

# Treatment of the Time Dependent Residual Layer and its Effects on the Calibration Procedures of Liquids and Gases Inside a Volume Prover

Anderson Ilha<sup>1</sup>, Mauro M Doria<sup>1,2</sup> e Valter Yoshihiko Aibe<sup>1</sup>

- 1- Divisão de Metrologia em Dinâmica de Fluidos, Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, Duque de Caxias 25.250-020 RJ Brazil  
Tel:55-21-2679-9149 , Fax:55-21-26791163, E-mail: aisantos@inmetro.gov.br
- 2- Instituto de Física – FIS, Universidade Federal do Rio de Janeiro, C.P. 68528, Rio de Janeiro 21941-972 RJ, Brazil Tel 55-21-2562-7335, Fax 55-21-2562-7368, E-mail:mmd@if.ufrj.br

**Abstract:** In order to minimize the uncertainty arising from measurements of volume provers, we consider the thin liquid films that form inside the prover's inner surfaces, such as the interior walls of standard tanks and bell provers. These thin films adhere to the surface and may carry a given amount of mass and volume which can impact on the prover-side measurement uncertainties.

**Keywords:** thin films, surface physics, prover calibration

## 1. Introduction

Today's global economy put severe requirements on the accuracy of fluid flow and volume meters such as tanks and bell provers. In such meters, as the liquid it previously contained draws off, a thin, surface tension-driven film naturally forms on the surfaces which were in contact with the fluid. These layers can carry an residual amount of mass and volume that may impact on the estimates of the prover's uncertainty by adding or subtracting small bits of mass or volume from the prover's measurement budget.

This residual layer, which affects mainly deliver-type volume provers, can be studied in many degrees of complexity using several approaches, such as lubrication and thin liquid film theories. The thin liquid layer that adheres to the surface as it drains out of a container gives rise to several types of phenomena, from the onset of ruptures, the consequent creation of voids, the spreading of fronts, and the development of fingers. In this work we study a very simple model able to describe the full time evolution of the thin layer thickness from its initial known value to a final constant asymptotic value. In its simplicity the model does not consider breaking of the film due to these complex phenomena because its asymptotic thickness is larger than the capillary length. Therefore the present model is interesting to estimate the prover's uncertainty because it provides a scenario for maximum loss.

## 2. General considerations

The mathematical treatment of such small scale flows has great general interest as it is typical of many industrial, physical and biological processes. They are found in applications ranging from ball-bearing lubrication models to the use of paints and other surface coatings, including several nano and biological applications [1,5].

A very convenient way to generate these residual layers is by the drawing of a flat sheet at constant speed out of a liquid bath. Therefore, although our primary interest is in the thin liquid

layers left inside provers, we will develop here a simpler model for the drawing of a flat plate out of a bath since these ideas can be readily generalized to provers of arbitrary shape.

This problem has been extensively considered in the literature of surface science and it is in fact part of some standard textbooks on fluid mechanics, with and without surface tension and for Newtonian and non-Newtonian fluids [6,7]. In these treatments one of the main interests is the final thickness of the thin film, which undergoes an evolution dictated by the Navier-Stokes equations. These equations are subjected to an approximation in which the film flow thickness  $h(x,t)$  is much smaller than its typical horizontal and vertical length scales,  $L_y$  and  $L_z$ , respectively, that is,  $h(x,t) \ll L_i, i=y,z$ . By following this assumption, one can arrive at

$$\left(\frac{h}{L}\right)^2 Re \ll 1 \quad (1)$$

From Eq.(1) we can see that, even though the conventional Reynolds number  $Re$  may turn out to be quite large, viscous forces will still predominate provided  $(h/L)$  is sufficiently small. Surface tension is another force that plays a dominant role in thin film flows. Such effects are incorporated via boundary conditions on the film surface. At the fluid-air interface, the tangential stresses on the fluid free surface coming from viscous drag of air layers can be safely ignored. On the other hand, it must balance tensions arising from local gradients of the surface tension. In the same way, the normal stress must be balanced by surface tension forces coming from the curvature of the interface:

$$\vec{n} \cdot \vec{T} \cdot \vec{n} = \sigma (\vec{\nabla} \cdot \vec{n}); \quad \vec{n} \cdot \vec{T} \cdot \vec{t} = \vec{\nabla} \sigma \cdot \vec{t} \quad (2)$$

where  $\vec{n}$  and  $\vec{t}$  are the normal and tangential unit vectors, respectively,  $\sigma$  is the surface tension and  $\vec{T}$  is the stress tensor.

