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Resonance of a liquid-liquid interface

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(Reçu le 7 septembre 1987, accepté sous forme définitive le 8 janvier 1988)

Résumé. — On observe la résonance d’une interface eau/décane dans un tuyau. Lorsque la ligne de contact est stationnaire, on peut retrouver la réponse expérimentale en fréquence par un calcul basé sur une théorie harmonique simple.

Abstract. — We have observed the resonance of a water/decane interface in a pipe. The measured frequency response can be understood with a simple harmonic theory when the contact line is stationary.

1. Introduction.

The interface between two immiscible fluids may be regarded as a geometric surface in space. The work required to change the surface area an infinitesimal amount is \( dW = \gamma \, dS \) where \( \gamma > 0 \) and is called the surface tension. Consider now an interface in a pipe and let us assume that the contact line (the perimeter of the interface) is stationary. If the interface is flat in equilibrium and then distended, the surface tension will act like a spring to restore it to its flat configuration. If the fluids in the pipe have inertial mass, then for small perturbations (and ignoring damping) the interface and the fluids should oscillate harmonically with frequency \( \omega_0 \sim (\gamma/M)^{1/2} \). (As will be seen later, this is still true for the general case of an interface that is not flat in equilibrium.) A resonance should therefore be observed if the interface undergoes forced oscillations.

We have observed precisely this phenomenon with a water/decane interface in a pipe. If we apply an oscillatory pressure difference \( \Delta P(t) = \Delta P_0 + \Delta P_\omega(t) e^{-i\omega t} \) across the length of the pipe and measure the linear response of both the mean velocity of the fluid and the pressure difference between the ends of the pipe, we observe a resonance in the frequency response \( V(\omega)/\Delta P(\omega) \). (This is analogous to measuring the impedance of an electric circuit.) The resonance occurs at \( \sim 1 \) Hz in pipes measuring between 2.8 mm and 4.8 mm inner diameter (ID). If the contact line is stationary (for which it is necessary, but not sufficient, that \( \omega_0 = 0 \)), then it is possible to describe the motion of the interface in terms of a simple harmonic theory. This theory is developed in section 2. Section 3 describes the experiment, section 4 discusses the results, and section 5 summarizes the paper.

2. Theory.

First, let us consider the classical solution for the oscillatory flow of a single fluid in a pipe of radius \( R \) and length \( L [1, 2] \). We start with the Navier-Stokes equations for an isotropic, incompressible, viscous fluid:

\[
\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = -\frac{1}{\rho} \nabla P + \frac{\eta}{\rho} \nabla^2 \mathbf{v}
\]  

(4a)

\[
\nabla \cdot \mathbf{v} = 0.
\]  

(4b)

Here, \( \mathbf{v} = \mathbf{v}(x, t) \) is the fluid velocity, \( P = P(x, t) \) is the pressure, \( \rho \) is the density, and \( \eta \) is the dynamic viscosity. In addition, we have the boundary condition that \( \mathbf{v} = 0 \) at a stationary surface. If we apply an oscillatory pressure difference with \( \Delta P_0 = 0 \), then \( \nabla P(x, t) = (\Delta P_\omega(t)/L) e^{-i\omega t} \hat{z} \) where \( \hat{z} \) is the axis of the pipe. At sufficiently low frequencies so that the flow is laminar, symmetry and flux conservation

JOURNAL DE PHYSIQUE. — T. 49, N° 5, MAI 1988

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphys:01988004905077700
equation (4b) require that the velocity has the solution $v(x, t) = u(r, \omega) e^{-i\omega t}$ with boundary condition $u(R, \omega) = 0$. The geometry of a pipe is such that the non-linear term in equation (4a) vanishes for this solution. Solving for $u(r, \omega)$, we find

$$u(r, \omega) = -i \Delta P_s(\omega) \rho L \omega \left[ 1 - \frac{J_0(\sqrt{i} r/\xi)}{J_0(\sqrt{i} R/\xi)} \right]$$

(5)

where $\xi = (\eta/\rho \omega)^{1/2}$ is the penetration depth (boundary layer width), and $J_0$ is the Bessel function of order zero. When $\omega = 0$, this function correctly reduces to the well-known parabolic velocity profile for Poiseuille flow. The mean velocity is $\bar{v}(\omega) = \frac{2}{R^2} \int_0^R u(r, \omega) r \, dr$ and, of course, $\Delta P(\omega) = \Delta P_s(\omega)$. The dynamics in this case are completely determined by viscous forces. If we write

$$\bar{v}(\omega) = -\frac{\kappa(\omega)}{\eta L} \Delta P(\omega)$$

(6)

(the AC version of Darcy’s Law), then the permeability $\kappa(\omega)$ is found to be

$$\kappa(\omega) = \frac{i R^2}{\omega/\omega_c} g(\omega/\omega_c),$$

(7)

$$g(y) = 1 - \frac{2}{\sqrt{y}} \frac{J_1(\sqrt{i} y)}{\sqrt{i} y J_0(\sqrt{i} y)}$$

where

$$\omega_c = \frac{\eta}{\rho R^2}$$

(8)

is the characteristic frequency of the pipe. When $f = \omega/2\pi < \omega_c$ (not $\omega < \omega_c$), the flow is viscous dominated and $\kappa(\omega)$ is flat:

$$\kappa(\omega) \approx R^2/8.$$  

(9)

When $f > \omega_c$, the flow is inertia dominated and

$$\kappa(\omega) \approx i \eta/\rho \omega.$$  

(10)

The high and low frequency expansions for $g(y)$ are given in appendix A.

