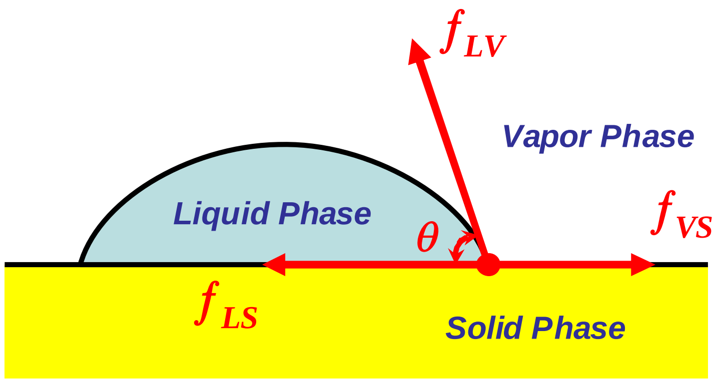
Principles of
Video Contact Angle Analysis

AST Products, Inc.

What is Contact Angle Analysis?

To Determine surface energy indirectly with the shape of a drop placed on the surface

- Three interfacial forces balance at the edge of a drop.
- Two are in opposite directions and the third one forms a particular angle to the surface.
- That particular angle is called Contact Angle.



$$\cos\theta = \frac{f_{VS} - f_{LS}}{f_{LV}} \quad \text{Young's Equation}$$

f_{LV} — interfacial force of drop and vapor

f_{LS} — interfacial force of drop and test surface

f_{VS} — interfacial force of test surface and vapor

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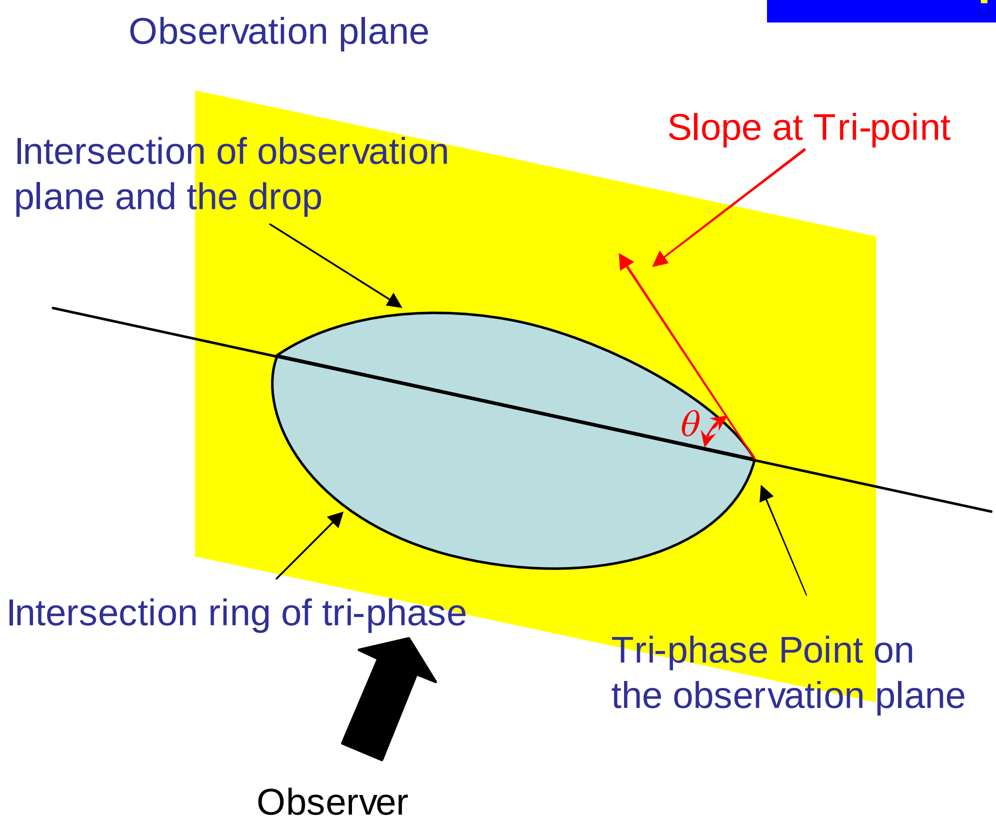
Applications of Contact Angle Analyzer

