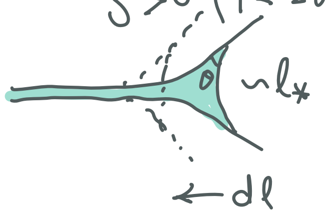
Elasto capillarity

· Elasto adhesion

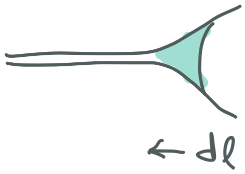
$S>0$, $(\Gamma < 2\gamma\cos\theta)$



$(2\gamma_{sv} - 2\gamma_{sl})dl$

$= 2\gamma\cos\theta \, dl$

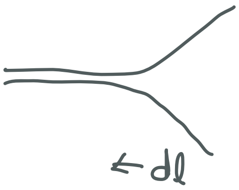
$S<0$ $(\Gamma > 2\gamma\cos\theta)$



$(2\gamma_{sv} - \gamma_{ss})dl$

$= \Gamma dl$

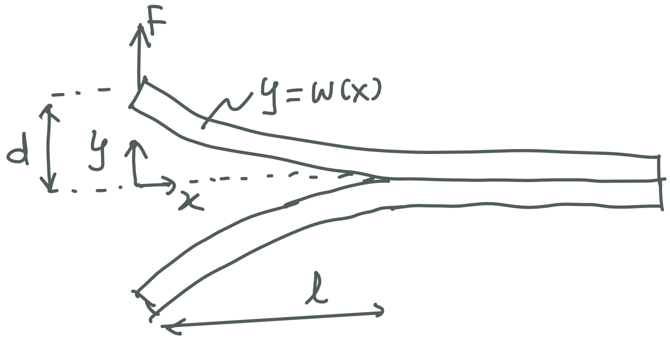
Dry adhesion (Γ)



$(2\gamma_{sv} - \gamma_{ss})dl$

$= \Gamma dl$

When $l_* \ll L$ (some length in the system), we may consider this problem from a simple energetic point of view.



$\mathcal{E}_{Bend} = \frac{1}{2}BK^2$, $K = -w''$
$\sim \frac{d}{l^2}$

$$\mathcal{F} = U_{Bending} + U_{Surface} - \cancel{Fd} \nearrow \text{(Displ. control)}$$

$$= 2\int_0^l \frac{1}{2} B K^2 dx + (2\gamma_{sv} - \gamma_{ss})\, l$$

$$= \underbrace{2\int_0^l \frac{1}{2} B w''^2 dx}_{\sim \frac{Bd^2}{l^3}} + \Gamma l$$

$\sim \frac{Bd^2}{l^3}$ $\quad \sim \Gamma l \quad \Rightarrow \quad \frac{d}{l^2} \sim \left(\frac{\Gamma}{B}\right)^{1/2} \sim l_{ec}^{-1}$

$\nearrow$ Favoring large l $\qquad$ $\uparrow$ Favoring small l.

The required force: $Fd \sim \Gamma l \sim \frac{Bd^2}{l^3} \rightarrow F \sim \Gamma \frac{l}{d} \sim \frac{\Gamma}{d}\left(\frac{Bd^2}{\Gamma}\right)^{1/4} = \boxed{\left(\frac{B\Gamma^3}{d^2}\right)^{1/4}}$

$$\delta F = \underbrace{\int_0^l 2Bw''\,\delta w''\,dx}_{①} + \left(Bw''^2\big|_l + \Gamma\right)\delta l$$

$$① = \int_0^l 2Bw''\,d\,\delta w' = 2Bw''\,\delta w'\Big|_0^l - \int_0^l 2Bw'''\,d\,\delta w$$

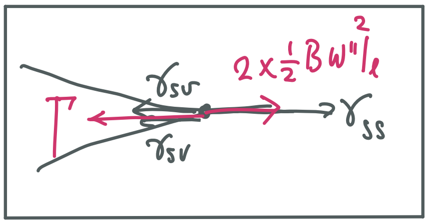
$$= \underbrace{2Bw''\,\delta w'\Big|_0^l}_{\overset{\shortparallel}{-2Bw''^2\big|_l\,\delta l}} - \underbrace{2Bw'''\,\delta w\Big|_0^l}_{\overset{\shortparallel}{0}} + \int_0^l 2Bw''''\,\delta w\,dx$$

