Capillarity: Measurements

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Outline

- **Physical Measurements**
  - Errors
  - Accuracy & Precision
  - Presentation

- **Surface Tension Measurement**
  - Pendant Drop (shape measurement)
  - Wilhelmy Plate (force measurement)
  - Maximum Bubble Pressure

- **Contact Angle Measurement on Flat Surfaces**
  - Sessile Drop (shape measurement)
  - Wilhelmy Plate (force measurement)

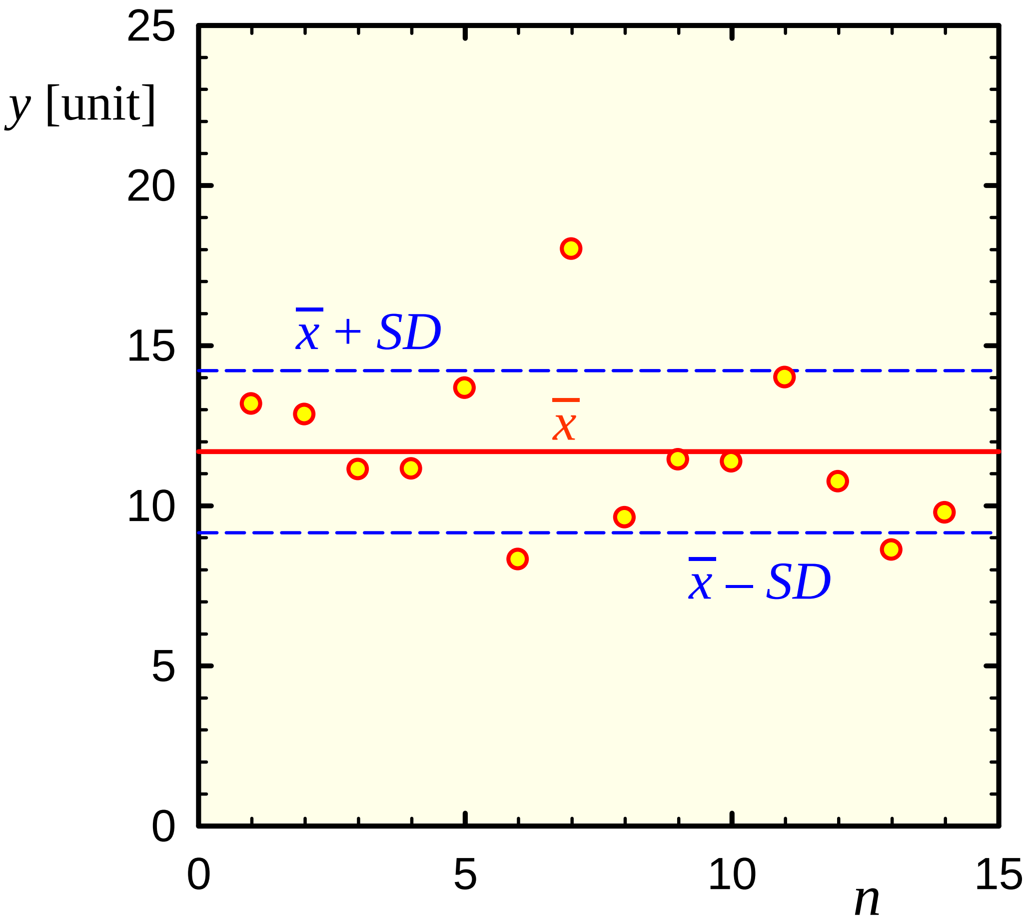
- **Contact Angle Measurement on Powders**
  - Skin Flotation
  - Static Capillary pressure
  - Washburn Method

1. Physical Measurements

- Mean & Standard Deviation
- SD versus SE
- Error Propagation
- Precision & Accuracy

Mean & Standard Deviation

Consider n identical and independent measurements (x_i, i = 1,…,n):



$$\overline{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

$$SD = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2}$$

Standard Deviation or Standard Error?

There are different measures of the data spread:

Standard Deviation: $x = m \pm SD$ Gives a 68% probability of finding a single measurement

Standard Error: $x = m \pm \frac{SD}{\sqrt{n}}$ Gives a 68% probability of finding an average measurement

Confidence Interval: $x = m \pm t_{\alpha/2,n-1} \frac{SD}{\sqrt{n}}$ Gives a (1–α) probability of finding an average measurement

Any option is valid as long as it is properly quoted!

How Good Is a Measurement?

Best Value — Absolute Error

$$y = \bar{y} \pm \Delta y$$

Relative Error

$$\varepsilon = \frac{\Delta y}{y}$$

Value	Error	Relative Error [%]	Quality
10.0	0.5	5	OK (maybe)
500.0	0.5	0.1	Good
0.5	0.5	100	Unacceptable

Error Propagation

The values, *a* and *b*, and their errors, Δa and Δb, are known. What is the error of *y*?

Relation	Maximum Error	Most Probable Error
$y = a + b$	$\Delta y = \Delta a + \Delta b$	$(\Delta y)^2 = (\Delta a)^2 + (\Delta b)^2$
$y = a - b$	$\Delta y = \Delta a + \Delta b$	$(\Delta y)^2 = (\Delta a)^2 + (\Delta b)^2$
$y = ab$	$\Delta y/y = \Delta a/a + \Delta b/b$	$(\Delta y/y)^2 = (\Delta a/a)^2 + (\Delta b/b)^2$
$y = a/b$	$\Delta y/y = \Delta a/a + \Delta b/b$	$(\Delta y/y)^2 = (\Delta a/a)^2 + (\Delta b/b)^2$

The general case:

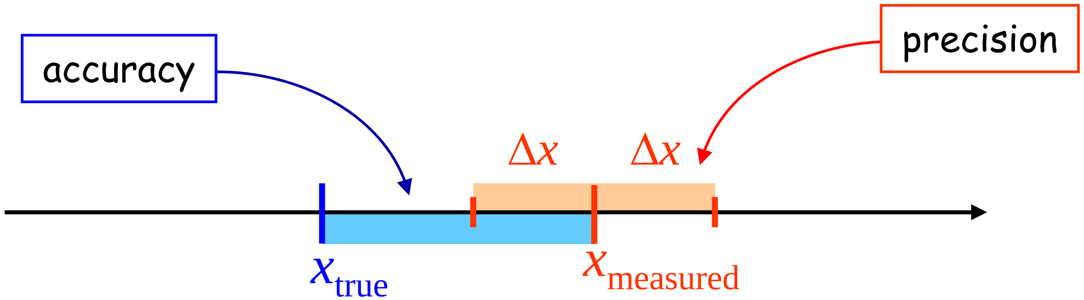
$$y = f(a,b)$$

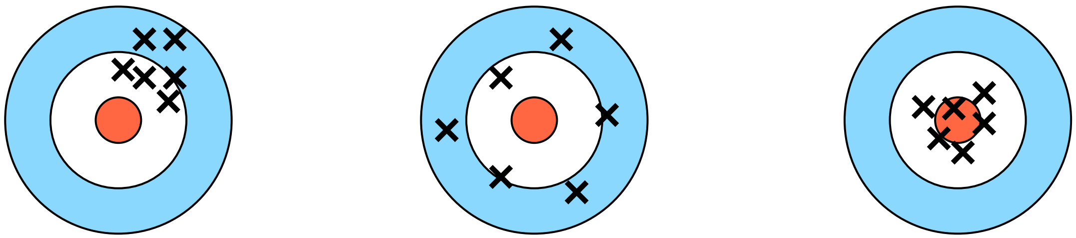
$$dy = \frac{\partial f}{\partial a} da + \frac{\partial f}{\partial b} db$$

$$\Delta y = \left|\frac{\partial f}{\partial a}\right| \Delta a + \left|\frac{\partial f}{\partial b}\right| \Delta b$$

$$\Delta y^2 = \left(\frac{\partial f}{\partial a}\right)^2 \Delta a^2 + \left(\frac{\partial f}{\partial b}\right)^2 \Delta b^2$$

Precision & Accuracy





precise | accurate | precise & accurate

	Origin	Problem	Solution
Precision	random errors	lack of reproducibility	repeat measurements
Accuracy	systematic errors	lack of standard	use complementary techniques

Data Presentation

284.7 ± 3.2936 ✗

- How many measurements (e.g. 3 or 300)?
- Standard error, standard deviation or confidence interval?
- Rounding off the error:

$3.293617 \rightarrow 3$
$29.01 \rightarrow 30$
$8.234 \rightarrow 8$
$1.34 \rightarrow 1.3$

- Rounding off the average:

✓

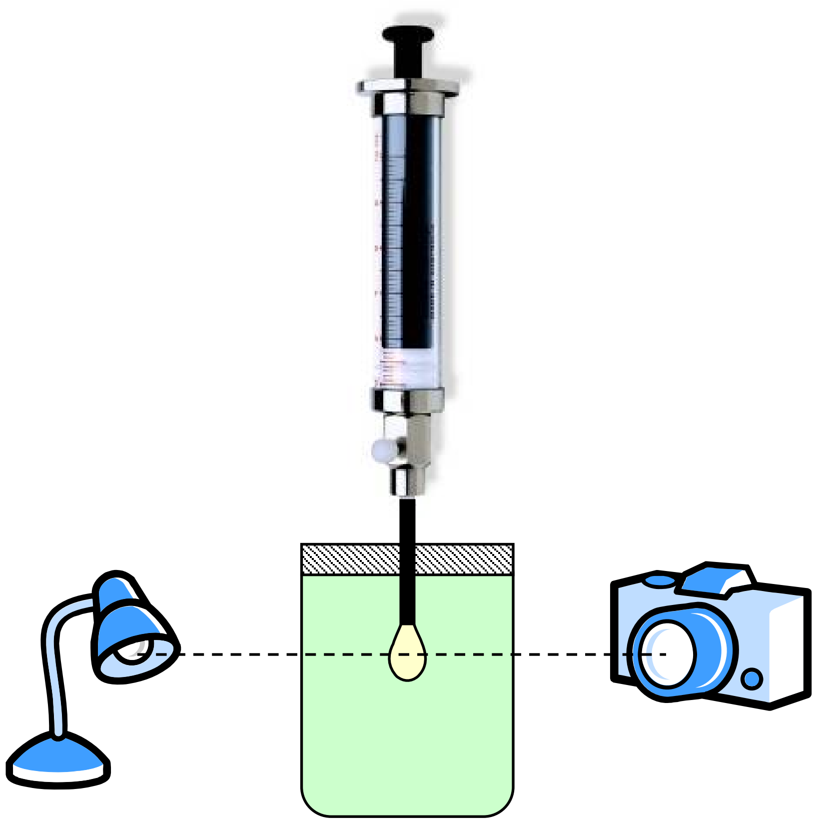
285 ± 3	285 (3)
25.2 ± 0.3	25.2 (3)
6.83 ± 0.07	6.83 (7)

2. Surface Tension Measurement

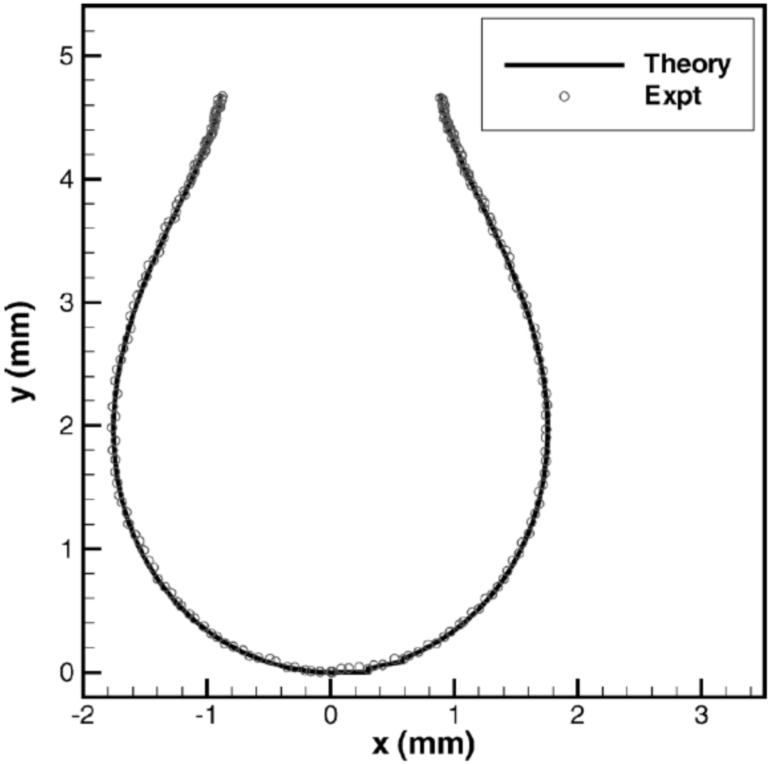
- Pendant Drop
- Wilhelmy Plate
- Maximum Bubble Pressure

Pendant Drop Method

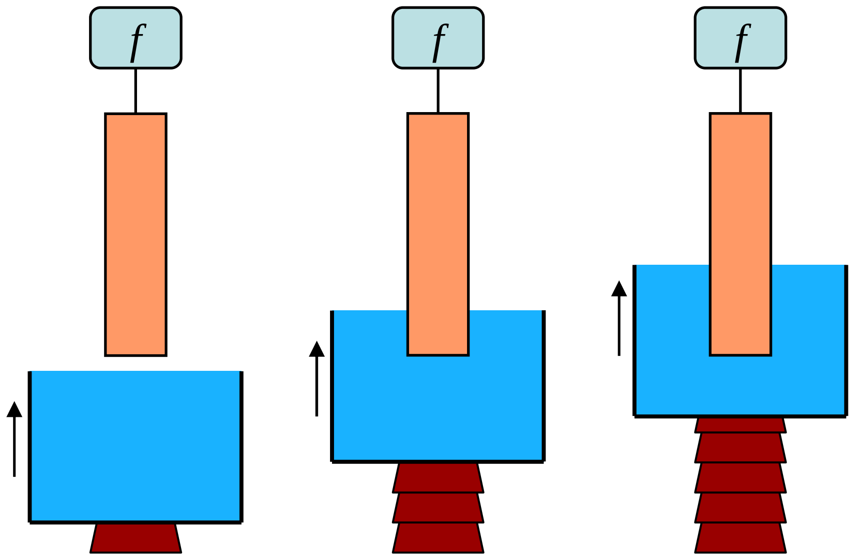
A digital image of the drop silhouette is obtained and fitted with Laplace equation.



The density is an input parameter.
The surface tension is a fitting parameter.



Wilhelmy Plate Method ($\theta = 90°$)

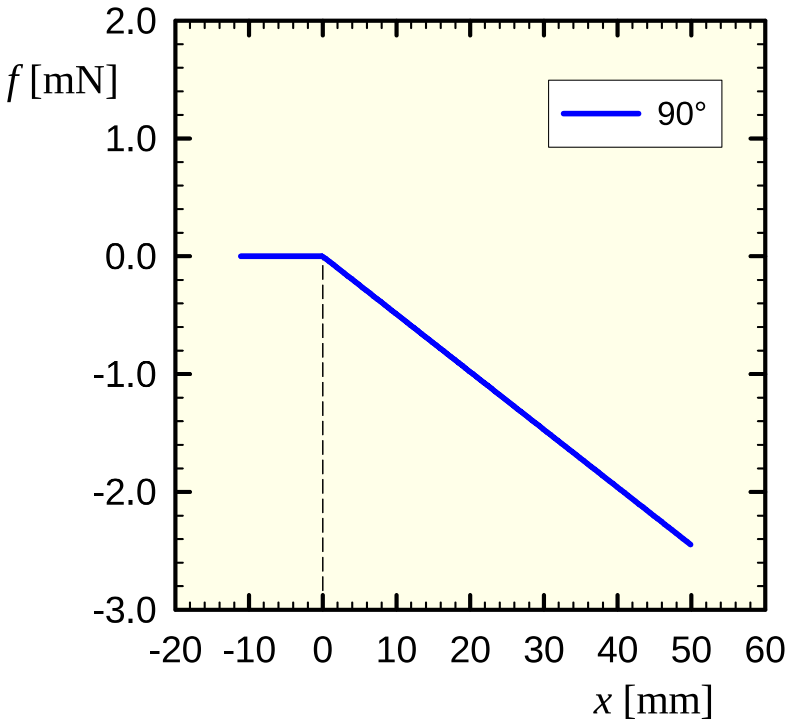


The total force is:

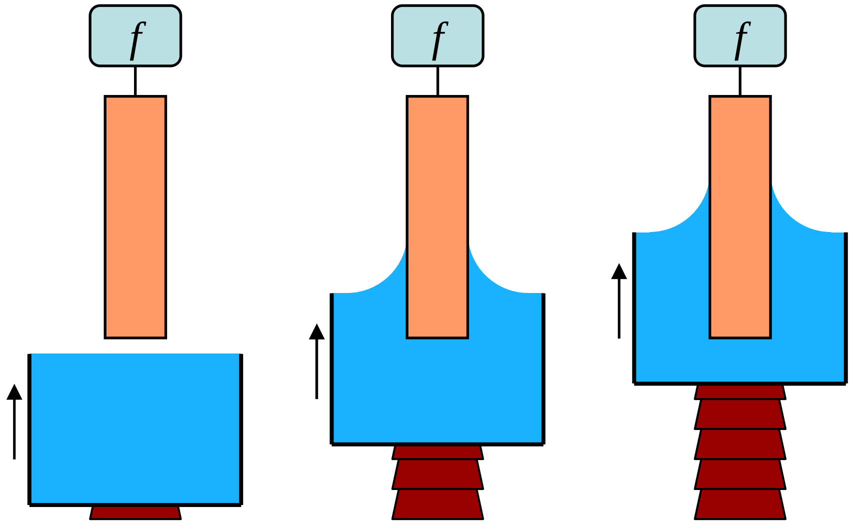
$$f_{total} = m_0 g - f_{buoyancy} = $$
$$= m_0 g - \rho_L A g x$$