Now let us consider the case of two fluids in a pipe but with no flow as shown in figure 1. The equilibrium contact angle $\theta_0$ made by the interface with the pipe is determined by the balance of local forces, i.e., $\gamma \cos \theta_0 = \gamma_{BP} - \gamma_{AP}$ where $\gamma_{AP}$ and $\gamma_{BP}$ are the surface tensions of fluids A and B with the pipe respectively. Thus, if $\gamma_{BP} > \gamma_{AP}$ (that is, fluid A is the wetting fluid), then $\cos \theta_0$ is positive or $\theta_0 < 90^\circ$ as in the figure. Now, in general, there will be a pressure jump across an interface given by $P_B - P_A = \gamma (1/R_1 + 1/R_2)$ where $P_A$ and $P_B$ are the pressures of fluids A and B respectively, and $R_1$ and $R_2$ are the radii of curvature of the interface [3]. For the geometry of a pipe, the interface forms a spherical cap and $R_1 = R_2 = R/cos \theta$. This pressure difference is now called the capillary pressure and is given by (see also appendix B),

$$\Delta P_c = P_B - P_A = 2 \gamma \cos \theta_0/R.$$  

(11)

The pressure is lower in the wetting fluid.

We can now consider the case where there is an applied oscillatory pressure difference and the interface is undergoing forced oscillations. We shall assume that the contact line is stationary and that the contact angle is oscillating. The physics of this will be discussed later. It will also be assumed that the interface is always a spherical cap, even dynamically. We shall ignore the end effects of the interface on the velocity profile. (These and all other approximations made in this paper are discussed in appendix C.) Thus, if $\theta(i) = \theta_0 + \delta \theta(\omega) e^{-i\omega t}$ where $\delta \theta(\omega)$ is small (see appendix C), we can write

$$\cos(\theta_0 + \delta \theta(\omega) e^{-i\omega t}) \equiv$$

$$\cos \theta_0 - \sin \theta_0 \delta \theta(\omega) e^{-i\omega t}$$

(12)

so the AC amplitude of the capillary pressure is just

$$\Delta P_{c}(\omega) = -2(\gamma / R) \sin \theta_0 \delta \theta(\omega).$$

(13)

There is, however, a dynamical correction to the capillary pressure due to viscous stresses given by [3]

$$\Delta P_v = (\sigma_{h,ik} - \sigma_{h,ik}) n_k$$

(14)

where

$$\sigma_{ik} = \eta (\partial v_i/\partial x_k + \partial v_k/\partial x_i)$$

(15)

is the viscous stress tensor and $n_i$ is the $i$-th component of the unit vector normal to the interface. It will be shown in appendix C that in our experiments this term is very small and may be neglected. There will also be a correction of a form similar to Bretheron’s [4]

$$\Delta P_{Br} \approx \frac{\gamma}{R} \left[ \frac{\eta \bar{v}}{\gamma} \right]^{2/3}$$

(16)

resulting from the ejection of fluid near the contact line. It, too, is small (see appendix C).

The measured pressure difference is now $\Delta P(\omega) = \Delta P_s(\omega) + \Delta P_c(\omega)$. We can express $\bar{v}(\omega)$ in terms of $\Delta P_s(\omega)$ as follows. Since the fluid flux must remain constant, the mean velocity of fluid A
must be the same as fluid B. From equation (6) we have

\[ \bar{v}(\omega) = -\frac{\kappa_A(\omega)}{\eta_A L_A} \Delta P_A(\omega) = -\frac{\kappa_B(\omega)}{\eta_B L_B} \Delta P_B(\omega) \]  

(17)

where \( \Delta P_A(\omega) \) and \( \Delta P_B(\omega) \) are the viscous pressure drops across fluids \( A \) and \( B \) respectively, and \( L_A \) and \( L_B \) are the lengths of each fluid in the pipe such that \( L_A + L_B = L \). Also, the total viscous pressure drop must be equal to the applied pressure, so \( \Delta P(\omega) = \Delta P_A(\omega) + \Delta P_B(\omega) \). Eliminating \( \Delta P_A(\omega) \) and \( \Delta P_B(\omega) \) and solving for \( \bar{v}(\omega) \), we find

\[ \bar{v}(\omega) = -\frac{\Delta P_\delta(\omega)}{\eta_A L_A / \kappa_A(\omega) + \eta_B L_B / \kappa_B(\omega)}. \]  

