the expansion pulse in the first two frames. Breakoff occurs in frame 12, and then the meniscus rebounds. The third-to-last frame shows how important the sharp outside orifice edge is as a boundary to wetting over the side of the nozzle. The fluid is PEI in water, pressure is 3 inches of water, and this is the standard alumina nozzle.

One simple way to eject continuous drops at a set frequency is to load an arbitrary waveform generator with the desired drop ejection waveform (as discussed above), and the trigger the arbitrary waveform generator with a pulse generator at the intended drop ejection frequency. This trigger can also be used to produce the inspection strobe, using a variable delay circuit.

Once drops are ejecting from the orifice, the level of positive pressure can be adjusted by changing the variable pressure source level (as, for example, by changing a manometer level). Ideal operating pressure at the orifice is usually between 0 and 5 inches of water. Direct observation of drop quality (stability, satellite formation, velocity) informs the pressure decision. For a typical binder fluid height of 4 inches, the manometer pressure would be set between –4 and 1 inches.

Further, drop velocity can be measured by observing drop position at two different strobe delay values, as shown in Figure 38. Drop size can be calculated by measuring flow rate m/t at a given drop ejection frequency f (for example, by ejecting drops into a small sample capsule for a known amount of time, and then weighing the capsule), then deducing drop diameter.



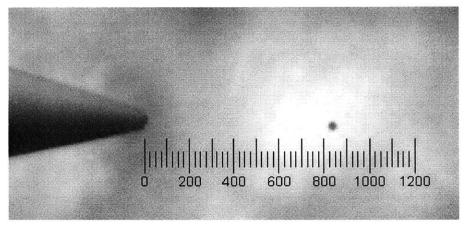


Figure 38. Velocity measurement. At a strobe delay of 200 microseconds (top), the drop is 350 micrometers from the orifice. Next, at a strobe delay of 300 microseconds (bottom), the drop is 850 micrometers from the orifice. The drop velocity is 500 micrometers per 100 microseconds, or 5 meters per second. This demonstration uses water as the fluid and the standard alumina nozzle, with positive pressure of 4 inches of water.

6. Conclusions

This work was motivated by the special 3DPTM need for the ability to print drops reliably with non-standard fluids. Many 3DPTM processes call for binder fluids which are either loaded with dissolved polymer or are solvent-based, or both. Standard inkjet printheads, and all previous generations of 3DPTM printheads, operate on a negative pressure principle to keep the printed fluid from wetting the orifice face. This method does not work satisfactorily for low surface energy fluids, such as the desired solvents. Also, many commercial inkjet printheads cannot run without some periodic (automated) cleaning of the orifice area. This frequent cleaning is not practical for 3DPTM processes and materials.

In response to these shortcomings of available printheads, a positive pressure Drop-on-Demand printhead has been developed to meet these special printing needs of various 3DPTM processes. Specifically, the printhead provides a stable means of ejecting drops of low surface energy and polymer-loaded binder fluids.

Maintaining the fluid meniscus in and around the orifice is a top priority. The details of the orifice geometry and materials greatly affect the way this meniscus behaves, both statically and dynamically. A small land surrounding the orifice provides a surface which is intentionally wetted by the application of positive pressure to the fluid in the printhead. The outside edge of this land is the boundary which controls the wetting, and therefore must be sharp. All features should scale with the orifice diameter. Further, since drop size is closely related to the orifice size, all dimensioning should start with the

orifice. An accurate static model for fluid behavior at the orifice has been developed, and several features of the dynamic behavior of the meniscus have been identified as well.

In fact, through improvements made in fabrication of the printheads, consistency and quality of printheads has increased dramatically. Important features of the printhead have been identified, and either outside vendors have been selected or in-house techniques have been developed to improve quality control. The ceramic nozzles are custom made by a vendor specializing in such devices. Similarly, the piezos are outsourced to specialists. Consistent stainless steel tubes as close to the right size as possible have been purchased, and several simplifications have been made so that minimal machining is necessary.

Assembly of the various elements is at least as much of a decisive factor in the final printhead quality as the selection of the elements themselves. Low temperature solder is used to avoid de-poling the piezo. Interference fits with hard stops are preferred because they eliminate guesswork, as well as the introduction of extra fasteners or solvent-incompatible materials such as epoxies.

