Capillary Phenomena in Assemblies of Parallel Cylinders

I. Capillary Rise between Two Cylinders

H. M. PRINCEN

Lever Brothers Company, Research and Development Division, Edgewater, New Jersey 07020

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The capillary rise of liquid in the gap between two closely spaced parallel cylinders has been calculated as a function of distance of separation and contact angle. The solutions are valid only when the height of the meniscus is much greater than the radius of the cylinders. With the same restriction, the capillary rise between a cylinder and a flat plate has been evaluated.

INTRODUCTION

Capillary phenomena associated with the presence of limited amounts of liquid in fibrous media are of importance in a number of fields, such as wetting of and wicking in textiles and paper (1–3). Especially in woven textiles the fibers are more or less parallel inside a yarn, whereas in certain materials the individual fibers are close to cylindrical, e.g., in most synthetic textiles.

We have recently embarked on a study of these phenomena, using the model of perfectly parallel and cylindrical rigid rods. Although this model does not reflect completely the detailed structure of these fibrous materials, it can hopefully lead to a better understanding of the behavior of liquids in more realistic systems.

The treatment will be limited to equilibrium conditions. In this first part the relatively simple problem of capillary rise between two vertical rods will be investigated. To our knowledge this system has not yet been studied in detail. In future reports we intend to consider the equilibrium configurations of liquid between two horizontal rods; the number of cylinders considered will also be increased.

THEORY

Capillary Rise between Two Identical Rods.

When two vertical cylinders are placed in a liquid, capillary rise of the liquid will occur in the space between the cylinders, provided the contact angle \( \theta \), measured through the liquid, is smaller than \( 90^\circ \) (Fig. 1a). When \( \theta > 90^\circ \), capillary depression takes place and the configuration will be a mirror image of Fig. 1a.

The meniscus is saddle-shaped and will reach an equilibrium height \( z_2 \) above the horizontal liquid surface. The radius of the cylinders is \( r \), and the distance between the cylinders is \( 2d \). It is assumed that the contact angle \( \theta \) is the same all along the line of three-phase contact.

The problem will be solved only for systems in which

\[
\frac{z_2}{r} \gg 1. \tag{1}
\]

In this case the dimensions of the meniscus are negligible compared to \( z_2 \), and the liquid surface will be essentially vertical from just above the bulk surface to just below the meniscus. Therefore, in this region one of the radii of curvature of the surface is infinite, and the other is given by the radius \( R \) of the circular arcs in the horizontal cross section. Figure 1b shows such a cross section for the case of complete wetting, which will be treated first.

The angle between the line connecting the centers of the cylinders and the radius pointing to the liquid/solid/gas boundary...
is \( \alpha \). The radius \( R \) is related to \( \alpha \) according to

\[
R = \frac{r + d}{\cos \alpha} - r \tag{2}
\]
or

\[
\frac{R}{r} = 1 + \frac{d}{r} \cos \alpha - 1. \tag{3}
\]

As the capillary pressure across the interface must equal the hydrostatic pressure, \( R \) is determined by the height \( z \) in the liquid column through

\[
\frac{\gamma}{R} = z \rho g, \tag{4}
\]

where \( \gamma \) is the surface tension, \( \rho \) is the density of the liquid, and \( g \) is the acceleration due to gravity. Equation [4] can be written in dimensionless form

\[
\frac{z}{r} = \frac{1}{cr^2} \cdot \frac{r}{R}, \tag{5}
\]

where

\[
c = \rho g / \gamma. \tag{6}
\]

Hence \( R \) is simply inversely proportional to \( z \). When the cylinders touch \( (d/r = 0) \) this relationship will hold whatever the height above the plane liquid surface and the capillary rise is "infinite." When \( d/r \) is finite, however, the surfaces form a saddle-shaped meniscus at a certain height \( z_2 \). At this height \( \alpha = \alpha_2 \) and \( R = R_2 \) (Fig. 1c), so that from Eqs. [3] and [5]

\[
\frac{R_2}{r} = 1 + \frac{d}{r} \cos \alpha_2 - 1 \tag{7}
\]

and

\[
\frac{z_2}{r} = \frac{1}{cr^2} \cdot \frac{r}{R_2}. \tag{8}
\]

To obtain the relationship between the capillary rise \( z_2/r \) (or \( r/R_2 \)) and \( d/r \), we use the principle that the weight of the liquid column directly below the shadowed area in Fig. 1c must be supported by the upward force due to surface tension in the meniscus region. Knowledge of the detailed shape of the saddle-shaped meniscus is not required for this purpose.