- Bio-medical
  - Wettability improvement of contact lens and product quality assurance.
  - Bio-compatibility of human implants
  - Micro-fluidity studies of bio-chips
- Interfacial Chemistry
  - Surface Tension and Wettability of Detergents and Surfactants
  - Adhesive strengthen and pre-adhesion treatment studies
  - Studies on Waterproof Agents
  - Die and color fastenization
- TFT-LCD Display Panel Industry
  - Glass panel cleanliness inspection and process quality assurance.
  - Pre-coating surface quality assurance of TFT printed circuitry, color filter, ITO conducting films.
- Erosion Control Studies
  - Studies of Surface Corrosion Factors
  - Surface Water Repellency Studies
- Cosmetics
  - Skin wettability and spreading of lotions
  - Wettability studies on powders
- Hard Disk Drives
  - Wettability and Spreading of Lubricant on Disk Surface
  - Surface Cleanliness
- Plating, Painting, and Printing
  - Surface cleanliness quality assurance
  - Surface adhesion quality assurance
  - Ink speading and adhesion studies
  - Color ink-jet tranparency development
- Plastics Inductry
  - Surface modification of polymers and process quality assurance
- Semiconductors
  - Wafer cleanliness
  - HMDS process control
  - Photo-resist and developer studies
  - CMP process development
- IC Packaging
  - Substrate cleanliness
  - BGA welding surface
  - Epoxy adhesion
  - Oxidation identification of bonding
- Nano Technology
  - Lotus effect on surface nano-structure
  - Surface Repellency of Nano-composites

Observing Contact Angle

What one observes is actually a 2D projection of 3D drop



- At least one is liquid phase
- Test surface is solid phase or another liquid phase
- Third phase is vapor phase (drop vapor and air) or another liquid phase

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Drop Surface Tension and Surface Energy of Test Surface

