Brief introduction to liquid surfaces & liquid/liquid interfaces, Special open lectures on "Selected Topics in Physical Chemistry of Interface".
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References:

1. **"Physics & Chemistry of Interfaces", Hans-Jürgen Butt, Karlheinz Graf & Michael Kappl, 2003, Wiley-VCH.**
2. **"Physical Chemistry of Surfaces", Arthur W. Adamson & Alice P. Gast, 1997, Wiley.**
3. **"Principles of Colloid & Surface Chemistry", 2nd edition, Paul C. Hiemenz, 1986, Dekker.**
4. **"Introduction to Colloid and Surface Chemistry, 4th edition", Duncan J. Shaw, 1992, Butterworth-Heinemann.**

1. Bulk properties of liquid; volume contraction (density increase) and vapor pressure increase on pressure.

2. Lifetime of a gas molecule on its liquid surface at equilibrium.

3. Estimate of surface tension from the molar enthalpy of vaporization, $\Delta\overline{H}_{vap}$.

4. Young-Laplace equation; equilibrium shape of liquid surface.

5. Kelvin equation; vapor pressure from curved liquid surface, capillary condensation and capillary force.

1. Bulk properties of liquid; volume contraction (density increase) and vapor pressure increase on pressure.

Bulk properties of liquids under external pressure at the isothermal condition

- Volume contraction or density increase

κ_T (isothermal compressibility) $\equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T$ ← $V = m/\rho$, $dV = -\frac{m}{\rho^2}d\rho$

Thus, T const

$\frac{dV}{V} = -\kappa_T dP$, $\ln\frac{V}{V_0} = -\kappa_T(P-P_0) = -\kappa_T\Delta P$ ← assume $\kappa_T \neq f(P)$

$1 - \frac{V}{V_0} = \frac{\Delta V}{V_0} = 1 - e^{-\kappa_T\Delta P} \approx \kappa_T\Delta P$ if $\kappa_T\Delta P << 1$

$\frac{d\rho}{\rho} = \kappa_T dP$, $\ln\frac{\rho}{\rho_0} = \kappa_T(P-P_0) = \kappa_T\Delta P$ ← assume $\kappa_T \neq f(P)$

$\frac{\rho-\rho_0}{\rho_0} = \frac{\Delta\rho}{\rho} = e^{\kappa_T\Delta P} - 1 \approx \kappa_T\Delta P$ if $\kappa_T\Delta P << 1$

Example: Water at 298K, $\kappa_T = 4.63\cdot10^{-5}\ atm^{-1}$

When $\Delta P = 10^2$ atm, $\frac{\Delta V}{V_0} = 1 - e^{-4.63\cdot10^{-3}} = 0.00463$

Contraction of $\approx 0.46\%$

$\frac{\Delta\rho}{\rho_0} = e^{4.63\cdot10^{-3}} - 1 = 0.00463$

increase of $\approx 0.46\%$

$\Delta P = 10^3$ atm, $\Delta V/V_0 = 0.0474$, 4.7% contraction

$\Delta\rho/\rho_0 = 0.0474$, 4.7% increase

- Vapor pressure increase

$d\mu_l = -S_m dT + V_m dP$, $d\mu_V = RT\frac{dp}{p}$

P = external pressure, p = vapor pressure

T = const, $RT\frac{dp}{p} = V_m dP$, $RT\ln\frac{p}{p^\circ} = V_m(P-P^\circ)$

Example: Water at 298K, $V_m = 18\cdot10^{-6}\ m^3/mol$

$RT = 2.48\ kJ/mol$

$p = p^\circ e^{V_m \Delta P / RT}$, $\frac{\Delta p}{p^\circ} = e^{V_m \Delta P / RT} - 1$

$\Delta P = 10^2$ atm, $\frac{V_m \Delta P}{RT} = 0.0735$, $\frac{\Delta p}{p^\circ} = 0.076$

