Multiphase Flow and Heat Transfer

Introduction

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Multiphase Flow and Heat Transfer

Prerequisites: Thermodynamics, Heat and Mass Transfer

References

- Van P Carey, *Liquid-Vapor Phase-Change Phenomena*, Second Edition, CRC Press, Taylor & Francis, 2007.
- Incropera FP and Dewitt DP, *Fundamentals of Heat and Mass Transfer*, Fifth edition, John Wiley and Sons, 2010.
- Mostafa G, *Two-Phase Flow, Boiling and Condensation*, Cambridge University Press. http://dx.doi.org/10.1017/CBO9780511619410

Class Timings: ME546

Mon, Tue:	11 AM to 12 PM	Room-105
Fri:	12 PM to 1 PM,	Room-105

Course Material: http://www.iitp.ac.in/∼sudheer/teaching.html

Course Content

Pool Boiling

- Classification
- Boiling Regimes
- Correlations
- Enhancement of Boiling Heat Transfer

Degasification

- Henry's law
- Degassing Techniques

Liquid-vapor interface

- Interfacial tension
- Capillary, Interface shape

Wettability

- Contact angle
- Bubble formation

Condensation

Two phase flow

- Flow regimes
- Flow models

Basics

Phase

Macroscopic state of matter which is homogeneous in chemical composition and physical structure. Gas, Liquid & Solid.

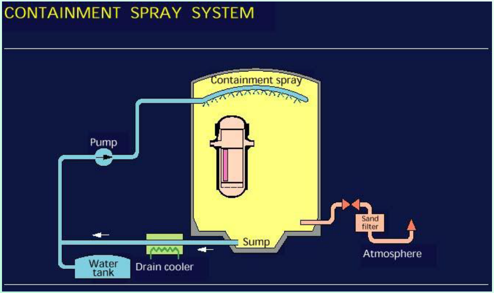
Gas-Liquid
  Steam and water; Air and water

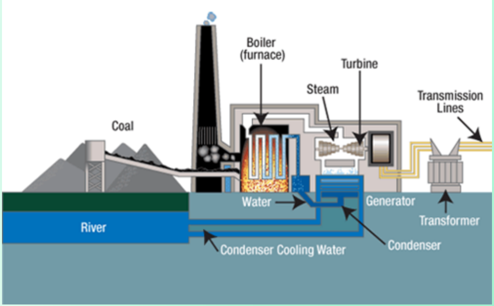
Liquid-Solid
  Plasma and platelets (Blood)

Liquid-Liquid
  Oil and water

Industrial Applications

Spray cooling ''Emergency Shutdown" of nuclear power plant





Steam power plant

Industrial Applications

- Steam generators and condensers
- Steam turbines (power plants)
- Coal fired furnaces
- Refrigeration
- Liquid sprays
- Cryogenics
- Material processing - Quenching
- Process plants - Chemical/petroleum
- Electronic component cooling
- Medical applications

Everyday Examples

- Dust storms
- Rain, Clouds, snow
- Ocean waves
- Geysers, boiling water
- Inkjets
- Tire splash
- Sloshing

Multiphase Flow and Heat Transfer

Boiling

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Basics

Phase

Macroscopic state of matter which is homogeneous in chemical composition and physical structure. Gas, Liquid & Solid.

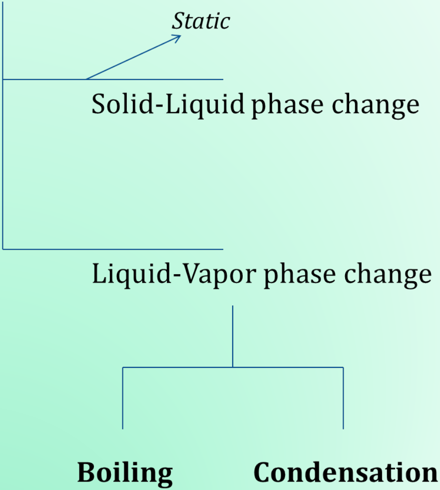
Gas-Liquid
  Steam and water; Air and water

Liquid-Solid
  Plasma and platelets (Blood)

Liquid-Liquid
  Oil and water

Phase Change

Melting and Solidification → No



Static

Solid-Liquid phase change

Liquid-Vapor phase change

Boiling

Condensation

Continuous, also energy equation

motion

Boiling and Condensation

Thermodynamics

- When the temperature of a liquid at a specified pressure is raised to the saturation temperature T_{sat} at that pressure, Boiling occurs.
- Liquid-Vapor transformation: $T_s > T_{sat}$ at a given pressure.

- When the temperature of a vapor is lowered to T_{sat}, Condensation occurs.
- Vapor-Liquid transformation: $T_s < T_{sat}$ at a given pressure.

Typical Values of Heat Transfer Coefficient

$$q_{conv} = hA_s \left(T_s - T_\infty\right)$$

Process	**h (W/m^2 K)**
Free convection	
Gases	2-25
Liquids	50-1,000
Convection with phase change	
Boiling and Condensation	2,500-100,000

Physical Considerations

Free and Forced convection depends on

$\rho, C_p, \mu, k_{fluid}$

Boiling/Condensation Heat Transfer depends on

- $\rho, C_p, \mu, k_{fluid}$
- $\Delta T = |T_s - T_{sat}|$
- Latent heat of vaporization, h_{lv}
- Surface tension at the liquid-vapor interface, σ
- body force arising from the liquid-vapor density difference, $g(\rho_l - \rho_v)$

$$h = h[\Delta T, g(\rho_l - \rho_v), h_{lv}, \sigma, L, \rho, C_p, k, \mu]$$

10 variables in 5 dimensions $\implies 5$ pi-groups.

Dimensionless Parameters

$$\frac{hL}{k} = f\left[\frac{\rho g(\rho_l - \rho_v)L^3}{\mu^2}, \frac{C_p \Delta T}{h_{lv}}, \frac{\mu C_p}{k}, \frac{g(\rho_l - \rho_v)L^2}{\sigma}\right]$$

$$\mathsf{Nu}_L = f\left[\frac{\rho g(\rho_l - \rho_v)L^3}{\mu^2}, \mathsf{Ja}, \mathsf{Pr}, \mathsf{Bo}\right]$$

Jakob number

Ratio of max sensible energy absorbed by liquid (vapor) to latent energy absorbed by liquid (vapor) during boiling (condensation).

Bond number

Ratio of the buoyancy force to the surface tension force.

Unnamed parameter

Represents the effect of buoyancy-induced fluid motion on heat transfer.

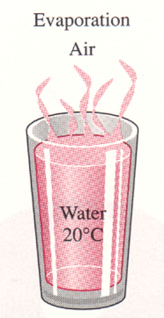
Boiling and Evaporation

Boiling

- The process of addition of heat to a liquid such a way that generation of vapor occurs.
- Solid-liquid interface
- Characterized by the rapid formation of vapor bubbles

Evaporation

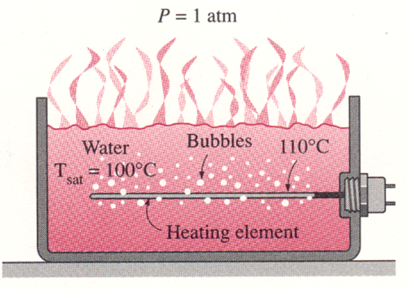
- Liquid-vapor interface
- $P_v < P_{sat}$ of the liquid at a given temp
- No bubble formation or bubble motion



Boiling

Boiling occurs

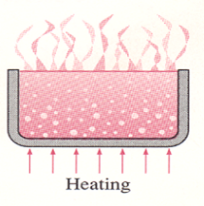
- Solid-liquid interface
- when a liquid is brought into contact with a surface at a temperature above the saturation temperature of the liquid

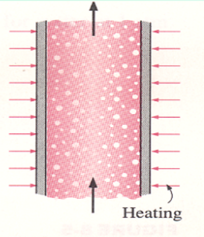


Bubble

- The boiling processes in practice do not occur under equilibrium conditions.
- Bubbles exist because of the surface tension at the liquid vapor interface due to the attraction force on molecules at the interface toward the liquid phase.
- The temperature and pressure of the vapor in a bubble are usually different than those of the liquid.
- Surface tension $\downarrow \quad \uparrow$ Temperature
- Surface tension $= 0$ at critical temperature
- No bubbles at supercritical pressures and temperatures

Boiling - Classification





Pool boiling

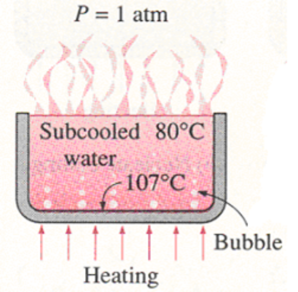
- Fluid is stationary
- Fluid motion is due to natural convection currents
- Motion of bubbles under the influence of buoyancy

Flow boiling

- Fluid is forced to move in a heated pipe or surface by external means such as pump
- Always accompanied by other convection effects