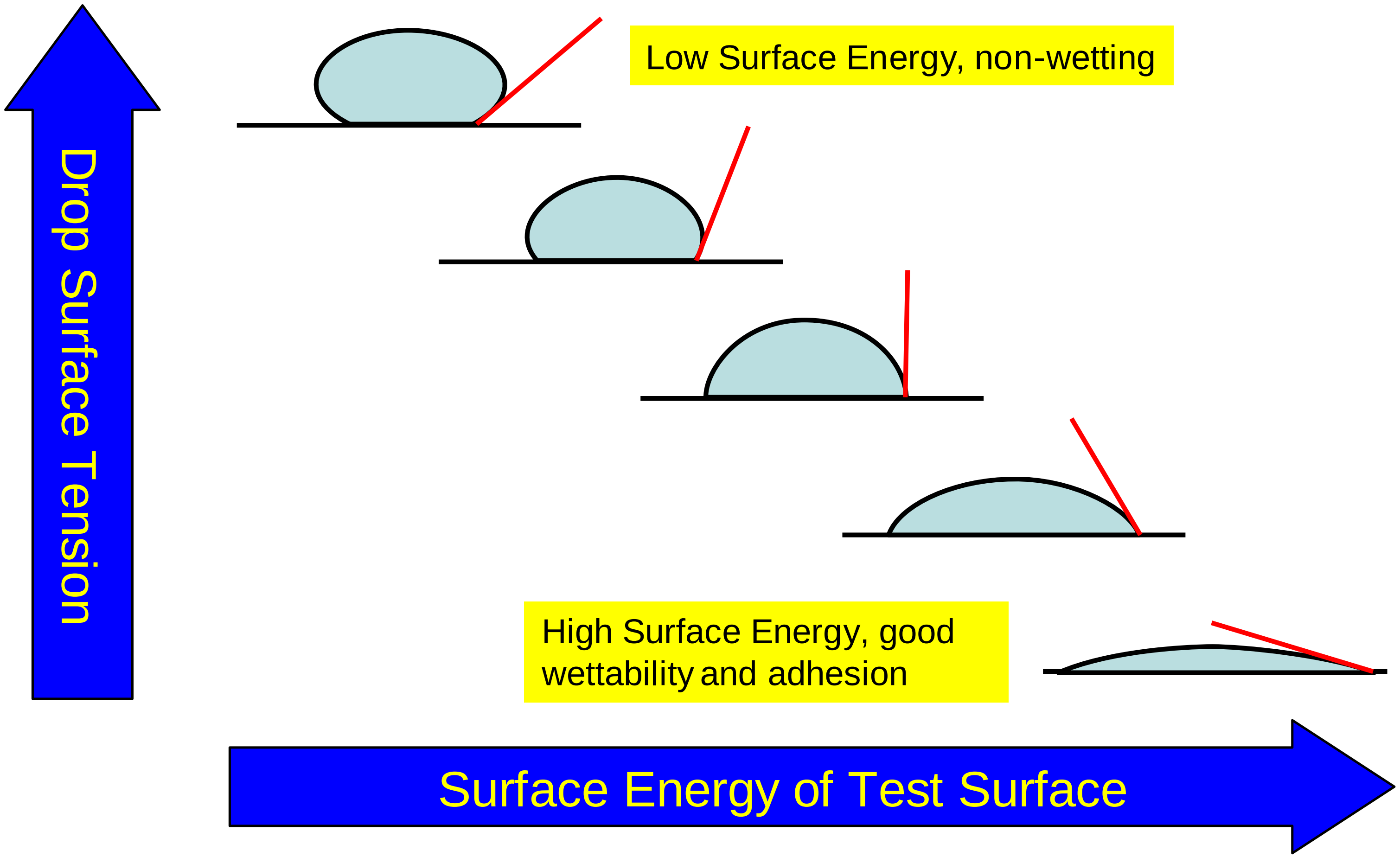

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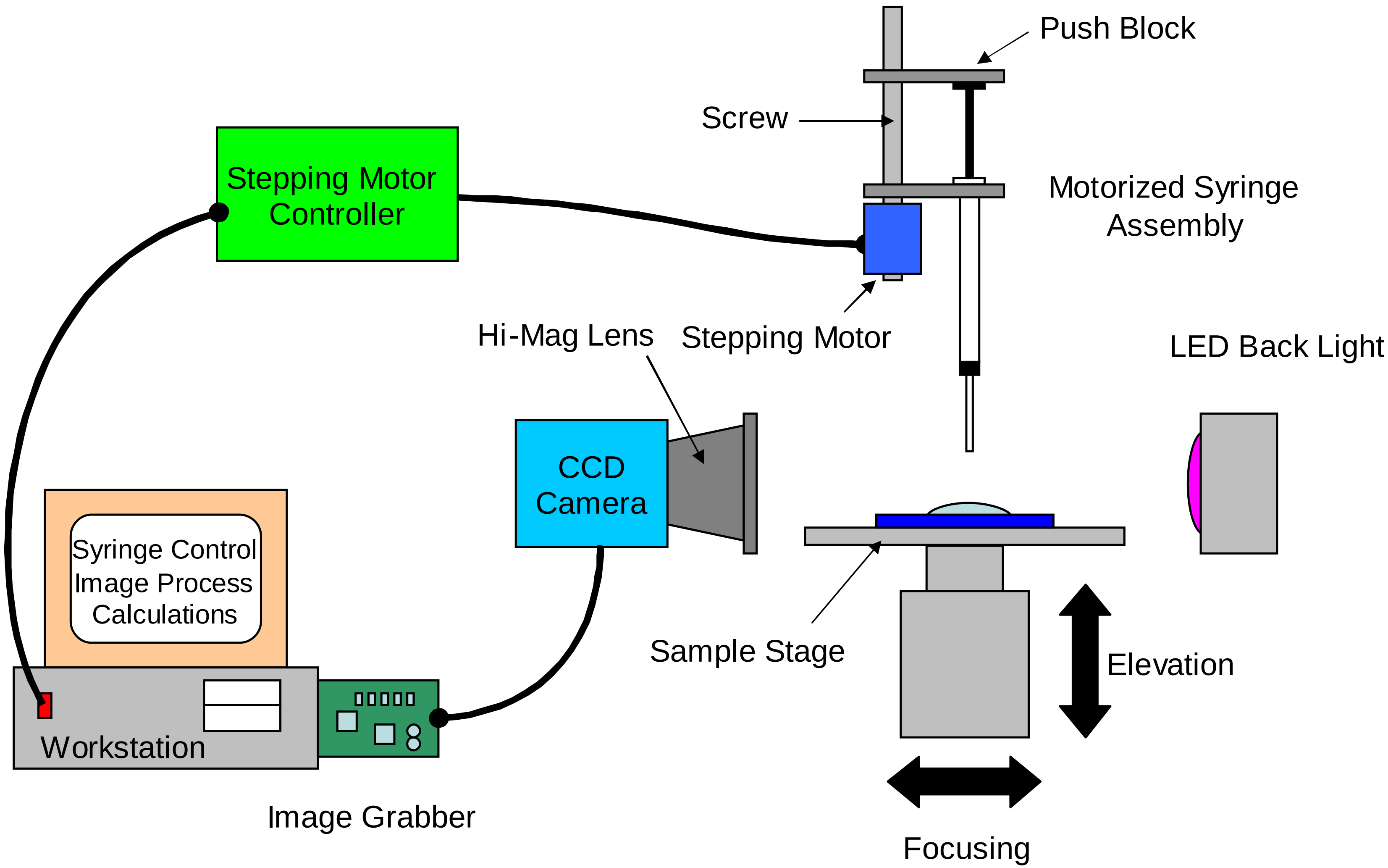
Diagram of Video Contact Angle Analyzer



