

Lecture: P1_Wk3_L1

Tip-Sample Interactions:
the Water Meniscus

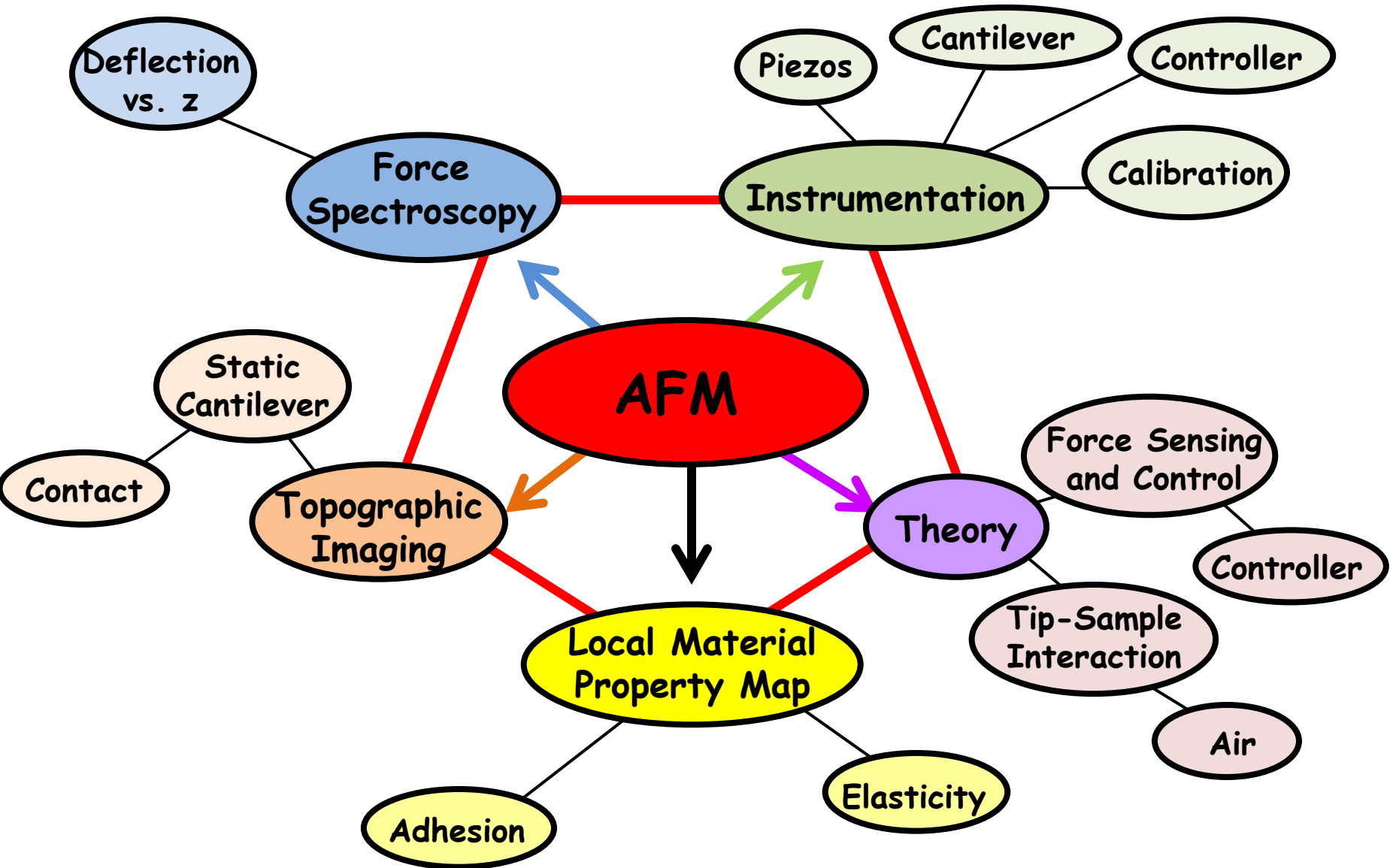
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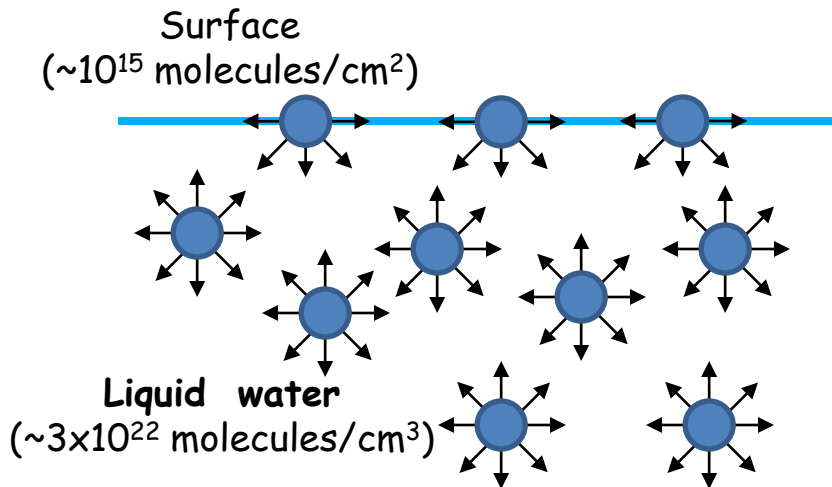
2012

Week 3 Overview

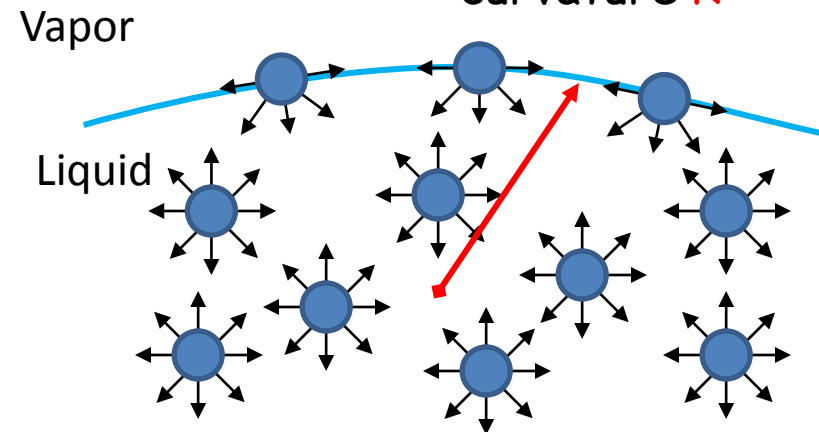


The asymmetry in number density at a liquid-vapor surface gives rise to a pressure differential and a surface curvature

Vapor ($\sim 2 \times 10^{19}$ molecules/cm³)



Local radius of curvature R



Solid substrate ($\sim 6 \times 10^{22}$ atoms/cm³)

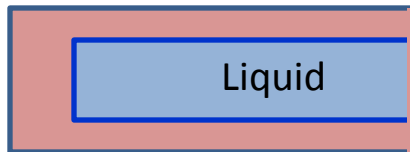
The "Curvature" of a Liquid's Surface has far reaching consequences

See Appendix for a general discussion on how to quantify the curvature of a surface using the **radius of curvature**. Two important consequences:

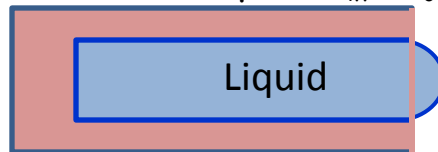
1. If the surface of a liquid is curved, there must be a pressure difference: **Young-Laplace Equation**

b) Liquid/vapor interface in equilibrium

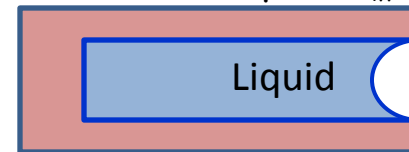
a) Fill tube with liquid:



Curvature implies $P_{in} > P_{out}$



Curvature implies $P_{in} < P_{out}$



$$(P_{in} - P_{out}) = \gamma \left(\frac{1}{R_2} + \frac{1}{R_1} \right)$$

for a spherical surface, $R_1 = R_2 = R$ and

$$\Delta P \equiv (P_{in} - P_{out}) = 2\gamma \left(\frac{1}{R} \right)$$

see Appendix 2 for derivation

Implications of the Young-Laplace Equation

- If the shape of a liquid surface is known, its curvature is known and the pressure difference can be calculated.
- In equilibrium, the pressure is the same everywhere in a liquid (otherwise there would be a flow of liquid to regions of lower pressure). Thus, P_{in} is constant and the Young-Laplace equation tells us that the surface of the liquid must have the same curvature everywhere.