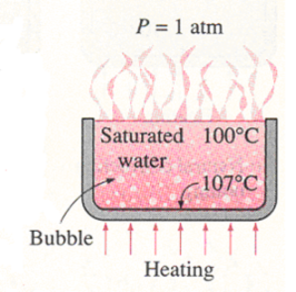
Boiling - Classification

Subcooled boiling



$$T_{\text{bulk of liquid}} < T_{sat}$$

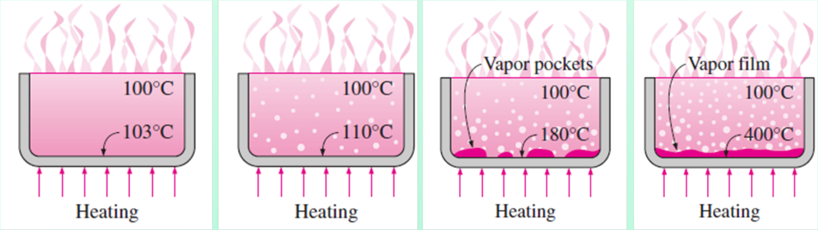
Saturated boiling



$$T_{\text{bulk of liquid}} = T_{sat}$$

Boiling Regimes

Boiling curve for saturated water at atmospheric pressure

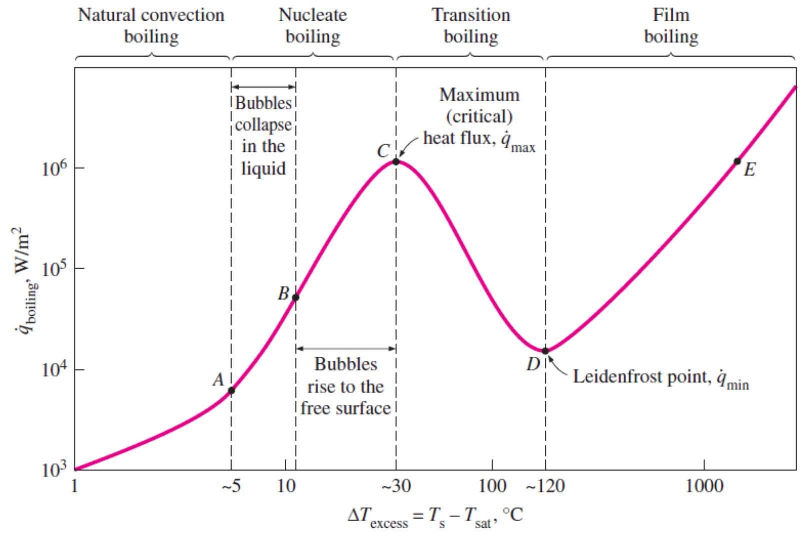


Natural convection boiling **Nucleate boiling** **Transition boiling** **Film boiling**

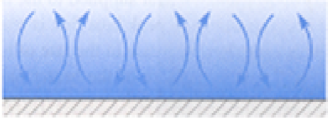
Nichrome (1500 K), Platinum (2045 K)

Nukiyama, 1934: Nichrome, Platinum

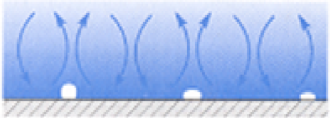
Boiling curve for saturated water at atmospheric pressure



Boiling Regimes - Nukiyama, 1934



1. Natural convection



Onset of boiling

2. Individual bubble regime

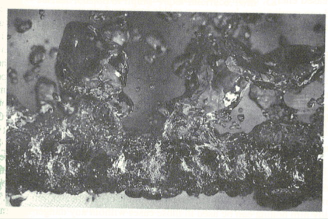
3. Regime of slugs and bubbles

4. Transition film boiling

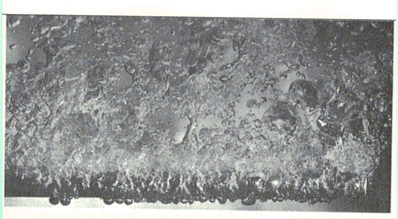
5. Stable film boiling

Boiling Regimes

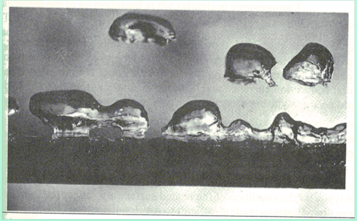
Methanol on horizontal 1 cm steam-heated copper tube



Nucleate boiling

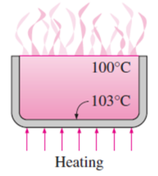


Transition boiling



Film boiling

Boiling Regimes

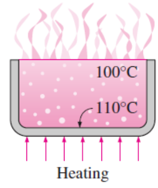


Natural convection

- Governed by natural convection currents.
- Heat transfer from the heating surface to the fluid is by natural convection.
- Natural convection ends at $\Delta T = 5°\text{C}$.

Nucleate boiling

- Onset of nucleate boiling (ONB)
- Stirring and agitation caused by the entrainment of the liquid to the heater surface increases h, q''.
- High heat transfer rates are achieved.

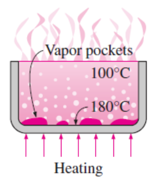


Boiling Regimes

Nucleate boiling

- $A - B$, isolated bubbles are formed at various preferential nucleation sites on the heated surface
- Bubbles collapse in the liquid.
- $B - C$, bubbles form at great rates forming continuous columns of vapor.
- Move all the way up to the free surface, where they break up and release their vapor content.
- **Critical/maximum heat flux (CHF)**, $\dot{q}''_{max}$
- For water, CHF $=$ 1 MW/m^2 at 30 K excess temperature.
- $h = \dot{q}''_{max}/\Delta T_{sat} = 3.3 \times 10^4$ W/m^2 K.

Boiling Regimes

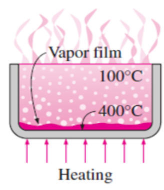


Transition boiling

- Large fraction of the heater surface is covered by a vapor film.
- Both nucleate and film boiling partially occur.
- Unstable film boiling regime.
- Avoided in practice.

Film boiling

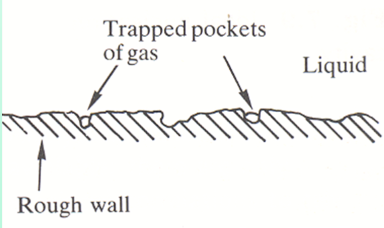
- Vapor film is responsible for the low heat transfer
- $\dot{q}$ increases with increasing ΔT as a result of heat transfer from the heated surface to the liquid through the vapor film by radiation.



Boiling Nucleation - Boiling Inception

The process of bubble formation is called Nucleation

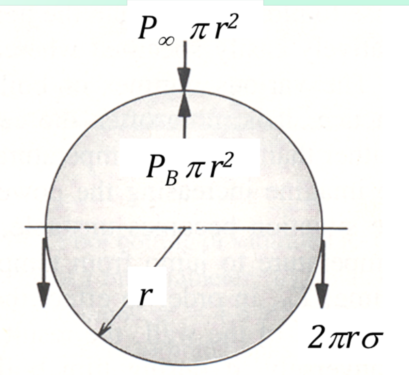
Enlarged view of a boiling surface



- The cracks and crevices do not constitute nucleation sites for the bubbles. Must contain pockets of gas/air trapped
- It is from these pockets of trapped air that the vapor bubbles begin to grow during nucleate boiling
- These cavities are the sites at which bubble nucleation occurs

Boiling Nucleation - Boiling Inception

When a liquid contacts the surface, surface tension forces prevent the liquid from entering the smaller cavities in which air or other gases are trapped.



r	radius of the bubble
σ	surface tension
P_B	pressure inside the bubble
P_∞	pressure in the liquid or the ambient pressure

Boiling Nucleation - Boiling Inception

For static equilibrium, the surface tension force balances the net pressure force:

$$2\pi r\sigma = (P_B - P_\infty)\,\pi r^2$$

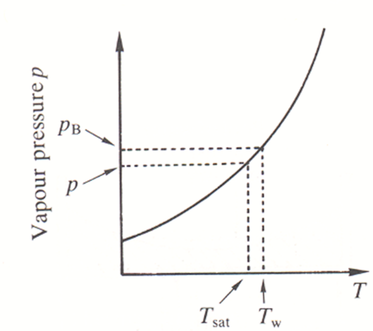
$$\boxed{\boldsymbol{P_B = P_\infty + \frac{2\sigma}{r}}}$$

Young-Laplace equation

P_B is maximum when $r = R$ (the cavity radius)

The wall temperature T_w must be high enough to vaporize the liquid at a pressure of P_B.