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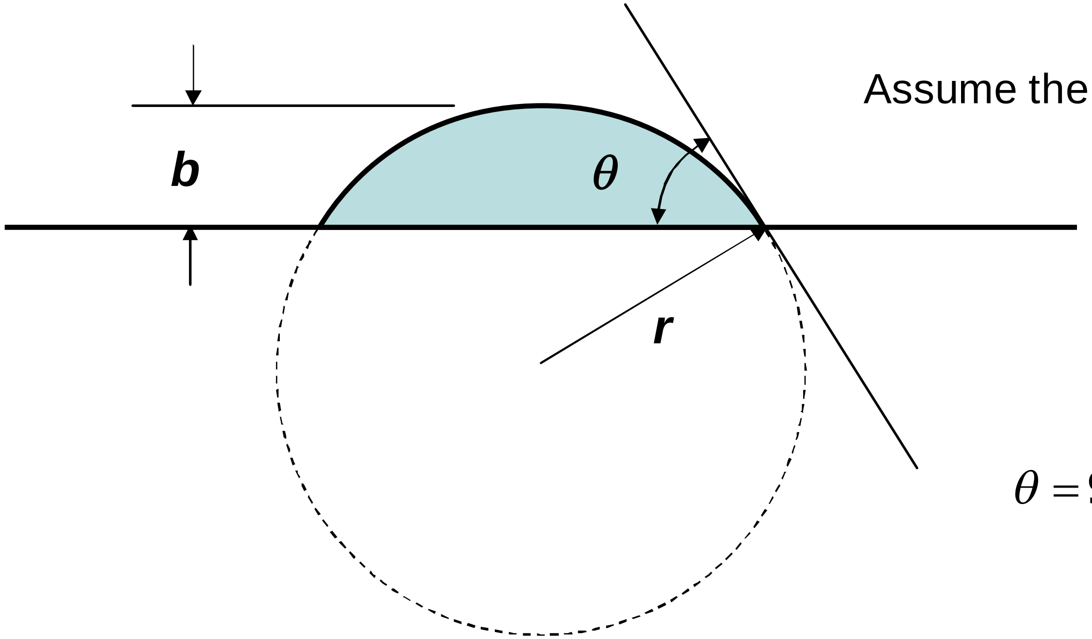
Simple Theoretical Model



Assume the drop is part of a sphere

$$\theta = 90 - \tan^{-1}\left(\frac{r-b}{\sqrt{2rb-b^2}}\right)$$

- Contact angle analysis software in general assume the drop is part of a sphere.
- However, due to gravitation and molecular dispersion, the shape of a drop is close but not exactly a part of a sphere.
- The hidden assumption: when the drop volume is small, the gravitational effect can be ignored.
- Improved on sphere model has been replaced by ellipsoid model to simulate gravitational effect. But, what about the molecular dispersion?

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Drop Shape Determination by AutoFAST Algorithm

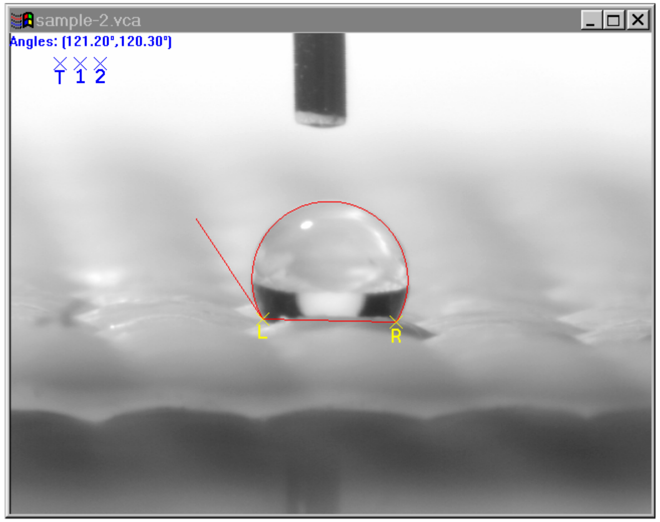
To keep the calculation objective, AutoFAST algorithm uses second-order binary curves to simulate the shape of drop without any theoretical modeling