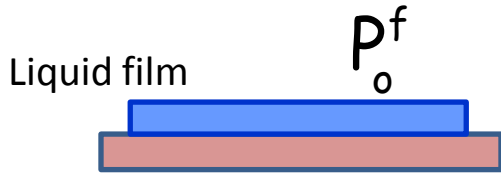
Example: Calculate the pressure difference that develops for a spherical drop of water at STP with a radius of $1 \mu\text{m}$?

$$\begin{aligned}\Delta P &= (P_{in} - P_{out}) = 2\gamma \left(\frac{1}{R} \right) = 2 \times (75 \times 10^{-3} \text{ J / m}^2) \left(\frac{1}{1 \times 10^{-6} \text{ m}} \right) \\ &= 1.5 \times 10^5 \text{ N / m}^2 = 1.5 \times 10^5 \text{ Pa} \times \frac{1 \text{ atm.}}{1 \times 10^5 \text{ Pa}} \\ \Delta P &\approx 1.5 \text{ atmospheres pressure drop across interface}\end{aligned}$$

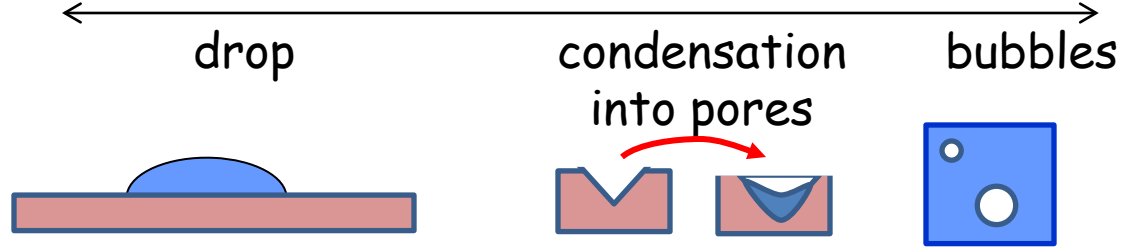
- Using the Young-Laplace equation, the equilibrium **shape of a liquid surface** can be calculated if we know the pressure difference and boundary conditions (volume of liquid and its contact line).

2. It may not be so obvious, ... but if the surface of a liquid is curved, the equilibrium vapor pressure of the liquid must also change: **Kelvin Equation**

Flat interface:



Curved interfaces:



The equilibrium vapor pressure measures a liquid's evaporation rate: smaller drops evaporate faster

$$\frac{R_{\text{gas}} T}{V_{\text{mol}}} \ln \left(\frac{P_{\text{vap}}^c}{P_o^f} \right) = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

$T = \text{temperature in K}$

$R_1, R_2 = \text{radii of curvature of liquid surface}$

see Appendix 3 for derivation

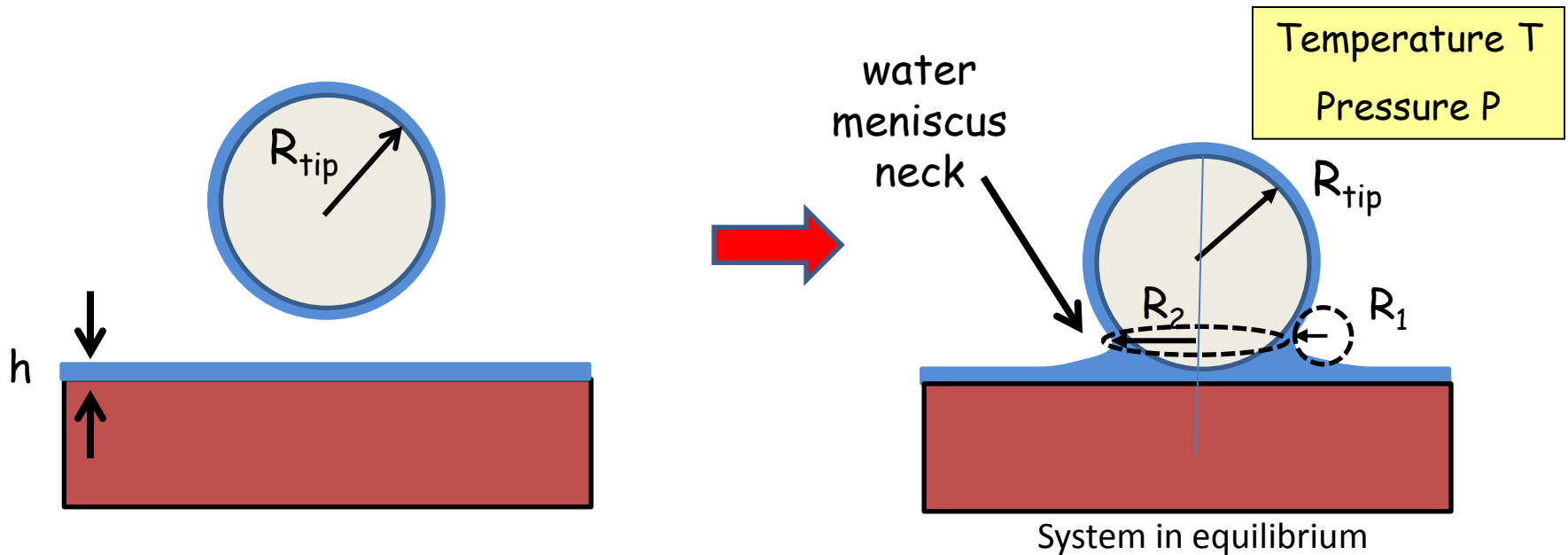
$$\gamma_{H_2O} = 0.072 \text{ J/m}^2$$

$$V_{\text{mol}}|_{H_2O} = 18 \text{ cm}^3 / \text{mole}$$

$$R_{\text{gas}} = 8.314 \text{ J/K} \cdot \text{mole}$$

Application to AFM

In humid air, both tip and substrate will be coated with thin layer of adsorbed water. When the tip contacts the surface, the adsorbed water will form a **meniscus neck** around the AFM tip.

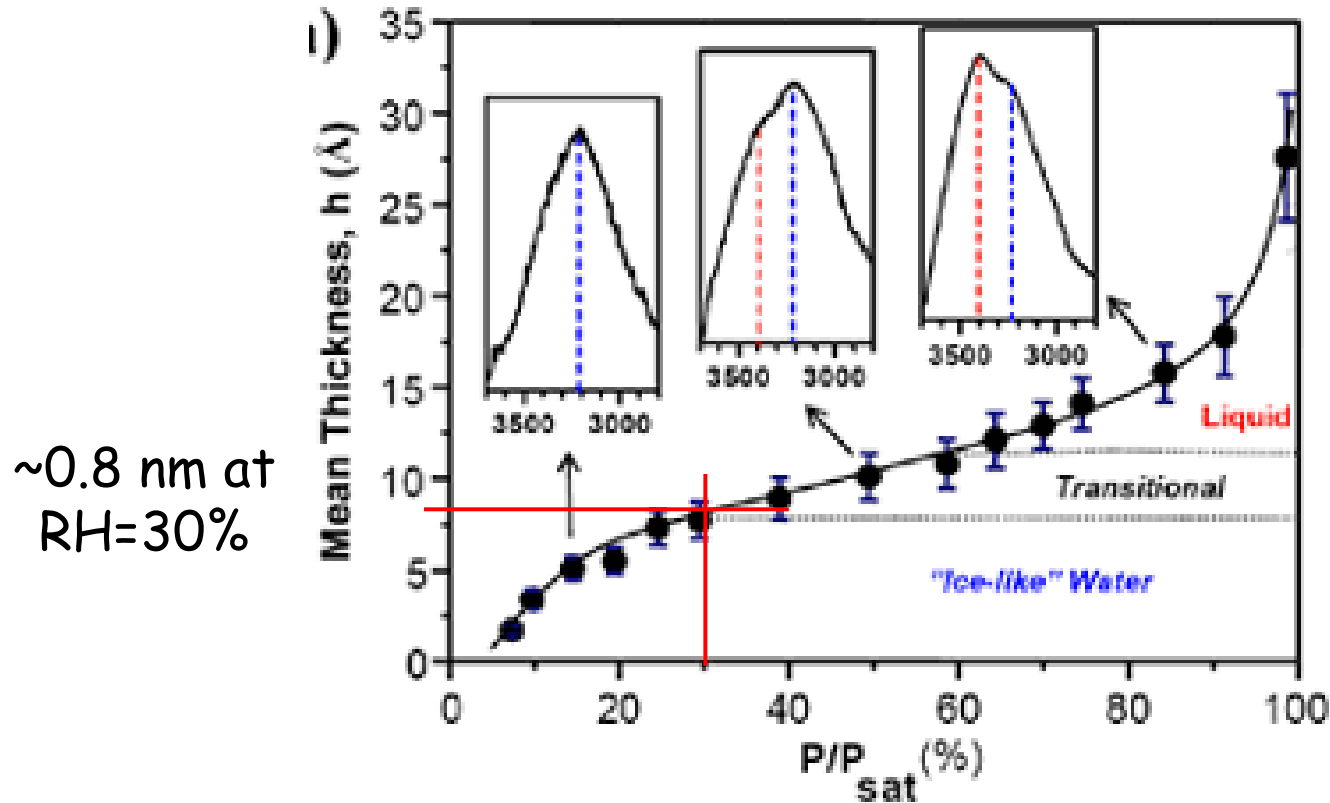


Sign convention for radius: R_1 is negative, R_2 is positive

How thick is h ?

(measured thickness of water layer on a silicon oxide substrate)

Asay and Kim, J. Phys. Chem B 109, 16760 (2005)



How long does it take for this layer of water to form? The answer depends on relative humidity, but for a typical ambient humidity of say 30%, the time is very fast, much less than one second - see Appendix 3.

At contact - what determines R_1, R_2 ?