The recorded force is:

$$f = f_{total} - m_0 g = -\rho_L A g x$$

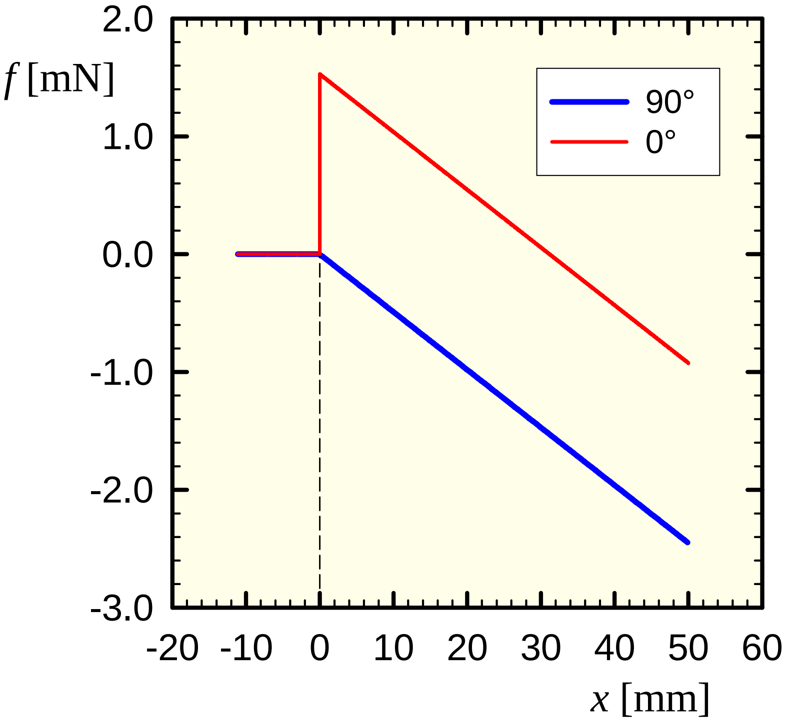


Wilhelmy Plate Method



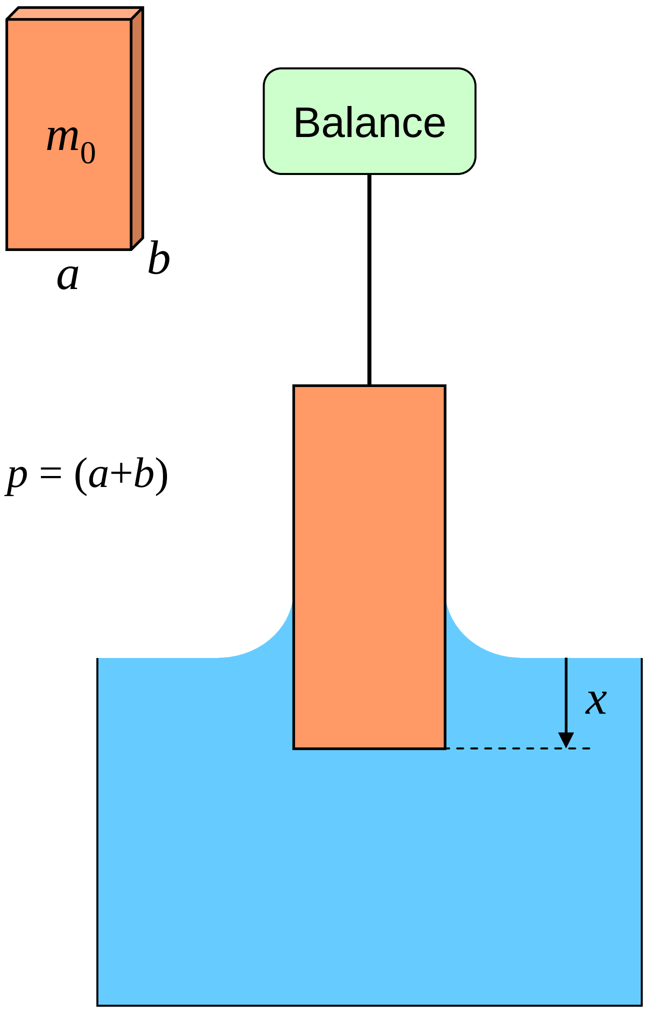
The recorded force is:

$$f = f_{\text{buoyancy}} + f_{\text{capillary}} =$$
$$= -\rho_L Agx + p\gamma\cos\theta$$



If the contact angle is not 90° there is also a capillary force.

Wilhelmy Plate: Calculations



The recorded force is:

$$f = -\rho_L A g x + p\gamma\cos\theta$$

The extrapolated force is:

$$f(x=0) = p\gamma\cos\theta$$

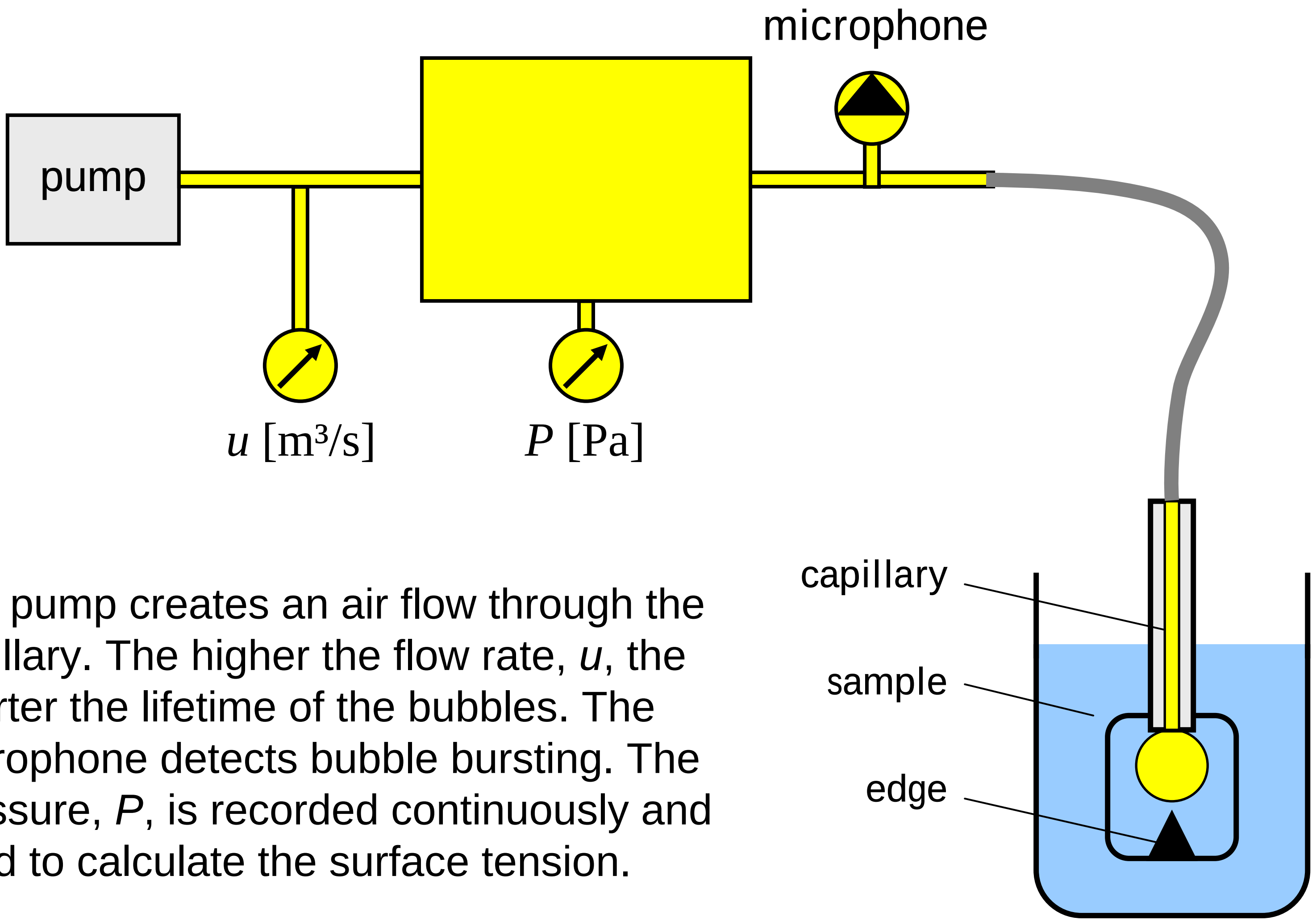
$\theta = 0$ → $$\gamma = \frac{f(x=0)}{p}$$

Surface Tension

known γ → $$\cos\theta = \frac{f(x=0)}{p\gamma}$$

Contact Angle

Maximum Bubble Pressure Method



The pump creates an air flow through the capillary. The higher the flow rate, *u*, the shorter the lifetime of the bubbles. The microphone detects bubble bursting. The pressure, *P*, is recorded continuously and used to calculate the surface tension.