Algorithm:

- Find points at the edge of drop
- Fit a curve to the drop edge.
- Find points at the contact boundary
- Fit a curve to the contact boundary
- Find the intersections of the two curves and calculate the slopes at the two intersections

Second-order Binary Equation

$$a_5 x^2 + a_4 xy + a_3 y^2 + a_2 x + a_1 y + a_0 = 0$$



The AutoFAST algorithm automatically determines drop edge and contact boundary. The RED lines are the actual simulated curves. Mark L and R are left and right intersections of curves, respectively.

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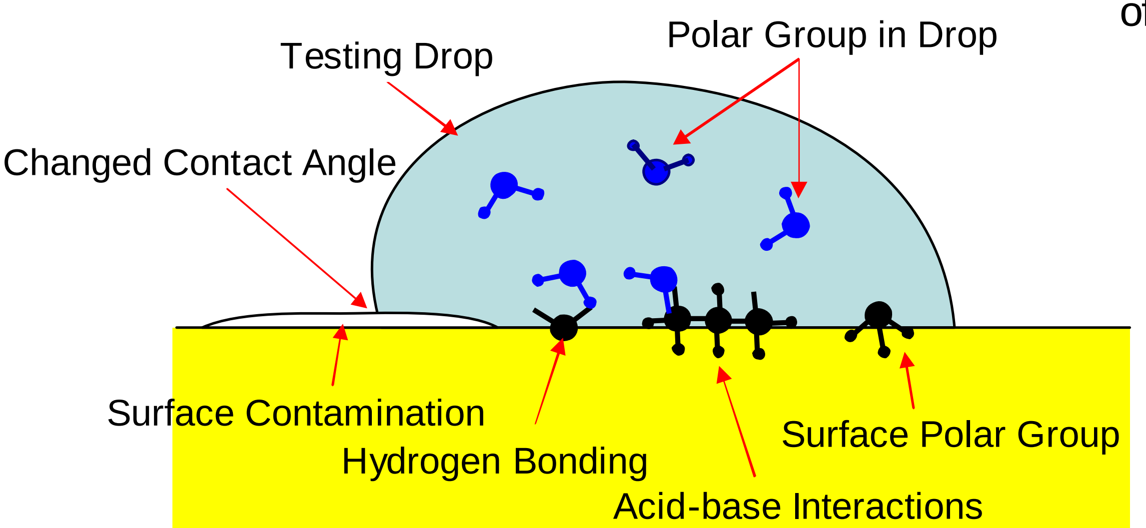
Interactions Between Drop and Testing surface

Surface energy is the combination of dispersion (non-polar) and polar energy

- Coulomb interactions of polar groups
  - Dipole-Dipole Interactions
  - Dipole-Induced Dipole Interaction
  - Hydrogen Bonding
  - Acid-Base Interactions

Dispersion Energy : Surface energy that results from non-polar interactions of molecules

Polar Energy : Surface energy that results from interactions of polar groups



Dispersion energy exists between all molecules but polar energy exists only when polar groups are present.

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Surface Energy Calculations

- **Fox-Zisman Theory**
  - Free energy of adhesion is equal to the projection of surface tension of drop at testing surface.
  - Assume that the interaction between the drop and the testing surface is greater than the internal force of drop (low contact angle).
  - Suitable for low contact angle surfaces.

- **Geometric Mean Theory**
  - Free energy of adhesion is equal to the Geometric Mean of cohesive energy of separated phases
  - Suitable for testing surfaces with similar ionization potential.

- **Harmonic Mean Theory**
  - Free energy of adhesion is equal to the Harmonic Mean of cohesive energy of separated phases
  - Suitable for non-polar low-energy testing surfaces.

- **Acid-Base Theory**
  - Evaluate polar energy based on energy interchange model of acid and base.