- Vapor pressure in handbooks are measured for liquids having a flat surface
- Vapor pressure depends on the curvature of the liquid's surface
- Use Kelvin equation - derived from the Young-Laplace Equation:

$$R_{\text{gas}} T \ln \left(\frac{P_{\text{vap}}^c}{P_o^f} \right) = \gamma V_{\text{mol}} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

P_{vap}^c = vapor pressure of liquid having curved surface with radii R_1, R_2

P_o^f = vapor pressure of liquid having flat surface

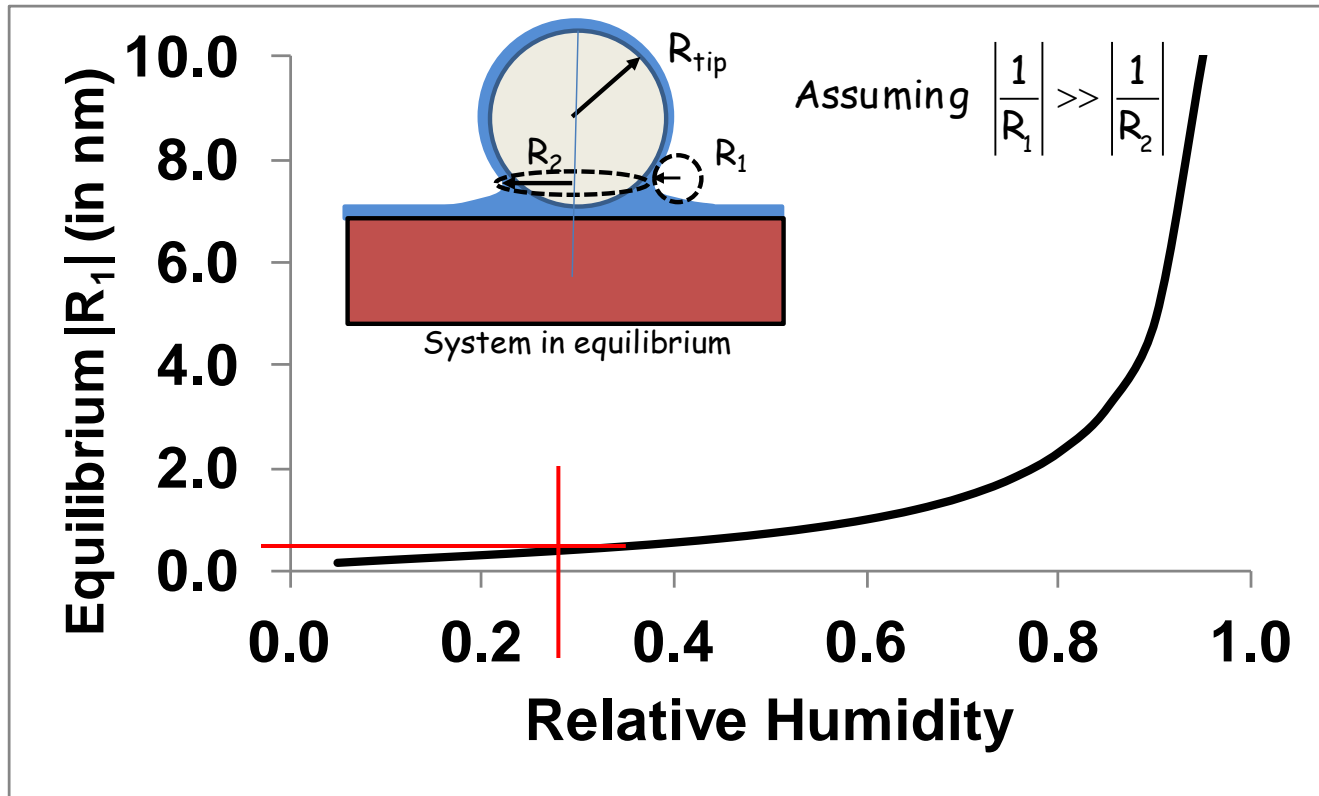
$$\frac{P_{\text{vap}}^c}{P_o^f} \equiv \text{Relative Humidity}$$

for water:

$$\gamma \frac{V_{\text{mol}}}{R_{\text{gas}} T} \Big|_{\text{water}} = \left(0.072 \frac{\text{J}}{\text{m}^2} \right) \cdot \left(\frac{1 \text{ m}}{10^9 \text{ nm}} \right)^2 \times \frac{\left(\frac{18 \text{ cm}^3}{\text{mole}} \right) \cdot \left(\frac{1 \text{ nm}}{10^{-7} \text{ cm}} \right)^3}{8.314 \frac{\text{J}}{\text{K} \cdot \text{mole}} \cdot 300 \text{ K}} = 0.52 \text{ nm}$$

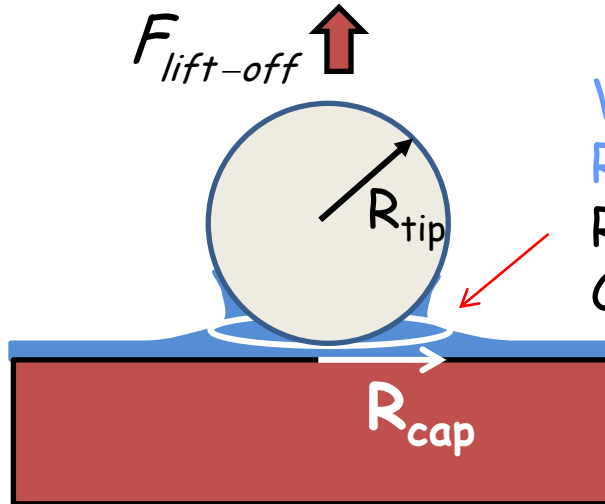
$$P_{\text{vap}}^c = P_o^f e^{0.52 \left(\frac{1}{R_1} + \frac{1}{R_2} \right)}; \quad R_1, R_2 \text{ in nm}$$

Results for water meniscus



Will the liquid evaporate from the meniscus neck? No, the liquid will not evaporate due to the curvature of the air/vapor interface.

Conclusion: A capillary meniscus force binds a sphere to a flat plane



Water meniscus forms:
 R_1 is small (and negative)
 R_2 is large (and positive)
 Curvature implies $P_{in} < P_{out}$

$$P_{Laplace} = \text{Laplace pressure} \equiv \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{R_{gas} T}{V_{mol}} \ln \left(\frac{P_{vap}^c}{P_o^f} \right)$$

$$F_{capillary} = P_{Laplace} A = \frac{R_{gas} T}{V_{mol}} \ln \left(\frac{P_{vap}^c}{P_o^f} \right) \pi R_{cap}^2$$

Relative humidity

R_{cap} will depend on h, R_{tip}, R_1 and R_2

Estimate magnitude of capillary force (see Appendix 4 for geometric details)

$$F_{capillary} \approx P_{Laplace} A = \frac{R_{gas} T}{V_{mol}} \left| \ln \left(\frac{p_{vap}^c}{p_o^f} \right) \right| \pi R_{cap}^2$$

$$= \frac{R_{gas} T}{V_{mol}} \left| \ln \left(\frac{p_{vap}^c}{p_o^f} \right) \right| \left[\pi \left(2 \sqrt{R_{tip} (h + R_1)} \right)^2 \right]$$

$$= \left(4\pi\gamma R_{tip} \right) \left[\frac{R_{gas} T}{\gamma V_{mol}} (h + R_1) \left| \ln \left(\frac{p_{vap}^c}{p_o^f} \right) \right| \right] = \left(4\pi\gamma R_{tip} \right) \left[\frac{(h + R_1)}{0.52 \text{ nm}} \left| \ln \left(\frac{p_{vap}^c}{p_o^f} \right) \right| \right]$$

Relative Humidity

(1.3/0.5) x 1.2 ~ 3

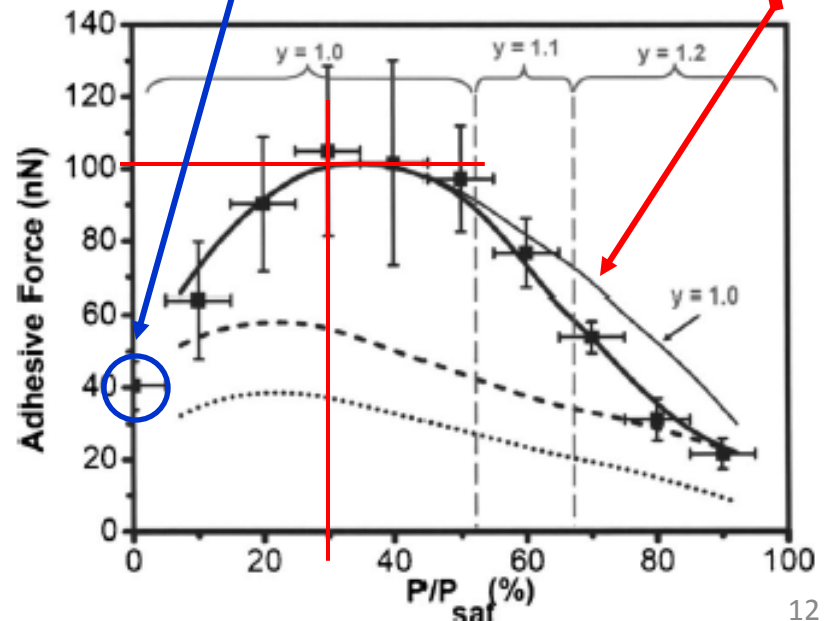
Compare to:

$$F_{vdW} \text{ (Derjaguin)} = 4\pi\gamma R_{tip} \left. \begin{array}{l} \text{independent} \\ \text{of RH} \end{array} \right\}$$