Boiling Nucleation - Boiling Inception



Vapor pressure curve: superheat required for nucleation

For the bubble to grow, the required condition:

$$T_w > T_{sat} + \frac{dT}{dp}\left(P_B - P_\infty\right)$$

Boiling Nucleation - Boiling Inception

Slope of the vapor pressure curve from the Clausius-Clapeyron eq.

$$\boxed{\frac{dp}{dT} = \frac{h_{lv}}{(v_v - v_l)T_{sat}}}$$

h_{lv}	latent heat of vaporization
T_{sat}	saturation temperature
v_l	specific volume of the liquid
v_v	specific volume of the gas

Then, if $v_v \gg v_l$ and, since $v_v = \frac{1}{\rho_v}$

$$\frac{dp}{dT} = \frac{h_{lv}}{(v_v - v_l)T_{sat}} \implies \frac{dT}{dP} = \frac{T_{sat}}{\rho_v h_{lv}}$$

$$T_w > T_{sat} + \frac{dT}{dp}(P_B - P_\infty)$$

$$\implies T_w > T_{sat} + \frac{T_{sat}}{\rho_v h_{lv}}\frac{2\sigma}{R}$$

Critical Radius for Nucleation

If ΔT_{sat} is the value of $(T_w - T_{sat})$ at which nucleation starts, then the cavity radius given by:

$$\boxed{R = \frac{2\sigma T_{sat}}{\rho_v h_{lv} \Delta T_{sat}}}$$

For water at 1 bar, $T_{sat} = 373$ K, $\sigma = 0.059$ N/m, $h_{lv} = 2.256 \times 10^6$ J/kg, $\rho_v = 0.598$ kg/m^3, $\Delta T_{sat} \approx 5$ K.

$$R = 6.5 \ \mu\text{m}$$

Typically, cavity sizes are in the micron range. If the cavity size is known, then clearly the wall superheat required to start nucleate boiling can be calculated.

Critical Radius for Nucleation

Real surfaces, of course, can contain a range of cavity sizes. As the wall superheat is increased, cavities of smaller and smaller radius are able to become active and initiate nucleation.

Maximum size of active nucleation sites on smooth metallic surfaces:

Water $\sim 5\mu\text{m}$
Organics and refrigerants $\sim 0.5\mu\text{m}$
Cryogenic fluids on aluminum or copper $\sim 0.1 - 0.3\mu\text{m}$

Heat Transfer in Nucleate Boiling

Rohsenow postulated:

- Heat flows from the surface first to the adjacent liquid, as in any single-phase convection process
- High h is a result of local agitation due to liquid flowing behind the wake of departing bubbles

Thus, it may be possible to adapt a single-phase forced convection heat transfer correlation to nucleate pool boiling, if we could specify the appropriate length and velocity scales associated with the convection process.

Heat Transfer in Nucleate Boiling

$$\mathsf{Nu} = f(\mathsf{Re}, \mathsf{Pr})$$

$$\mathsf{Nu} = \frac{hL_b}{k_l}; \quad \mathsf{Re} = \frac{\rho_v u_b L_b}{\mu_l}; \quad \mathsf{Pr} = \frac{\mu_l \ C_{Pl}}{k_l}$$

Velocity is taken as the liquid velocity towards the surface which is to supply the vapor that is being produced so:

$$u_b \sim \frac{\dot{q}''}{h_{lv}\rho_v}$$

Length scale is taken to be,

$$L_b \sim \left[\frac{\sigma}{g(\rho_l - \rho_v)}\right]^{\frac{1}{2}}$$

Heat Transfer in Nucleate Boiling

$$\mathsf{Nu} = \frac{hL_b}{k_l} = \frac{h}{k_l}\left[\frac{\sigma}{g(\rho_l - \rho_v)}\right]^{\frac{1}{2}}$$

$$\mathsf{Re} = \frac{\rho_v u_b L_b}{\mu_l} = \frac{\rho_v}{\mu_l}\frac{\dot{q}''}{h_{lv}\rho_v}\left[\frac{\sigma}{g(\rho_l - \rho_v)}\right]^{\frac{1}{2}}$$

$$\mathsf{Pr} = \frac{\mu_l\ C_{Pl}}{k_l}$$

$$\mathsf{Nu} = \frac{1}{C_{sf}}\,\mathsf{Re}^{1-m}\,\mathsf{Pr}^{-n}$$

$$h = \frac{\dot{q}''}{T_s - T_{sat}} = \frac{\dot{q}''}{\Delta T_{sat}}$$

Rohsenow's Correlation

$$\boxed{\frac{C_{Pl}\Delta T_{sat}}{h_{lv}} = C_{sf}\left[\frac{\dot{q}''}{\mu_l\ h_{lv}}\sqrt{\frac{\sigma}{g(\rho_l-\rho_v)}}\right]^m\left[\frac{\mu_l\ C_{Pl}}{k_l}\right]^{1+n}}$$

$$\boxed{\frac{\dot{q}''}{\mu_l\ h_{lv}}\sqrt{\frac{\sigma}{g(\rho_l-\rho_v)}} = \left(\frac{1}{C_{sf}}\right)^{\frac{1}{m}}\left[\frac{C_{Pl}\Delta T_{sat}}{h_{lv}}\right]^{\frac{1}{m}}\mathrm{Pr}^{-\frac{1+n}{m}}}$$

$m = 0.33$ and $1+n = 1$ for water and 1.7 for other fluids.
Applicable only for clean surfaces

C_{sf} is the surface-fluid constant. Typically: 0.0025 and 0.015.

For a given ΔT_{sat}, $\dot{q}'' \propto C_{sf}^{-3}$.
$\because C_{sf}$ can vary by a factor of 10, $\dot{q}''$ can vary by a factor of 1000.

Rohsenow's Correlation

$$\boxed{\frac{C_{Pl}\Delta T_{sat}}{h_{lv}} = C_{sf}\left[\frac{\dot{q}''}{\mu_l\ h_{lv}}\sqrt{\frac{\sigma}{g(\rho_l-\rho_v)}}\right]^m \left[\frac{\mu_l\ C_{Pl}}{k_l}\right]^{1+n}}$$

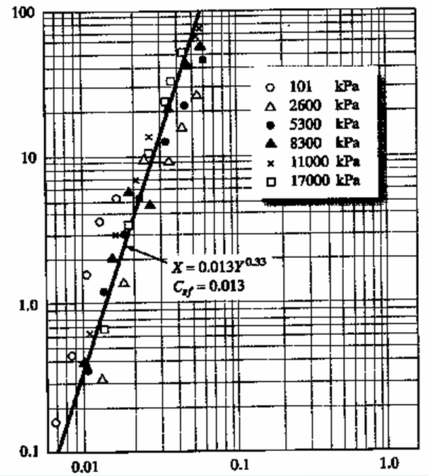
$$\boxed{\frac{\dot{q}''}{\mu_l\ h_{lv}}\sqrt{\frac{\sigma}{g(\rho_l-\rho_v)}} = \left(\frac{1}{C_{sf}}\right)^{\frac{1}{m}} \left[\frac{C_{Pl}\Delta T_{sat}}{h_{lv}}\right]^{\frac{1}{m}} \mathsf{Pr}^{-\frac{1+n}{m}}}$$

When used to estimate q'', errors can amount to $\pm 100\%$.
The errors for estimating ΔT_{sat} reduce by a factor of 3

$$\because \Delta T_e \propto (q_s'')^{1/3}$$

Rohsenow’s Method: Platinum Wire-Water

$$\left[\frac{q''}{\mu_l\, h_{lv}}\sqrt{\frac{\sigma}{g(\rho_l-\rho_v)}}\right]$$



$$\frac{C_{pl}\left(T_w - T_{sat}\right)}{h_{lv}\,\mathrm{Pr}}$$

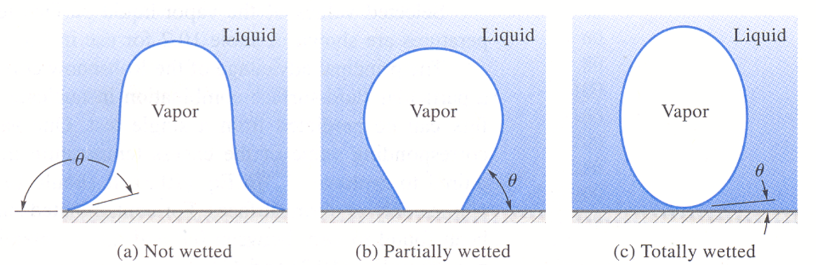
Coefficient in Rohsenow's Correlation

The most important variables affecting C_{sf} are:

- Surface roughness of the heater which determines the number of nucleation sites at a given temperature.
- Angle of contact between the bubble and heating surface, a measure of wettability of a surface with a particular fluid.