Fox-Zisman Theory

- Free energy of adhesion is equal to the projection of surface tension of the drop at testing surface.
- Assume that the interaction between the drop and the testing surface is greater that the internal force (low contact angle), and energy of the interaction is negligible compared to testing surface energy
- Suitable for testing surfaces with low contact angle.
- Requires at least two drops of low contact angle.

$$\cos\theta_i = \frac{\gamma_s}{\gamma_i} \qquad i = 1, 2$$

θ_i : contact angle of testing drop

γ_i : surface tension of testing drop

γ_s : surface tension of testing surface

Geometric-Mean Method

- Free energy of adhesion between phases is equal to the **Geometric Mean** of two separated phases.
- Owen, Wendt, Rabel and Kaelble (OWRK) Method
- Suitable for testing surfaces with similar ionization potential.
- Require at least two kinds of drops that have similar ionization potential with the testing surface

$$\gamma_i(1+\cos\theta_i) = 2\left(\sqrt{\gamma_i^{\mathrm{d}}\gamma_s^{\mathrm{d}}} + \sqrt{\gamma_i^{\mathrm{p}}\gamma_s^{\mathrm{p}}}\right) \quad i = 1, 2$$

$$\gamma_i = \gamma_i^{\mathrm{d}} + \gamma_i^{\mathrm{p}} \quad i = 1, 2$$

$$\gamma_s = \gamma_s^{\mathrm{d}} + \gamma_s^{\mathrm{p}}$$

θ_i : contact angle of testing drop i

γ_i : surface tension of testing drop i

$\gamma_i^{\mathrm{d}}, \gamma_i^{\mathrm{p}}$: dispersion and polar energy of testing drop i

$\gamma_s^{\mathrm{d}}, \gamma_s^{\mathrm{p}}$: dispersion and polar energy of testing surface

Harmonic-Mean Method

- Free energy of adhesion between phases is equal to the **Harmonic Mean** of two separated phases.
- Wu's Method
- Suitable for non-polar low energy surfaces.
- Require at least two kinds of drops with different surface tensions.

$$\gamma_i(1+\cos\theta_i) = 4\left[\frac{\gamma_i^{\mathrm{d}}\gamma_s^{\mathrm{d}}}{\gamma_i^{\mathrm{d}}+\gamma_s^{\mathrm{d}}} + \frac{\gamma_i^{\mathrm{p}}\gamma_s^{\mathrm{p}}}{\gamma_i^{\mathrm{p}}+\gamma_s^{\mathrm{p}}}\right] \quad i = 1, 2$$

$$\gamma_i = \gamma_i^{\mathrm{d}} + \gamma_i^{\mathrm{p}} \quad i = 1, 2$$

$$\gamma_s = \gamma_s^{\mathrm{d}} + \gamma_s^{\mathrm{p}}$$

θ_i : contact angle of testing drop i

γ_i : surface tension of testing drop i

$\gamma_i^{\mathrm{d}}, \gamma_i^{\mathrm{p}}$: dispersion and polar energy of testing drop i

$\gamma_s^{\mathrm{d}}, \gamma_s^{\mathrm{p}}$: dispersion and polar energy of testing surface

Acid-Base Theory

- Evaluate polar energy based on energy interchange model of acid and base.
- Suitable for materials with polar surface
- Requires at least three drops of different surface tensions, at least two of them must be polar fluid.

$$\gamma_i(1+\cos\theta_i) = 2\left(\sqrt{\gamma_i^{d}\gamma_s^{d}} + \sqrt{\gamma_i^{\oplus}\gamma_s^{\Theta}} + \sqrt{\gamma_i^{\Theta}\gamma_s^{\oplus}}\right)$$