(18)

Now, if \( X_i \) is the position of the interface (see Fig. 1), then \( L_A = X_i \) and \( L_B = L - X_i \). Thus, \( \bar{v}(\omega) \) will depend on the position of the interface, which is undesirable. Clearly, as the interface oscillates, \( X_i \) will not be well defined. This will obviously not be a problem as long as \( \delta X_i \ll L \). Also, we can keep the interface very near one end of the pipe or the other so that \( X_i \approx 0 \) or \( L \) and the pipe is occupied mostly by one fluid. In that case equation (18) becomes simply

\[ \bar{v}(\omega) = -\frac{\Delta P_\delta(\omega)}{\kappa_i(\omega) / \eta_i L} \]  

(19)

where the subscript \( i \) denotes fluid \( A \) or \( B \), whichever is occupying most of the pipe. (We could also match the viscosities and densities of the fluids so that \( \kappa_A(\omega) = \kappa_B(\omega) \) but this is difficult in practice.)

We can now relate all the relevant terms to the mean interface displacement \( \bar{a}(\omega) \) since the fluid is incompressible (see appendix C) and the contact line is stationary. First, we have \( \bar{v}(\omega) = -i\omega \bar{a}(\omega) \). Next, the change in the volume of the spherical cap formed by the interface (see appendix B) can be expressed as

\[ \delta V = -\pi R^2 \bar{a}(\omega) \equiv \left(\frac{dV}{d\theta}\right)|_{\theta = \theta_0} \delta \theta(\omega), \]

yielding \( \delta \theta(\omega) \equiv (\bar{a}(\omega)/R)(1 + \sin \theta_0)^2 \). Combining this result with equations (13) and (19), we can write the frequency response as

\[ \frac{\bar{v}(\omega)}{\Delta P(\omega)} = \frac{-i\omega \bar{a}(\omega)}{\Delta P_c(\omega) + \Delta P_\delta(\omega)} = (i\omega) \frac{-\bar{v}(\omega)}{\eta_i L / \kappa_i(\omega)} \]

\[ = (2 \frac{\gamma}{R}) \sin \theta_0 \delta \theta(\omega) - \bar{v}(\omega) \eta_i L / \kappa_i(\omega) \]

\[ = (2 \frac{\gamma}{R^2}) \sin \theta_0 (1 + \sin \theta_0)^2 + i \omega \eta_i L / \kappa_i(\omega) \].

(20)

As expected, the frequency response is independent of \( \bar{a}(\omega) \) since this is a linear theory. Substituting equation (7) for \( \kappa(\omega) \), we find

\[ \frac{\bar{v}(\omega)}{\Delta P(\omega)} = \frac{i \omega / \rho_i L}{\omega_0^2 - \omega^2 / \rho_i \nu_i R^2} \]  

(21)

where

\[ \omega_0^2 = \frac{2 \gamma}{\rho_i R^2} \sin \theta_0 (1 + \sin \theta_0)^2 \]  

(22)

is the resonant frequency. The characteristic frequency \( \omega_c = \eta_i / \rho_i R^2 \) (see Eq. (8)) now controls the damping. The peak position \( \omega_p \) is \( \omega_p / \omega_0 = (9/17)^{1/2} \approx 0.85 \) as \( \omega_c \to \infty \) and \( \omega_p / \omega_0 = 1 \) as \( \omega_c \to 0 \). If we set \( y = \omega / \omega_c \) and \( Q = \omega_0 / \omega_c \), we can rewrite equation (21) in the scaled form

\[ \frac{\bar{v}(\omega)}{\Delta P(\omega)} = \left(\frac{R^2}{\eta_i L}\right) F(y), \]

\[ F(y) = \frac{i y}{Q^2 - y^2 / \theta(y)}. \]  

(23)

Basically, this result is no different from the usual damped harmonic oscillator problem except that here the damping coefficient is complex and a function of the driving frequency. It is difficult to determine the criteria for critical damping since this depends on the form of the transient response, but by analogy with the harmonic oscillator, one can argue that this happens for \( Q \approx 4 \).

3. Experiment.

A schematic of the experiment is shown in figure 2. The tubing was all pyrex glass coupled with positive pressure O-ring seals (solid bars). The system was initially filled with distilled water with as few air bubbles as possible. Beginning at the far right in figure 2, there was a water reservoir \( R_1 \) that could be used as a source for DC flow. When the valve \( V_1 \) was closed (as it was through the course of most of these experiments), only AC flow was possible (i.e., \( \Delta P_\delta = \bar{v} = 0 \)). The oscillatory drive was an ordinary audio speaker with a 2 mm diameter piston attached to its cone. The piston pressed on a latex membrane held taut over a port in the tubing. Capillary \( C_2 \) was used to measure the mean velocity of the liquid as will be described below. By opening the valve to the decane reservoir \( R_2 \), an interface could be moved into capillary \( C_1 \). Once inside \( C_1 \), it was kept at one end or the other so as to implement equation (19). Due to end effects (see appendix C), the interface could not be placed too close to the end of the capillary, so there was some compromise here. The liquid finally emptied into another reservoir \( R_3 \).