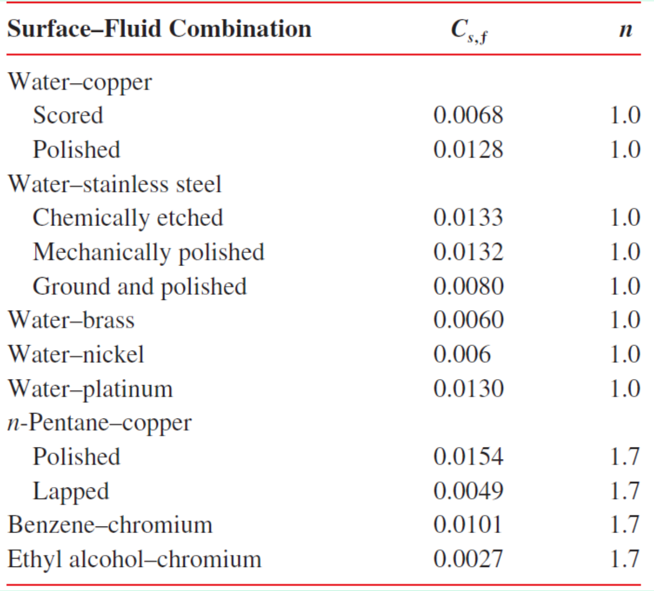
Surface is hydrophilic (wetted),if $\theta < 90^\circ$

Surface is hydrophobic (not wetted),if $\theta > 90^\circ$



(a) Not wetted (b) Partially wetted (c) Totally wetted

Coefficient in Rohsenow's Correlation



Surface–Fluid Combination	$C_{s,f}$	n
Water–copper		
Scored	0.0068	1.0
Polished	0.0128	1.0
Water–stainless steel		
Chemically etched	0.0133	1.0
Mechanically polished	0.0132	1.0
Ground and polished	0.0080	1.0
Water–brass	0.0060	1.0
Water–nickel	0.006	1.0
Water–platinum	0.0130	1.0
n-Pentane–copper		
Polished	0.0154	1.7
Lapped	0.0049	1.7
Benzene–chromium	0.0101	1.7
Ethyl alcohol–chromium	0.0027	1.7

Coefficient in Rohsenow's Correlation

- For contaminated surfaces, the exponent of Prandtl number of liquid $(1+n)$ is found to vary between 0.8 and 2.0.
- Contamination also affects the other exponent in the equation and C_{sf}
- If no data is available, then consider, $C_{sf} = 0.013$

Heat Transfer in Nucleate Boiling

Another frequently quoted Forster-Zuber correlation

$$\dot{q}'' = 0.00122 \left(\frac{k_l^{0.79} C_{Pl}^{0.45} \rho_l^{0.49}}{\sigma^{0.5} \mu_l^{0.29} h_{lv}^{0.24} \rho_v^{0.24}} \right) [T_w - T_{sat}(P_l)]^{1.24} \, \Delta P_{sat}^{0.75}$$

ΔP_{sat} is the difference in saturation pressure corresponding to a difference in saturation temperature equal to the wall superheat $T_w - T_{sat}(P_l)$.

k_l - W/m K

C_{Pl} - kJ/kg K

ρ - kg/m^3

P - Pa

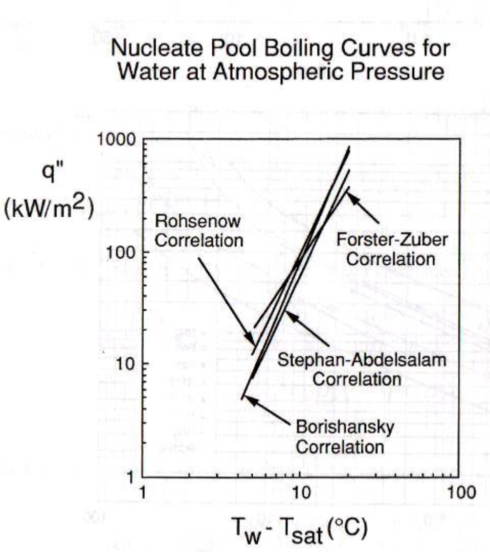
σ - N/m

μ - Ns/m^2

h_{lv} - kJ/kg

$\dot{q}''$ - kW/m^2

Heat Transfer in Nucleate Boiling



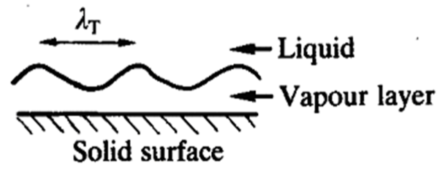
Critical Heat Flux in Nucleate Boiling

- Rohsenow's correlation is restricted to nucleate boiling
  - Does not reveal the ΔT_{sat} at which the $\dot{q}''_{max}$
  - Limiting heat flux: when nucleate boiling breaks down and an insulating vapor film forms
- For a $\dot{q}''$ controlled surface, the ΔT_{sat} rise after $\dot{q}''_{max}$ can be very large (can be > 1000 K)

Instability of Vapor Layer

The light fluid in a layer which has a heavy fluid on top of it is unstable.

The layer breaks down by the formation of waves on its surface as in the figure.



Taylor waves

Reyleigh-Taylor instability

During boiling, disturbances of all wavelengths are present, there will be some disturbances at small wavelength and long wavelength that will amplify and cause the interface to be unstable.

Rayleigh-Taylor Instability

Condition for the interface instability of a motionless liquid overlaying a motionless vapor region:

$$\alpha > \alpha_c = \left[\frac{(\rho_l - \rho_v)g}{\sigma}\right]^{\frac{1}{2}}$$

This condition is called Reyleigh-Taylor Instability

Corresponding critical wavelength:

$$\lambda_c = \frac{2\pi}{\alpha_c} = 2\pi\left[\frac{\sigma}{(\rho_l - \rho_v)g}\right]^{\frac{1}{2}}$$

The most dangerous wavelength, as they grow most rapidly,

$$\lambda_D = \sqrt{3}\ \lambda_c$$

At 1 bar:

$\sigma = 0.058988$ N/m

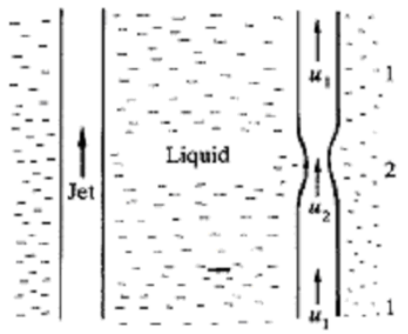
$\rho_l = 958.63$ kg/m^3

$\rho_v = 0.59034$ kg/m^3

$\lambda_c = 15.7$ mm

$\lambda_D = 27.2$ mm

Kelvin-Helmhotz Instability



A parallel sided jet is not stable.

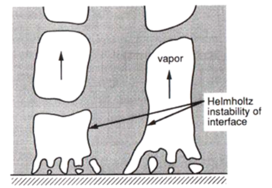
Consider the random thinning of the jet as illustrated.

By continuity, $u_2 > u_1$ and therefore, from Bernoullis equation $p_2 < p_1$.

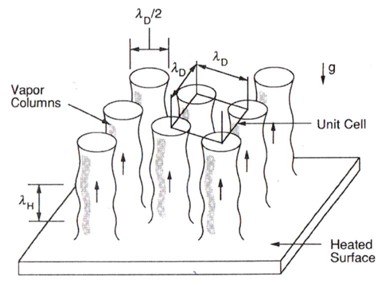
- If the jet is in equilibrium at 1, then the liquid pressure at 2 will push the 'neck' further in and disrupt the jet completely, thus breaking it up. This is a Kelvin-Helmhotz instability.
- This argument would imply that the vapor jet is always unstable, but the effects of surface tension, which has a stabilizing effect, have been neglected.

Zuber's Model

1. $\dot{q}''_{max}$ when the interface of columns - Helmholtz unstable.
2. Centerline spacing of columns $=$ most dangerous λ_D of Taylor instability.
3. Columns diameter $= \lambda_D/2$.
4. The Helmholtz unstable λ imposed on the columns $=$ Taylor wave node spacing λ_D.



Postulated Helmholtz instability CHF mechanisms



Vapor column spacing in the Zuber critical heat flux model

Zuber's Model Analysis: Consider Unit Cell

Critical Helmholtz velocity for vertical vapor and liquid flow:

$$u_c = |\bar{u}_l - \bar{u}_v| = \left(\frac{\sigma \alpha (\rho_l + \rho_v)}{\rho_l \rho_v} \right)^{\frac{1}{2}}$$

Assuming $\rho_l \gg \rho_v$ and substituting $\alpha = 2\pi/\lambda$:

$$u_c \left(\frac{2\pi\sigma}{\rho_v \lambda} \right)^{\frac{1}{2}}$$

The most dangerous wavelength from Taylor instability for liquid in contact with vapor:

$$\lambda_D = 2\pi \left[\frac{3\sigma}{(\rho_l - \rho_v) g} \right]^{\frac{1}{2}}$$

Zuber's Model Analysis: Consider Unit Cell

Critical heat flux, the rate of heat supply to the area, A_{surf}:

$$\dot{q}''_{max} A_{surf} \approx h_{lv} \rho_v u_v A_{col}$$

$$\dot{q}''_{max} = \frac{\pi}{16} h_{lv} \rho_v u_v$$

- Since the downward liquid velocity is much smaller than the upward vapor velocity, due to the large density difference between the phases, $u_c \approx u_v$.
- The Helmholtz unstable wavelength imposed on the columns is equal to the Taylor wave node spacing λ_D.

$$\dot{q}''_{max} = \frac{\pi}{16(3)^{1/4}} h_{lv} \rho_v \left[\frac{\sigma(\rho_l - \rho_v) g}{\rho_v^2} \right]^{1/4}$$

works well for the flat horizontal plates.