The area is given by

\[
A = 2r^2[(1 + R_2/r)^2 \sin \alpha_2 \cos \alpha_2 - \alpha_2 - (\pi/2 - \alpha_2)(R_2/r)^2]. \tag{9}
\]

Therefore, the weight of the liquid column is

\[
F_1 = z \rho g A. \tag{10}
\]

The force due to surface tension consists of two terms.
1) An upward force resulting from the contact of the liquid and the cylinders along AC and BD. This force equals

\[ F_{21} = 4\gamma r \alpha_2. \]  \[ 11 \]

2) A downward force due to the free vertical liquid surfaces along AB and CD which tend to pull down the liquid column, leading to

\[ F_{22} = -4\gamma (\pi/2 - \alpha_2) R_2. \]  \[ 12 \]

Substituting for \( \alpha_2 \) and \( A \) in Eq. [10] according to Eqs. [8] and [9], equating \( F_1 \) and \( F_{21} + F_{22} \), and rearranging, one obtains

\[ \left( \frac{R_2}{r} \right)^2 \left( \sin \alpha_2 \cos \alpha_2 - \alpha_2 + \frac{\pi}{2} \right) + 2 \left( \frac{R_2}{r} \right) (\sin \alpha_2 \cos \alpha_2 - \alpha_2) + \sin \alpha_2 \cos \alpha_2 - \alpha_2 = 0. \]  \[ 13 \]

From this quadratic equation \( R_2/r \) can be calculated as a function of \( \alpha_2 \), and the corresponding value of \( d/r \) can be obtained from Eq. [7]. We followed a somewhat different path, however. Instead of \( \alpha_2 \), we selected \( d/r \) as the independent variable.

As Eqs. [8] and [10] still apply one obtains by the same procedure

\[ (R_2/r)^2(\pi/2 - (\theta + \alpha_2)) + \sin (\theta + \alpha_2) \cos (\theta + \alpha_2) \]

\[ + 2(R_2/r)[\sin \alpha_2 \cos (\theta + \alpha_2)] \]

\[ - \alpha_2 \cos \theta] + \sin \alpha_2 \cos \alpha_2 - \alpha_2 = 0. \]  \[ 13a \]

Equations [7a] and [13a] are then solved for various values of \( d/r \) and \( \theta \).

**Capillary Rise between a Rod and a Plate.**

Above, we have concentrated on the system of two rods of equal diameter and equal contact angles. The same analysis can be applied to two vertical rods of different diameter and/or different wettabilities. As an example of such systems we have considered only the capillary rise between a completely wettable rod and plate. Figure 3 shows a horizontal cross section just below the meniscus in this system. The distance between the cylinder and the plate is 2d.

The equivalent equations for Eqs. [7],
Fig. 3. Cross section just below the meniscus between a cylinder and a plate (θ = 0°).

[9], [11], and [12] are

\[
\frac{R_2}{r} = \frac{1 + 2d/r - \cos \alpha_2}{1 + \cos \alpha_2} \tag{7b}
\]

\[A = r^2((1 + d/r)^2 - (R_2/r)^2) \tan \alpha_2 \]

\[F_{21} = 2\gamma r(\alpha_2 + (1 + R_2/r) \sin \alpha_2) \tag{11b}\]

\[F_{22} = -2\gamma r(\pi - \alpha_2)R_2/r. \tag{12b}\]

This, finally, leads to the equivalent for Eq. [13]:

\[(R_2/r)^2(\sin \alpha_2 \cos \alpha_2 - \alpha_2 + \pi) \]

\[+ 2(R_2/r)(\sin \alpha_2 \cos \alpha_2 - \alpha_2) \tag{13b}\]

\[+ \sin \alpha_2 \cos \alpha_2 - \alpha_2 = 0; \]

which again has to be solved in conjunction with Eq. [7b].

**Force versus Free Energy Approach.** In the above analysis the problem was solved on the basis of a balance of gravitational and surface tension forces. An alternative approach is the minimization of the free energy of the system. It will be shown that the latter approach leads to the same result by considering the free energy change in the system when the meniscus is displaced over an infinitesimal distance \(dz\) from its equilibrium position.

The resultant change in gravitational energy is

\[dF_1 = z_2A \rho g dz, \tag{14}\]

where \(A\) is defined as in Eq. [9a].

In this process the liquid column, the cross section of which is shown in Fig. 2, is extended by an element \(dz\), resulting in the wetting of an area \((AC + BD)\) \(dz\) of the originally nonwetted cylinders and in the creation of an area \((AB + CD)\) \(dz\) of free liquid surface. The corresponding free energy change is given by

\[dF_2 = [(AC + BD)(\gamma_{SL} - \gamma_{SV}) \]

\[+ (AB + CD)\gamma_{LV}] dz, \tag{15}\]

where \(\gamma_{SL}\) and \(\gamma_{SV}\) are the solid/liquid and solid/vapor interfacial tensions, and \(\gamma_{LV} = \gamma\) is the liquid/vapor surface tension.

According to Young's equation

\[\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta. \tag{16}\]

Hence, Eq. [15] can be written in the form

\[dF_2 = [(AB + CD) \]

\[- (AC + BD) \cos \theta] \gamma dz. \tag{17}\]

As the total change in free energy \(dF_1 + dF_2\) must be zero at equilibrium, one finds

\[z_2A \rho g + [(AB + CD) \]

\[- (AC + BD) \cos \theta] \gamma = 0. \tag{18}\]

When \(z_2, A, AB, CD, AC,\) and \(BD\) are expressed in terms of \(R_2\) and \(\alpha_2\), this leads to the same equilibrium condition as found previously, i.e., Eq. [13a].

