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E. M. Blokhuis

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LETTERS TO THE EDITOR

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COMMENTS

Comment on ''Effect of gravity on contact angle: A theoretical investigation'' [J. Chem. Phys. 109, 3651 (1998)]

E. M. Blokhuis[a)]
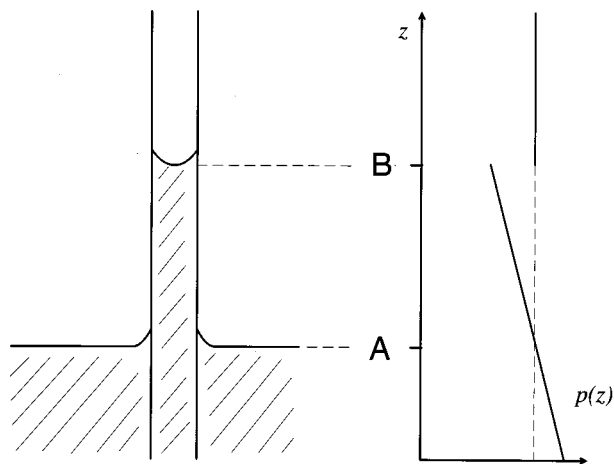*Colloid and Interface Science Leiden Institute of Chemistry, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

The validity of Young's law for the contact angle[1] has been a continued subject of scrutiny (for references see Ref. 2) since its formulation by Sir Thomas Young in 1805. Young's equation has been questioned as a general rule and in the presence of a gravitational field. Its validity has been investigated using integral relations and arguments have been given for the introduction of a microscopic contact angle. It is now recognized that for very small liquid droplets on a substrate, Young's law indeed has to be modified to account for the presence of the line tension of the triple line.[3] For macroscopically large droplets and for macroscopically large distances from the triple line, however, the contact angle is given by Young's law.

In the theoretical analysis by Ward and Sasges[4] a vapor phase in a capillary is considered in between two liquid phases. The authors find in their analysis that the contact angle θ_l of the *lower* liquid and the contact angle θ_u of the *upper* liquid are different sometimes by as much as 20°. In experiments a difference in contact angle is also observed but usually interpreted in terms of the difference between the advancing and receding contact angle. Ward and Sasges offer their theoretical analysis as an alternative interpretation for this effect and show, in an accompanying paper,[5] how the experimental results can be understood in terms of their calculation. To explain their theoretical results the authors correctly state that the calculated difference in contact angle is *not* due to a modification of Young's equation in the presence of gravity, but rather due to the fact that the three surface tensions in Young's equation are height dependent. This effect, however, is expected to be extremely small if the difference in height is of the order of centimeters, so that the reader still may be left to question the validity of Young's equation in a gravitational field. The purpose of this comment is to remove such doubts by showing that in a proper analysis the upper and lower contact angle are determined by Young's law so that the upper and lower contact angle are equal.

Before we turn to the analysis by Ward and Sasges in more detail, we remind ourselves of the usual capillarity effect as shown in Fig. 1. The shape and height, $H = B - A$, of the liquid surface at **B** are determined by solving the Laplace equation, $\Delta p = \sigma_{lv}(1/R_1 + 1/R_2)$, with Δp the pressure difference at the capillary axis, σ_{lv} is the liquid–vapor surface tension, and $1/R_1$, $1/R_2$ are the two principal radii of curvature at the surface. In order to solve the Laplace equation three conditions are required: (1) one needs to determine Δp; (2) and (3) *two* boundary conditions are needed since the Laplace equation is a *second*-order differential equation for the surface height profile. The pressure difference Δp is related to the height of the surface via $\Delta p = -\Delta \rho g H$ (see the pressure profile in Fig. 1), where $\Delta \rho$ is the difference in density between the liquid and the vapor, and g is the gravitational constant. Furthermore the derivative of the height profile is zero at the cylinder axis due to the cylindrical symmetry and, finally, the derivative of the height profile at the wall is determined by Young's equation. With the height profile thus fully determined by the three surface tensions and the diameter of the capillary, the pressure difference Δp and capillary rise can be (numerically) calculated.

In the analysis by Ward and Sasges a liquid phase is also present *above* the vapor phase. This situation is sketched in Fig. 2 (although Ward and Sasges consider the capillary closed at the bottom and at the top). The same procedure as the one described above is now followed to determine the shape of the *lower* height profile **B**. By construction the lower contact angle is then given by Young's equation. Then, however, it is argued that the pressure in the upper liquid phase (**C**) ''is the same as it would have been if the vapor phase were not there'' (see Fig. 2 in Ref. 4). As a consequence they find that the pressure difference at **C** is no longer a variable but determined by the height difference between **B** and **C**. This results in the pressure difference at **C** being larger than at **B** so that solving the Laplace equation now gives an upper contact angle different from the lower contact angle leading to the apparent violation of Young's equation.