Zubers Correlation for Critical Heat Flux

Zuber's correlations for flat horizontal plate:

$$\boxed{q''_{\mathsf{max}} = 0.149 h_{lv} \rho_v \left[\frac{\sigma(\rho_l - \rho_v) g}{\rho_v^2} \right]^{1/4}}$$

works well for the flat horizontal plates.

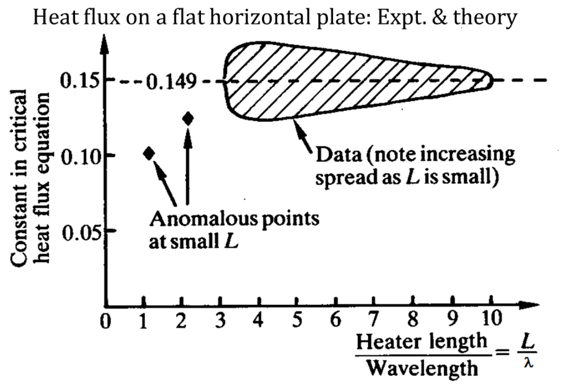
The coefficient is modified for better fit for different geometries:

$$\boxed{q''_{\mathsf{max}} = 0.131 h_{lv} \rho_v \left[\frac{\sigma(\rho_l - \rho_v) g}{\rho_v^2} \right]^{1/4}}$$

Critical Heat Flux on a Flat Plate

$$q''_{\text{max}} = C h_{lv} \rho_v \left[\frac{\sigma(\rho_l - \rho_v) g}{\rho_v^2} \right]^{1/4}$$

$C = 0.149$ for flat, horizontal heater


Heat flux on a flat horizontal plate: Expt. & theory

$$\lambda = 2\pi \left[\frac{\sigma}{(\rho_l - \rho_v) g} \right]^{\frac{1}{2}}$$

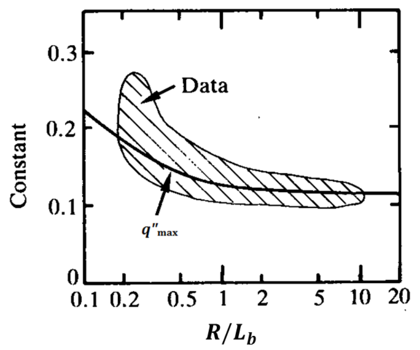
$$= 2\pi L_b$$

Critical Heat Flux Outside Horizontal Cylinders

$$q''_{\max} = C h_{lv} \rho_v \left[\frac{\sigma(\rho_l - \rho_v) g}{\rho_v^2} \right]^{1/4}$$

Boiling outside horizontal cylinders: expt. & theory

$$C = 0.116 + 0.3 \exp\left\{-3.44 \sqrt{\frac{R}{L_b}}\right\}$$



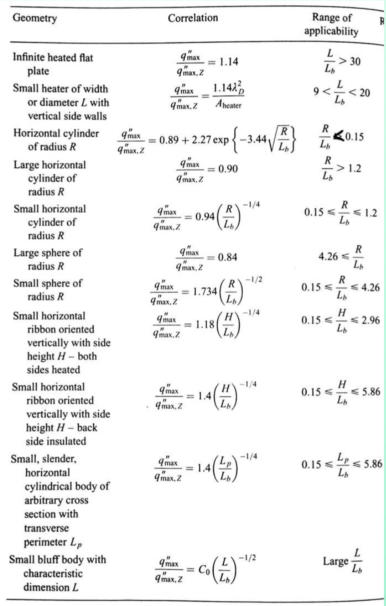
Correlations for Critical Heat Flux

$$\frac{q''_{max}}{q''_{max,z}} = f(L/L_b)$$

where $q''_{\text{max,z}} = 0.131 h_{lv}\rho_v \left[\frac{\sigma(\rho_l-\rho_v)g}{\rho_v^2}\right]^{1/4}$ and $L_b \sim \left[\frac{\sigma}{g(\rho_l-\rho_v)}\right]^{\frac{1}{2}}$
$= \frac{\lambda_D}{2\pi\sqrt{3}}$

- The ratio L/L_b indicates the size of the heater relative to the expected spacing of the vapor columns carrying vapor away from the surface near the critical condition.
- For heaters of finite size, variation of the value of this dimensionless group (*i.e.*, the Bond number) is expected to significantly alter the CHF condition particularly if its value is near or below one.

CHF for Different Geometries of Heater

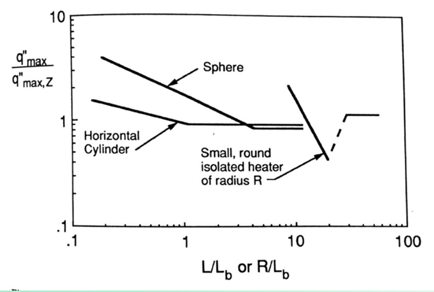


Geometry	Correlation	Range of applicability
Infinite heated flat plate	$\frac{q''_{\max}}{q''_{\max,Z}} = 1.14$	$\frac{L}{L_b} > 30$
Small heater of width or diameter L with vertical side walls	$\frac{q''_{\max}}{q''_{\max,Z}} = \frac{1.14\lambda_D^2}{A_{\text{heater}}}$	$9 < \frac{L}{L_b} < 20$
Horizontal cylinder of radius R	$\frac{q''_{\max}}{q''_{\max,Z}} = 0.89 + 2.27\exp\left\{-3.44\sqrt{\frac{R}{L_b}}\right\}$	$\frac{R}{L_b} \nless 0.15$
Large horizontal cylinder of radius R	$\frac{q''_{\max}}{q''_{\max,Z}} = 0.90$	$\frac{R}{L_b} > 1.2$
Small horizontal cylinder of radius R	$\frac{q''_{\max}}{q''_{\max,Z}} = 0.94\left(\frac{R}{L_b}\right)^{-1/4}$	$0.15 \leqslant \frac{R}{L_b} \leqslant 1.2$
Large sphere of radius R	$\frac{q''_{\max}}{q''_{\max,Z}} = 0.84$	$4.26 \leqslant \frac{R}{L_b}$
Small sphere of radius R	$\frac{q''_{\max}}{q''_{\max,Z}} = 1.734\left(\frac{R}{L_b}\right)^{-1/2}$	$0.15 \leqslant \frac{R}{L_b} \leqslant 4.26$
Small horizontal ribbon oriented vertically with side height H – both sides heated	$\frac{q''_{\max}}{q''_{\max,Z}} = 1.18\left(\frac{H}{L_b}\right)^{-1/4}$	$0.15 \leqslant \frac{H}{L_b} \leqslant 2.96$
Small horizontal ribbon oriented vertically with side height H – back side insulated	$\frac{q''_{\max}}{q''_{\max,Z}} = 1.4\left(\frac{H}{L_b}\right)^{-1/4}$	$0.15 \leqslant \frac{H}{L_b} \leqslant 5.86$
Small, slender, horizontal cylindrical body of arbitrary cross section with transverse perimeter L_p	$\frac{q''_{\max}}{q''_{\max,Z}} = 1.4\left(\frac{L_p}{L_b}\right)^{-1/4}$	$0.15 \leqslant \frac{L_p}{L_b} \leqslant 5.86$
Small bluff body with characteristic dimension L	$\frac{q''_{\max}}{q''_{\max,Z}} = C_0\left(\frac{L}{L_b}\right)^{-1/2}$	Large $\frac{L}{L_b}$

$$\frac{q''_{max}}{q''_{max,z}} = f(L/L_b)$$

$$q''_{\text{max,z}} = 0.131 h_{lv}\rho_v\left[\frac{\sigma(\rho_l-\rho_v)g}{\rho_v^2}\right]^{1/4}$$

$$L_b \sim \left[\frac{\sigma}{g(\rho_l-\rho_v)}\right]^{\frac{1}{2}}$$

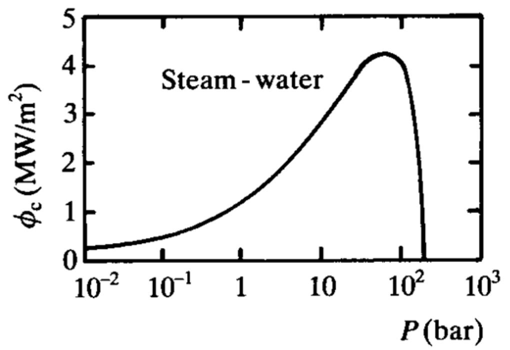


Variation of CHF with Pressure

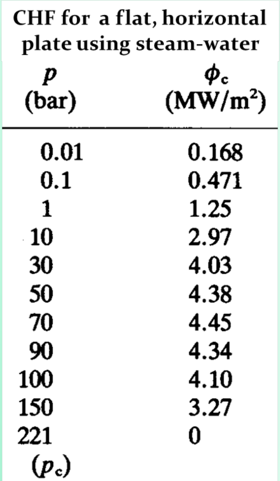
As the system pressure rises:

h_{lv} falls slowly at first & falls steeply at critical point;

ρ_v increases; σ and $(\rho_l - \rho_v)$ fall monotonically



For both pool & flow boiling, the max. CHF occurs at ∼70 bar.