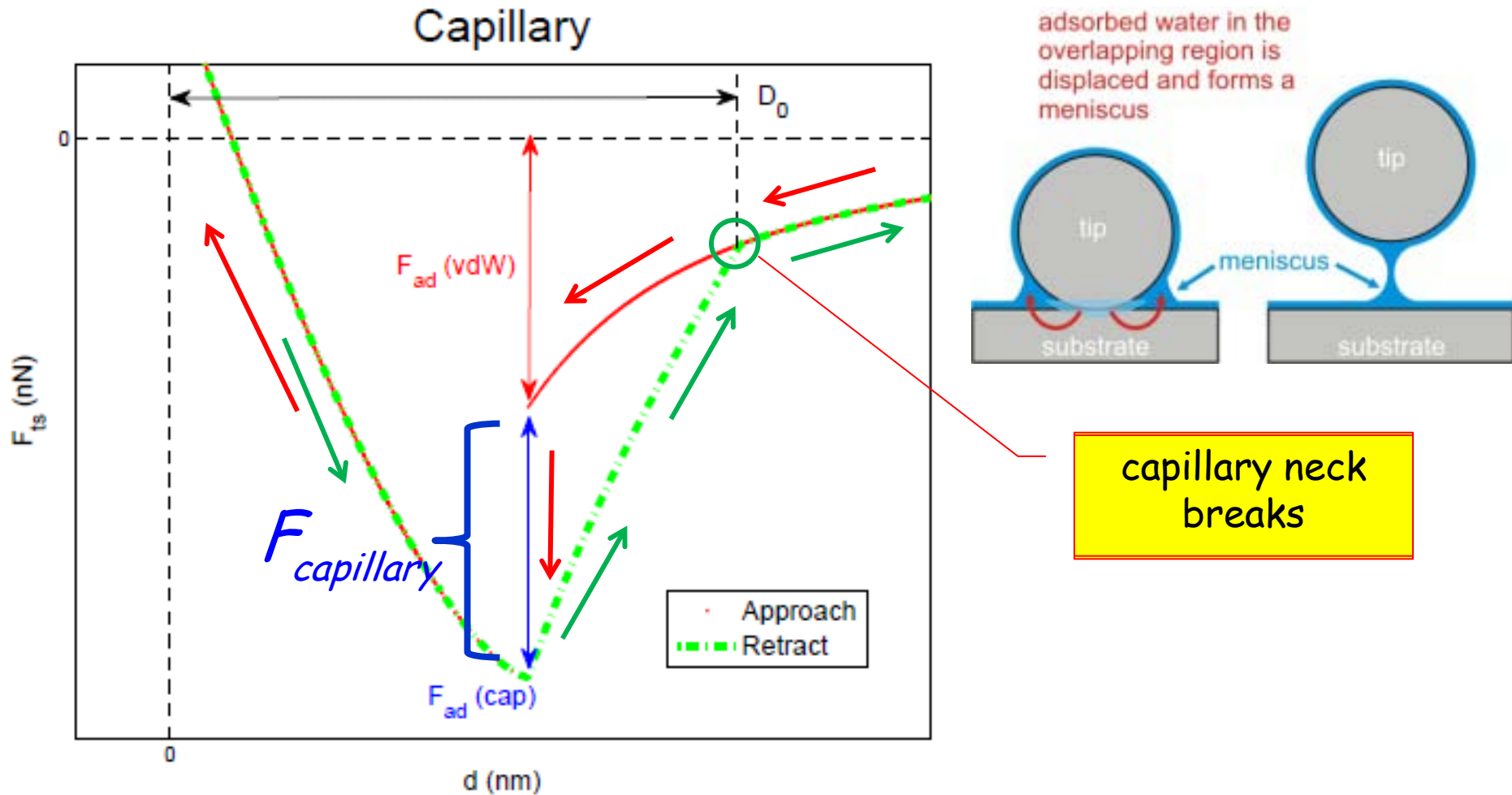
$$F_{JKR} = 3\pi\gamma R_{tip}$$

DATA:

Asay and Kim, J. Phys. Chem B **109**, 16760 (2005)
He et al., J. Chem. Phys. **114**, 1355 (2001).



Effect of capillary condensation - important modifications to the DMT model

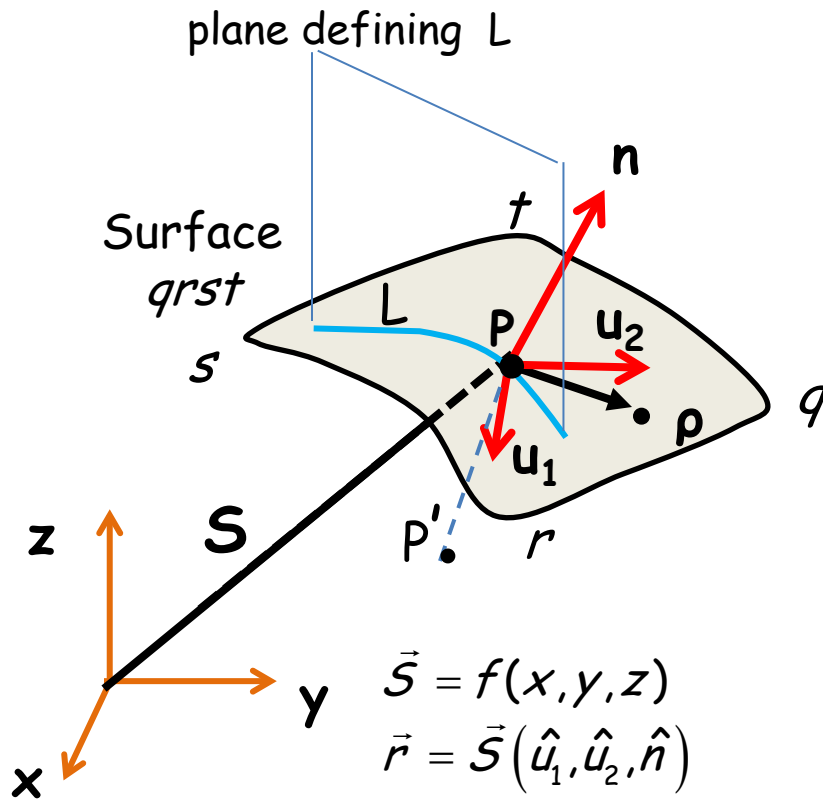


- Capillary force models range from simple to complex
- Strong dependence on humidity

Next Lecture: An overview of VEDA -
the online AFM simulation software

Appendix 1: Defining the “Curvature” of a Surface in 3D?