~8% increase, $p =$

$\Delta P = 10^3$ atm $\frac{V_m \Delta P}{RT} = 0.735$, $\frac{\Delta p}{p^\circ} = 1.08$

~110% increase or log about twice

Example: Hg at 20°C, $V_m = 14.81 \cdot 10^{-6}$ m^3/mol

$RT = 2.44$ kJ/mol

$\Delta P = 10^2$ atm, $\frac{V_m \Delta P}{RT} = 6.16 \cdot 10^{-2}$, $\frac{\Delta p}{p^\circ} = 0.0635$

~6% increase

$\Delta P = 10^3$ atm $\frac{V_m \Delta P}{RT} = 0.616$, $\frac{\Delta p}{p^\circ} = 0.852$

~85% increase

Example: Hg at 100°C, $V_m = 15.02 \cdot 10^{-6}$ m^3/mol

$RT = 3.10$ kJ/mol

$\Delta P = 10^2$ atm, $\frac{V_m \Delta P}{RT} = 4.9 \cdot 10^{-2}$, $\frac{\Delta p}{p^\circ} = 0.050$

5% increase

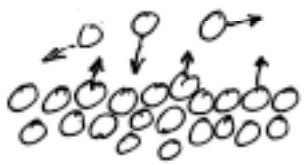
$\Delta P = 10^3$ atm, $\frac{V_m \Delta P}{RT} = 0.49$ $\frac{\Delta p}{p^\circ} = 0.632$

~63% increase

2. Lifetime of a gas molecule on its liquid surface at equilibrium.

Estimate of the life time of a molecule on its liquid surface:

- Start with the equilibrium rate of adsorption & desorption (evaporation) of molecules to & from the liquid surface under isothermal condition



Example: water surface w/ vapor at 25°C

$P_{vap}(25°, \text{water}) = 23.76$ mm Hg

Effusion rate of an ideal gas molecule through an orifice of area A under P,

$$R = \frac{PA}{\sqrt{2\pi m k_B T}}$$

$P = P_{vap} = \frac{23.76}{760} \cdot 1.013 \cdot 10^5$ Pa

$A = 10 Å^2 = 10(10^{-10} m)^2 = 10^{-19} m^2$

$m = 0.018 kg / 6.022 \cdot 10^{23}$

$k_B T = 4.1 \cdot 10^{-21} J$ (at 298K)

$$R = \frac{\frac{23.76}{760} \cdot 1.013 \cdot 10^5 \ \frac{N}{m^2} \cdot 10^{-19} m^2}{\left(2\pi \cdot \frac{0.018 kg}{6.022 \cdot 10^{23}} \cdot 4.1 \cdot 10^{-21} J\right)^{1/2}} = 1.14 \cdot 10^7 s^{-1}$$

$$\approx \frac{\frac{25}{75} \cdot 1 \cdot 10^{4+19} \cdot kg \frac{m}{s^2}}{\left(6 \cdot \frac{0.02}{6 \cdot 10^{23}} \cdot 4 \cdot 10^{-21} kg \cdot kg \frac{m^2}{s^2}\right)^{1/2}} \approx \frac{\frac{1}{3} \cdot 10^{15} \ kg m/s^2}{(8 \cdot 10^{-46})^{1/2} \ kg m/s}$$

$$\approx \frac{10^{15}/s}{3 \cdot 3 \cdot 10^{-23}} \approx 10^{-15+22}/s = 10^7/s$$

$10 Å^2 \approx$ water molecule cross-section

∴ Adsorption rate of water at 25°C = desorption rate of water at 25°C $= 10^7$ molecules/s