All our measurements were made with distilled water and 99+% pure n-decane. For some of the measurements, the decane was dyed with azulene to make the interface more visible. (The azulene had
no measurable effect on the decane’s fluid properties (or the surface tension.) The kinematic viscosity \( \nu = \eta / \rho \) of both the water and the decane was measured at room temperature with an Ubbelohde viscometer yielding \( \nu_{H2O} = 0.94 \times 10^{-2} \) stokes (cm\(^2\)/sec) and \( \nu_{decane} = 1.21 \times 10^{-2} \) stokes. With \( \rho_{H2O} = 1.00 \) g/cm\(^3\) and \( \rho_{decane} = 0.73 \) g/cm\(^3\), we deduced that \( \eta_{H2O} = 0.94 \times 10^{-2} \) poise (g/cm-sec) and \( \eta_{decane} = 0.88 \times 10^{-2} \) poise. The surface tension of water/decane was measured with a spinning drop tensiometer with the result \( \gamma = 41 \) dynes/cm.

The pressure differences \( \Delta P_1(\omega) \) and \( \Delta P_2(\omega) \) across C1 and C2 respectively were measured by tapping the fluid at the ends of each capillary and connecting these leads to transducers T1 and T2. These were both Omega PX170 piezoresistive differential pressure transducers which have a nominal response time of 1 ms. They require a 10V DC power supply \( V_s \). Since the transducers can be damaged by contact with water, the pressure taps were filled with oil (either decane or mineral oil). This introduced an interface between water and oil in the arms leading to T1 and T2. This will produce a static pressure associated with the capillary pressure drop across this interface but since the transducers ideally have infinite « impedance », no flow occurs in these arms, and hence does not effect the ac measurements. However it does complicate determining the equilibrium contact angle from the measured dc pressure using equation 11. Therefore we weren’t able to get an accurate measure of the static contact angle. The requirement for infinite impedance broke down above 5 Hz, consequently, in analysing the data, we only included points measured below 5 Hz.

The two pressure signals were amplified and conditioned with 100 Hz low-pass filters. The frequency response was measured automatically from 0.1 to 10 Hz by a Hewlett-Packard 3562A dynamic signal analyzer in log swept-sine mode. The signal from its output was amplified and used to drive the speaker. Since we measured the ratio of signals from two nominally identical transducers, any systematic variations in response would tend to cancel out. This method of measurement also eliminated the drive (speaker) response from the problem.

The diameter of C2 was at largest 500 \( \mu \). Thus from equation (8), \( \omega_{c2} \approx 15 \) Hz so its permeability is effectively given by \( \kappa_2(\omega) = R_2^2/8 \) below 10 Hz (see Eq. (9)). From equation (6), the mean velocity of the fluid in C2 is therefore \( \bar{v}_2(\omega) = -R_2^2 \Delta P_2(\omega)/8 \eta_2 L_2 \). The mean velocity in C1 is then

\[
\bar{v}_1(\omega) = -R_1^2 \Delta P_2(\omega)/8 \eta_2 L_2 R_2^2
\]  

(24) since the total fluid flux \( \Phi = \pi R_1^2 \bar{v}_1 = \pi R_2^2 \bar{v}_2 \) must be conserved. The frequency response we calculated in equation (23) corresponds here to \( \bar{v}_1(\omega)/\Delta P_1(\omega) \). We actually measure \( \Delta P_2(\omega)/\Delta P_1(\omega) \), so using equations (23) and (24) we have

\[
\Delta P_2(\omega)/\Delta P_1(\omega) = -8 \eta_2 L_2 R_1^2 \bar{v}_1(\omega) / R_2^2 \Delta P_1(\omega) = - (\beta/\omega_c1) F(\omega/\omega_c1)
\]  

(25)

where \( \omega_c1 = \eta_1/\rho_1 R_1^2 \)

(26)

and

\[
\beta = 8 \eta_2 L_2 R_2^2 / \rho_1 R_1 L_1.
\]

(27)

We have defined \( \beta \) to be independent of \( \eta_1 \). The reasons for this will be made clear later.

Fig. 2. — Schematic of the experiment. The details are described in the text.
When the interface was inside Cl and the drive was on, we could see it stretching and contracting by eye with no apparent motion of the contact line (at least in some pipes: see Sect. 4). The interface in the largest pipe (4.82 mm ID) was visibly distorted by gravity (see appendix C) which restricted how large our pipes could be. For pipes smaller than our smallest (2.82 mm ID), the harmonic approximation equation (12) could not be satisfied and still have a reasonable signal. We checked for harmonicity by lowering the drive amplitude and observing any changes in the frequency response. We did observe a change in the 2.82 mm ID pipe and accordingly lowered the drive amplitude till there was none. Anharmonic effects would appear as higher harmonics in equations (2) and (3) but we did not look for them. The measurements were often repeated several times and were always reproducible. There was no significant background (i.e., source off) signal.