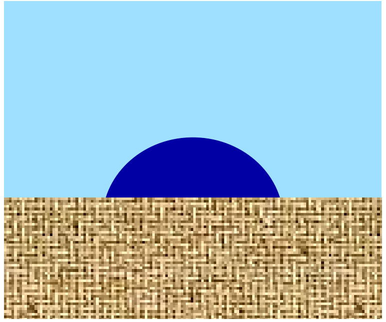
3. Contact Angle on Flat Surfaces

- Sessile Drop Method
- Wilhelmy Plate Method
- Vibrated Contact Angles

Sessile Drop Technique

Protocol:

- Deposit a droplet of liquid on the surface;
- Take an image of the droplet shape;
- Determine the contact angle.

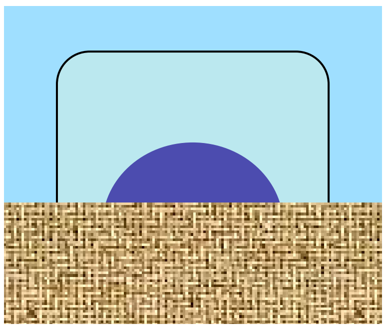


Problems:

- Which angle was measured?
- Was evaporation significant?
- What is the correct droplet size?
- Is the value of θ representative?
- Has the liquid affected the surface?

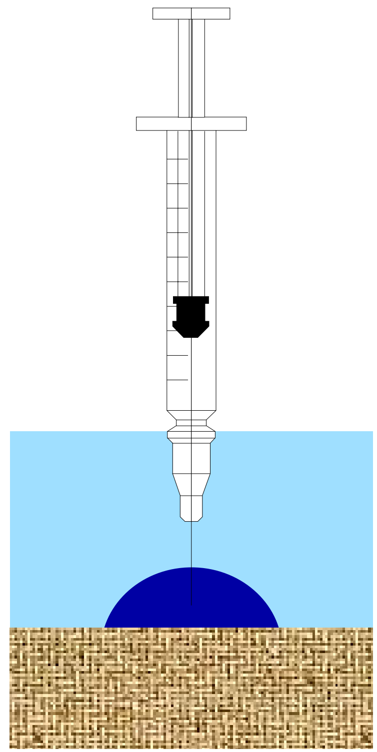
Sessile Drop Technique

Eliminate/reduce evaporation

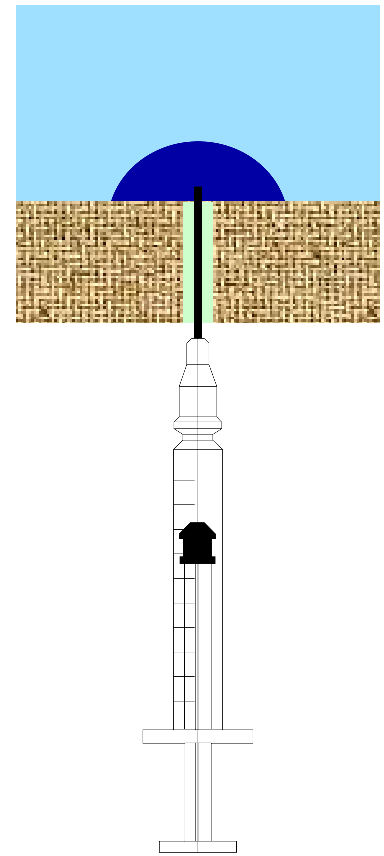


inconvenient

Advance/recede the contact line



most popular



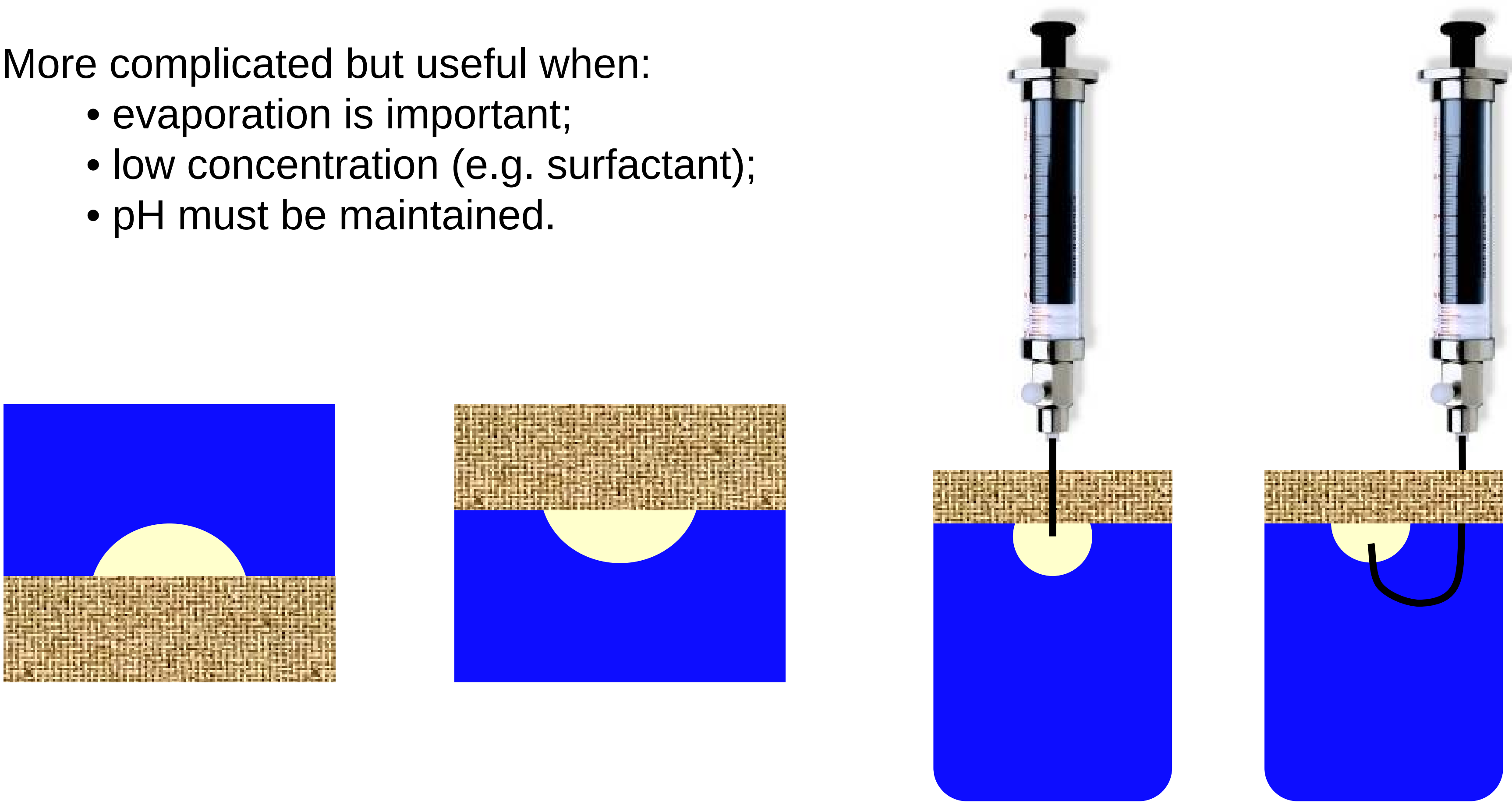
stable/inconvenient

Captive Bubble

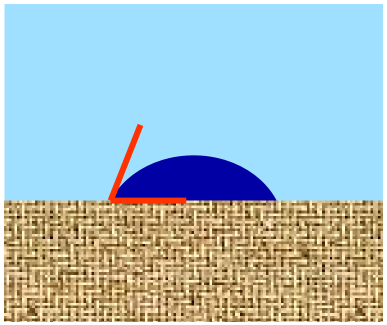
The captive bubble is an “inverted” sessile drop technique.