Further, careful operation of the positive pressure Drop-on-Demand printhead is critical to its success. Once a particular geometry is determined for the printhead, selection of the proper positive pressure, waveform, fluids, and drop frequency becomes important. These parameters determine first, whether the printhead will eject drops at all, and then what size, what velocity, and of what quality they will be. Drop quality includes such features as whether or not there are satellites and how consistent the drops are over time. When the proper adjustments have been made, it is typical for the printhead to run continuously for five or more days, without need for adjustment or cleaning. Proactive

heating of the reservoir ensures that new air bubbles do not form while the printhead is operating.

In some processes it is desirable to have a high flow rate of binder while maintaining a small drop size. Drops must be small for the sake of resolution, so higher flow rate from a single printhead can only be achieved by increasing drop frequency. Several studies of the factors that limit the maximum reliable drop frequency have been carried out, including investigation of printhead resonances, meniscus oscillations, and supply tube reflections. There are clearly multiple relevant features of the printhead system, but modifications to the supply tubing alone have allowed the maximum drop frequency to increase by a factor of two or more. More work in this area, as suggested in the next section, will certainly broaden the Drop-on-Demand horizon.

Finally, the positive pressure Drop-on-Demand printhead has been tested under many operating conditions, including both printing low-surface-energy chloroform from a static printhead to make lines in PMMA, and printing PEI-loaded binder from a moving printhead in both vector and raster modes. These tests show the printhead to be quite robust once it has started up.

6.1. Future work

The Drop-on-Demand system is a challenging one with many important independent parameters. Although many of these parameters have been thoroughly studied and isolated as much as possible, the entire parameter space is vast, and many areas remain unexplored. Among the many parameters that have been examined are the printhead and orifice geometry and materials, binder fluid properties, and operating

conditions (including pressure levels, piezo waveform, temperatures, drop frequency, and printhead motion).

The following is a partial list of possibilities for future work which would further inform the understanding and development of the positive pressure Drop-on-Demand printhead.

- 1. Model the complex fluid dynamics of drop ejection. This task is particularly difficult because surface tension, viscosity, and inertia all seem to be important. Also, until the pressure wave reflections are well understood, the pressure profile reaching the orifice during a drop ejection event is not known.
- 2. Understand all pressure wave reflections, both long and short, and fast and slow. The pressure pulses originating from the piezo expansion and contraction propagate in two directions through a variety of media (binder fluid, stainless steel printhead body, polymer supply tube). Along the way, each wave partially reflects from every interface (supply end of the printhead, orifice end of the printhead, and reservoir end of the supply tube). Is the important short reflection from the supply tube end or the nozzle end? A better understanding of these reflections would allow higher frequency printing at more consistent flow rate and velocity, as well as a simplified, more efficient piezo waveform. Further optimization of the printhead (piezo, stainless steel, supply tube and nozzle) geometry would be possible.

- 3. Investigate heating of printhead by piezo. There has been at least one occasion where the vigorous activity of the piezo has been suspected of overheating wire connections. However, any heating at all of the printhead by the piezo could be quite destructive in that it would encourage air bubbles to form in the printhead (the opposite effect the intentional heating of the reservoir). These air bubbles could be one cause of slowing and ceasing drop formation, a phenomenon that has been observed occasionally.
- 4. Investigate effects of other fluid properties more completely. Some surface tension effects have been studied extensively, but it would be helpful to understand the importance of other fluid properties, particularly viscosity.
- 5. Look more carefully at the meniscus oscillations. Again, a better understanding of the fluid dynamics of drop ejection would be possible if the oscillations of the meniscus at the orifice after drop ejection could be correlated to drop ejection frequency, or even to single-drop waveforms with an expansion pulse that pulls the meniscus back before pushing it out into a drop.
- 6. Printhead consistency. An investigation should be undertaken, first, into what fabrication factors most affect printhead performance, and second, into how to eliminate these variables. Is it the variation among piezo elements, stainless steel tube segments, the soldering process, the location of the piezo on the stainless steel

tube, or some combination? Can some of these variables be eliminated by requesting tighter tolerances from vendors, or through a more precise soldering technique?