Among the theories formulated to describe a flat plane substrate emerging from a large bath of a non-volatile liquid is the classical work of Landau and Levich [8,9], who predicted the dependence of the initial thickness of the adhered liquid layer,  $h_0$  in terms of the the withdrawal velocity,  $U_0$ , the viscosity of the bath,  $\mu$ , the density of the fluid,  $\rho$ , the surface tension,  $\sigma$ , the acceleration of gravity,  $g$ , and an overall undetermined constant. This theoretical law predicts that the thickness of the adhered liquid layer increases with the withdrawal speed. According to Landau and Levitch we have that,

$$h_0 = C \frac{(\mu U_0)^{2/3}}{(\rho g)^{1/2} \sigma^{1/6}},$$

where  $C$  is proportionality constant. We shall not use this Landau-Levitch prediction and will take the initial thickness of the adhered liquid layer,  $h_0$ , to be a free independent parameter whose time evolution needs to be found.

### 3. The thin film model

The model presented here assumes that, at any given time  $t$ , the thin liquid layer adheres to the flat plane with a constant thickness  $h(t)$  over all its extension. This simplifying assumption helps to attain an analytical solution to the problem.

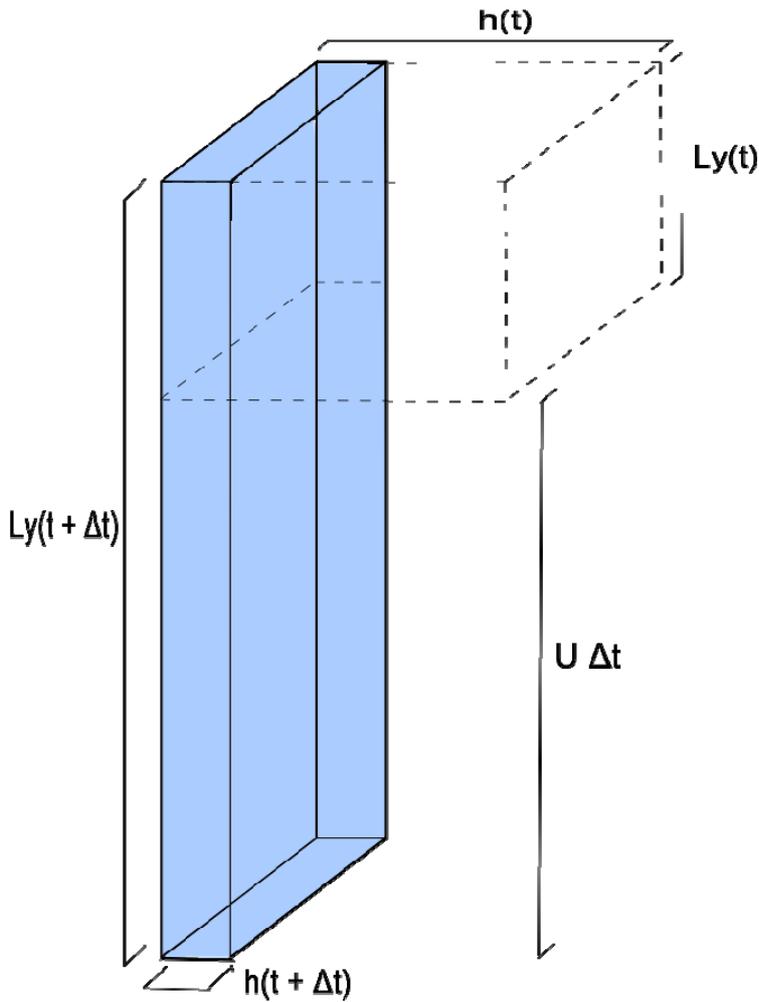


Fig. 1 Removal of a flat plate from a bath and the mass conservation parameters

A flat plate with width  $L_y$  and height  $L_z$  is held vertically inside a liquid container. We attach the  $z$ -axis to the vertical direction and the  $x$ -axis perpendicular to the flat plane. At the time  $t_0$  the flat plane is drawn out of the bath with constant velocity  $U$ , such that a thin layer of liquid of constant height  $h(t_0)$  covers it. At the next time  $t_0 + \Delta t$ , as this layer drains off the flat plate, its thickness  $h(t_0 + \Delta t)$  becomes progressively thinner.