More complicated but useful when:

- evaporation is important;
- low concentration (e.g. surfactant);
- pH must be maintained.

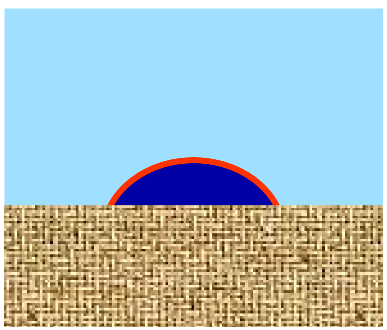


Drop Shape Analysis



Draw the tangent numerically (fit the droplet profile with an empirical function):

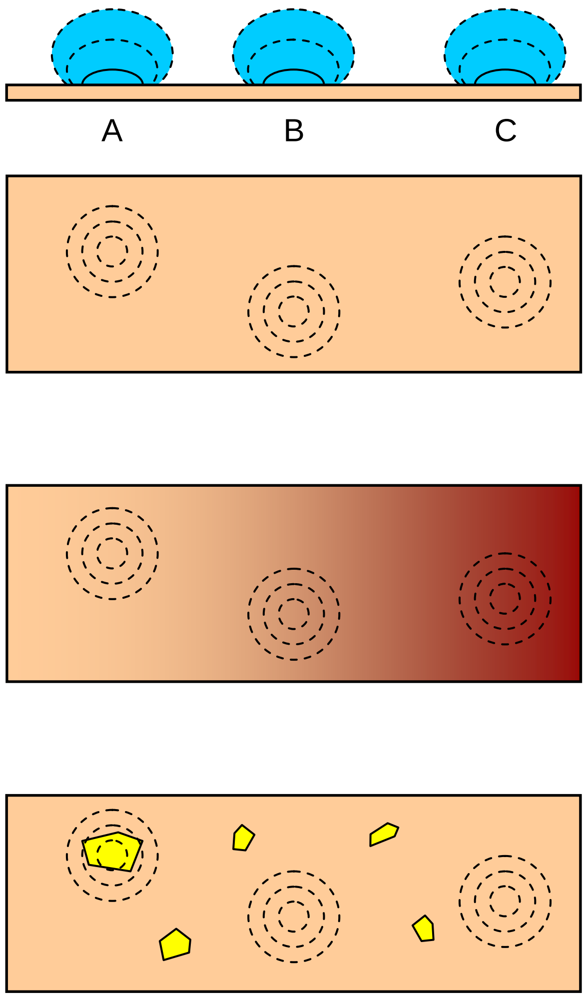
- empirical 👎;
- tolerates shape asymmetry 👍.

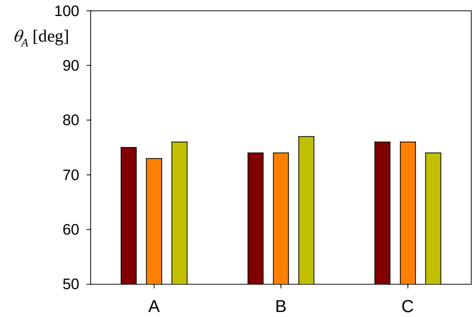


Fit the drop silhouette with Laplace equation:

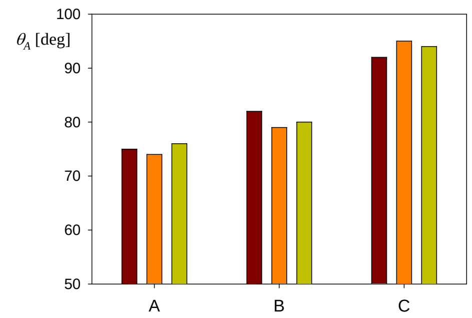
- conceptually superior 👍;
- suitable for axisymmetric shapes only 👎.