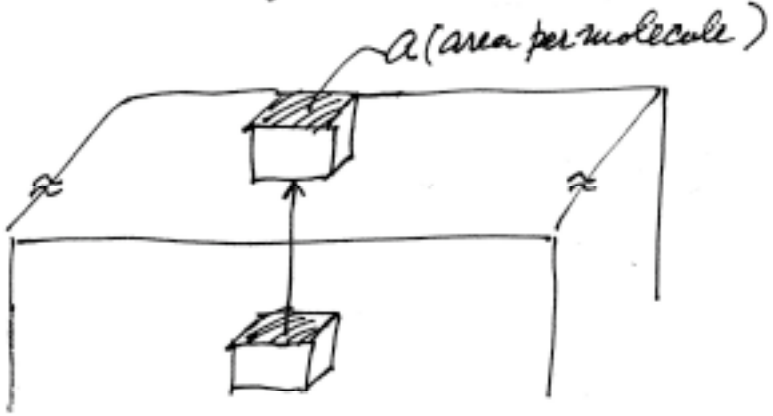
Average life-time $= 1/R = 10^{-7} s = 0.1 \mu s = 100 ns$

3. Estimate of surface tension from the molar enthalpy of vaporization, $\Delta\overline{H}_{vap}$.

Estimate of surface tension of an organic liquid.

Start from the molar enthalpy of vaporization of cyclohexane & arrive at an estimate of its surface tension

- $\Delta\bar{H}_{vap}$ = the enthalpy required to release a mole of liquid to vapor, releasing their interaction energy in liquid state
- $dG^\sigma = \gamma dA$, dG^σ = Gibbs free energy change for increasing surface by dA where γ is proportionality constant
- Envision a process of bringing a molecule from the bulk liquid to the surface under isothermal condition



- Assuming the liquid state packing is cubic, so each molecule is interacting with 6 nearest neighbors

- $dG^\sigma = dH^\sigma - TdS^\sigma \approx dH^\sigma$, $\Delta h^\sigma = \dfrac{\Delta\bar{H}_{vap}}{6 \cdot N_A}$, $\gamma = \dfrac{\Delta h^\sigma}{a}$

Example with cyclohexane

$\Delta\bar{H}_{vap} = 30.5\ kJ/mole$

$M = 72+12 = 84\ g/mol = 0.084\ kg/mol$

$\rho = 0.773\ g/cm^3 = 773\ kg/m^3$

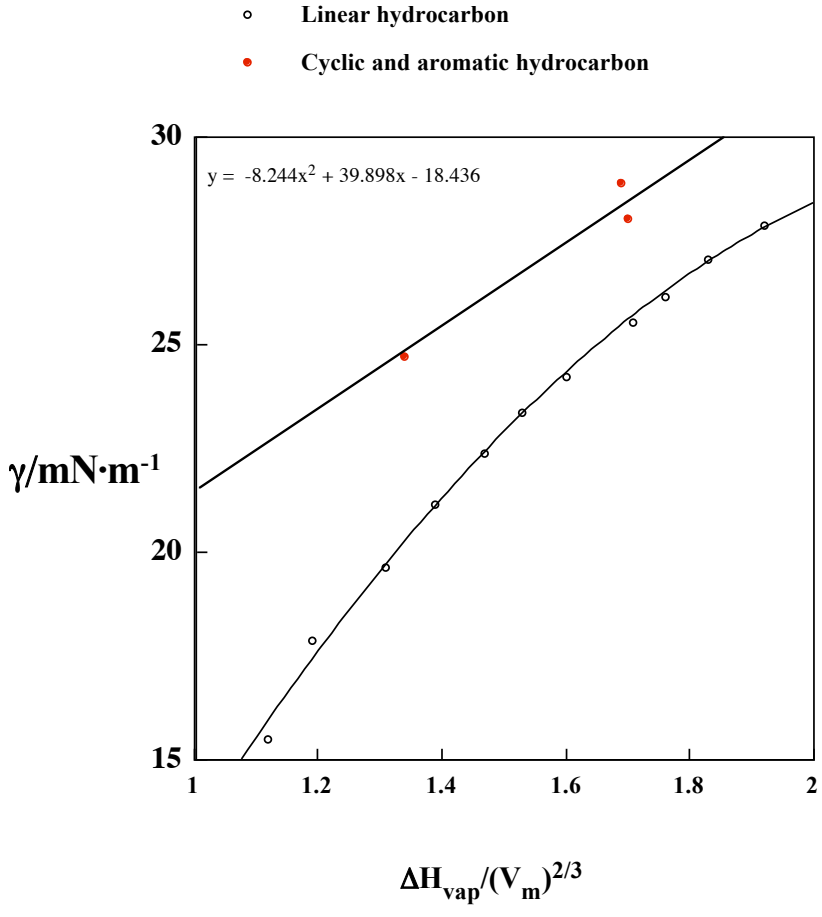
$$\Delta h_{surface} = \frac{30.5\cdot10^3\ J/mol}{6\cdot 6.02\cdot10^{23}/mol} = 8.44\cdot10^{-21}\ J$$