In order to make the simplest possible treatment of this problem, we assume that, for any given time  $t$ , the thin film thickness  $h(t)$  remains instantaneously the same along the flat plane. In other words, the film thickness has a flat profile that decreases homogeneously with  $t$  all over the plate. As one can see in Fig.(1), the film width  $L_z$  is constant (since it is the same as the plate's) and its vertical extension  $L_y$  increases by the speed  $U$  of the descending fluid. The volumes of the thin layer at the moments  $t$  and  $t + \Delta t$  are given by  $V(t) = L_y L_z h(t)$  and  $V(t + \Delta t) = L_y (L_z + U \Delta t) h(t + \Delta t)$ , respectively. Since the liquid density is constant, the volume is always the same by mass conservation,  $V(t) = V(t + \Delta t)$ . Thus, by considering an infinitesimal time  $\Delta t \rightarrow dt$ , it follows that

$$\frac{d \ln h}{dt} = -\frac{U}{L_z}. \quad (3)$$

To determine the speed  $U$  we invoke the Navier-Stokes equations to describe the draining thin liquid layer, assumed to be an incompressible Newtonian fluid of constant density  $\rho$  and constant viscosity  $\mu$ :

$$\frac{D\bar{u}}{Dt} = \frac{\partial \bar{u}}{\partial t} + \bar{u} \cdot \nabla \bar{u} = -\frac{1}{\rho} \bar{\nabla} p + \frac{\mu}{\rho} \nabla^2 \bar{u} - g \hat{z} \quad (4)$$

that must satisfy the mass conservation law,

$$\bar{\nabla} \cdot \bar{u} = 0. \quad (5)$$

Another approximation is the standard assumption of no acceleration of thin films,  $D\bar{u}/Dt = 0$ , and also of no pressure variation inside the film. In this way the last two terms must cancel each other yielding a vanishing net total force. Inside the thin layer the motion is purely vertical and only depends with distance to the flat plane,  $\bar{v} = v_z(x) \hat{z}$  as it must vanish at the flat plane – liquid interface because of the no slip condition. These assumptions reduce the problem to solving the equation,  $d^2 u_z / dx^2 = \rho g / \mu$ , whose first integration gives that  $du_z / dx = (\rho g / \mu) x + c_1$ , where the constant  $c_1$  is still to be determined. At this point we introduce surface tension considerations that apply to the external interface liquid-air. Using the gradient of the surface tension condition previously discussed, such that the symmetric tensor is  $T_{ij} = -p \delta_{ij} + \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$  and  $i$  and  $j$  represent the three possible directions. Taking that the normal and tangent directions are given by  $\hat{n} \equiv \hat{x}$  and  $\hat{t} \equiv \hat{z}$ , respectively, the gradient surface tension condition becomes,

$$\mu \frac{du_z}{dx} \Big|_{x=h} = \frac{d\sigma}{dz}. \quad (6)$$

Added to the no slip condition,  $u_z \Big|_{x=0} = 0$ , results in the following expression for the velocity,

$$u_z = \bar{u}_z + U_0, \quad \bar{u}_z = \frac{\rho g}{\mu} \left( \frac{x^2}{2} - xh \right) + \frac{1}{\mu} \frac{d\sigma}{dz} x + U_0 \quad (7)$$

In this simplified model the divergence-free Eq.(5) just is  $\partial u_z / \partial z = 0$ , and so,  $d\sigma/dz$  must independent of the height  $z$ , therefore a constant. Notice the overall constant  $U_0$  added upon integration to describe the vertical removal of the flat plane from the bath. Once in possession of the velocity  $u_z$ , with all the required boundary conditions satisfied, we proceed to further

considerations. The speed contains both the raise of the flat plane and the fall of the thin liquid layer, which means that  $\bar{u}_z < 0$  rendering the following condition for the thickness,

$$h \geq h^*, \quad h^* \equiv \frac{2}{g\rho} \frac{d\sigma}{dz}, \quad \text{and} \quad H \equiv \frac{3}{4} h^* \quad . \quad (8)$$

This condition sets limitations to the present model which does not apply to a layer thinner than  $h^*$ . We also define the time scale below useful in our considerations:

$$\tau \equiv \frac{4}{3} \frac{\mu\rho g L_z}{\left(\frac{d\sigma}{dz}\right)^2} \quad . \quad (9)$$

At this point we define the speed  $U$ , used before in Eq.(3) to determine the time evolution of the thickness  $h$  and defined here through the average flow:

$$U = -\frac{1}{h} \int_0^h dx \bar{u}_z = \frac{\rho g}{3\mu} h^2 - \frac{1}{2\mu} \frac{d\sigma}{dz} h \quad . \quad (10)$$