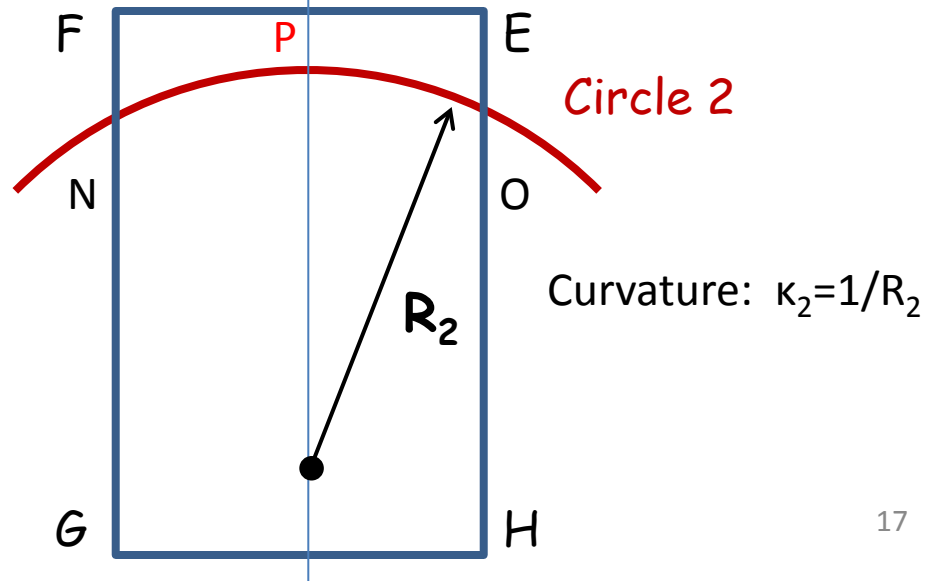
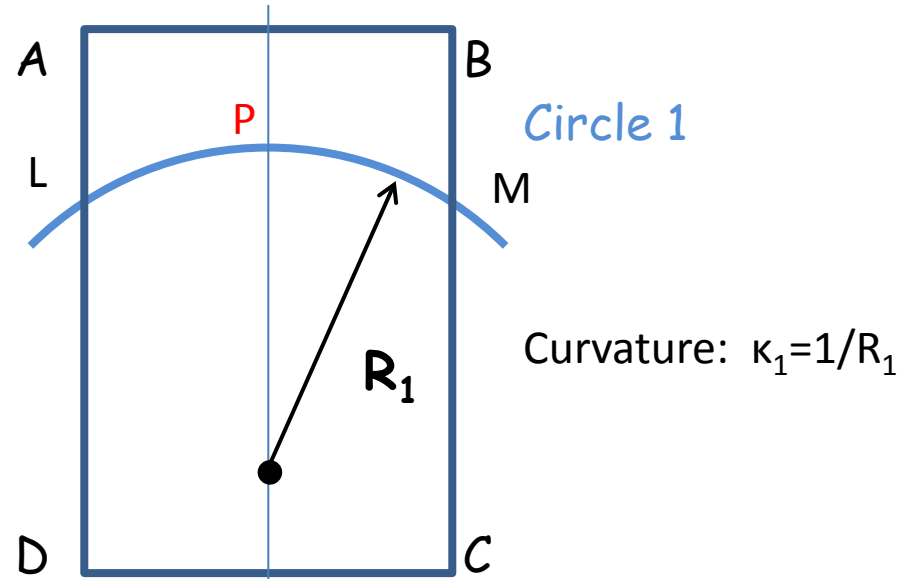
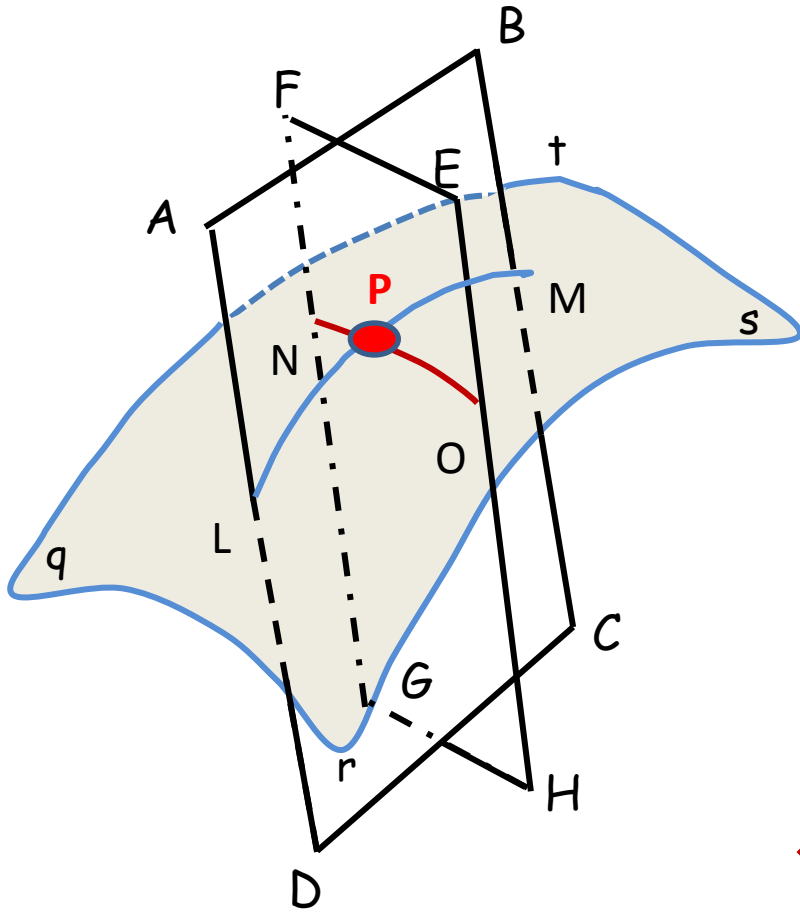
Surprisingly, the “curvature” of any surface can be specified by two numbers, the two radii of curvature at a point P .



- Define a point *P* on surface *qrst* by the vector *S*.
- Define the orientation of the surface by the normal vector *n*.
- Define two tangent unit vectors *u*₁ and *u*₂ that are normal to each other and to *n*.
- This local coordinate system (*u*₁, *u*₂, *n*) can be used to specify any point *p* on the surface.
- How much a surface "bends and twists" along a **line L** can be defined by the largest circle tangent to the line (positive radius when located on the concave side of the surface).

- The reciprocal of the tangent circle radius $R=PP'$ is called the curvature ($\kappa=1/R$ units: radians/m) of the surface along the line at the point *P*. For gently curving surfaces, the curvature is basically the second derivative of the line *L* at the point *P*.
- The curvature of the surface will be a continuous function as the plane defining *L* is rotated through 180°.
- As the plane is rotated, there will be a maximum and a minimum radius of curvature. These two **extrema** are called the **principal curvatures** at the point *P*.

Defining the curvature of $qrst$ requires finding the radii of two circles tangent to the surface.



Mean radius of curvature:

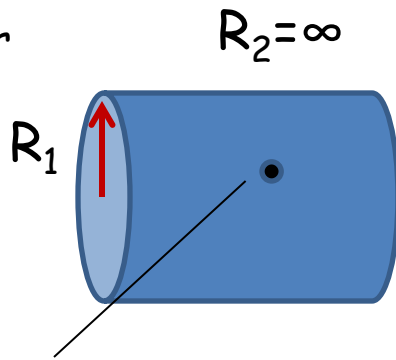
$$\frac{1}{R_{mean}} = \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

Gaussian curvature: $K = \kappa_1 \kappa_2$

Further Considerations

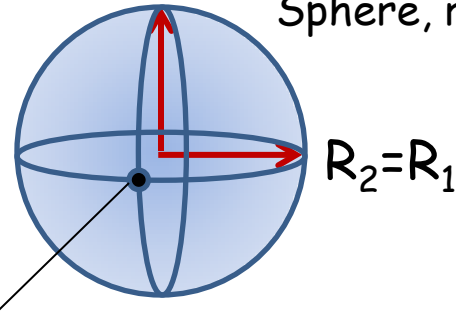
1. An important theorem in differential geometry proves that so long as plane $ABCD$ is perpendicular to plane $FEHG$ (see previous slide), the **mean radius of curvature is invariant**, independent of the alignment of the two planes wrt the surface $qrst$.
2. Once the curvature is known at a point, it can be used to derive a differential equation that describes the equation of the surface at that point.
3. A few surfaces with their of radii of curvature:

Cylinder



$$\frac{1}{R_m} = \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{1}{2} \cdot \frac{1}{R_1}$$

R_1



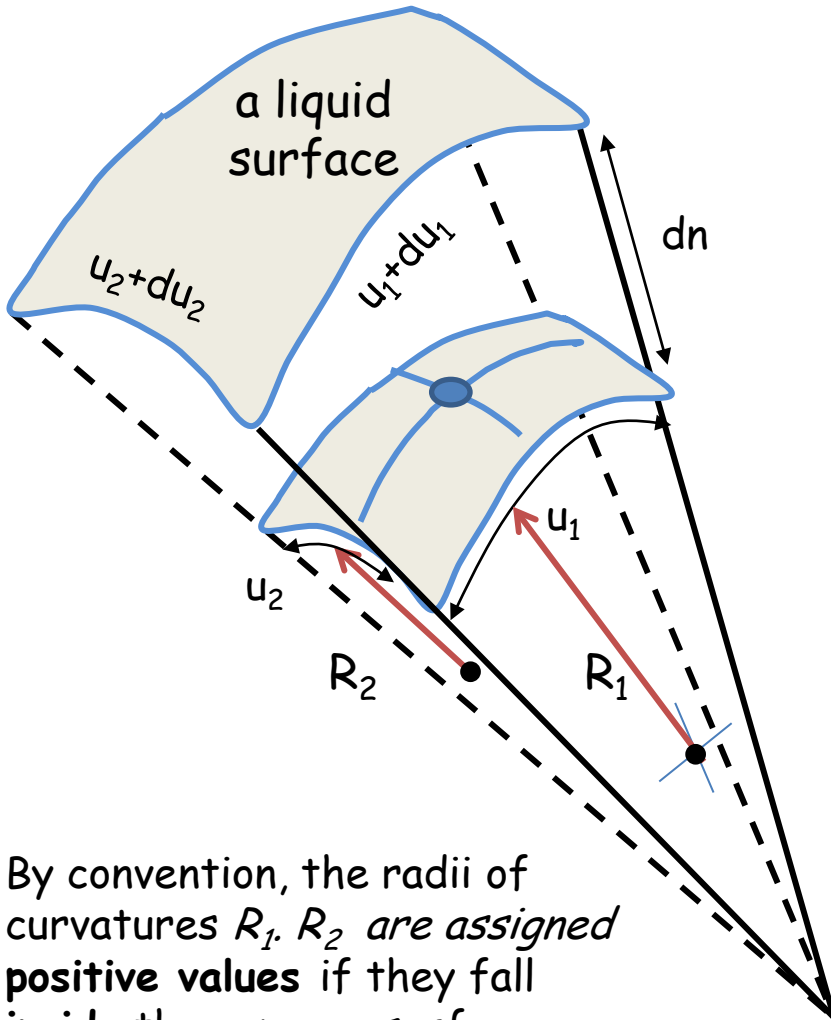
$$\frac{1}{R_m} = \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{1}{2} \cdot \frac{2}{R} = \frac{1}{R}$$

Appendix 2: Derivation of Young-Laplace and Kelvin Equations

1. If the surface of a liquid is curved, there must be a pressure difference: **Young-Laplace Equation**
2. If the surface of a liquid is curved, the equilibrium vapor pressure of the liquid must also change: **Kelvin Equation**