$$a = \left(\frac{M}{\rho N_A}\right)^{2/3} = \left(\frac{0.084\ kg/mol}{773\ kg/m^3 \cdot 6.022\cdot10^{23}/mol}\right)^{2/3} = 3.19\cdot10^{-19}\ m^2$$

$$\gamma = \frac{8.44\cdot10^{-21}}{3.19\cdot10^{-19}} = 2.65\cdot10^{-2}\ J/m^2 = 26.5\ mN/m \text{ (estimate)}$$

$24.7\ mN/m$ (expt'l)

Correlation of surface tension & Enthalpy of vaporization per molar area



4. Young-Laplace equation and equilibrium shape of liquid surface.

- In equilibrium and neglecting gravity, the curvature of a liquid surface is constant and given by the Young-Laplace equation.
- The radii of curvature, R_1 and R_2, are prescribed by two orthogonally intersecting planes.
- For a liquid surface with a finite curvature, there is a pressure difference across the interface, and the pressure is higher on the concave side of the interface.

$$\Delta P = \gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \text{ or } \Delta P = \frac{2\gamma}{R} \text{ (for sphere)}$$

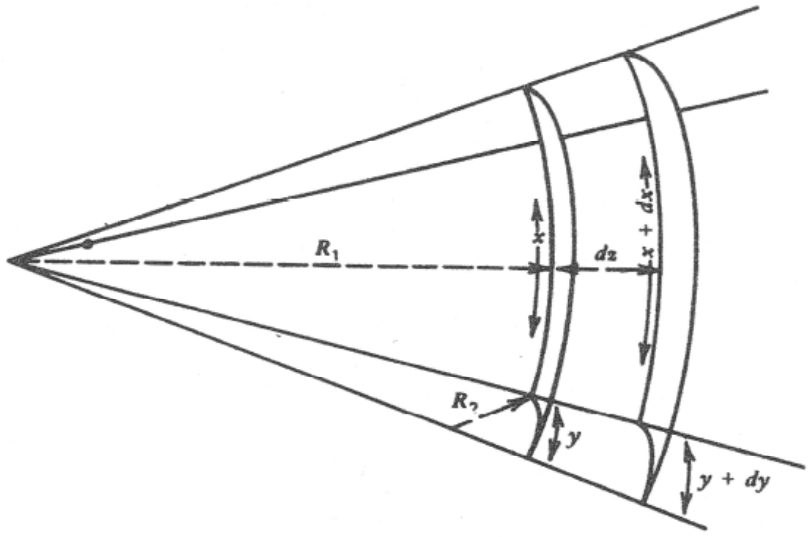


Fig. II-3. Condition for mechanical equilibrium for an arbitrarily curved surface.