Notice the negative sign describing the descending motion of the draining thin layer. Eqs (3) and (8) result into the following integral equation

$$\int_{h_0}^h \frac{dh}{h^3 - \frac{3}{2\rho g} \frac{d\sigma}{dz} h^2} = -\frac{\rho g}{2\mu L_z} \int_{t_0}^t dt \quad (11)$$

$$\frac{t-t_0}{\tau} = \frac{H}{h_0} - \frac{H}{h} + \ln \left( \frac{1 - \frac{H}{h_0}}{1 - \frac{H}{h}} \right) \quad (12)$$

Thus the solution presents the following features. At the initial time  $t_0$  the thin layer has arbitrary thickness  $h_0$  that however has to be larger than the critical one,  $h_0 > H$ . For times near to the initial one the behavior is parabolic:

$$\frac{t-t_0}{\tau} \approx \frac{1}{2} \left[ \left( \frac{H}{h} \right)^2 - \left( \frac{H}{h_0} \right)^2 \right] \quad (13)$$

For very long times,  $t \gg t_0$ , the behavior is logarithm and the thin layer reaches its asymptotic minimum thickness, given by  $H$ :

$$\frac{t-t_0}{\tau} \approx \ln \left( \frac{1-\frac{H}{h_0}}{1-\frac{H}{h}} \right) \quad (14)$$

#### 4. Discussion

The discussion is set in terms of the Bond number ( $Bo$ ) which compares the strength of gravity and of the surface tension:  $Bo = \rho g a^2 / \sigma$ . This is a dimensionless number which contains a lengthscale,  $a$ . The situation that gravity and surface tension become comparable is,  $Bo=1$ , defines the capillary length:

$$a_c = \sqrt{\frac{\sigma}{\rho g}} \quad (15)$$

Qualitatively speaking the capillary length prescribes the situation where inhomogeneities naturally arise in the liquid caused by surface tension and sets that they must be smaller than the capillary length. Thus as the thin layer becomes progressively smaller, the relative importance of surface tension increases causing that surface tension effects are dominant in microscale processes. For instance for water the capillary length is  $a_c \approx 2.0 \text{ mm}$

Concerning its shape, the thin layer is not expected to keep an upright position and instead must bent over at the bottom, acquiring a drop shape, therefore thicker in the bottom as compared to the top. However this is not the case in our simplified study, which only takes into account a constant  $d\sigma/dz$ . In fact the surface tension  $\sigma$  itself is not present in the present treatment.

We introduce here an extra assumption to our model, namely, that the derivative of the surface tension along the vertical direction is proportional to the surface tension itself. The simplest possible hypothesis is that

$$\frac{d\sigma}{dz} = \frac{\sigma}{L_z}. \quad (16)$$

This naive treatment implies that the longer the thin layer the less important it becomes the surface tension effect. Under this condition the fundamental length and time scales become,

$$H = \frac{3}{2} \left( \frac{a_c}{L_z} \right) a_c, \quad \text{and} \quad \tau = \frac{4}{3} \left( \frac{L_z}{a_c} \right)^3 \frac{\mu}{\rho g a_c} \quad (17)$$

As we are interested in large vertical lengths, much larger than the capillary length,  $L_z \gg a_c$ , we see that the asymptotic thickness can reach values much smaller than by the capillary length,  $H \ll 3a_c/2$ . This shows that our extra assumption of Eq.(16) is not a good one as we expect that

the present theory should work at most for  $H \sim a_c$ . We will proceed with the Eq.(16) assumption aware of its limitations. The two fundamental scales have the following proportionalities with the vertical length:  $H \sim 1/L_z$  and  $\tau \sim L_z^3$ . Thus for very long times, the longer the thin layer, the thinner will be the final layer and the longer it will take to reach this value.

#### 4. Results and discussions

Notice that according to Eq.(17) the time scale is determined by the ratio  $\mu/(a_c \rho g)$ . Let us consider some known liquids to determine its value, as shown in Table 1.

Table. 1 Fundamental time and length scales

liquid	Specific weight $\rho g$ ( $10^3 \text{ N/m}^3$ )	surface tension $\sigma$ (N/m)	capillary length $a_c$ ( $10^{-3} \text{ m}$ )	Viscosity $\mu$ ( $10^{-3} \text{ N s m}^{-2}$ )	Time $\mu/(a_c \rho g)$ (s)
water	9.81	0.073	2.7	1.002	$3.7 \times 10^{-5}$
Glycerin	12.4	0.063	2.3	1490	$0.5 \times 10^{-4}$
Benzene	8.59	0.029	1.8	0.652	$1.3 \times 10^{-12}$
Mercury	133.7	0.47	1.9	1.554	$0.64 \times 10^{-8}$

The time evolution of the model, described by Eq.(12) is depicted in Figure 2, which shows the time evolution of the adhered thin layer for several starting thickness  $h_0$  in units of the fundamental time scale,  $\tau$ , and length scale,  $H$ .