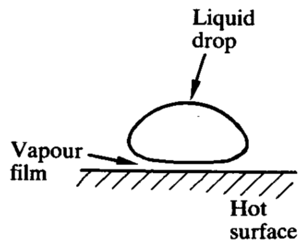
CHF for a flat, horizontal plate using steam-water

p (bar)	ϕ_c (MW/m^2)
0.01	0.168
0.1	0.471
1	1.25
10	2.97
30	4.03
50	4.38
70	4.45
90	4.34
100	4.10
150	3.27
221 (p_c)	0

Leidenfrost Temperature

Rewetting of hot surfaces: Liquid does not wet hot surface.

- Liquid is separated from the plate by a thin film of vapor so that the friction for sideways motion of the drop is very small and the heat transfer across the vapor film is poor.
- The vapor film, of course moves outwards, and fresh vapor is generated by evaporation at the underside of the drop due to heat conduction across the film and radiation from the plate to the drop.



Leidenfrost Temperature

- If the plate is allowed to cool down, it will eventually reach a temperature at which the vapor film collapses, and then very intense boiling takes place which rapidly leads to the evaporation of all the liquid.
- The surface temperature at which this sudden wetting of the plate occurs is the Leidenfrost Temperature.

$$q''_{\mathsf{min}} = C h_{lv} \rho_v \left[\frac{\sigma(\rho_l - \rho_v) g}{(\rho_l + \rho_v)^2} \right]^{1/4}$$

C is a non-dimensional constant which lies between 0.09 and 0.18.

$C = 0.09$ provides a better fit.

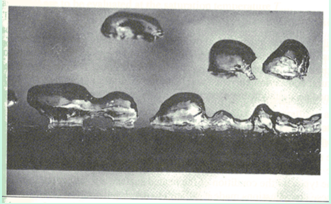
$C = 0.13$ is sometimes taken as an intermediate value

Prof. Dr. Johann G. Leidenfrost (1715-1794)

- Father - Minister
- Started off with Theological studies
- PhD thesis, ‘’On the Harmonious Relationship of Movements in the Human Body”
- Professor at University of Duisburg
- Areas of influences:
    - Theologian
    - Physician (Private Medical practice)
    - As a Prof. taught: Medicine, Physics, and Chemistry

70 publications

Film Boiling for Large Horizontal Surfaces



$$q''_{\text{film boiling}} = 0.425\ \Delta T_{sat} \left[\frac{\rho_v(\rho_l - \rho_v) g h'_{lv} k_v^3}{\mu_v \Delta T_{sat}} \sqrt{\frac{(\rho_l - \rho_v) g}{\sigma}} \right]^{1/4}$$

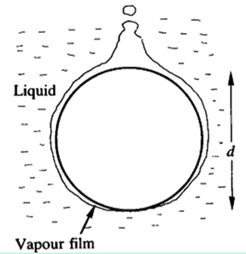
The effective latent heat of vaporization allows for the inclusion of sensible heating effects in the vapor film.

$$h'_{lv} = h_{lv} + 0.5 C_{p,v}(T_s - T_{sat})$$

Vapor properties are evaluated at the film temperature,

$$T_f = (T_s + T_{sat})/2.$$

Film Boiling



$$q''_{\text{film boiling}} = C_{\text{film}} \; \Delta T_{sat} \left[\frac{\rho_v(\rho_l - \rho_v) g h'_{lv} k_v^3}{\mu_v \Delta T_{sat}} \frac{1}{D} \right]^{1/4}$$

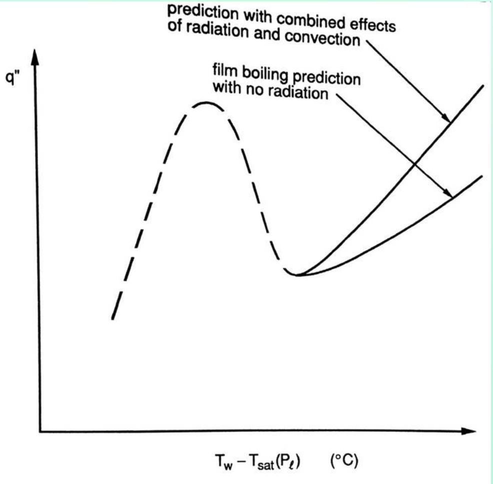
$C_{\text{film}} = 0.62$ for horizontal cylinders
$C_{\text{film}} = 0.67$ for spheres

$$h'_{lv} = h_{lv} + 0.4 C_{p,v}(T_s - T_{sat})$$

To be precise, properties at $T_f = (T_s + T_{sat})/2$

Radiation Effects in Film Boiling

$$h_{\text{total}} = h_{\text{film conv}} + \frac{3}{4} h_{\text{rad}} \qquad h_{\text{rad}} = \frac{\varepsilon_s \sigma (T_s^4 - T_{sat}^4)}{T_s - T_{sat}}$$



Saturated Water-Steam on Flat Heater

$T_w = 300°\text{C}$

Physical properties of water at 1 atm and 100°C:

$$
\begin{aligned}
T_{sat} &= 100°\text{C} \\
h_{lv} &= 2257 \text{ kJ/kg} \\
k_v &= 0.0251 \text{ W/m K} \\
\mu_v &= 12.3 \times 10^{-6} \text{ Pa s} \\
\rho_v &= 0.598 \text{ kg/m}^3 \\
\rho_l &= 958 \text{ kg/m}^3 \\
\sigma &= 0.0589 \text{ N/m} \\
C_{Pv} &= 2.029 \text{ kJ/kg K}
\end{aligned}
$$

$$q''_{\text{max}} = 0.149 h_{lv} \rho_v \left[\frac{\sigma(\rho_l - \rho_v)g}{\rho_v^2}\right]^{1/4}$$

$$q''_{\text{min}} = C h_{lv} \rho_v \left[\frac{g\sigma(\rho_l - \rho_v)}{(\rho_l + \rho_v)^2}\right]^{1/4}$$

$$q''_{\text{film}} = 0.425\ \Delta T_{sat} \left[\frac{\rho_v(\rho_l - \rho_v) g h'_{lv} k_v^3}{\mu_v \Delta T_{sat}} \sqrt{\frac{(\rho_l - \rho_v)g}{\sigma}}\right]^{1/4}$$

$$h'_{lv} = h_{lv} + 0.5 C_{p,v}(T_s - T_{sat})$$

Saturated Water-Steam on Flat Heater

$$\dot{q}''_{max} = 1.26 \text{ MW/m}^2$$

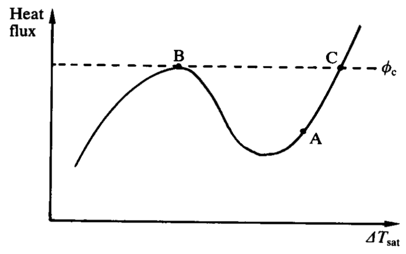
$$h_{max} = 17.5 \text{ kW/m}^2 \text{ K}$$

$$\dot{q}''_{min} = 19.03 \text{ kW/m}^2$$

$$h_{min} = 226 \text{ W/m}^2 \text{ K}$$

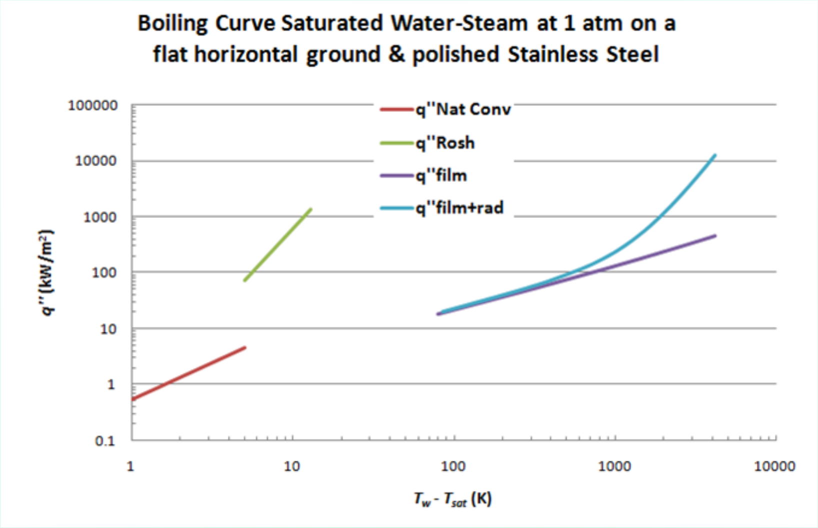
$$\dot{q}''_{film} = 39.39 \text{ kW/m}^2$$