$$\gamma_i = \gamma_i^{d} + 2\sqrt{\gamma_i^{\oplus}\gamma_i^{\Theta}}$$

$$\gamma_s = \gamma_s^{d} + 2\sqrt{\gamma_s^{\oplus}\gamma_s^{\Theta}}$$

γ_i : surface tension of testing drop i

γ_i^{d} : dispersion portion of surface tension

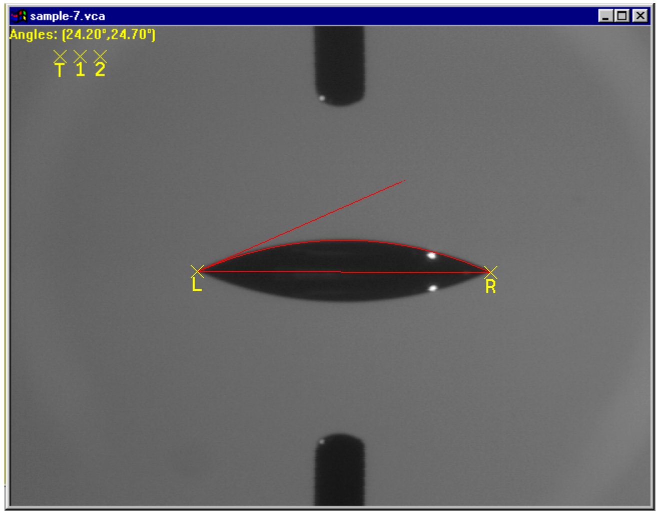
$\gamma_i^{\oplus}$: surface tension contributed by acid

γ_i^{Θ} : surface tension contributed by base

References on Contact Angle Theories

- S. Wu, "Polymer Interface and Adhesion," Marcel Dekker, New York (1982).
- R.J. Good, in "Modern Approaches to Wettability: Theory and Applications," Eds. M.E. Schrader and G.I. Loeb, p. 1-27, Plenum Press, New York, (1992).
- K.L. Mittal, Ed., "Contact Angle, Wettability and Adhesion," VSP BV, The Netherlands, (1993).

AutoFAST Options



Drop on a reflective surface

"Reflective Surface" Option

- Assumes the drop image possesses horizontal mirror symmetry and the axis of symmetry is the contact boundary

"Low Contact Angle" Option

- Assume at low contact angle, the drop image possess vertical mirror symmetry

When measuring advancing and receding contact angles with tilting stage, do not choose either "Reflective Surface" or "Low Contact Angle" Option.

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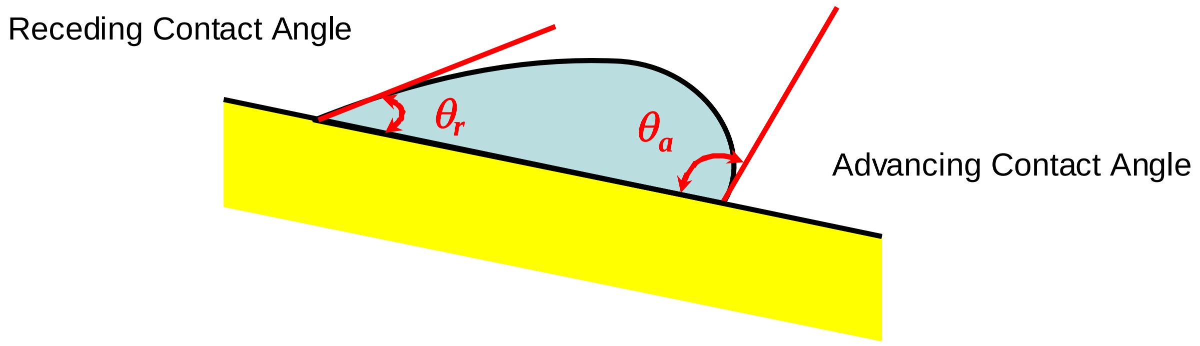
Advancing and Receding Contact Angles

When the testing surface is tilted, contact angles at either sides of the drop differ.

Advancing Contact Angle relates to surface energy and wettability.

Receding Contact Angle relates to surface roughness and repellency.