When the interface is outside Cl, this is equivalent to setting \( \gamma = 0 \). Hence, \( \omega_0 = Q = 0 \) and equation (25) just reduces to measuring the frequency response of a single fluid in a pipe, namely equation (6). Figure 3(a) shows a measurement of the magnitude of the frequency response of a 2.82 mm ID pipe with the interface outside Cl. The solid line shows a fit to the magnitude of equation (25) with \( \omega_0 = 0 \) and \( \beta \) and \( \omega_e \) as adjustable parameters [5]. Figure 3(b) shows the exact same measurement but with the interface now inside Cl. The solid line is a fit to equation (25) but now with three parameters: \( \beta \), \( \omega_0 \), and \( \omega_e \). We clearly observe a resonance. To show this more explicitly, we present in figure 4 the same data shown in figure 3 but on the same scale. Note that the two data sets overlap at high frequencies where the effects of the surface tension become less important.

4. Discussion.

The interface displayed some interesting and still puzzling features even before we made any measurements. First, the wetting properties varied from pipe to pipe. Some pipes were strongly water wet and others not so. The pipe material (glass, quartz), the chemicals used in cleaning (nitric acid, acetone, etc.), and even heat treatment (firing the ends of the pipe) seemed to affect the wetting properties. It appeared, for example, that quartz was less strongly water wet than glass. Furthermore, it was found that if the pipe was sufficiently water wet, the contact line would move and the interface would simply slide back and forth without changing shape. In contrast, if the interface was relatively flat (i.e., the pipe was
wet equally well by water or decane), the contact line always remained stationary. Obviously, we used these pipes in the experiments.

Why does the contact line ever remain stationary? Evidently, there must be some kind of pinning occurring at the surface of the pipe. One explanation is that since the pipe surface is rough microscopically, there are locally preferred metastable sites for the contact line [6]. If we oscillate the system at low enough amplitudes, there is not enough push to get over the energy barrier to another metastable site. Also, the microscopic contact angle actually never changes and the apparent oscillation of the macroscopic contact angle arises from the large changes in the curvature of the interface resulting from the microscopic motion of the contact line in its well. Of course, by increasing the amplitude of the drive we could always force the contact line to move. There appeared to be a critical value of the amplitude at which the contact line de-pinned. At this point, the contact line was visibly moving, if only slightly, and the width of the resonance, as measured by the fitted values of \( \omega_c \), broadened significantly as shown in figure 5. This implies some extra dissipation. It is well known that macroscopic motion of the contact line dissipates energy [7] and is the most likely source of the excess dissipation.

Table I shows the results of fitting the magnitude of equation (25) to the magnitude of the frequency response in four different pipes where the contact line was apparently pinned. The quality of the data and the fits were all comparable to those shown in figure 3. When the interface is not in C1, the fitted values for \( \beta \) and \( \omega_c \) are in reasonable agreement with the values calculated from equations (26) and (27).

(No such measurement is presented for the 4.82 mm ID pipe because the pressure signal was too noisy.) When the interface is inside C1, we note the following general features. First, the oscillations are always underdamped as inferred from the values of \( Q = \omega_c/\omega_0 \). Second, when the interface is moved from one end of the pipe to the other (mostly water to mostly decane), the fitted values of \( \beta \), \( \omega_0 \), and \( \omega_c \) all increase as predicted by equations (22), (26) and (27) though not always in the correct ratios. Third, the characteristic frequency \( \omega_c \) is considerably larger than it ought to be in the 2.82 and 4.82 mm ID pipes and at least once in the 3.87 mm ID pipe.

Table I. — Fit results and predicted values. There is a 5 % systematic error in \( \omega_c \) due to the uncertainty in \( \gamma \). The statistical error in \( \omega_0 \) is \( \pm 1^\circ \). W = mostly water, D = mostly decane, WNI = all water, no interface.