FIG. 1. Pressure profile $p(z)$ of a liquid in a capillary.

FIG. 2. Pressure profile $p(z)$ of a liquid in a capillary with additional vapor bubble.

We believe that the arguments leading to the pressure in the upper liquid phase being ''the same as it would have been if the vapor phase were not there'' are incorrect. We now discuss in more detail the analysis by Ward and Sasges which is based on three equations. The first equation shows the decomposition of the total chemical potential into the ''intrinsic'' chemical potential[6], μ_{int}, and the external potential [Eq. (1) in Ref. 4]

$$\mu_{int}(z) + W g z = \mu. \tag{1}$$

The second and third equations relate the intrinsic chemical potential to the variation of the pressure in the liquid (l) and vapor (v) regions

$$\mu_{int}^l(z) = \mu_{int,0}^l + \nu_\infty^l (p^l(z) - p_0^l),$$
$$\mu_{int}^v(z) = \mu_{int,0}^v + R T \ln\left(\frac{p^v(z)}{p_0^v}\right), \tag{2}$$
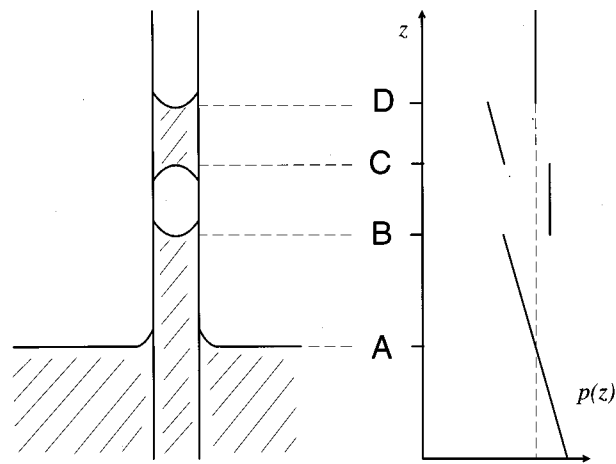
where we have used the notation of Ref. 4. Since μ_{int} is a *potential*, it is defined up to a constant. It is important to realize that the above-mentioned relations are therefore *only* defined with respect to a reference state. Therefore, if we now derive the pressure in the liquid and vapor regions from Eqs. (1) and (2),

$$p^l(z) = p_0^l - \frac{W g}{\nu_\infty^l}(z - z_0^l),$$
$$p^v(z) = p_0^v \exp\left(-\frac{W g}{R T}(z - z_0^v)\right), \tag{3}$$

the reference state is chosen at $z = z_0^l$, where $p^l = p_0^l$ for the liquid region and $z = z_0^v$, where $p^v = p_0^v$, for the vapor region. The reference state should be chosen appropriately for each phase in such a way that the intrinsic chemical potential is a continuous function at the interface between the liquid and vapor regions.

In the system considered by Ward and Sasges, two liquid phases are present and in each of these liquid phases the

reference state should be chosen independently. However, in the analysis by Ward and Sasges the reference state for the upper liquid phase is chosen to be the *same* as for the lower liquid phase. As a consequence the pressure in the upper liquid is equal to the pressure the liquid *would have* if the vapor were not present and replaced by liquid (see also the pressure profile shown in Fig. 2 in Ref. 4). This result is clearly unphysical since the pressure at the base of a capillary filled with liquid differs significantly when part of the liquid above is replaced by vapor.

The correct pressure profile $p(z)$ is shown in Fig. 2. The pressure of the liquid at **C** is equal to the pressure of the liquid at **B** and not equal to the pressure the liquid would have if the vapor were to be replaced by liquid. The difference in pressure, Δp, between the liquid and the vapor at **B** and **C** (and at **D** for that matter) is the same and *determined* by Young's equation.

Finally, we mention that one could also *experimentally* investigate whether the observed contact angle difference[5] is due to contact angle hysteresis or explainable in terms of the theoretical analysis by Ward and Sasges. For this, consider the same experimental setup as used in the theoretical analysis by Ward and Sasges but now instead of *one* vapor region one prepares the system such that there are *two* vapor regions present in the capillary. According to the analysis by Ward and Sasges the contact angle should be progressively larger at each higher liquid–vapor interface, whereas we predict that all contact angles should be equal in equilibrium or, in the case of hysteresis, be pairwise equal with both upper contact angles being the same and both lower contact angles being the same.

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