Young - Laplace Equation:

Pressure difference across a curved interface



$$\Delta A = (u_1 + du_1)(u_2 + du_2) - (u_1 u_2)$$

$$\approx u_1 du_2 + u_2 du_1$$

$$\left. \begin{aligned} \frac{u_1 + du_1}{R_1 + dn} &= \frac{u_1}{R_1} \Rightarrow du_1 = u_1 \frac{dn}{R_1} \\ \frac{u_2 + du_2}{R_2 + dn} &= \frac{u_2}{R_2} \Rightarrow du_2 = u_2 \frac{dn}{R_2} \end{aligned} \right\} \text{similar triangles}$$

$$\text{Work} = (P_{in} - P_{out})(A)dn = (P_{in} - P_{out})(u_1 u_2)dn$$

$$\equiv \gamma \Delta A \approx \gamma (u_1 du_2 + u_2 du_1) \quad \text{see P1_Wk2_L2}$$

$$= \gamma \left(u_1 \left(u_2 \frac{dn}{R_2} \right) + u_2 \left(u_1 \frac{dn}{R_1} \right) \right)$$

$$(P_{in} - P_{out}) = \gamma \left(\frac{1}{R_2} + \frac{1}{R_1} \right) \quad (\text{Laplace Pressure})$$

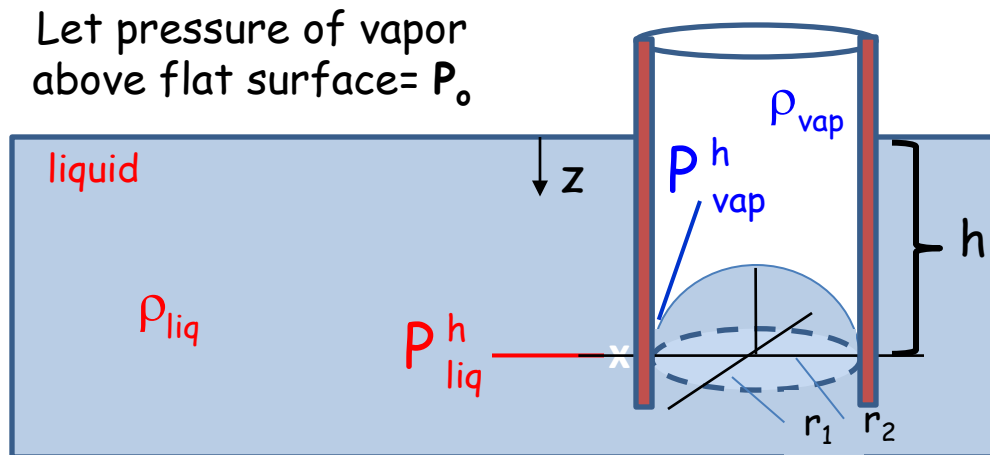
for a spherical surface, $R_1 = R_2 = R$ and

$$\Delta P = (P_{in} - P_{out}) = 2\gamma \left(\frac{1}{R} \right)$$

By convention, the radii of curvatures R_1, R_2 are assigned **positive values** if they fall **inside** the concave surface under consideration.

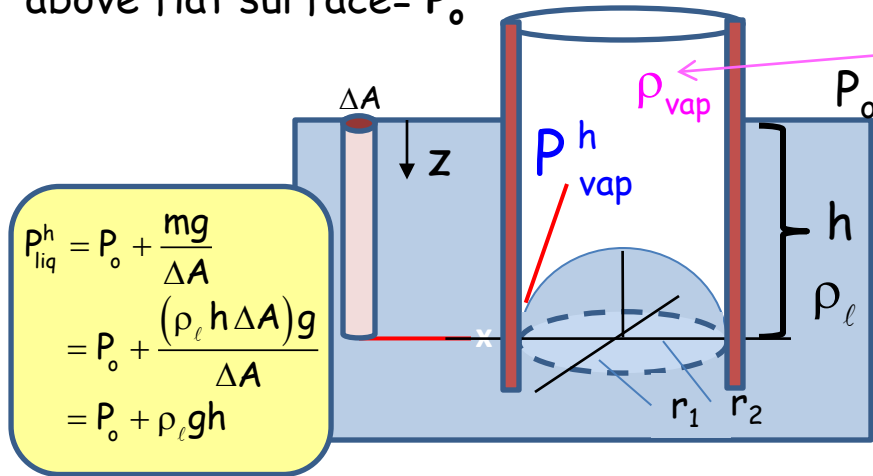
The vapor pressure above a curved surface: the Kelvin equation

The situation: Insert open tube into liquid. Assume the liquid does not wet the tube. Liquid will fill tube to a depth h as shown. In general, the vapor-liquid interface will be curved, and will be characterized by the radii of curvature r_1 and r_2 . In equilibrium at temperature T , the pressure difference between the **vapor** at depth h (P_{vap}^h) and the **liquid** at depth h (P_{liq}^h) must be described by the Young - Laplace Equation. Let the vapor/liquid density be designated by ρ_{vap} , ρ_{liq} respectively.



Note: The end result is completely general and is identical to that obtained using more general arguments that are not so physically transparent.

Pressure of vapor above flat surface = P_o



$$\begin{aligned} P_{liq}^h &= P_o + \frac{mg}{\Delta A} \\ &= P_o + \frac{(\rho_l h \Delta A)g}{\Delta A} \\ &= P_o + \rho_l gh \end{aligned}$$

In equilibrium:

$$P_{liq}^h - P_{vap}^h = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (\text{Young - Laplace})$$

$$(P_o + \rho_l gh) - P_{vap}^h = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

$$\rho_l gh = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + (P_{vap}^h - P_o)$$

$$h = \frac{\gamma}{\rho_l g} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{(P_{vap}^h - P_o)}{\rho_l g}$$

small - neglect

What is P_{vap}^h ?

vapor density = $\rho_{vap} = \frac{\text{molar mass}}{\text{molar volume}} = \frac{M}{V_m}$

for ideal gas: $P_{vap} V_m = P_{vap} \left(\frac{M}{\rho_{vap}} \right) = n R_{gas} T \Big|_{n=1}$

$$\rho_{vap} = \frac{M P_{vap}}{R_{gas} T}; \quad \text{now, } P_{vap}(z) = P_o + \rho_{vap} gz$$

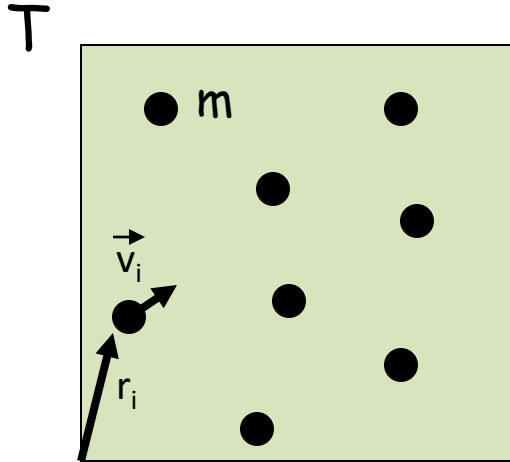
$$\frac{dP_{vap}(z)}{dz} = \rho_{vap} g = \frac{M P_{vap}}{R_{gas} T} g$$

$$\int_{P_o}^{P_{vap}^h} \frac{dP_{vap}}{P_{vap}} = \int_0^h \frac{M}{R_{gas} T} g dz \Rightarrow \ln \left(\frac{P_{vap}^h}{P_o} \right) = \frac{M}{R_{gas} T} gh$$

$$\begin{aligned} \ln \left(\frac{P_{vap}^h}{P_o} \right) &\approx \frac{M}{R_{gas} T} \frac{\gamma}{\rho_l} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \\ &= \frac{V_{mol}}{R_{gas} T} \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \end{aligned}$$

$$R_{gas} T \ln \left(\frac{P_{vap}^h}{P_o} \right) = \gamma V_{mol} \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

Appendix 3: Kinetic Theory of Gases



How to describe velocity of
 N gas molecules of mass m at
a temperature T : Maxwell
Speed Probability
Distribution function (1852)