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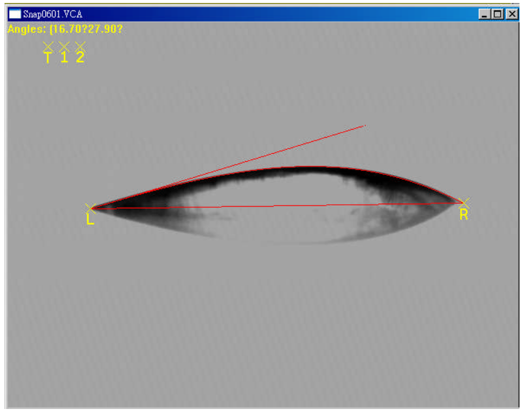
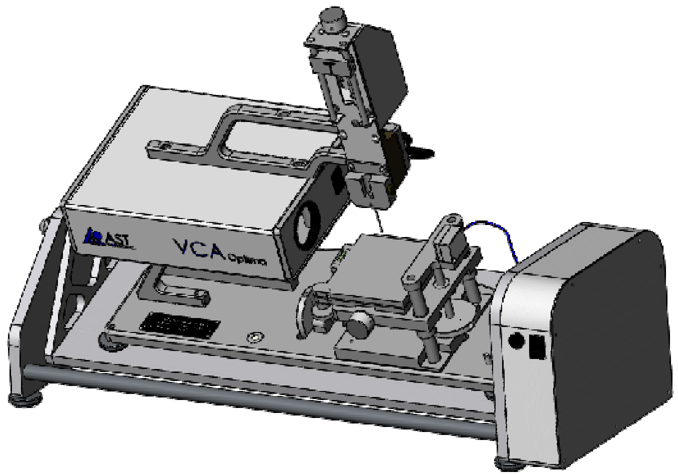
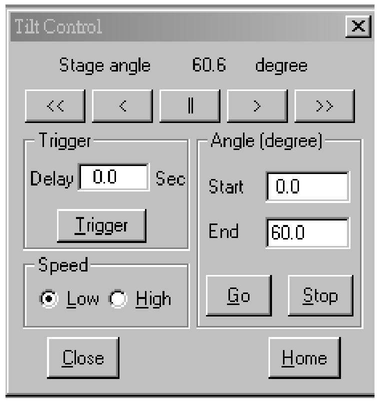
Measuring Advancing and Receding Contact Angle with the Tilting Stage assmebly





VCA Optima software calculates asymmetrical drop image with accuracy. The advancing contact angle at right is 27.9° while the receding contact angle at left, 16.7°. The critical titling angle is 87°.



Tilting Stage Control Interface

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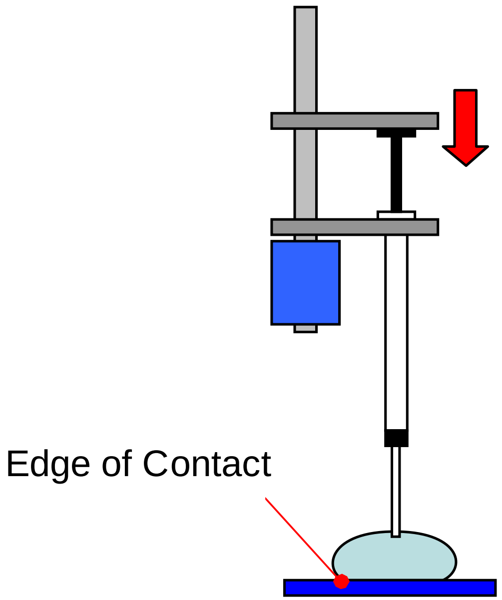
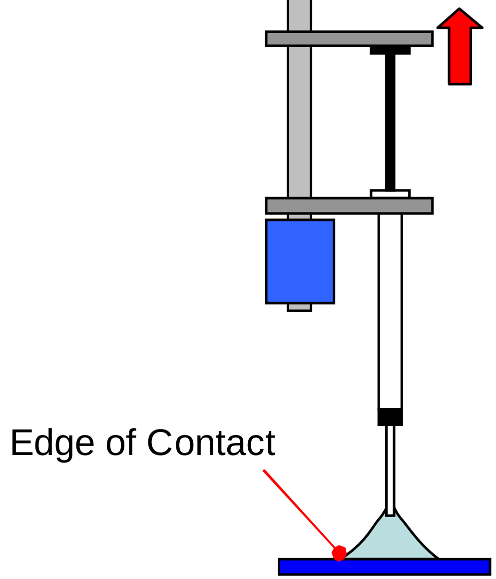
Measuring Advancing and Receding Contact Angle with Motorized Syringe



Advancing Contact Angle

The critical angle at which
the edge of contact expands



Receding Contact Angle

The critical angle at which
the edge of contact retracts

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Industry Standards of Contact Angle Measurements

- ASTM D724-99 Standard Test Method for Surface Wettability of Paper (Angle-of-Contact Method)
- ASTM D5725-99 Standard Test Method for Surface Wettability and Absorbency of Sheeted Materials Using an Automated Contact Angle Tester
- ASTM C813-90(1994)e1 Standard Test Method for Hydrophobic Contamination on Glass by Contact Angle Measurement
- ASTM D5946-96 Standard Test Method for Corona-Treated Polymer Films Using Water Contact Angle Measurements
- TAPPI T458 Surface Wettability of Paper (Angle of Contact Method) (TAPPI web site: www.tappi.org)