$$h_{film} = 185 \text{ W/m}^2 \text{ K}$$

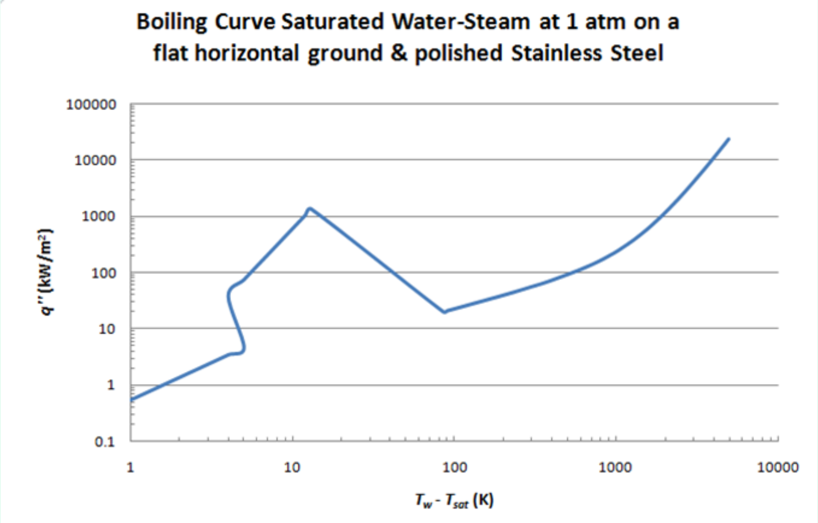


- So, although the plate is very hot, it is carrying only a fraction of the critical heat flux. So we are around point A on the boiling curve.
- The point C, which has the same heat flux as at point B, can be found.
- T_C is so high that radiative heat transfer is very important.

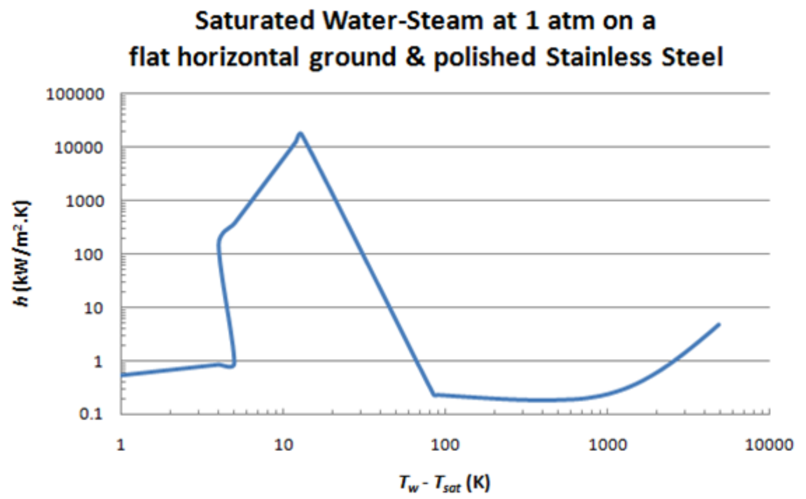
Saturated Water-Steam on Flat Heater



Saturated Water-Steam on Flat Heater



Saturated Water-Steam on Flat Heater



Effect of Liquid Subcooling

Natural convection portion will shift upward as driving $\Delta T_{sub} \uparrow$

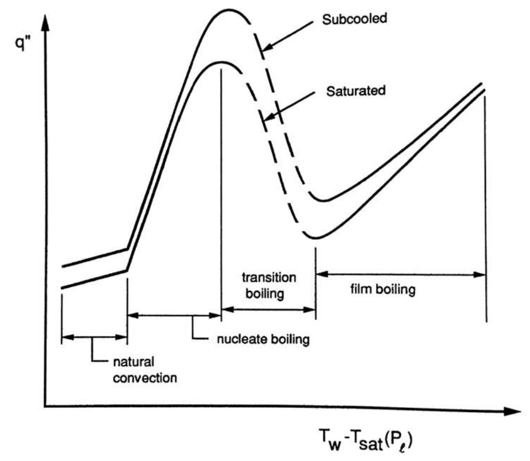
Nucleate boiling: slight influence as $\Delta T_{\text{sub}} \uparrow$

A change of $\sim$300% in ΔT_{sub} produces $\sim$20% in $\Delta q''$

Maximum heat flux: strong influence

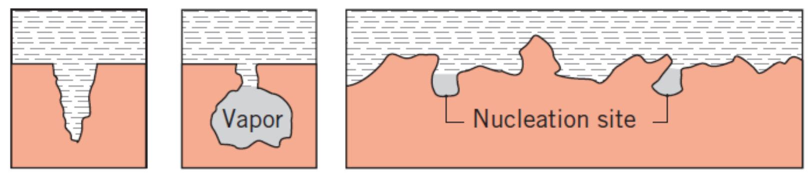
Vapor raises and condenses - easy pathway for liquid to flow towards the surface

Effect of Liquid Subcooling

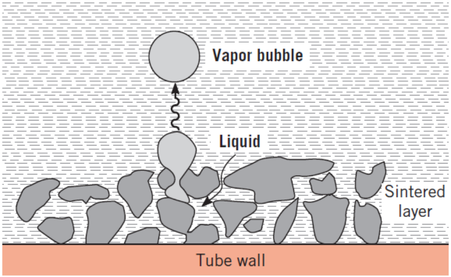


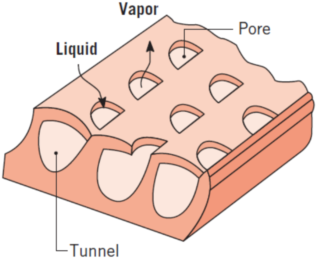
$$q''_{\text{max}} = 0.16 h_{lv} \rho_v \left[\frac{\sigma(\rho_l - \rho_v) g}{\rho_v^2} \right]^{1/4} \left[1 + .065 \left(\frac{\rho_l}{\rho_v} \right)^{0.75} \frac{C_{Pl} \Delta T_{sub}}{h_{lv}} \right]$$

Enhancement of Heat Transfer

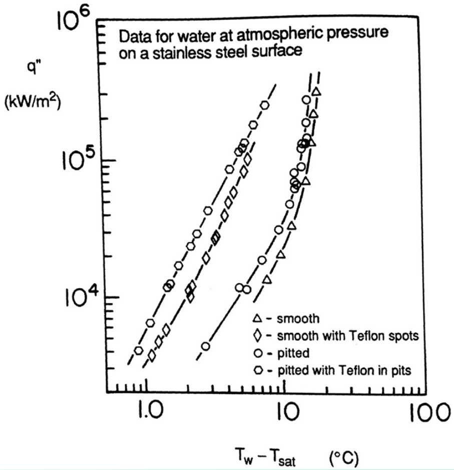


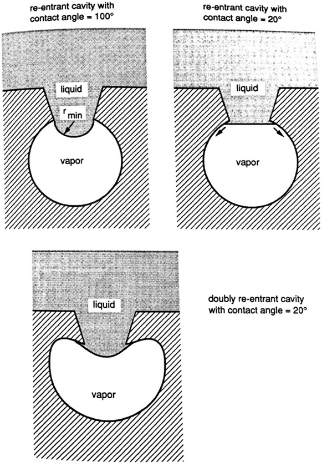
- Roughening or structuring or coating of the heating surface
- Production of artificial nucleation sites by sintering and
- Addition of gases or liquids or solids



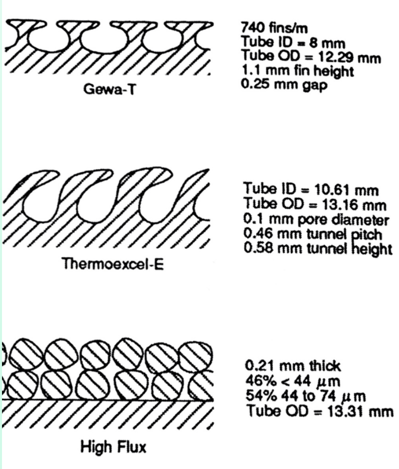


Enhancement of Heat Transfer





Enhancement of Heat Transfer

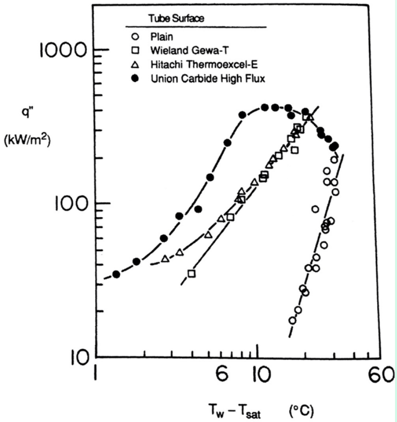


740 fins/m
Tube ID = 8 mm
Tube OD = 12.29 mm
1.1 mm fin height
0.25 mm gap

Tube ID = 10.61 mm
Tube OD = 13.16 mm
0.1 mm pore diameter
0.46 mm tunnel pitch
0.58 mm tunnel height

0.21 mm thick
46% < 44 μm
54% 44 to 74 μm
Tube OD = 13.31 mm

Pool boiling data for P-xylene at atmospheric pressure



Deviation from Classical Boiling Curve

The classical boiling curves are characteristic of heat surfaces that satisfy:

1. they must be at least partially wetted by the liquid in the surrounding pool and
2. the characteristic dimension of the heat L must be large compared with the capillary length scale $L_b = \sqrt{\sigma/(\rho_l - \rho_v)g}$

If the surface does not satisfy these conditions, the resulting boiling curve can be very different from the classical curves.