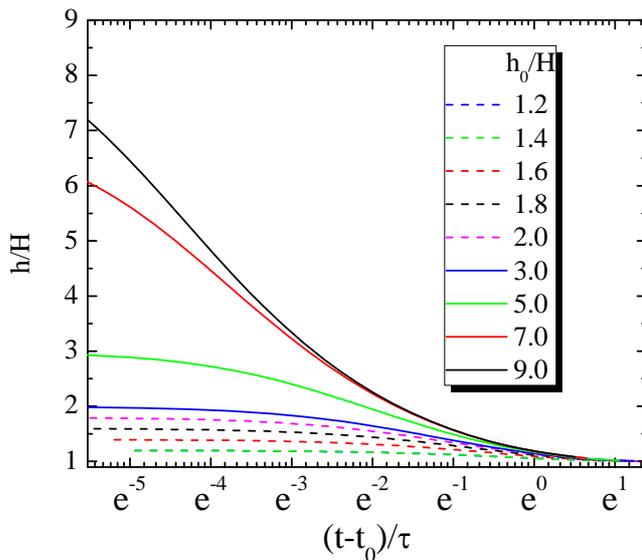


Fig. 2 Time evolution of the thickness of the film layer for several initial starting values in units of the fundamental time scale,  $\tau$ , and length scale,  $H$  as described by the present model

For a vertical length a thousand times larger than the capillary length, that is  $L_z/a_c \sim 10^3$ , we find the following values for the time  $\tau$  needed to reach the layer thickness H: 4.8x194 s (water), 6.5x10<sup>4</sup> s (glycerin), 1.7x10<sup>-3</sup> s (benzene) and 8.0 s (mercury).

## 5. Conclusion

We have developed here a very simple model to describe a thin liquid layer that adheres to a flat plane surface set in the upright position as it is lifted from a bath. The model is meant to determine the remaining layer left inside containers and provers.. The liquid starts its descending motion due to gravity and the thickness reaches a final asymptotic value due to the derivative of the surface tension. The thickness is assumed to remain the same throughout the whole process. The model gives a full description of the time evolution of the thickness, although it is an oversimplification of the real situation. We believe that its usefulness is to describe the maximum error found in the loss of liquids inside provers and containers. We expect that present view to be useful as long as the thickness is larger than the capillary length. Thus the model offers an estimative for the maximum error in calibration facilities for large tanks and containers.

...

## Acknowledgments

The authors wish to thank Faperj (Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), Brazilian research agencies, for support in this research.

## References

- [1] O'Brien SBG; Schwartz LW, "Theory and modeling of thin liquid films," Encyclopedia of Surface and Colloid Science, CRC Press; 1st edition, pp. 5283-5297 (2002).
- [2] Oron A; Davis SH; Bankoff G, "Long-scale evolution of thin liquid films," Rev. Mod. Phys. **69**, No. 3, pp. 931-938 (1997).
- [3] Atherton RW; Homsy GM, "On the derivation of evolution equations for interfacial waves," Chem. Eng. Commun. **2**, pp. 57-77 (1976).
- [4] McCallum MS; Voorhees PW; Miksis MJ; Davis SH; Wong H, "Capillary Instabilities in Solid Thin Films: Lines," J. Appl. Phys. **79**, pp. 7604-7611 (1996).
- [5] Ali MA; Jameel AT; Ahmadun FR, "Stability and rupture of nano-liquid film (NLF) flowing down an inclined plane," Computers and Chemical Engineering **29**, pp. 2144-2154 (2005).
- [6] Acheson DJ, "Elementary Fluid Dynamics," Clarendon Press: Oxford (1990).
- [7] de Gennes P; Brochard-Wyart M; Quéré D; "Gouttes, bulles, perles et ondes," Éditions Belin (2005).
- [8] Landau L; Levich B, "Dragging of a liquid by a moving plate," Acta Physicochim. **17**, pp. 42-54 (1942).
- [9] Qu D; Ramé H; Garoff S, "Dip-coated films of volatile liquids," Phys. Fluids **14** pp. 1154-1165 (2002).