7. Decipher printhead startup process. Once printheads startup and begin producing good drops, they will often run for days without trouble. However, the startup process is still somewhat mysterious, in that a given printhead may start up easily one day, and completely refuse to produce a decent drop stream the next day. These incidents are greatly reduced with the more standardized printheads, but better understanding of what makes a good startup would allow for more predictable process time, and even possible automation of the startup procedure.

7. References

- Body, D. B., and Talke, F. E. "Experimental and Theoretical Study of Wave Propagation Phenomena in Drop-on-Demand Ink Jet Devices," IBM Journal of Research and Development, Volume 28, Number 3, 1984.
- 2. Morgan Matroc, Inc. "Guide to Modern Piezoelectric Ceramics," 1993.
- 3. Wallace, David B. "A Method of Characteristics Model of a Drop-on-Demand Ink-Jet Device Using an Integral Method Drop Formation Model," American Society of Mechanical Engineers #89-WA/FE-4, 1989.

8. Appendices

8.1. Appendix A. Printing Lines

Lines have been printed using the very low surface tension binder chloroform using the positive pressure Drop-on-Demand printhead. The powder material used was poly-methyl-methacrylate (PMMA). Three layers were printed, the unbound powder blown away with air, and the resulting lines observed. Figure 39 shows a well-stitched line.

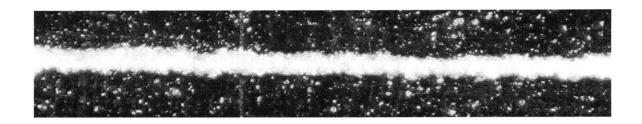


Figure 39. PMMA line printed with chloroform (three layers) at 10 millimeters per second traverse rate and 1000 Hertz drop frequency. Positive pressure is 3 inches of water and the nozzle is standard alumina.

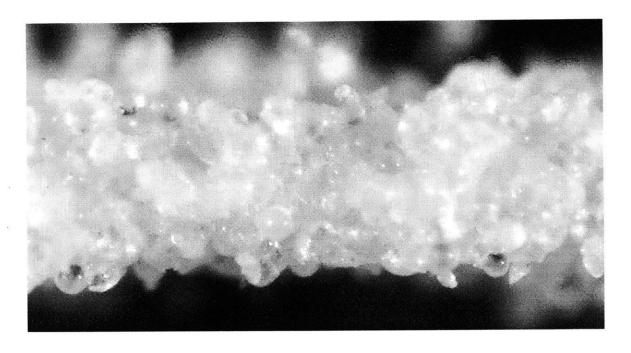


Figure 40. Close-up of PMMA line printed with chloroform. Powder size is 65 micrometers and overall line width is 300 micrometers.

Appendix B. Gaiser Nozzle 8.2.

The best-to-date nozzle for use with the positive pressure Drop-on-Demand

printhead is a custom vacuum pickup tool made by Gaiser Tool Company. Following is

their contact information, and the detailed drawing from which they fabricate the custom

tool.