Derivation:

Let the inner surface be displaced by a small dz outward.
The area change, $\Delta A = (x+dx)(y+dy) - xy = xdy + ydx + dxdy \approx xdy + ydx$

$dG^\sigma = \gamma(xdy + ydx)$

Work $= \Delta P dV = \Delta P xy dz$ ← must be equal at equilibrium

$\frac{x+dx}{R_1+dz} = \frac{x}{R_1}$, $1+\frac{dx}{x} = 1+\frac{dz}{R_1}$, $\frac{dx}{x} = \frac{dz}{R_1}$, $dx = \frac{xdz}{R_1}$

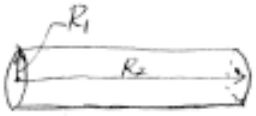
$\frac{y+dy}{R_2+dz} = \frac{y}{R_2}$, ⟶ $dy = \frac{ydz}{R_2}$

$\gamma\left[x\frac{ydz}{R_2} + y\frac{xdz}{R_1}\right] = \Delta P xy dz$, $\Delta P = \gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$

Examples of R_1 + R_2

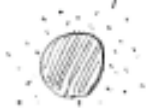
Sphere: $R_1 = R_2$, $\Delta P = \frac{2\gamma}{R}$

Cylinder: R_1 = finite, R_2 = infinite $\Big\} \Delta P = \frac{\gamma}{R_1}$



Plane: $R_1 = R_2 = \infty$, $\Delta P = 0$

Liquid drop suspended in its vapor

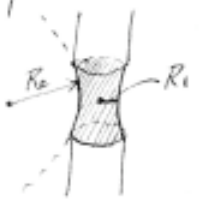


$P_l > P_g$, $\frac{1}{R} > 0$, $\Delta P = \frac{2\gamma}{R} > 0$

Gas bubble suspended in liquid

$P_l < P_g$, $\frac{1}{R} < 0$, $\Delta P = \frac{-2\gamma}{R} < 0$

Liquid trapped between two cylinders



$R_1 > 0$, $R_2 < 0$

If $|R_2| > R_1$, $\Delta P = \gamma\left(\frac{1}{R_1} - \frac{1}{R_2}\right) > 0$

If $|R_2| < R_1$ $\Delta P = \gamma\left(\frac{1}{R_1} - \frac{1}{R_2}\right) < 0$

For a large body, the hydrostatic pressure must be included

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \rho g h$$

Bubble pressure in water at 25°C, $\gamma = 72\ mN/m$

diameter = 2 mm, $\Delta P = \frac{2 \cdot 0.072\ N/m}{1 \cdot 10^{-3}\ m} = 144\ N/m^2 = 144\ Pa \simeq 10^{-3}\ atm$

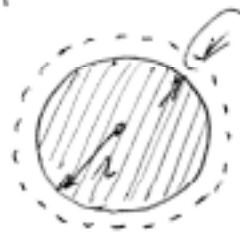
diameter = 20 nm $\Delta P = \frac{2 \cdot 0.072\ N/m}{10 \cdot 10^{-9}\ m} = 1.44 \cdot 10^9\ Pa \simeq 10^4\ atm$

5. Kelvin equation; vapor pressure from curved liquid surface, capillary condensation and capillary force.

- **Liquid vapor pressure from curved surface**

Vapor pressure dependence on curved surface

P_0 : liquid vapor pressure from flat surface
P_r : liquid vapor pressure from a drop



Situation: a drop increases its size by addition of dn moles of liquid, thus its surface area increases resulting in dG^σ

$$RT\ln\frac{P_r}{P_0}=\frac{2\gamma V_m}{r},\quad \boxed{P_r=P_0\exp\left(\frac{2\gamma V_m}{RTr}\right)}$$

Derivation;
T const
Vapor: ideal gas, dP change, $d\mu_v = RT\frac{dP}{P}$
Liquid: drop size increases by condensation of dn moles of the gas, $dG^\sigma=\gamma dA=\gamma\cdot d(A\pi r^2)=8\pi\gamma r\,dr$

