Laplace-Young and Bashforth-Adams Equations

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Interfacial tension can be measured from drop profiles using a set of equations which originated with Laplace. This note will review the solution methods and the choices available within the algorithms. The following work is taken from *Physical Chemistry of Surfaces*, Fifth Edition, by Arthur Adamson, ISBN 0-471-61019-4. There is now a sixth edition available. The text has been translated into other languages, including Chinese.

Laplace Equation

The solution starts with the Laplace equation which states the interfacial pressure ΔP across an interface because of its interfacial tension γ and radii of curvature R_1 and R_2:

$$\Delta P = \gamma (1 / R_1 + 1 / R_2)$$

The radii of curvature are not easy to describe except in the case of a sphere where they are both equal to the radius of the sphere. Adamson has illustrations to assist in visualizing them.

Laplace-Young or Young and Laplace Equation

Within a drop or capillary that is symmetric about the central vertical axis, the pressure ΔP may be written also as a function of gravity and the densities of the drop and the surrounding media. If $\Delta\rho$ is the difference in densities, g the acceleration of gravity, and h the height in the drop,

$$\Delta P = \Delta\rho\ g\ h$$

The combination of the two equations is commonly called the Laplace-Young equation.

$$\Delta\rho\ g\ h = \gamma (1 / R_1 + 1 / R_2)$$

h is normally measured from the apex of the drop. $\Delta\rho$ and g are known, γ is what we desire, and R_1 and R_2 can presumably be measured from the profile, but this will turn out to not be trivial. When the radii of curvature are expressed in X-Y coordinates of the drop profile (the height h is in the y direction), a differential equation results with no analytical solution:

$$\Delta\rho\ g\ h = \gamma \left[\{y'' / (1 + y'^2)^{3/2}\} + \{y' / (1 + y'^2)^{1/2}\} \right]$$

where $y' = dy/dx$ and $y'' = dy^2/dx^2$.

Because <u>no</u> closed-form solution exists, <u>all</u> answers are <u>numerical approximations</u>. Because this is a differential equation, the approximation process is called an integration of the equation.

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Bashforth-Adams Equation

Bashforth-Adams were the first people to put forth a numerical solution to the Laplace-Young equation. They made the following variable substitutions: the $z = y - h$ and b = radius of curvature at the apex. The Laplace-Young equation can then be rewritten *exactly* as

$$\Delta\rho\ g\ z\ +\ 2\ \gamma / b = \gamma\,(1/R_1 + 1/R_2)$$

and following Adamson, with $x / \sin\phi = R_2$ and $\beta = \Delta\rho\ g\ b^2 / \gamma$:

$$1 / (R_1 / b) + \sin\phi / (x / b) = \beta\,(z / b) + 2$$

This Bashforth-Adams equation is exact — it is equally valid as the Laplace-Young formulation.

The Bashforth-Adams Integration Tables

These are solution tables for the Laplace-Young equation, improved and extended over time. These tables provide 5 decimal places. FTÅ uses these tables because they are proven, having been examined by many experts, provide rapid calculations, and are free from software bugs. Furthermore, the accuracy of the final answer is not compromised in any way by using these tables: interfacial tension depends on knowing densities and magnification accurately. Except for water, density is rarely known to better than 1%, two decimal places. Magnification, errors of which affect the answer to the third power, is not known to better than 0.1%, if only because of lens aberrations and electronic camera noise. So even if one could integrate the equations better than the tables, it would not help because *other factors limit overall accuracy*.

The Classical Bashforth-Adams Method Applied to Photographic Prints

Many people confuse the Bashforth-Adams equation (exact and uncompromised) with the method applied to the first drop shape analysis, which was performed on photographic images using scales to measure the shape. Fordham derived tables which expressed γ in terms of the maximum drop diameter and the diameter at the height h equal to that diameter. This translation did not result in the loss of any real accuracy, but the physical measurements on images were difficult. More importantly, one measured only at two points on the profile, so much data was not used in some sense. This gave the method a bad name.

FTÅ Method

The algorithm determines the profile over the entire drop periphery, but places different weights on different portions, to avoid problems such as tip distortion. The method is always trying to find the best match of two parameters, say β and b (other formulations might by x/b and z/b), to the overall curve using an iterative process, which is the modern way. The FTÅ method then draws graphics and critiques the drop shape and size as if it were a classical photographic image. Note the FTÅ method works on sessile drops for which *there are no Fordham diameter tables*.

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