Local vs. Global Measurement

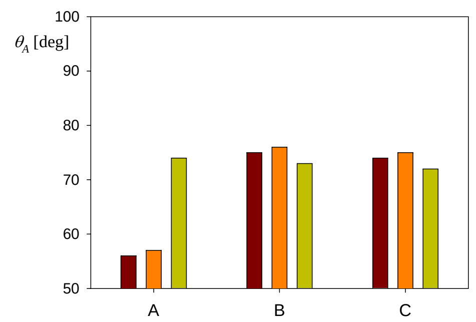




Uniform surface

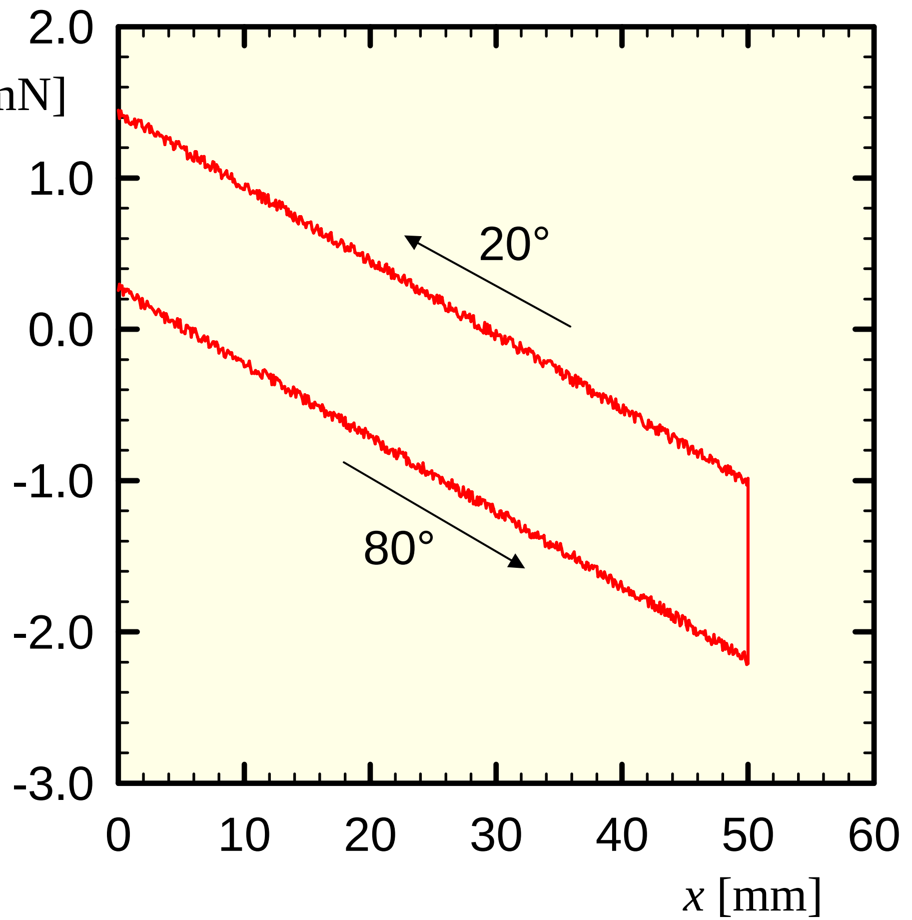


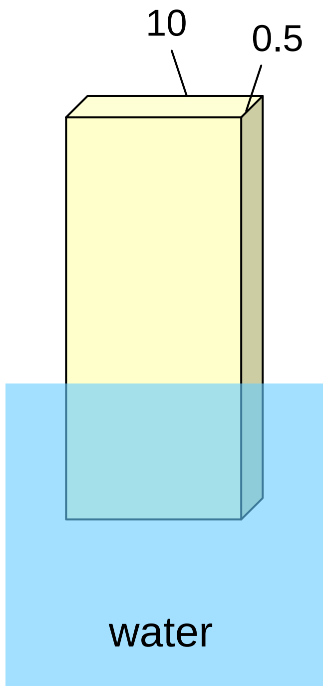
Surface with a gradient



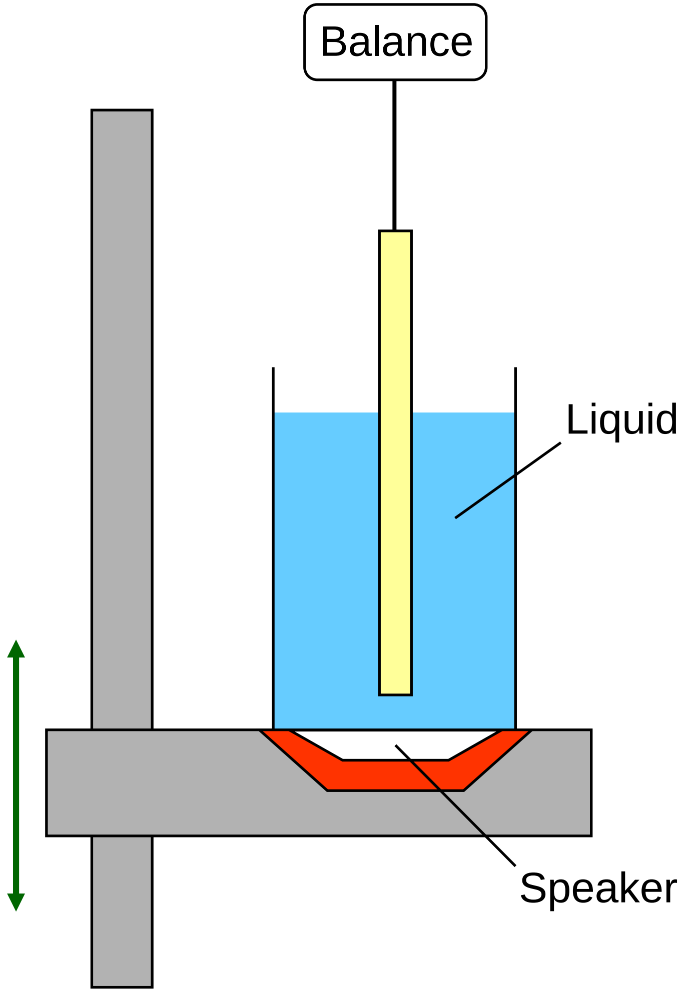
Heterogeneous surface

Wilhelmy Plate Method





Wilhelmy Plate with Vibrations

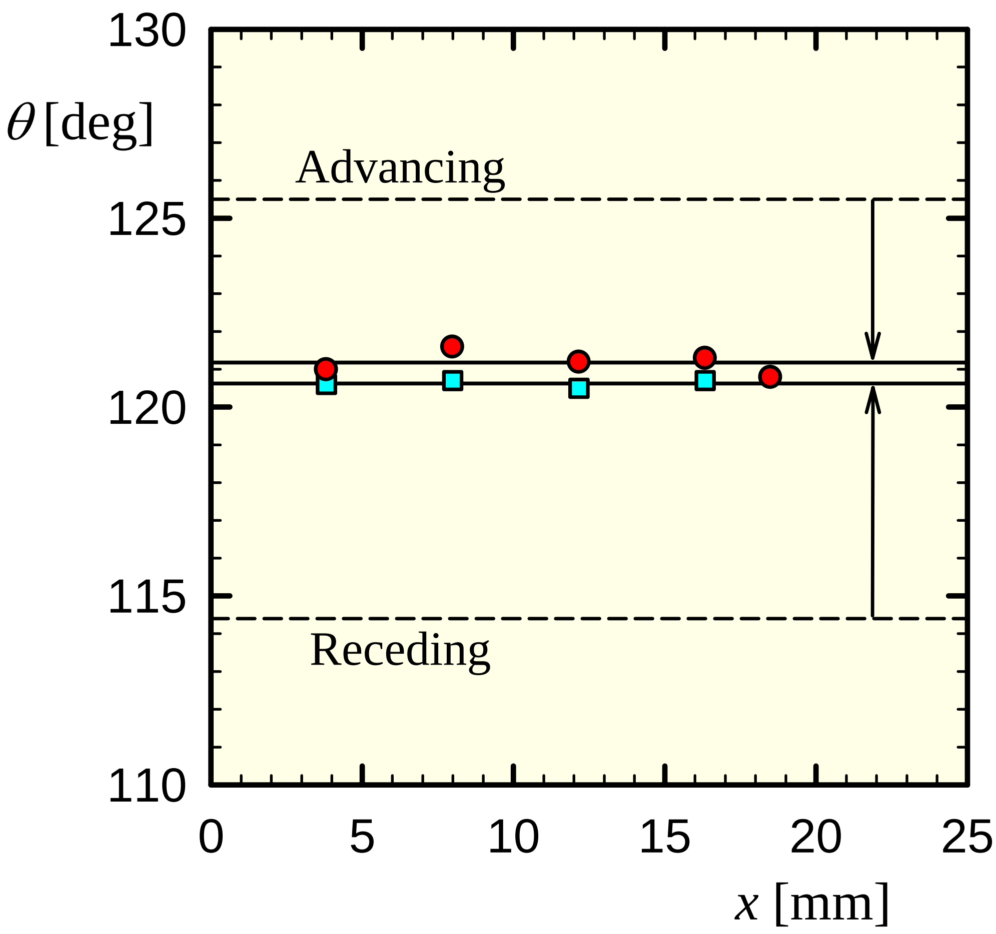


Measurement Protocol:

- drive stage (advance or recede);
- stop movement;
- apply acoustic vibrations;
- allow relaxation to occur;
- measure force.

$$\cos\theta_{A,R,V} = \frac{f_{A,R,V}}{p\gamma}$$

Vibrated Contact Angles



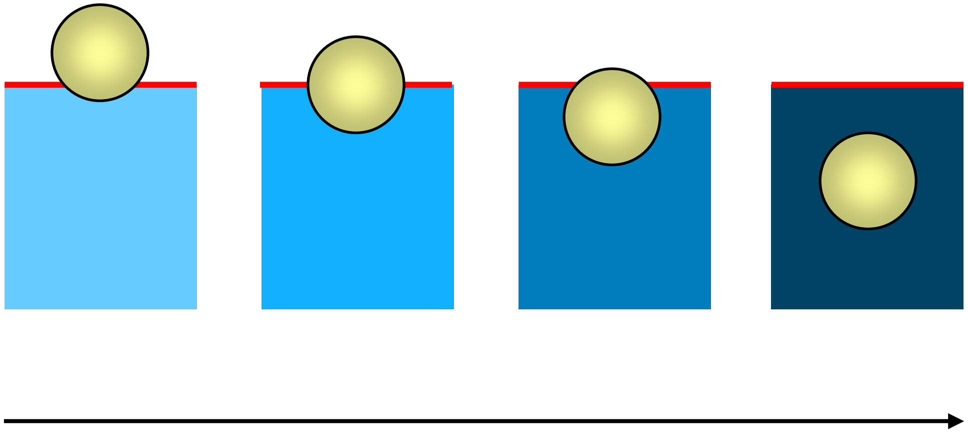
Fabretto et al (2003)

4. Contact Angle on Powders

- Skin Flotation
- Static Capillary Pressure
- Washburn Technique

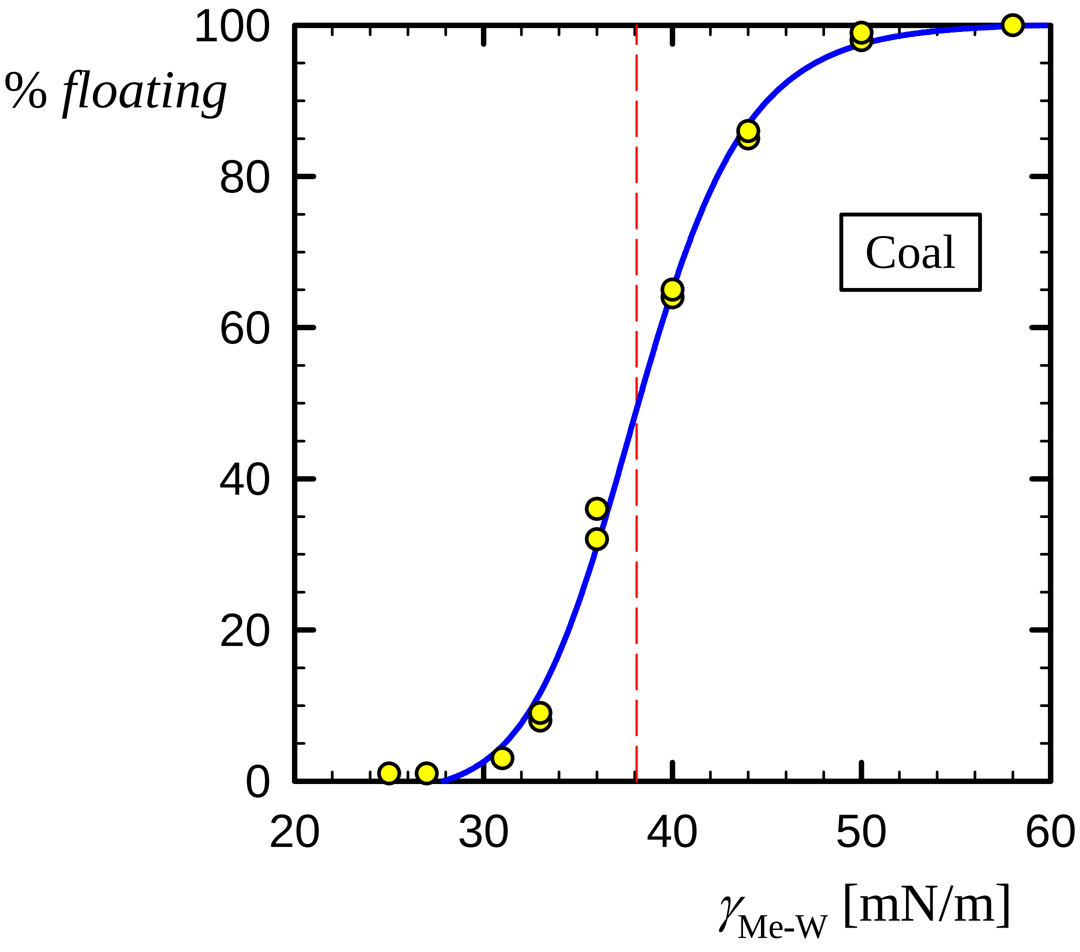
Skin Flotation Technique

Liquid mixtures (e.g. water/methanol) with decreasing surface tension, γ, are consecutively used to determine the critical surface tension, γ_C, of the particle surface.



