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PRINCIPLES of the SPINNING DROP TENSIO METER

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PRINCIPLE OF THE SPINNING DROP TENSIOMETER

The spinning drop geometry is described in figure 1, in which the rotation takes place around axis “x”, and axis “y” denotes the distance from the rotation axis. The drop shape exhibits a symmetry around axis “x”. The centrifugal acceleration is $\omega^2 y$ (ω is the rotational velocity), and it increases with the distance from the axis and is such that the natural gravity effect is negligible. Hence the influence of the density difference between the two fluids increases with the distance from the axis and produces a pull of the interface toward the axis. This results in the elongation of the drop along the “x” axis, which is opposed by the interfacial tension that tends to minimize the surface area, i.e. to make the drop shape more spherical.

The principle of measurement of interfacial tension with a spinning drop tensiometer will be discussed in the so-called Vonegut’s case of an elongated drop in which the central part of the drop is essentially cylindrical, i.e. the radius of curvature at equator point E in the plane of fig. 1 (R_M) is much larger than the radius of the slice cut (R_m), so that the curvature at point E may be approximated by the inverse of the radius of the cylinder ($1/R_m$). This approximation has been shown to be valid whenever the length of the drop is at least 4 times its diameter (which is roughly the case of the drop shown in figure 1).

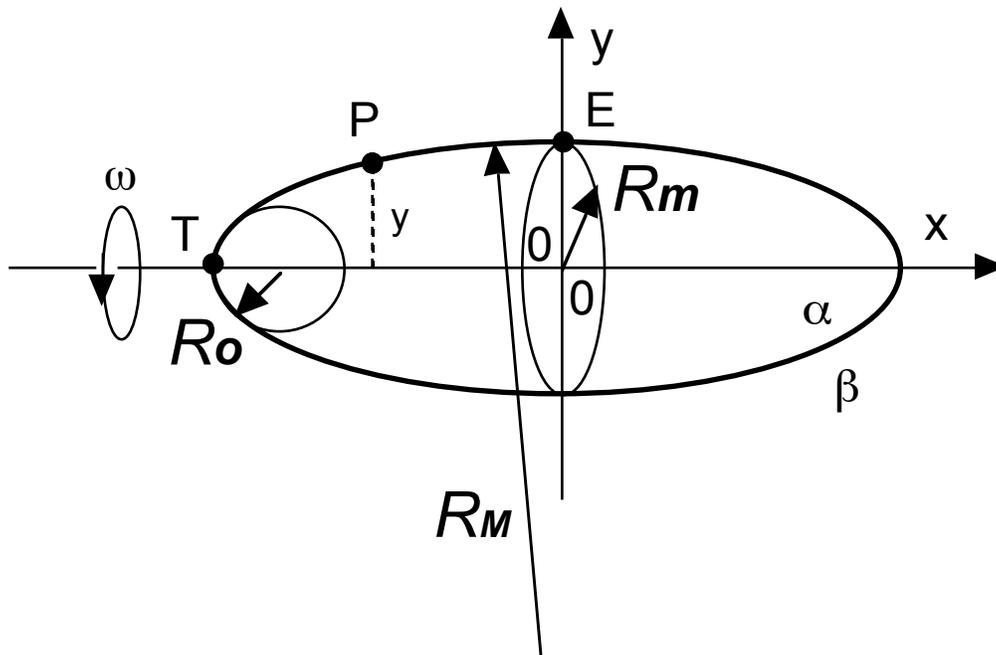


Figure 1. Geometry of a spinning drop of denser liquid α in less dense liquid β .

The densities of the phases are ρ_α and ρ_β (with $\rho_\alpha < \rho_\beta$ and $\Delta\rho = \rho_\beta - \rho_\alpha$) and R_0 is the radius of curvature at the tip of the drop.

Let's be p_T the pressure (reference) at point T on the axis at the tip of the drop, and p the pressure at any (P) point at the interface, located at distance “y” of the axis. The classical Pascal's formula to calculate the pressure difference between two points located in the same phase ($\Delta p = \rho g h$) is still valid if the centrifugal acceleration ($1/2 \omega^2 y$) replaces gravity g .

$$\text{In phase } \alpha \quad p_\alpha = p_{\alpha T} + 1/2 \rho_\alpha \omega^2 y^2 \quad [1]$$

$$\text{In phase } \beta \quad p_\beta = p_{\beta T} + 1/2 \rho_\beta \omega^2 y^2 \quad [2]$$

$$\text{By difference} \quad p_\alpha - p_\beta = p_{\alpha T} - p_{\beta T} - 1/2 \Delta\rho \omega^2 y^2 \quad [3]$$

Because of the concavity toward phase α , $p_\alpha > p_\beta$ at any point of the interface, and according to Laplace's law:

$$p_\alpha - p_\beta = 2 \gamma H = \gamma \left[\frac{1}{y\sqrt{1+y'^2}} - \frac{y''}{(\sqrt{1+y'^2})^3} \right] \quad [4]$$

H is the average curvature, i.e., $H = [1/R_1 + 1/R_2]/2$ where R_1 and R_2 are the principal (minimum and maximum) radii of curvature. y' and y'' indicate the first and second derivative of y with respect to x . In the expression in brackets, the first term is the curvature along a circle centered on the axis (not equal to “y” because the radius of curvature is measured along the normal vector, and thus is equal to y only if $y' = 0$), and the second one is the curvature of the generating curve, i.e., the curve shown in the plane of figure 1.