$$dn=dV/V_m=4\pi r^2 dr/V_m$$

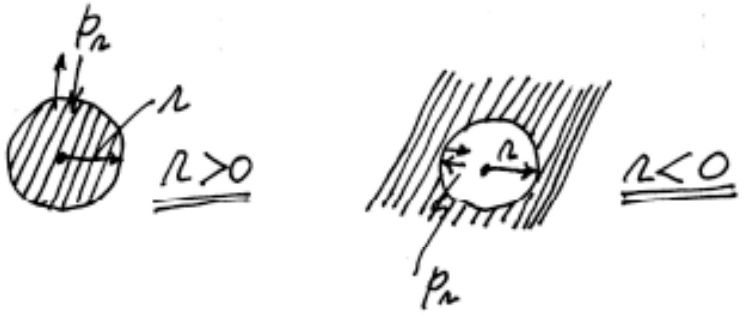
$$d\mu_l=8\pi\gamma r\,dr/4\pi r^2 dr\cdot V_m=2\gamma V_m/r=\Delta\mu_l$$

$d\mu_v = d\mu_l$ (equilibrium)

$$RT\int_{P_0}^{P_r}\frac{dP}{P}=\frac{2\gamma V_m}{r},\quad \boxed{RT\ln\frac{P_r}{P_0}=\frac{2\gamma V_m}{r}}$$

Concrete examples of vapor pressure increase and decrease with radius of droplet and bubbles. In the case of a bubble, the vapor pressure of liquid within constitutes a small portion of the total Laplace pressure.

Examples with water at 298K.
Relative vapor pressure of water droplets & that within bubbles immersed in water.

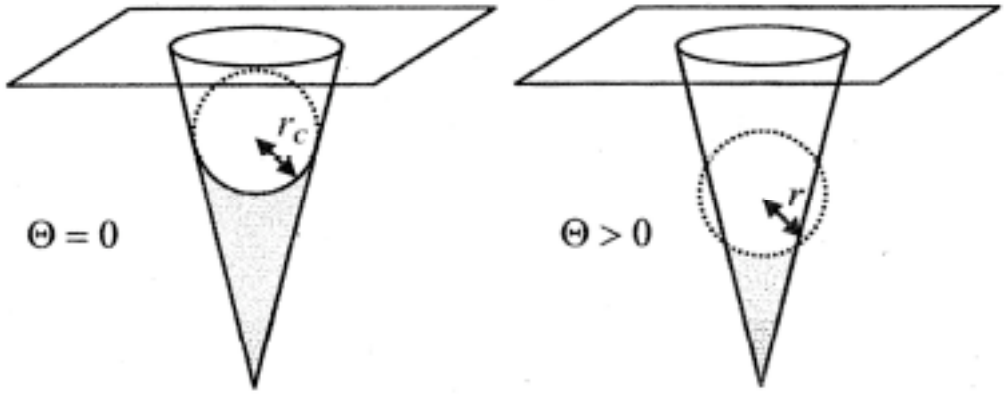


$V_m = 18 \cdot 10^{-6}\ m^3/mol$
$\gamma = 72 \cdot 10^{-3}\ N/m$
$RT = 2.48 \cdot 10^{3}\ N \cdot m/mol$

$$p_r/p_0 = \exp\left\{\pm \frac{2 \cdot \gamma \cdot V_m}{RT \cdot r}\right\}$$

	Droplet	Bubble
$r = 1\ \mu m$	$p_r/p_0 = \exp\left(\frac{2 \cdot 72 \cdot 10^{-3} \cdot 18 \cdot 10^{-6}}{2.48 \cdot 10^{3} \cdot 10^{-6}}\right)$	p_r/p_0
	$= \exp(+1.045 \cdot 10^{-3})$	$= \exp(-1.045 \cdot 10^{-3})$
	$= 1.001$	$= 0.999$
$r = 100\ nm$	1.011	0.990
$r = 10\ nm$	1.110	0.900
$r = 1\ nm$	2.84	0.352

- **Capillary condensation:**
  Kelvin's recognition that polysaccharide surfaces retain moisture at relative humidity well below saturation such as in vegetables, cotton clothes and oatmeal.
  An illustration of conical surfaces with full wetting & partial wetting