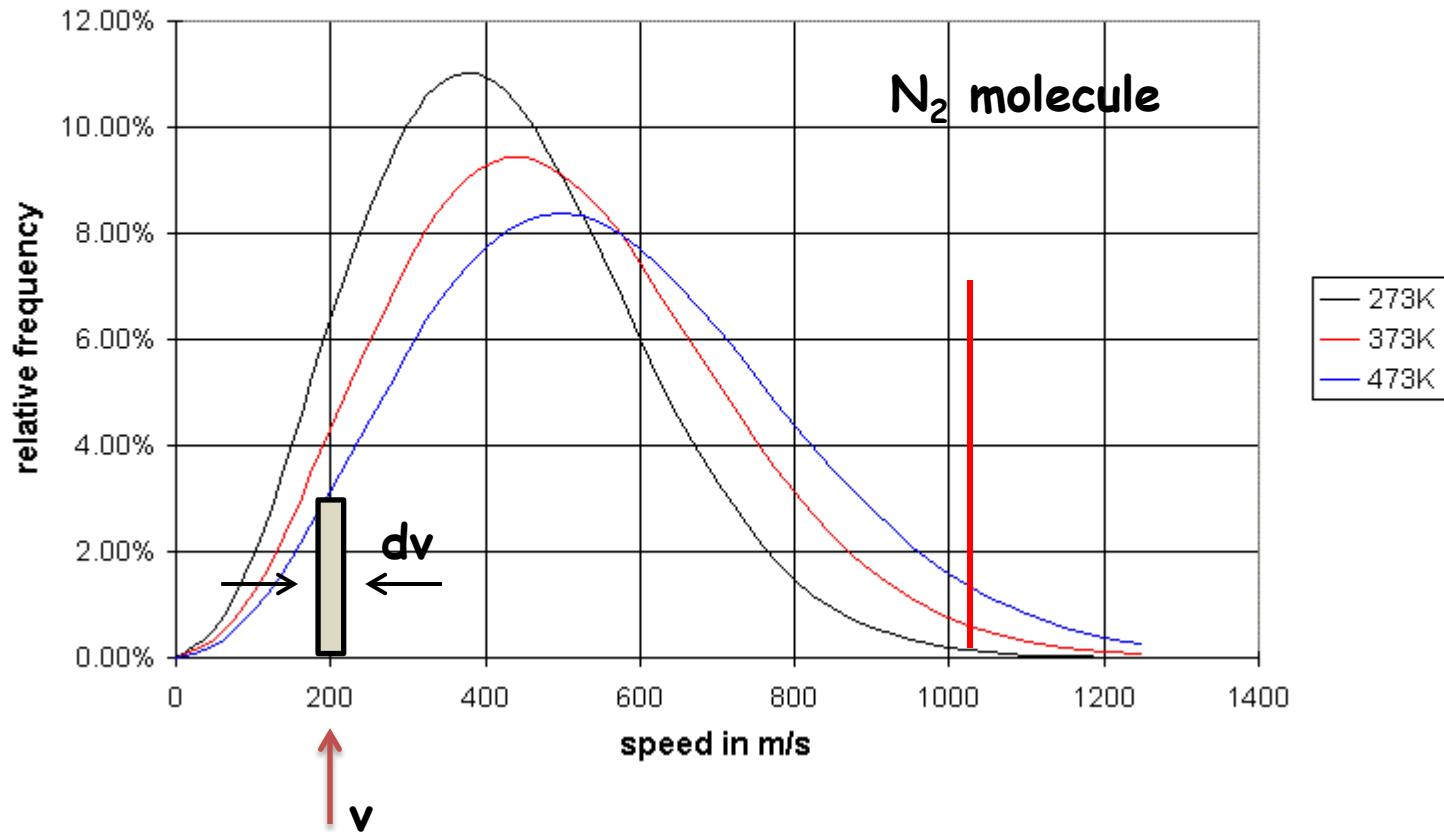
$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 e^{-mv^2/(2k_B T)}$$

$$v \equiv \sqrt{v_x^2 + v_y^2 + v_z^2} = \text{speed of gas molecule}$$

Maxwell Speed Distribution Function

Note asymmetry - there are more ways to get a large speed than a small one.

Maxwell-Boltzmann speed distribution



Shaded area represents probability that molecule will have a speed $v \pm dv/2$

Why Are Distribution Functions Useful?

Once you know $f(v)$, you can answer many questions:

$$P(v_1 \leq v \leq v_2) \equiv \int_{v_1}^{v_2} f(v) dv \quad \text{probability of finding molecule with velocity } v_1 \leq v \leq v_2$$

$$\langle x(v) \rangle \equiv \int_0^{\infty} x(v) f(v) dv$$

where $\langle x \rangle$ is the expected (average) value for some quantity x that you define.

For example, the average velocity will be

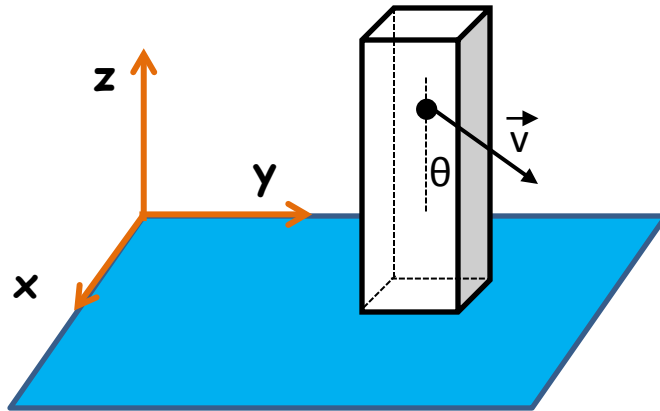
$$\langle v \rangle = v_{avg} \equiv \int_0^{\infty} v f(v) dv = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} \int_0^{\infty} v^3 e^{-mv^2/2k_B T} dv$$

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}; \quad n = 1; \quad a = \frac{m}{2kT}$$

$$\langle v \rangle = v_{avg} = \sqrt{\frac{8k_B T}{\pi m}}$$

Standard Results

$n = \text{molecules/volume}$



What is the mean value of velocity in the z-direction?

$$\langle v_z \rangle = \langle v \cos \theta \rangle = \langle v \rangle \langle \cos \theta \rangle = \frac{1}{2} v_{avg}$$

$$\langle \cos \theta \rangle = \frac{1}{2\pi} \int_0^{2\pi} d\phi \int_0^{\pi/2} \cos \theta \sin \theta d\theta = \frac{1}{2} \sin^2 \theta \Big|_0^{\pi/2} = \frac{1}{2}$$

What is the molecular flux (number of molecules/sec) that will hit a unit area of the plate?

For n molecules in the volume, $\frac{1}{2}$ will be moving up, the other half will be moving down

$$J = \text{Collision rate / unit area} = \frac{1}{2} n \langle v_z \rangle = \frac{1}{4} n v_{avg}$$

Assuming an ideal gas, how does n depend on T and P ?

$$PV = Nk_B T$$

$$n \equiv \frac{N}{V} = \frac{P}{k_B T}$$

Assuming an ideal gas, what is the number of molecules that fill a 1cm^3 volume at STP (0°C (273.15 K), 1 atm (100 kPa))?

$$n \equiv \frac{N}{V} = \frac{1\text{mole}}{22.4\text{liters}} \cdot \frac{6 \times 10^{23}\text{ molecules}}{\text{mole}} \cdot \frac{1\text{liter}}{0.001\text{m}^3} \cdot \frac{1\text{m}^3}{10^6\text{cm}^3} = 2.7 \times 10^{19}\text{ cm}^{-3}$$

Assuming an ideal gas, what is the incident molecular flux in the $-z$ direction?

$$J = \frac{1}{4}nv_{\text{avg}} = \frac{1}{4} \cdot \frac{P}{k_B T} \cdot \sqrt{\frac{8k_B T}{\pi m}} = \frac{P}{\sqrt{2\pi m k_B T}} \quad [\text{units: } s^{-1} m^{-2}]$$

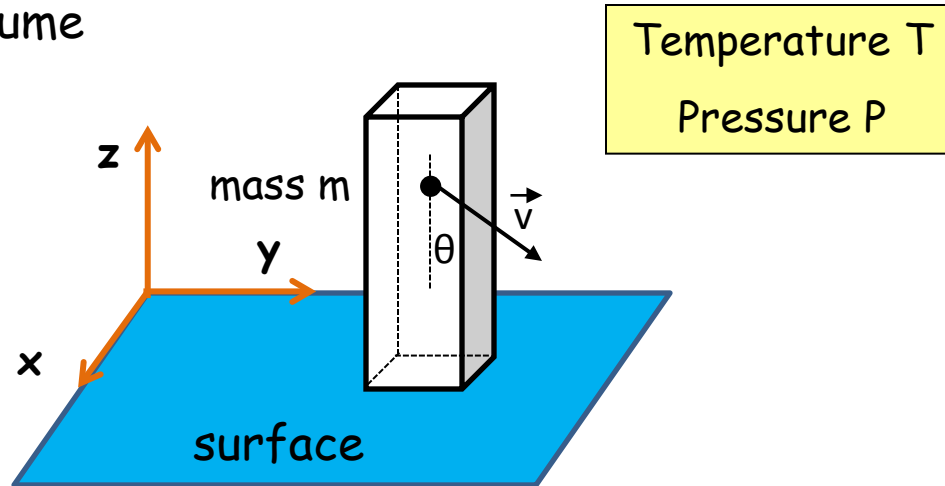
Assuming an ideal gas, how many molecules will strike a unit area of the surface in a time t ?

$$\Phi = \int_0^t J dt = \frac{P}{\sqrt{2\pi m k_B T}} t \quad [\text{units: } m^{-2}]$$

How many gas atoms strike a unit area of a surface in a given time t ?

J = molecular flux (number/unit area) in unit time

n = molecules/volume



The answer is found by integrating the molecular flux over the time t

$$\Phi = \int_0^t J dt = \frac{P}{\sqrt{2\pi m k_B T}} t \quad \left[\text{units : number / m}^2 \right]$$

If the gas has some fraction of water molecules, then it is not surprising that a thin layer of water will form on a surface.

Estimate the length of time for a monolayer of gaseous atoms to accumulate on a surface?