$$\left[\delta w'\big|_l = \delta w'(l) - w''\big|_l\,\delta l + O(\delta^2)\,;\ \ \delta w\big|_l = \delta w(l) - w'\big|_l\,\delta l\right]$$

$$\delta l \neq 0\,,\ \delta w \neq 0 \Rightarrow \boxed{Bw'''' = 0}$$

Subject to $w(0) \equiv d$, $w''(0) = 0$, $w(l) = 0$, $w'(l) = 0$

$$\Gamma = Bw''^2\big|_l \rightsquigarrow$$



Solution $w''' = C_1$

$$w'' = C_1 x + \cancel{C_2}^{\,0}$$

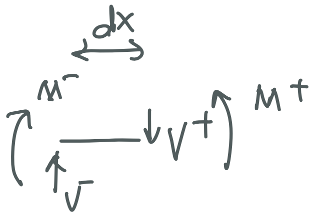
$$w' = \frac{1}{2}C_1 x^2 + C_3 = \frac{1}{2}C_1(x^2 - l^2)$$

$$w = \frac{1}{6}C_1 x^3 - \frac{1}{2}C_1 l^2 x + C_4 = \frac{1}{6}C_1(x^3 - l^3) - \frac{1}{2}C_1 l^2(x - l)$$

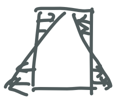
$$w(0) = \frac{1}{3}C_1 l^3 = d \rightarrow C_1 = \frac{3d}{l^3}$$

$$\Gamma = B(C_1 l)^2 \rightarrow \frac{d}{l^2} = \frac{1}{9}\left(\frac{\Gamma}{B}\right)^{1/2} = \frac{1}{9}\,l_{ec}^{-1}$$

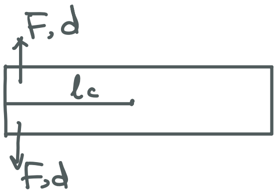
Let us then calculate the force required to produce this l.

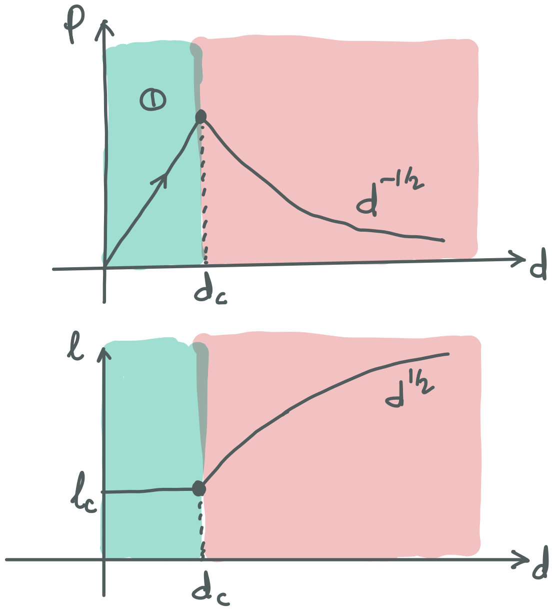


$$\rightarrow \frac{dV}{dx} = 0, \quad \frac{dM}{dx} = V, \quad M = Bw''$$



$$\rightarrow F = V(0) = \underbrace{Bw'''(0) = \frac{3Bd}{\ell^3}}_{\text{Elasticity}} = \overbrace{\frac{1}{9}\left(\frac{B\Gamma^3}{d^2}\right)^{1/4}}^{\text{Elastoadhesion}}$$

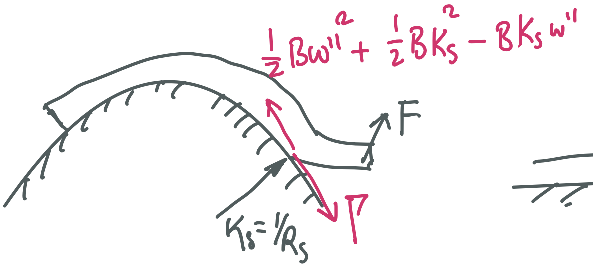


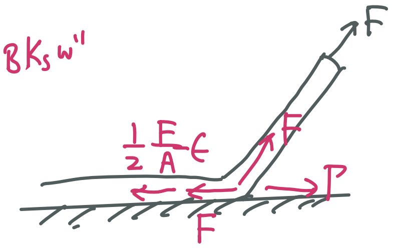


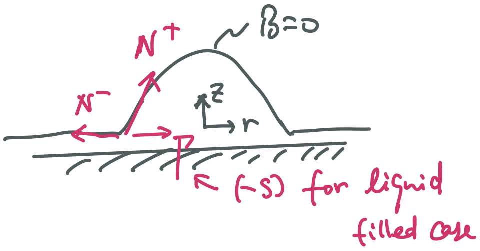
① $\ell \equiv \ell_0$, $P = \frac{3B}{\ell^3} d$