Totally wetting surface, $\Theta=0$, $RT\ln\left(\frac{p_r}{p_o}\right) = -\frac{2\gamma V_m}{r_c}$, r_c = capillary radius

Partially wetting surface, $\Theta>0$, $RT\ln\left(\frac{p_r}{p_o}\right) = -\frac{2\gamma V_m}{r}$, $r \equiv r_c \cdot \cos\Theta$

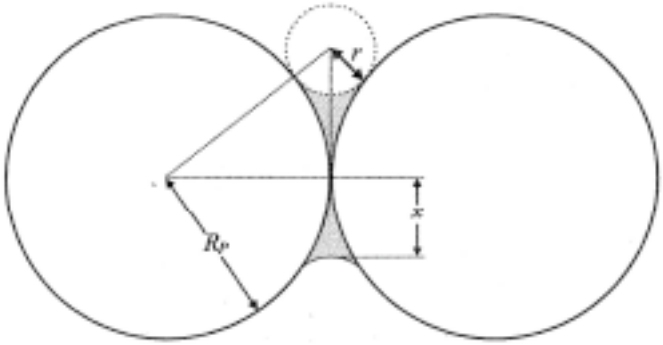
Wetting of capillary pores.
Suppose a porous solid with pores of all sizes placed in water vapor with RH of 90% at 20°C. What is the size of pores that are filled with water?
Assume that the pores are sufficiently hydrophilic to be wetted by water with $\Theta = 0$

$$RT\ln\frac{p_r}{p_o} = -\frac{2\gamma V_m}{r_c}, \quad r_c = -\frac{2\gamma V_m}{RT\ln(p_r/p_o)}$$

$$r_c = \frac{-2\cdot 72\cdot 10^{-3}\ N/m \cdot 18\cdot 10^{-6}\ m^3/mol}{8.314\cdot 293\ J/mol\cdot \ln(0.9)} \approx 10.1\ nm$$

$$\approx -\frac{2\cdot 70\cdot 20\cdot 10^{-9}\ N\cdot m^2/mol}{8\cdot 300\ -(0.1)\ N\cdot m/mol} \approx \frac{280\cdot 10^{-8}}{240}\ m \approx 11\ nm$$

- **Capillary force**



Two spherical particles adhesion via liquid meniscus

Capillary force is responsible for clay & other solid particles stick together in finite relative humidity. An example is given above with two spherical particles

$$\Delta P = +\gamma\left(-\frac{1}{R_p}-\frac{1}{r}\right) \approx -\frac{\gamma}{r} \quad \text{since } R_p >> r$$

Surface area $= \pi x^2$, 1/4 of a sphere with radius x

$$F = \Delta P \cdot \pi x^2 = -\frac{\gamma}{r}\cdot \pi x^2 \quad \text{(force is attractive)}$$

Note: $(R_p + r)^2 = (x+r)^2 + R_p^2$

$R_p^2 + 2rR_p + r^2 = x^2 + 2xr + r^2 + R_p^2 \approx x^2$ ($x >> 2r$)

$\therefore x^2 = 2rR_p$

$$F = -\frac{\gamma}{r}\cdot\pi\cdot 2rR_p = -2\pi\gamma R_p$$

The capillary force to bring particles together is indept of r & (P_v/P_o)!

Capillary force vs. gravitation force.

What would be the maximum particle size when the capillary force to hold glass particles together is no longer strong enough to separate them by gravity?

Glass density: $\rho = 3000\ kg/m^3$, water vapor at 298K

$$mg = \frac{4}{3}\pi R_p^3 \rho g = 1.23\cdot 10^5 \frac{kg}{m^2 s^2}\cdot R_p^3$$

$$F_{capillary} = 2\pi\gamma R_p = 0.45\ \frac{kg}{s^2}\cdot R_p$$

$mg = F_{capillary}$, the particles separate, $R_p = \left(\frac{0.45}{1.23\cdot 10^5}\ m^2\right)^{1/2}$

$= 1.9\ mm$