<table>
<thead>
<tr>
<th>( d ) (mm)</th>
<th>( L ) (cm)</th>
<th>Fluid</th>
<th>( \beta ) (Hz)</th>
<th>( \beta_{\text{calc}} )</th>
<th>( \omega_c ) (Hz)</th>
<th>( \omega^\text{calc}_c )</th>
<th>( \omega_0 ) (Hz)</th>
<th>( \theta_0 ) (deg)</th>
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<tbody>
<tr>
<td>2.82</td>
<td>24.5</td>
<td>WNI</td>
<td>117 ± 3</td>
<td>122</td>
<td>0.47 ± 0.01</td>
<td>0.47</td>
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<tr>
<td></td>
<td></td>
<td>W</td>
<td>123 ± 9</td>
<td>122</td>
<td>0.94 ± 0.13</td>
<td>0.47</td>
<td>18.5 ± 0.3</td>
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<tr>
<td></td>
<td></td>
<td>D</td>
<td>141 ± 13</td>
<td>167</td>
<td>1.18 ± 0.19</td>
<td>0.61</td>
<td>22.4 ± 0.4</td>
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<tr>
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<td></td>
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<td>133 ± 11</td>
<td>167</td>
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<td>WNI</td>
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<td>D</td>
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<td></td>
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<td>10.94 ± 0.03</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>324 ± 4</td>
<td>257</td>
<td>0.32 ± 0.01</td>
<td>0.32</td>
<td>11.29 ± 0.03</td>
<td>32</td>
</tr>
<tr>
<td>4.82</td>
<td>28.8</td>
<td>W</td>
<td>299 ± 4</td>
<td>304</td>
<td>0.46 ± 0.01</td>
<td>0.16</td>
<td>10.13 ± 0.01</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>357 ± 7</td>
<td>416</td>
<td>0.73 ± 0.02</td>
<td>0.21</td>
<td>13.10 ± 0.06</td>
<td>53</td>
</tr>
</tbody>
</table>
should be noted that $\omega_c$ is always too large, never too small. This implies another source of dissipation in addition to the viscosity of the liquids. Also, this extra dissipation must be associated with the presence of the interface since there is no evidence for it otherwise. It is possible, for example, that the contact line does, in fact, move microscopically as discussed above, and that there is some kind of dissipation associated with this motion also. Contamination of the fluids was ruled out as the cause by replacing them with fresh ones.

The amplitude $\beta$ can be calculated from equation (27) and there is reasonable agreement in most cases. Note that if we had fitted $\beta/\omega_c$ (which would contain a dissipative parameter) instead of $\beta$, there would be no agreement at all. This again implies that the problem is with $\omega_c$ alone, and hence, with extra dissipation.

From equation (22) and the fitted values for $\omega_0$, it is possible to extract the equilibrium contact angle $\theta_0$. The results are shown in table I. The values are not unreasonable and show a certain consistency for each pipe. As discussed earlier, different pipes have different wetting properties, so there is no reason to expect the same contact angle for all pipes. Unfortunately, as discussed earlier, it was difficult to obtain an independent measure of the contact angle. However, it was possible to change the apparent equilibrium contact angle by changing the mean position of the speaker piston; by measuring the dc pressure and correcting for the interface in the transducer arms, we could estimate the equilibrium contact angle. When the contact angle was increased, the resonant frequency also increased as predicted by equation (22). This was the only difference in the two measurements for the 3.4 mm ID pipe with an interface (see Tab. I).

Finally, we made some investigations with a superposed DC flow. The contact line did not remain stationary, of course, but had a constant mean velocity. The peak could still be seen stretching and contracting. The frequency response still showed a peak in this case but it was much broader than the pure AC flow response.

5. Summary.

When an interface is pinned in a pipe, the system can resonate much like a mass on a spring. Damping is provided by the viscosities of the fluids. For small perturbations, a simple harmonic theory can account for the observed frequency response. We find, however, that the damping frequency $\omega_c$ is often much larger than the predicted value, implying another source of dissipation. This may arise from microscopic motion of the contact line. From the resonant frequency, we can extract the equilibrium contact angle.

Acknowledgments.

It is a pleasure to thank S. Bhattacharya, E. Herbolzheimer, and M. O. Robbins for many invaluable discussions.

Appendix A: expansions for $g(y)$.

For general edification, we give the low and high frequency expansions for the function $g(y)$ defined in equation (7):

$$y \to 0 : g(y) = -i \frac{y^2}{8} + i \frac{y^4}{48} + i \frac{11}{3072} y^3 + o(y^4)$$

$$y \to \infty : g(y) = 1 - 2 \left( \frac{i}{y} \right)^{1/2} + o \left( \frac{1}{y} \right).$$

Appendix B: thermodynamics.

The result equation (11) can also easily be obtained by minimizing the thermodynamic potential $\Omega = -P_AV_A - P_B V_B + \gamma S$ [8]. We set

$$d\Omega = - P_A dV_A - P_B dV_B + \gamma dS = 0$$

and since $dV_A = -dV_B$ for an incompressible fluid, we have $P_A - P_B = \gamma dS/dV_B$. Simple geometry yields the following formulas for the surface area of an interface in a pipe and the volume of the spherical cap it forms as functions of the contact angle $\theta$:

$$S = \frac{2 \pi R^2}{1 + \sin \theta},$$

$$V = \frac{\pi R^2 \cos \theta (2 + \sin \theta)}{(1 + \sin \theta)^2}.$$

Solving for $(dS/d\theta)/(dV/d\theta)|_{\theta = \theta_0}$, we produce again equation (11).