The answer depends on the flux of gas atoms on the surface, the sticking probability of each gas atom, and the number of active adsorption sites on the surface. If the sticking probability is assumed to be 1, then a minimum estimate for the monolayer deposition time can be made. Furthermore, it is customary to assume there are $\sim 10^{19}$ adsorption sites per square meter on a surface, roughly equal to the number of atoms per square meter that characterize most surfaces.

$$J \times t_{\text{monolayer}} \approx 10^{19} \quad \text{where} \quad J = \frac{P}{\sqrt{2\pi m k_B T}}$$

$$t_{\text{monolayer}} \approx \frac{10^{19} \times \sqrt{2\pi m k_B T}}{P}; \quad \text{assume } 18 \text{ gm / mole} \Rightarrow m = m_{\text{H}_2\text{O}} = 3 \times 10^{-26} \text{ kg}; \quad T = 300\text{K}$$

Vacuum	P (Torr)	P (Pa)	n (m ⁻³)	t _{monolayer} (s)
atmospheric	760	1x10 ⁵	2.4x10 ²⁵	2.8x10 ⁻⁹
low	~1	130	3.1x10 ²²	2.2x10 ⁻⁶
medium	~1x10 ⁻³	0.13	3.1x10 ¹⁹	2.2x10 ⁻³
high	~1x10 ⁻⁶	1.3x10 ⁻⁴	3.1x10 ¹⁶	2.2
ultra-high	~1x10 ⁻¹⁰	1.3x10 ⁻⁸	3.1x10 ¹²	2.2x10 ⁴

Appendix 4: Geometric details required to calculate R_{cap}

Here, treat R_1 , R_2 as positive numbers

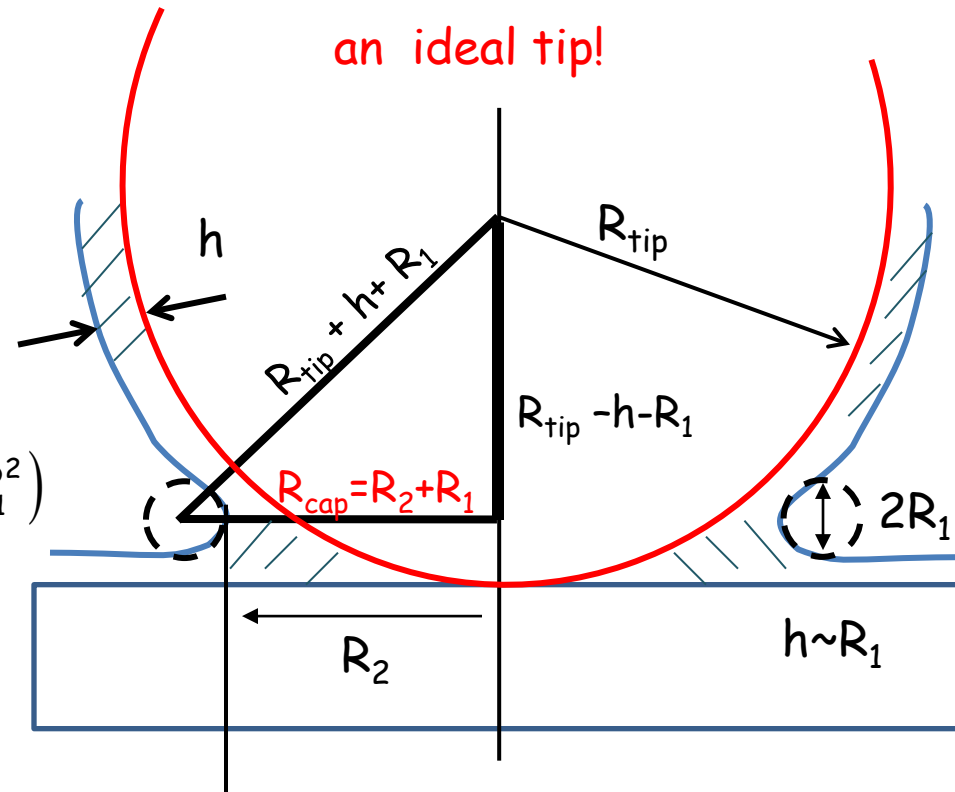
$$(R_{tip} + (h + R_1))^2 = (R_{tip} - (h + R_1))^2 + (R_2^2 + R_1^2)$$

$$R_2^2 + 2R_1R_2 + (R_1^2 - 4R_{tip}(h + R_1)) = 0$$

$$R_2 = \frac{-2R_1 \pm \sqrt{4R_1^2 - 4(R_1^2 - 4R_{tip}(h + R_1))}}{2}$$

$$= +2\sqrt{R_{tip}(h + R_1)} - R_1$$

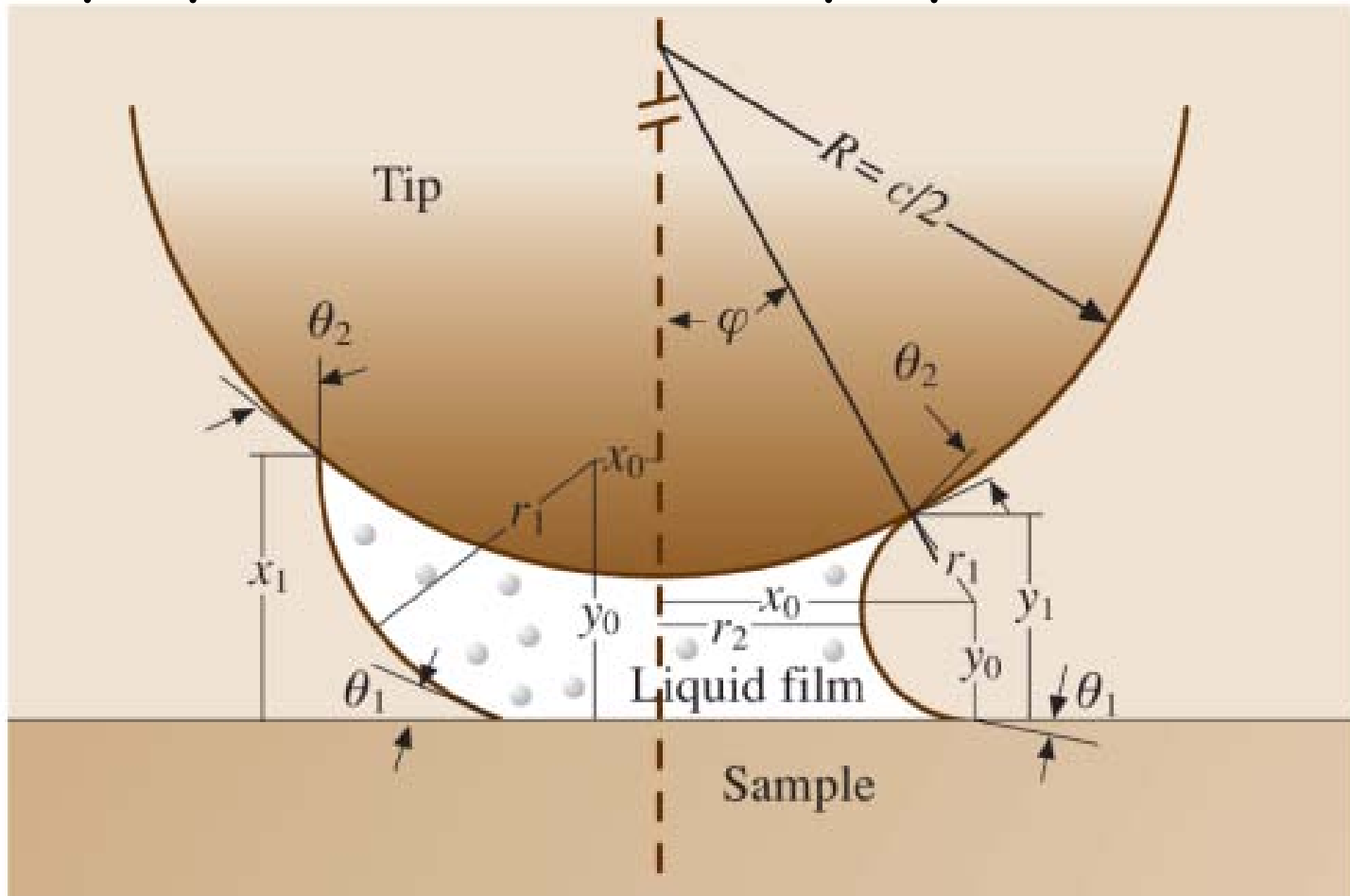
$$R_{cap} \approx R_1 + R_2 = 2\sqrt{R_{tip}(h + R_1)}$$



Appendix 5: Further Considerations

Hydrophobic surfaces

Hydrophilic surfaces



B. Bhushan, *Springer handbook of nanotechnology, 2nd Edition, Vol. 2; p. 960 (2007).*

Water Facts

A water molecule has a diameter d_0 of approximately 0.3 nm.[1,2]

The areal density of water is $x/(d_0)^2$, where x is the adsorbed water layer thickness.

A water "monolayer (i.e., $x=1$)" consists of about 11 molecules/nm².

[1]. Karis, T. E. "Water Adsorption on Thin Film Media," *Jour. Colloid Interface Sci.*, **225**, 196-203, (2000).

[2]. Adamson, A. W., Hu, P. and Tadros, M. E. "Adsorption and Contact Angle Studies," *Jour. Colloid Interface Sci.*, **49**, 184-195 (1974) .