② $\ell > \ell_c$, $P \propto d^{-1/2}$, $\ell \propto d^{1/2}$

- The concept of elastic "contact line" [Dai et al. JMPS 2019, IJSS 2022 Nat. Commun. 2021, Nano Lett. 2023]







$$\Rightarrow \Gamma = \frac{1}{2}B(K - K_s)^2$$

$$\Rightarrow \Gamma = F(1-\cos\theta) + \frac{1}{2}\frac{F^2}{EA}$$

(Kendall's peeling angle)

$$\Gamma = (-S) = N^- - N^+\cos\theta$$

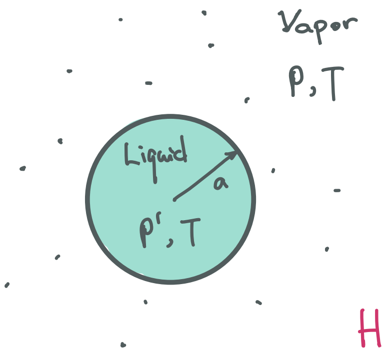
$[= N(1-\cos\theta)]$

If there's no jump in N.

Capillary condensation & nucleation

• Kelvin equation

describes the change in vapour pressure due to a curved liquid-vapor interface, such as the surface of a droplet. It explains capillary condensation - the phenomenon whereby a confined gas condenses to a liquid at a chemical potential below that corresponding to liquid-vapor coexistance in the bulk or Saturation vapor pressure (P_{SAT}).



In equilibrium $\mu_L = \mu_V$ ~ Chemical potential.

Thermodynamics $d\mu = -\underset{\text{entropy}}{s}\, d\overset{0}{\cancel{T}} + \overset{\text{molar volume}}{V_m}\, dp$

How is p different from P_{sat}?

For a drop, the curvature is convex, $p' - p = \frac{+2\gamma}{a}$.

$$\mu_i(T, p) = \mu_i(T, p_{sat}) + \int_{p_{sat}}^{p} V\, dp \quad , i = L \text{ or } V.$$

$$\begin{cases} \mu_L(T, p') = \mu_L(T, p_{sat}) + V_m(p' - p_{sat}) \\ \mu_V(T, p) = \mu_V(T, p_{sat}) + \int_{p_{sat}}^{p} \frac{RT}{p}\, dp = \mu_V(T, p_{sat}) + RT \ln \frac{p}{p_{sat}} \end{cases}$$

Note $\mu_L(T, P_{sat}) = \mu_v(T, P_{sat})$ and $\mu_L(T, p') = \mu_v(T, p)$ in equilibrium.

$$\longrightarrow \quad V_m(p' - P_{sat}) = RT \ln\frac{p}{P_{sat}}.$$

Rewrite $p' - P_{sat} = \underbrace{p' - p}_{\substack{\text{Known} \\ \simeq \frac{2\gamma}{a}}} + \underbrace{p - P_{sat}}_{\text{Interest}}$

We have $$\frac{2\gamma V_m}{a} + V_m(p - P_{sat}) = RT \ln\frac{p}{P_{sat}} \qquad (*)$$

In particular, when $\frac{2\gamma}{a} \gg p - P_{sat}$, (*) reads

$$\boxed{\ln\frac{p}{P_{sat}} = \frac{V_m}{RT}\,\frac{2\gamma}{a}}$$

Kelvin equation ($a\uparrow$, $p \to P_{sat}$, drop → bulk)

- If vapor is cooled, P_{sat} decreases, $p/P_{sat}\uparrow$, $a \to a_c$ (Nucleation)
- If curvature is concave, a is negative, $p < P_{sat}$

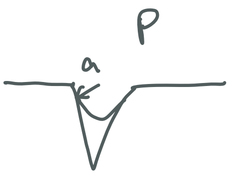
Major consequences:

① Ostwald Ripening

$$\mu_L - \mu_S = 2\gamma V_m\left(\frac{1}{a_L} - \frac{1}{a_S}\right) < 0$$

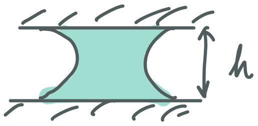
Larger bubbles/drops grow at expense of smaller bubbles/drops.