Gaiser Tool Company

4544 McGrath Street

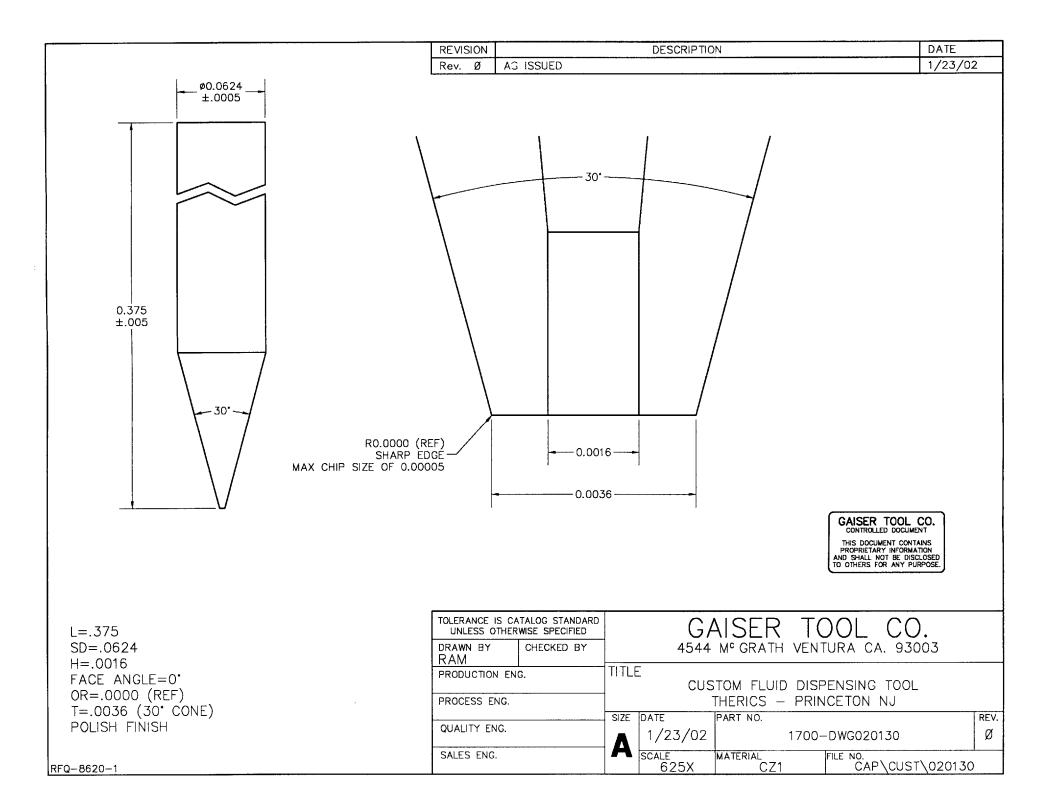
Ventura, CA 93003

Tel: 805-644-5583

Fax: 805-644-2013

The 3DPTM contact at Gaiser is Ryan Mitchell, extension 130

91



8.3. Appendix C. Derivation of Equation 6

Equation 6 claims:

$$P = \frac{2\sigma}{R_{face}} \sin(\alpha_{contact})$$

Following is the derivation of this equation for any angle α .

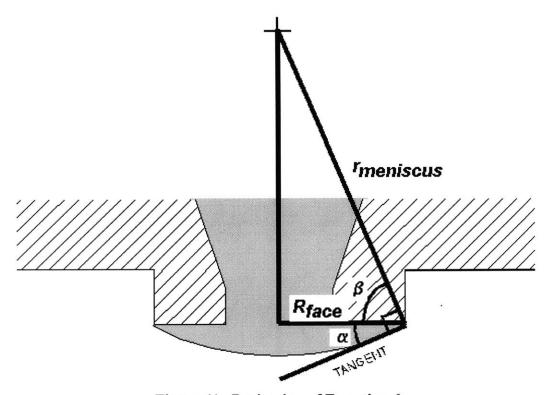


Figure 41. Derivation of Equation 6

The pressure necessary to maintain the meniscus at a particular radius is the Laplace pressure:

$$P = \frac{2\sigma}{r_{meniscus}}$$

For a particular meniscus contact angle α , (shown above between R_{face} and Tangent line),

$$\beta = (90 - \alpha)$$

and

$$\cos(\beta) = \frac{R_{face}}{r_{meniscus}},$$

so

$$\cos(90 - \alpha) = \sin(\alpha) = \frac{R_{face}}{r_{meniscus}}.$$

Substituting the Laplace pressure equation gives

$$\sin(\alpha) = \frac{R_{face}}{2\sigma/P},$$

and, after rearranging,

$$P = \frac{2\sigma}{R_{face}} \sin(\alpha).$$

8.4. Appendix D. Derivation of Equation 8

Equation 8 claims:

$$h_{cap} = \frac{2\sigma}{P} - \sqrt{\frac{4\sigma^2}{P^2} - R_{face}^2}$$

A simple geometric argument shows the above equation to be true.