**RESULTS AND DISCUSSION OF CAPILLARY RISE**

Table I gives the results for the rod-rod problem. The angle \(\alpha_2\) and \(r/R_2\) are tabulated as a function of \(d/r\) and for various contact angles. As \(r/R_2\) varies from infinity to zero, the table does not permit direct, accurate interpolation of this quantity. The parameter \(d/R_2 = (d/r)(r/R_2)\) is more suitable for this purpose, as it varies only between \(\cos \theta\) (at \(d/r = 0\)) and zero. The former limit arises from the fact that for very small values of \(d/r\) the capillary rise becomes identical to that between two flat plates at a distance \(2d\). Values of \(d/R_2\) are included for \(\theta = 0^\circ\) only. They are readily calculated for the other contact angles as well. In Fig. 4 we have plotted \(d/R_2\) versus \(d/r\) for five different contact angles and also for the rod-and-plate system (\(\theta = 0^\circ\)).

For certain \(d/r\), the table gives \(r/R_2\) (or \(d/R_2\)) and, therefore, the capillary rise \(z_2/r\) through Eq. [8]. The result is meaningful only if \(z_2/r\), thus calculated, is much greater...
### Table I

Parameters characterizing the capillary rise between two identical vertical rods.

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**Fig. 4.** \(d/R_2\) as a function of \(d/r\) for two cylinders \((\theta = 0^\circ, 30^\circ, 45^\circ, 60^\circ,\) and \(75^\circ\)). Upper curve refers to a cylinder-and-plate system for \(\theta = 0^\circ\).
than unity, as this is the underlying assumption in the whole above treatment. This may be illustrated by means of the practical example of the rise of water between two completely wetted glass rods at \(d/r = 0.1\). From the table one finds \(r/R_2 = 5.121\), so that \(z_2/r = 5.121/cr^2\). For this result to be reliable, \(cr^2\) must be much smaller than 5.121. As \(c \approx 14 \text{ cm}^{-2}\) for water, \(r^2\) must be much smaller than about 0.36 cm\(^2\), or \(r \ll 0.6\) cm.

It is seen in Table I that for each value of \(\theta\) there is an upper limit of \(d/r\) above which no values are given. This results from the observation that \(\alpha_2\) can never exceed \(90^\circ - \theta\).

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**TABLE II**

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</tr>
<tr>
<td>0.18</td>
<td>39.00</td>
<td>3.049</td>
<td>0.5488</td>
<td>5.0</td>
<td>157.15</td>
<td>0.0066</td>
<td>0.0329</td>
</tr>
<tr>
<td>0.20</td>
<td>41.94</td>
<td>2.688</td>
<td>0.5316</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(see Fig. 5), in which case \( R_2 = \infty \) and \( z_2/r = 0 \). As the capillary rise is zero, the net force due to surface tension \( (F_{21} + F_{22}) \) should then also be zero. In other words

\[
(AC) \cos \theta = (AB)
\]

or

\[
\alpha_2 \cos \theta = 1 + d/r - \cos \alpha_2,
\]

which leads to

\[
(d/r)_{\text{max.}} = (\pi/2 - \theta) \cos \theta + \sin \theta - 1. \quad [19]
\]

For complete wetting \( (d/r)_{\text{max.}} = \pi/2 - 1 = 0.5708 \). Although for \( d/r > (d/r)_{\text{max.}} \) some capillary rise does take place, it will never obey the condition \( z_2 \gg r \), so that for these large separations the above treatment breaks down, whatever the value of \( r \).

It must be mentioned that the effect of \( \theta \) on \( z_2 \) differs from that in a narrow closed capillary of circular cross section, where a simple \( \cos \theta \) term suffices. In the present system \( z_2 \) decreases more rapidly with increasing \( \theta \). This is shown clearly in Fig. 6, where the ratio \( (z_2)_{\theta}/(z_2)_{\theta=0} \) is plotted as a function of \( \theta \) for several values of \( d/r \), on the assumption that the capillary constant of the liquid \( (c) \) remains constant. When \( d/r \) approaches zero, the ratio does indeed tend to a value of \( \cos \theta \), but the larger the value of \( d/r \), the more rapidly does \( z_2 \) decrease with increasing \( \theta \).

In Table II the results are presented for a rod-and-plate combination. The table is used the same way, i.e., \( z_2/r \) is calculated from \( r/R_2 \) through Eq. [8]. However, in this case there is no finite value for \( (d/r)_{\text{max.}} \).

It is also noted that for equal \( d/r \) the capillary rise \( z_2 \) is higher in the rod-plate system than in the rod-rod system.

**CONCLUDING REMARKS**

In principle, capillary rise between two rods or between a rod and a plate can be used to measure surface and interfacial tensions. Compared to the conventional capillary rise method, it has the disadvantage that the rise is considerably smaller than that observed in a cylindrical capillary of diameter \( 2d \). Also, the rods experience an inward pull owing to capillary forces in the liquid column, so that the rods must be sufficiently rigid to ensure constant separation. On the other hand, the meniscus between two rods will always be in equilibrium with the bulk surface, which cannot be said for the isolated meniscus in a cylindrical capillary.

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**REFERENCES**