② Hard to dry out small cracks



$$\ln\frac{p}{P_{sat}} = -\frac{2\gamma V_m}{aRT}$$, $a\downarrow$ needs $p\downarrow$

Example:

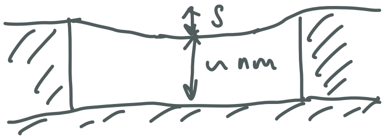


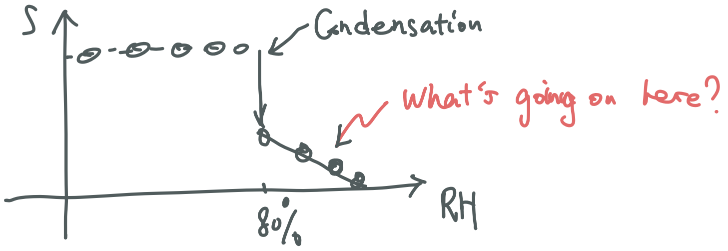
At 25°C, how dry must air be to evaporate the confined water?

$$\ln RH = - \frac{1 \times \overset{\gamma}{0.072\ J/m^2} \times \overset{V_w}{18 \times 10^{-6}\ m^3/mol}}{\frac{h}{2} \times \underset{R}{8.3\ J/(mol \cdot K)} \times \underset{T}{298K}}.$$

$h = 1\ \mu m$	$RH = 99.9\%$
100 nm	99 %
10 nm	90 %
1 nm	35 %

In Yang et al. Nature (2020), Kelvin equation is found to qualitatively valid.



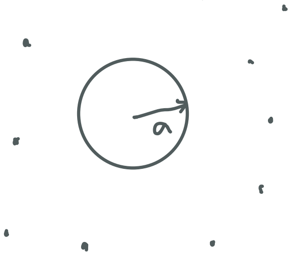


• Homogeneous nucleation

Nucleation - A process of localized formation of a distinct thermodynamic phase (gas, liquid, solid etc).

Homogeneous nucleation occurs without preferential nucleation site spontaneously and randomly.

Super-saturated vapor $p > P_{sat}(T)$



What is δG required to form a drop of radius a?

Aside:

$V_m = \frac{4\pi a^3}{3n}$

or $n = \frac{4\pi a^3}{3V_m}$

$$\Delta G = n(\mu_L - \mu_V) + 4\pi a^2 \gamma$$

Recall:

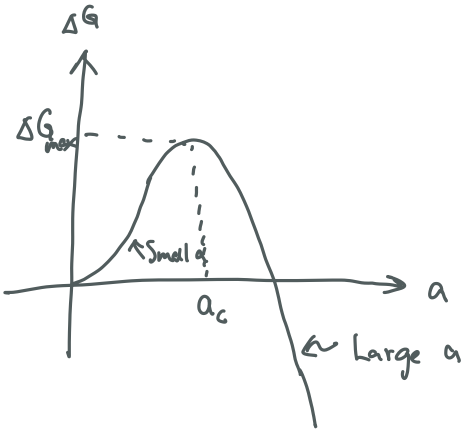
$$\mu_V(T, P_s) = \mu_V(T, P_{sat}) + RT \ln \frac{P_s}{P_{sat}}$$

$$\mu_L(T, P_s) = \mu_L(T, P_{sat}) + V_m(P_s - \overset{\text{often neglected.}}{\cancel{P_{sat}}}) \text{ (constant term)}$$

We then have

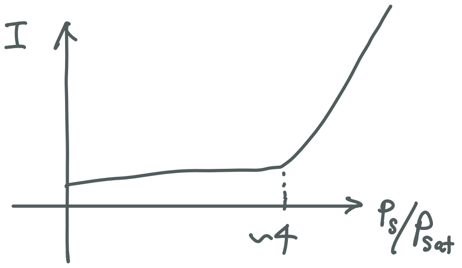
$$\Delta G = \underbrace{-\frac{4\pi a^3}{3V_m} RT \ln \frac{P_s}{P_{sat}}}_{P_s > P_{sat} \Rightarrow \text{Driving}} + \underbrace{4\pi a^2 \gamma}_{\text{Resisting}}$$