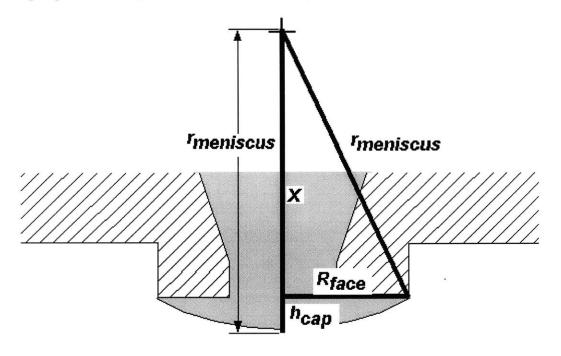


Figure 42. Derivation of Equation 8

Referring to the figure, the Pythagorean Theorem gives

$$X^2 = r_{meniscus}^2 - R_{face}^2,$$

which means

$$X = \sqrt{r_{meniscus}^2 - R_{face}^2} .$$

Also,

$$h_{cap} = r_{meniscus} - X = r_{meniscus} - \sqrt{r_{meniscus}^2 - R_{face}^2} \; . \label{eq:hcap}$$

By substituting the Laplace pressure expression

$$P = \frac{2\sigma}{r_{meniscus}}$$

into the previous equation to eliminate $r_{meniscus}$, it becomes clear that

$$h_{cap} = \frac{2\sigma}{P} - \sqrt{\frac{4\sigma^2}{P^2} - R_{face}^2} \; . \label{eq:hcap}$$

8.5. Appendix E. Derivation of Equation 9

Equation 9 claims:

$$V_{ratio} = \frac{V_{cap}}{V_{drop}} \approx \frac{\left(\pi R h^2 - \frac{\pi h^3}{3}\right)}{\left(\frac{4}{3}\pi a^3\right)} = \frac{3}{4} \frac{h^2}{a^2} \left(R - \frac{h}{3}\right).$$

Clearly, the volume of the drop is determined by its radius:

$$V_{drop} = \frac{4}{3}\pi a^3.$$

All that remains to find is the volume of the spherical cap, which is given by the following integral of the thin discs that make up the cap:

$$V_{cap} = \int_{0}^{h_{cap}} \pi r^{2} dh$$

where r is the radius of each disc and dh is the thickness of each disc. Since

$$r^2 = R^2 - (R - h)^2$$

for each disc,

$$V_{cap} = \int_{0}^{h_{cap}} \pi (R^2 - (R - h)^2) dh = \int_{0}^{h_{cap}} \pi (2Rh - h^2) dh.$$

Evaluating the integral gives

$$V_{cap} = \left[\pi (Rh^2 - \frac{h^3}{3})\right]_0^{h_{cap}} = \pi Rh_{cap}^2 - \frac{\pi h_{cap}^3}{3}$$

which completes the derivation.

8.6. Appendix F. Derivation of Equation 13

Equation 13 claims:

$$f_{meniscus} = \frac{1}{2\pi} \sqrt{\frac{2\sigma}{\frac{1}{2}m_{drop}}} = \frac{1}{2\pi} \sqrt{\frac{3\sigma}{\pi \rho a^3}}.$$

This equation is analogous to mass-spring simple harmonic motion governed by

$$m\ddot{x} + kx = 0$$
.

In the present case, the relevant mass is the mass of the hemisphere that oscillates:

$$m \leftrightarrow \frac{1}{2} m_{drop} \equiv M$$

The restoring force is dependent on the constant surface tension value given by the Laplace pressure:

$$k \leftrightarrow rP = 2\sigma$$
.

Finally, the independent variable which has a linear relationship with the restoring force is the curvature of the meniscus:

$$x \leftrightarrow \kappa = \frac{1}{r}$$
.

The governing equation is

$$M\ddot{\kappa} + 2\sigma\kappa = 0$$
,

which has the general solution

$$\kappa = A \sin \left(\sqrt{\frac{2\sigma}{M}} t \right) + B \cos \left(\sqrt{\frac{2\sigma}{M}} t \right).$$

The natural frequency of this system is then

$$\omega = \sqrt{\frac{2\sigma}{M}}$$

or

$$f = \frac{1}{2\pi} \sqrt{\frac{2\sigma}{M}} \; .$$

With M given as above,

$$M = \frac{1}{2} m_{drop} = \frac{2}{3} \pi a^3$$
.

Substituting gives

$$f = \frac{1}{2\pi} \sqrt{\frac{2\sigma}{\frac{1}{2} m_{drop}}} = \frac{1}{2\pi} \sqrt{\frac{3\sigma}{\pi \rho a^3}}.$$