Because of the axial symmetry at the tip T, both radii of curvature are equal and the average curvature $H_T = (1/R_0 + 1/R_0)/2$, hence:

$$p_{\alpha T} - p_{\beta T} = 2 \gamma H_T = 2 \gamma /R_0 \quad [5]$$

By substituting [4] and [5] in [3] an equation in ‘y’ is attained. At any point P of the interface:

$$2 \gamma /R_0 - 1/2 \Delta\rho \omega^2 y^2 = \gamma \left[\frac{1}{y\sqrt{1+y'^2}} - \frac{y''}{(\sqrt{1+y'^2})^3} \right] \quad [6]$$

By using dimensionless variables $X = x/R_0$, $Y = y/R_0$ and scaling parameter $K = \Delta\rho\omega^2 R_0^3/2\gamma$ and by multiplying by “y” and substituting in [6], the following equation is attained:

$$2 Y - K Y^3 = \frac{d}{dY} \left(\frac{Y}{\sqrt{1+Y'^2}} \right) \quad [7]$$

by integration
$$Y^2 - K Y^4/4 = \left(\frac{Y}{\sqrt{1+Y'^2}} \right) + cst \quad [8]$$

At the tip of the drop (point T) ($Y = 0$) hence, $cst = 0$,

Applying equation [8] at the equator of the drop (point E) where Y is maximum (Y_m) and where the derivative $Y' = 0$.

$$Y_m^2 - K Y_m^4/4 = Y_m \quad \text{or} \quad K Y_m^3 - 4 Y_m + 4 = 0 \quad [9]$$

By applying equation [7] at point E where $Y' = 0$

$$2 Y_m - K Y_m^3 = \frac{d}{dY}(Y) = 1 \quad [10]$$

Combining [9] and [10]

$$Y_m = 3/2, \quad y_m = R_m = 1.5 R_o \quad \text{and} \quad K = 16/27 = \Delta\rho \omega^2 R_o^3/2 \gamma \quad [11]$$

From which comes Vonnegut's formula :
$$\gamma = \Delta\rho \omega^2 R_m^3/4 \quad [12]$$

In formula [12] units are: γ (N/m), R_m (m), $\Delta\rho$ (Kg/m³), ω (rad/s)

R_m is the radius of the drop at equator (E) as indicated in figure 1. This formula has been shown to be valid within 0.1% if the length of the drop exceeds 4 times its diameter. In practice a more elongated drop is used which really looks like a cylinder, but it is worth remarking that the hemisphere at the tip of the drop has not the same radius than the cylinder at the center as indicated in figure 2 ($R_o = 2/3 R_m$). This is due to the fact that the centrifugal acceleration is not constant, but increases with the distance from axis.

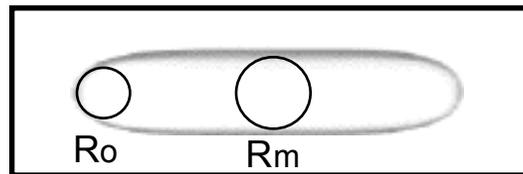


Figure 2. “Cylindrical” elongated drop curvature radii in Vonnegut’s approximation case.

It is worth noting that formula [12] does only require the evaluation of a distance (drop radius at center) and not the estimation of a curvature, which would implies the estimation of the first and second derivative of the shape of the drop, a much more difficult problem. It is also worth noting that this method is the only one in which the drop is not in contact with a solid surface, hence no contact angle has to be measured nor estimated.

Finally the formula indicates that low tension will be associated with small radius, i.e., an elongated drops and slow rotational velocity, whereas high tension would require a high rotational velocity and the drop might not be elongated enough to fall in the Vonnegut's formula case. This method is thus appropriate to measure low tensions, typically below 1 mN/m, and down to ultralow values ($\mu\text{N/m}$ or less) found in surfactant-oil-water systems containing microemulsions.

In practice the spinning tube, often a capillary of internal diameter equal or less than 1 mm, produces a lens effect than blows up the drop size, and a correction has to be applied to estimate the real radius.

The tension may be calculated for non elongated drops, by numerically solving the equation set without having to estimate the curvature.

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