- $\frac{\partial \Delta G}{\partial a} = 0 \Rightarrow a_c = \frac{2V_m\gamma}{RT\ln(P_s/P_{sat})}$
- $\Delta G_{max} = \frac{16\pi V_m^2 \gamma^3}{3[RT\ln(P_s/P_{sat})]^2}$



- For water at 300 K, $P_s/P_{sat} = 1.1$, $a_c \sim 11$ nm; $P_s/P_{sat} = 3$, $a_c \sim 1$ nm
- Rate of nucleation I

$$I \sim \exp\left(-\frac{\Delta G_{max}}{RT}\right)$$

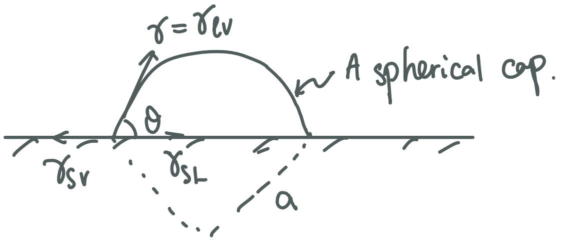


$$\sim \left(\frac{P_s}{P_{sat}}\right)^2 \exp\left[-\frac{16\pi}{3}\frac{\gamma^3 V_m}{(RT)^3 \ln^2(P_s/P_{sat})}\right]$$

• Heterogeneous nucleation

Occuring at nucleation sites on surface contacting the liquid or vapor, or even on suspended particles or minute bubbles.

Example.



$$\gamma_{sl} + \gamma\cos\theta = \gamma_{sv}$$

Now the free energy reads

$$\Delta G = n(\mu_L - \mu_v) + \gamma A_{lv} + (\gamma_{sl} - \gamma_{sv}) A_{sl}$$

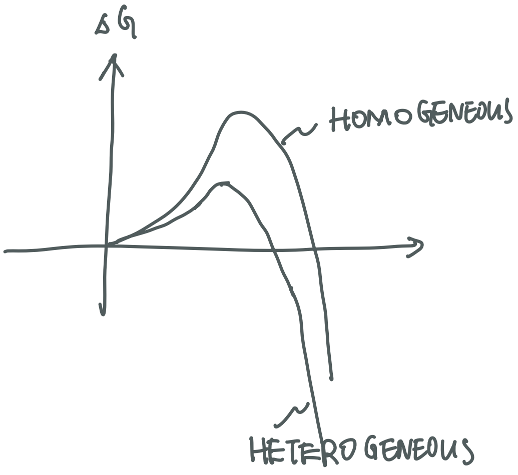
$$= \frac{V}{V_m}(\mu_L - \mu_v) + \gamma\left(A_{lv} \overbrace{- A_{sl}\cos\theta}^{\text{Sort of reduction}}\right)$$

In general, $V = \frac{4\pi a^3}{3} f(\theta)$, $A_{lv} = 4\pi a^2 g(\theta)$, $A_{sl} = 4\pi a^2 h(\theta)$

$$\rightarrow \quad \Delta G = -\frac{4\pi a^3}{3V_m} RT\ln\left(P_s/P_{sat}\right) f(\theta) + 4\pi a^2\gamma\left(g - h\cos\theta\right)$$

• $a_c = \frac{2V_m\gamma}{RT\ln(P_s/P_{sat})}\left(\frac{g - h\cos\theta}{f}\right)$

- $$\Delta G_{max} = \underbrace{\frac{16\pi}{3} \frac{\gamma^3 V_m^3}{[RT\ln(P_s/P_{sat})]^2}}_{\Delta G_{max} \text{ for homogeneous case}} \left(\frac{g - h\cos\theta}{f} \right)^3$$



$$= \Delta G_{HOMO} \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$$

$\theta = \frac{\pi}{2}$, $\Delta G_{HETER} = \frac{1}{2} \Delta G_{HOMO}$

$\theta = \pi$, $\Delta G_{HETER} = \Delta G_{HOMO}$