Both surface tension & contact angle decrease

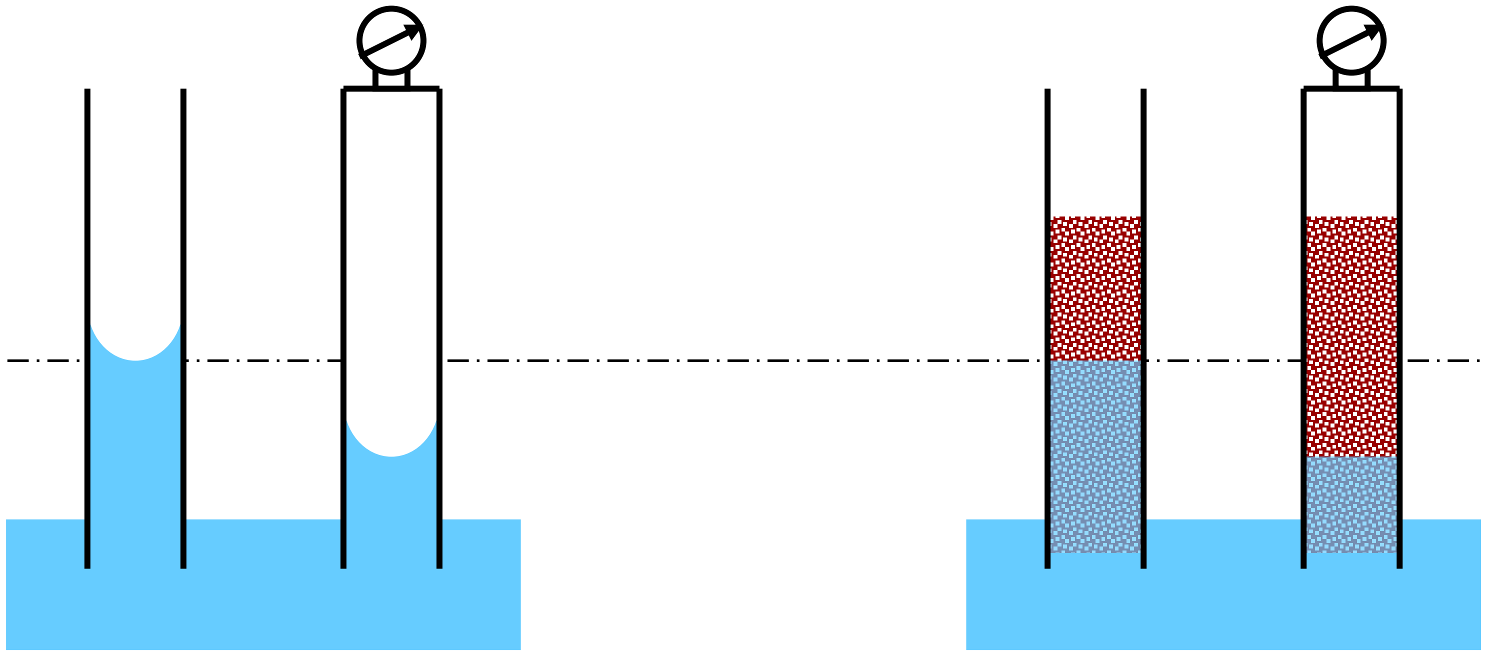
Skin (Film) Flotation – Example



Williams & Fuerstenau (1987)

Static Capillary Pressure Technique (SCPT)

Measure the pressure required to stop capillary penetration:

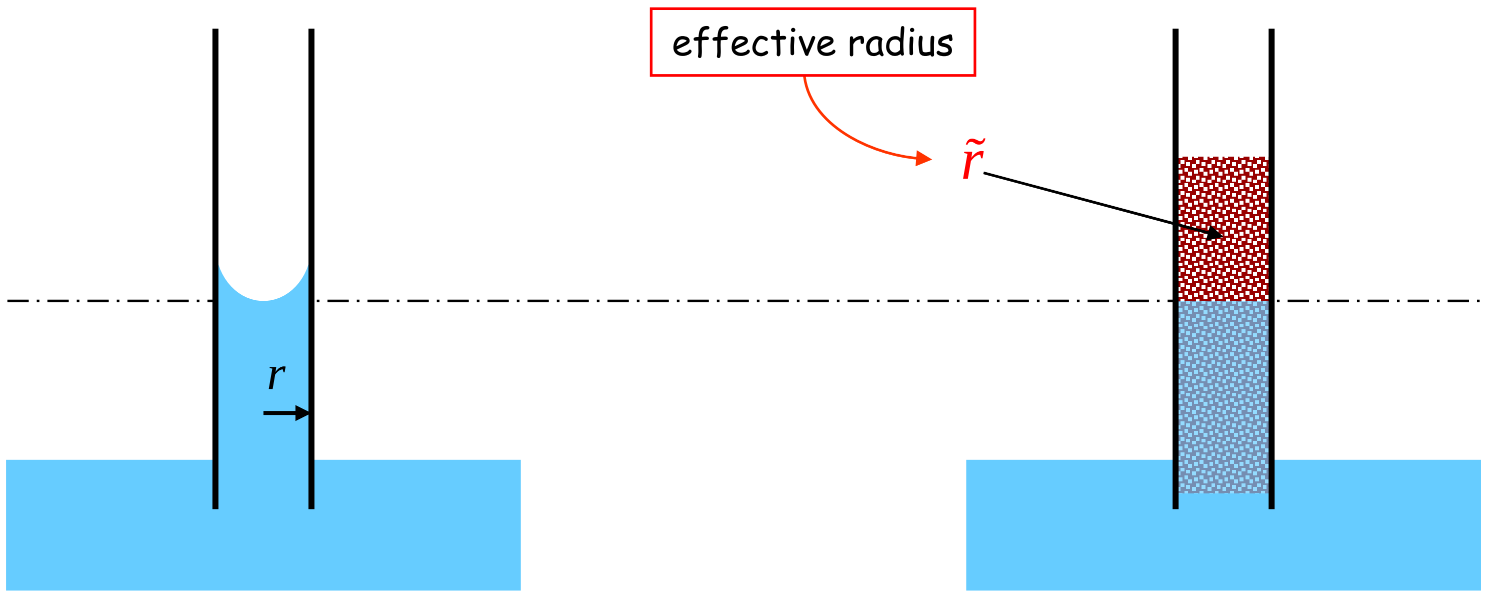


Bartell & Osterhof (1927)

Effective Capillary Radius

The capillary pressure, ΔP, is given by Laplace equation:

$$\Delta P = \frac{2\gamma}{r}\cos\theta \qquad\qquad \Delta P = \frac{2\gamma}{\tilde{r}}\cos\theta$$



Single Capillary

Porous Medium

SCPT – Advancing Liquid

$$\Delta P = \frac{2\gamma}{\tilde{r}} \cos\theta$$

Test liquid ($\theta_1 > 0$): $$\Delta P_1 = \frac{2\gamma_1}{\tilde{r}} \cos\theta_1$$