Going one step further, the second derivative of $\Omega$ will yield the curvature about the minimum. For a Hamiltonian $H = (A/2) q^2 + (B/2) \dot{q}^2$ with generalized variable $q$, the frequency of oscillations is just $\omega_0^2 = B/A$. If we take $\Omega$ as the potential energy and the contact angle as the generalized variable, then $B = d^2\Omega/d\theta^2|_{\theta = \theta_0}$. If the mass of the fluid is $M$, then its kinetic energy is $T = (M/2) \bar{V}^2$. If the contact line is stationary, $\bar{V} = \dot{V}/\pi R^2 = (1/\pi R^2)(dV/d\theta)|_{\theta = \theta_0} \dot{\theta}$ and since $A = d^2T/d\dot{\theta}^2$, we find after some calculation that

$$\omega_0^2 = \frac{2 \pi \gamma}{M} \sin \theta_0 (1 + \sin \theta_0)^2.$$

Since the mass of the fluid in a pipe is $M = \rho \pi R^2 L$, we arrive again at equation (22).

Appendix C: approximations.

We must check our approximations for self-consistency in worst case scenarios. We first need to know the total liquid volume displacement $\delta$. This was
measured both by observing the linear displacement of liquid in a capillary of known diameter and also by measuring the power spectrum of the mean velocity $\bar{v}(\omega)$ and converting this to a displacement. It was found that $\delta \approx 2 \times 10^{-3}$ cm$^3$ and was nearly constant up to 5 Hz. (It was decreased in the 2.82 mm ID pipe by a factor of 4 so we will use the 3.4 mm ID pipe in worst cases.) The mean linear displacement in a given pipe is therefore $\bar{u} = |\bar{v}(\omega)| = \delta / \pi R^2$ and the mean fluid velocity is then $\bar{v} = |\bar{v}(\omega)| = \omega \bar{u} = \omega \delta / \pi R^2$.

C.1 INCOMPRESSIBILITY. — We have assumed that the fluid is incompressible. This will be valid as long as:

(a) the mean velocity of the fluid $\bar{v}$ is less than the speed of sound $c$ in that fluid. This requires $\bar{v} < c$, or $\omega < c / \bar{u}$.

(b) in a non-steady system, the time it takes for sound to traverse the system is much shorter than the characteristic time of a disturbance. This requires $L / c < \omega^{-1}$, or $\omega < c / L$.

In general, $L > \bar{u}$, so we need only worry about condition (b). Typically, $c \sim 10^5$ cm/sec, and $L \sim 30$ cm, so we require that

$$f \ll \frac{c}{2\pi L} \sim \frac{10^5}{2\pi (30)} \sim 500 \text{ Hz}.$$  

We are therefore vindicated in our assumption. It should be noted that even air can be regarded as incompressible when $f \ll 150$ Hz. This makes the presence of any small air bubbles in our system unimportant.

C.2 LAMINAR FLOW (REYNOLDS NUMBER). — We have assumed that the flow is always laminar. This requires that the Reynolds number $Re$ be sufficiently small. For $R = 0.17$ cm, $\rho = 1$ g/cm$^3$, $\eta = 10^{-2}$ poise, and $f = 5$ Hz, we find

$$Re = \frac{2R\rho \bar{v}}{\eta} = \frac{2 \rho \omega \delta}{\pi \eta R} = \frac{2(1)(2\pi)(5)(2 \times 10^{-3})}{\pi (10^{-2})(0.17)} \approx 24.$$  

It is known that turbulent flow in a pipe does not begin until $Re \sim 1600$.

C.3 SPHERICAL CAP APPROXIMATION. — We have assumed that the interface is always a spherical cap, even dynamically. This will be true as long as the viscous pressure drop $\Delta P_v = \eta \bar{v} / \kappa$ over the length $\ell$ of the interface is much smaller than the equilibrium capillary pressure $\Delta P_c$. The length of the interface is just the height of the spherical cap, so $\ell = R \cos \theta_0 / (1 + \sin \theta_0)$ and

$$\frac{\Delta P_v}{\Delta P_c} \approx \frac{\eta \ell \bar{v} / \kappa}{\frac{2 \gamma \cos \theta_0 R}{\ell}} = \frac{\eta \omega \delta}{2 \pi \gamma \kappa (1 + \sin \theta_0)}.$$  

Since the resonant frequency is always well above the characteristic frequency of the pipes, we can use the high frequency approximation equation (10)

$$\kappa = |\kappa(\omega)| \sim \eta / \rho \omega.$$  

The above equation becomes

$$\Delta P_v \approx \frac{\rho \omega^2 \delta}{2 \pi \gamma} = \frac{(1)(2\pi)^2(5)^2(2 \times 10^{-3})}{2 \pi (41)} \approx 0.01$$  

so even in the worst case this approximation is valid.