Calibrating liquid ($\theta_2 = 0$): $$\Delta P_2 = \frac{2\gamma_2}{\tilde{r}} \cos 0$$

$$\cos\theta_1 = \frac{\gamma_2}{\gamma_1} \frac{\Delta P_1}{\Delta P_2}$$

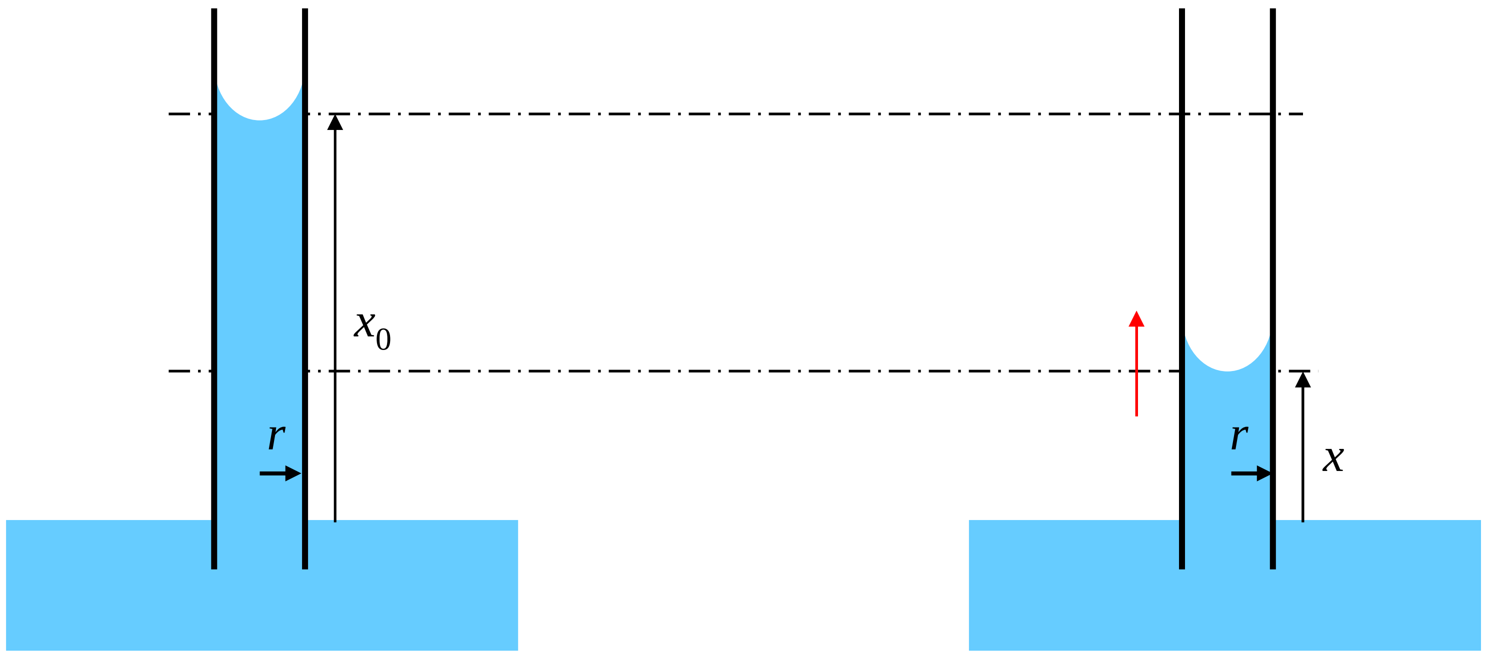
Driving Force for Capillary Penetration

Static Meniscus:

$$f = \frac{2\gamma}{r}\cos\theta - \Delta\rho g x_0 = 0$$

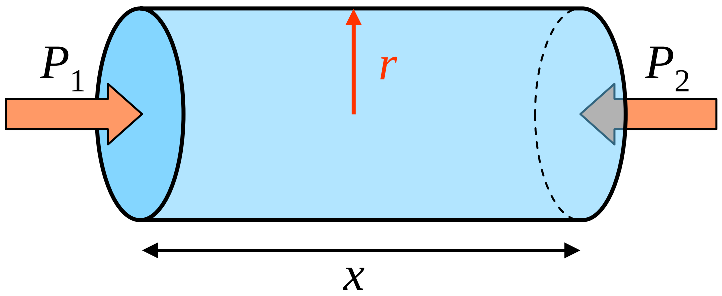
Dynamic Meniscus:

$$f = \frac{2\gamma}{r}\cos\theta - \Delta\rho g x > 0$$

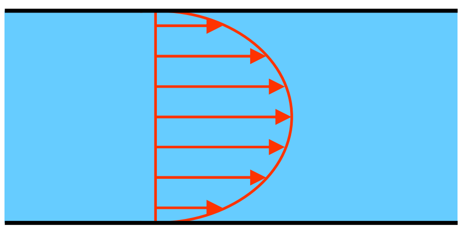


Poiseuille Flow

Circular Pipe



Velocity Profile



Poiseuille Equation

$$Q = \frac{\pi r^4}{8 \mu x} \Delta P$$

$$Q = \frac{V}{t} = \frac{Ax}{t} = A\overline{u} = \pi r^2 \overline{u}$$

$$\overline{u} = \frac{r^2}{8 \mu x} \Delta P$$

Washburn Equation

$$\frac{dx}{dt} \equiv \bar{u} = \frac{r^2}{8\mu x}\Delta P$$

Poiseuille Equation

Constant capillary pressure

$$\frac{dx}{dt} = \frac{r^2}{8\mu x}\left(\frac{2\gamma\cos\theta}{r} - \Delta\rho g x\right)$$

Gravity is unimportant

$$\frac{dx}{dt} = \frac{r\gamma\cos\theta}{4\mu x}$$

Integration

$$x^2 = \frac{r\gamma\cos\theta}{2\mu}t$$

Washburn Equation

Washburn Method

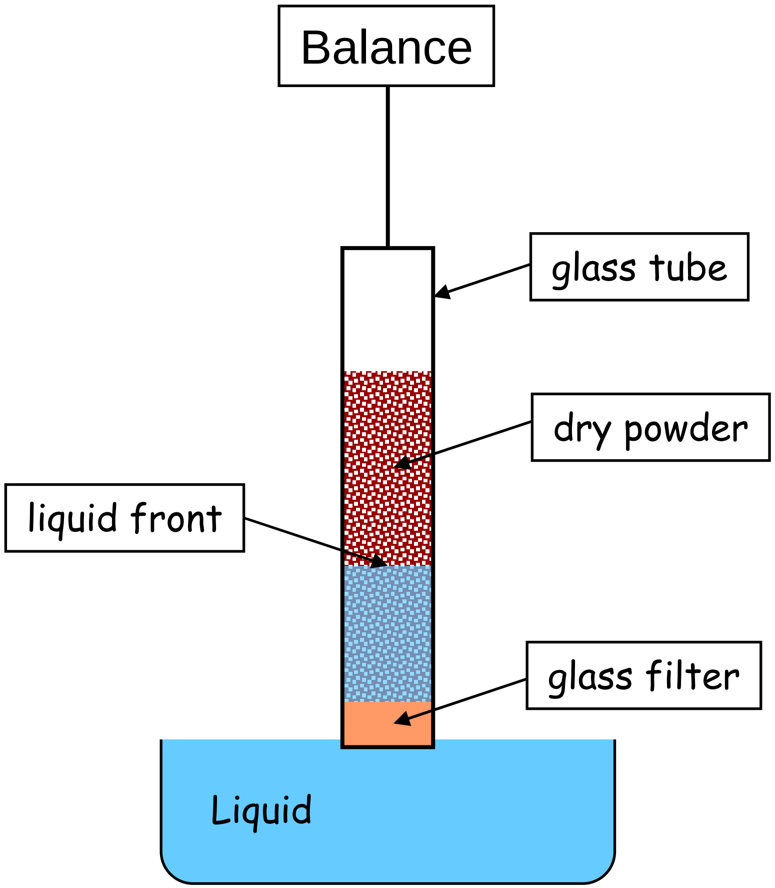
The contact angle is related to the geometry of the system ($2/\tilde{r}$), the known liquid properties (viscosity μ and surface tension γ) and a measurable quantity (x^2/t):

$$\cos\theta = \frac{2}{\tilde{r}} \frac{\mu}{\gamma} \frac{x^2}{t}$$

The geometry factor can be calibrated by using a liquid with $\theta_2 = 0$. Then :

$$\cos\theta_1 = \frac{\mu_1}{\mu_2} \frac{\gamma_2}{\gamma_1} \frac{\left(x^2/t\right)_1}{\left(x^2/t\right)_2}$$

Washburn Method – Gravimetric Version



<u>Assumptions</u>:

- gravity is ignored;
- flow is laminar;
- pore geometry is constant.

$$\cos\theta = \underbrace{\frac{2}{\varepsilon^2 A^2 \tilde{r}}}_{\text{geometry}} \underbrace{\frac{\mu}{\rho^2 \gamma}}_{\text{liquid}} \underbrace{\frac{m^2}{t}}_{\text{experiment}}$$

Conclusions

- The measuring technique must be regarded as part of the research approach;
- Sensitivity is (potentially) enormous but accuracy is typically low;
- Hysteresis must always be taken into account;
  - Surface may be rough and/or heterogeneous;
  - Surface may not be uniform;
  - Surface may be affected by the contact with the liquid;
  - Surface may be contaminated;
  - Contact line speed may be important (especially with viscous liquids or at high speed);
- Use complementary techniques whenever possible;
- Very few methods work for single particles; measurements on packed beds are often preferable.