C.4 HARMONICITY (LINEARITY). — We have assumed that the system is harmonic. The key to this assumption lies in keeping only the linear term in the expansion of the cosine equation (12). If $\delta \theta = |\delta \theta(\omega)|$, then to higher order we may write (ignoring the time dependence)

$$\cos (\theta_0 + \delta \theta) \approx \cos \theta_0 - \delta \theta \sin \theta_0 - \frac{1}{2} (\delta \theta)^2 \cos \theta_0 + \frac{1}{6} (\delta \theta)^3 \sin \theta_0 + \cdots.$$  

Requiring that both the $(\delta \theta)^2$ and $(\delta \theta)^3$ terms be small compared to the linear term, we have the conditions $\delta \theta \ll 2 \tan \theta_0$ and $(\delta \theta)^3 \ll 6$. If $\delta \approx (dV/d\theta)|_{\theta = \theta_0} \delta \theta$, then when $\theta_0 = 45^\circ$,

$$\delta \theta \approx \delta (1 + \sin \theta_0)^2 / \pi R^3 = (2 \times 10^{-3})(1 + 0.7)^2 / \pi (0.17)^2 \approx 0.4$$  

so $\delta \theta / 2 \tan \theta_0 \approx 0.2$. Clearly, this is something to worry about. We were always careful to lower the drive amplitude to see if there was any change in the frequency response.

C.5 VISCOUS STRESSES. — We have assumed that the viscous stress correction equation (14) is negligible. From the form for the viscous stress tensor equation (15), we see that $\Delta P_{vs} \sim \eta \bar{v}/R$. Since this is a dynamic term, it must be small compared to the fluctuations in the capillary pressure equation (13), and the viscous pressure (since it is dissipative). We have first, using the above result for $\delta \theta$,

$$\frac{\Delta P_{vs}}{\Delta P_c(\omega)} \sim \frac{\eta \bar{v}}{2 \gamma \sin \theta_0 \delta \theta R} = \frac{R \eta \omega}{2 \gamma \sin \theta_0 (1 + \sin \theta_0)^2} = \frac{(0.24)(10^{-2})(2 \pi)(5)}{2(41)(0.7)(1 + 0.7)^2} \approx 5 \times 10^{-4}.$$  

This is a very small effect. Comparing to the viscous pressure

$$\frac{\Delta P_{vs}}{\Delta P_v} \sim \frac{\eta \bar{v}}{\eta L \bar{v}/\kappa} = \kappa = \frac{R}{8L} = \frac{0.24}{8(30)} \approx 10^{-3}$$  

where we have taken $\kappa = R^2/8$, its maximum value. We can completely ignore the viscous stress correction.
C.6 Bretherton correction. — We have assumed that the Bretherton correction equation (16) is unimportant. Like the viscous stress correction, it also has dynamic origins and must be small compared to both the fluctuations in the capillary pressure and the viscous pressure. A calculation similar to the one above shows that \( \Delta P_{Br}/\Delta P_c(\omega) \sim 0.01 \). Comparing to the viscous pressure, we note that the worst case occurs at low frequency. When \( f = 0.5 \) Hz, well below the resonance, we find \( \Delta P_{Br}/\Delta P_v \sim 0.05 \) so we see that this correction is small on both counts.

C.7 End effects. — The velocity profile of a fluid moving in a pipe will be perturbed by the presence of an interface. This effect will be unimportant if the pressure drop \( \Delta P_m \) caused by the change in momentum of fluid at the interface is small compared to the fluctuations in the capillary pressure. We have then

\[
\frac{\Delta P_m}{[\Delta P_c(\omega)]} \sim \frac{\rho \nu^2}{2 \gamma \sin \theta \delta / \sqrt{R}} = \frac{\rho \omega^2 \delta}{2 \pi \gamma \sin \theta (1 + \sin \theta)} \frac{(1)(2 \pi^2)(5)(2 \times 10^{-3})}{2 \pi(41)(0.7)(1 + 0.7)^2} \approx 4 \times 10^{-3}
\]

so this effect is not a problem.

When fluid enters a pipe, there is a distance over which it has not yet established its equilibrium velocity profile. This distance, called the entry length, has been found empirically to be \( x \approx (R/15) Re [9] \). Thus,

\[
x = \frac{2 \rho \omega \delta}{15 \pi \eta} = \frac{2(1)(2 \pi)(5)(2 \times 10^{-3})}{15 \pi (10^{-2})} \approx 0.3 \text{ cm}
\]

We always kept the interface 2-3 cm from the ends of the pipe.

C.8 Gravity. — We have ignored gravity in our calculations. We know from visual inspection that gravity clearly distorted the interface in the 4.82 mm ID pipe. The gravitational pressure difference across the diameter of the pipe (remember the pipes were horizontal) is \( \Delta P_g = 2(\rho_B - \rho_A) g R \) so compared to the capillary pressure when \( \theta_0 = 45^\circ \),

\[
\frac{\Delta P_c}{\Delta P_g} = \frac{2(\rho_B - \rho_A) g R}{2 \gamma \cos \theta / \sqrt{R}} = \frac{(\rho_B - \rho_A) g R^2}{\gamma \cos \theta_0} = \frac{(1 - 0.73)(980)(0.24)^2}{(41)(0.7)} \approx 0.5.
\]

Clearly, gravity is important, especially in the larger tubes. Unfortunately, there was nothing to be done about it.

References

[5] JAYASINGHE, D. A. P., LETELIER, M. and LEUTH-