Influence of Contact Angle

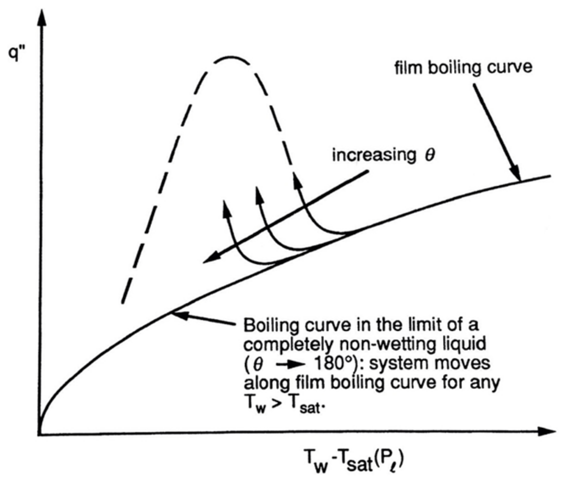
Boiling curve for a non-wetting liquid (Linear plot)

- $q''\uparrow$ monotonically with superheat
- Eventually merges with the "classical" film boiling curve

Hydrophobic:

- Water surface coated
- Mercury on Teflon

Influence of Contact Angle

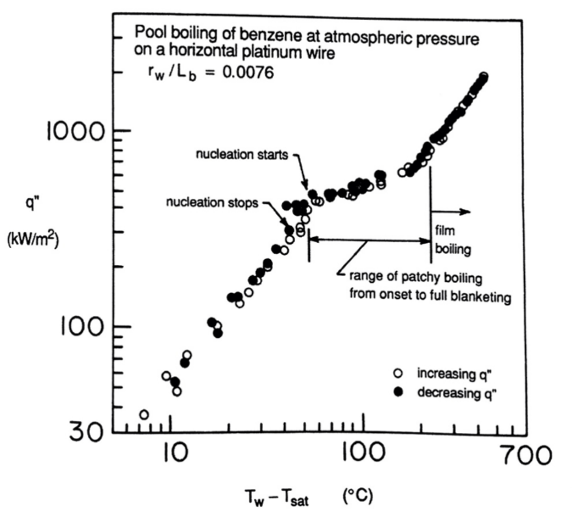


Influence of Smaller Heater

Length scale, $L_b \ll 50 D_b$ (Bubble departure diameter)

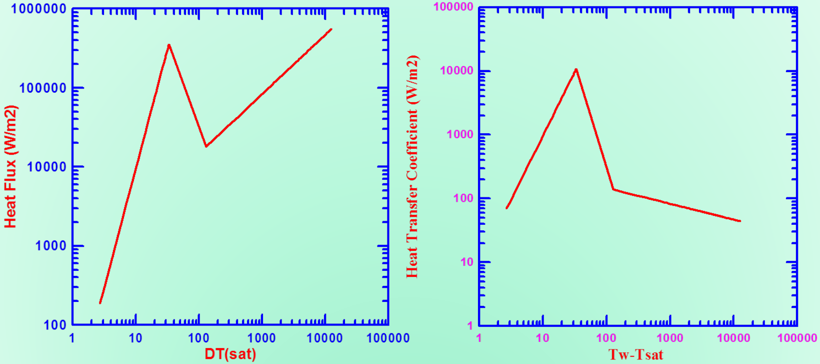
- Growing bubble completely covers the heater
- ONB initiates a film-type boiling
- No Nucleating regime
- No Transition regime
- No $\dot{q}''_{\text{max}}$

Influence of Smaller Heater



Pool Boiling curve of Benzene

Pool Boiling curve of Benzene at 1 bar & $T_{sat} = 80°\text{C}$



Problem

The bottom of a copper pan, 0.3 m in diameter, is maintained at 118°C by an electric heater. Estimate the power required to boil water in this pan. What is the evaporation rate? Estimate the critical heat flux.

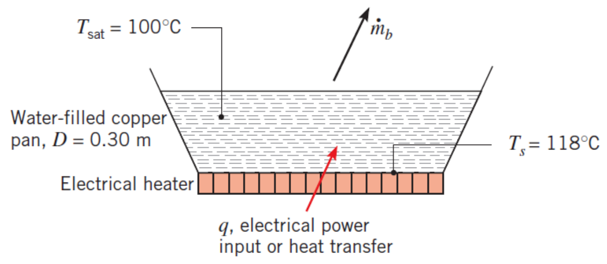
Saturated water, liquid at 100°C:
$\rho_l = 957.9$ kg/m^3, $C_{P,l} = C_{P,g} = 4.217$ kJ/kg K,
$\mu_l = 279 \times 10^{-6}$ N s/m^2, $\mathrm{Pr}_l = 1.76$,
$h_{lv} = 2257$ kJ/kg, $\sigma = 0.0589$ N/m,

Saturated water, vapor at 100°C:
$\rho_v = 0.5955$ kg/m^3

Solution

Saturated water, liquid at 100°C:
$\rho_l = 957.9$ kg/m$^3, C_{P,l} = C_{P,g} = 4.217$ kJ/kg K,
$\mu_l = 279 \times 10^{-6}$ N s/m^2, Pr$_l = 1.76$,
$h_{lv} = 2257$ kJ/kg$, \sigma = 0.0589$ N/m,

Saturated water, vapor at 100°C:
$\rho_v = 0.5955$ kg/m^3



Solution

Saturated water, liquid at $100°$C:
$\rho_l = 957.9$ kg/m^3, $C_{P,l} = C_{P,g} = 4.217$ kJ/kg K,
$\mu_l = 279 \times 10^{-6}$ N s/m^2, Pr$_l = 1.76$,
$h_{lv} = 2257$ kJ/kg, $\sigma = 0.0589$ N/m,

Saturated water, vapor at $100°$C:
$\rho_v = 0.5955$ kg/m^3

$$\frac{\dot{q}''}{\mu_l \; h_{lv}} \sqrt{\frac{\sigma}{g(\rho_l - \rho_v)}} = \left(\frac{1}{C_{sf}}\right)^{\frac{1}{m}} \left[\frac{C_{Pl} \Delta T_{sat}}{h_{lv}}\right]^{\frac{1}{m}} \mathrm{Pr}^{-\frac{1+n}{m}}$$

$$1/m = 3, 1+n = 1, C_{sf} = 0.0068$$

$$q_s'' = 5.589 \text{ MW}$$

$$\dot{m}_{\text{evap}} = \frac{q_s}{h_{lv}} = 630 \text{ kg/h}$$

Solution

Saturated water, liquid at $100°$C:
$\rho_l = 957.9$ kg/m^3, $C_{P,l} = C_{P,g} = 4.217$ kJ/kg K,
$\mu_l = 279 \times 10^{-6}$ N s/m^2, Pr$_l = 1.76$,
$h_{lv} = 2257$ kJ/kg, $\sigma = 0.0589$ N/m,

Saturated water, vapor at $100°$C:
$\rho_v = 0.5955$ kg/m^3

$$q''_{\text{max}} = 0.149 h_{lv} \rho_v \left[\frac{\sigma(\rho_l - \rho_v)g}{\rho_v^2} \right]^{1/4}$$

$$= 1.26 \text{ MW/m}^2$$

$$q''_{\text{min}} = 0.09 h_{lv} \rho_v \left[\frac{\sigma(\rho_l - \rho_v)g}{(\rho_l + \rho_v)^2} \right]^{1/4}$$

$$= 18.9 \text{ kW/m}^2$$

Solution

Saturated water, liquid at $100°\text{C}$:
$\rho_l = 957.9$ kg/m^3, $C_{P,l} = C_{P,g} = 4.217$ kJ/kg K,
$\mu_l = 279 \times 10^{-6}$ N s/m^2, Pr$_l = 1.76$,
$h_{lv} = 2257$ kJ/kg, $\sigma = 0.0589$ N/m,

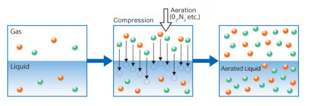
Saturated water, vapor at $100°\text{C}$:
$\rho_v = 0.5955$ kg/m^3

$$q''_{\text{max}} = 1.26 \text{ MW/m}^2 \quad \Delta T_{sat} = 10.96 \text{ K}$$

$$q''_{\text{min}} = 18.9 \text{ kW/m}^2 \quad \Delta T_{sat} = 82.72 \text{ K}$$

$$\boxed{q'' = 0.45 \text{ MW/m}^2 \quad \Delta T_{sat} = 0.45 \text{ K}}$$

Multiphase Flow and Heat Transfer



Degasification

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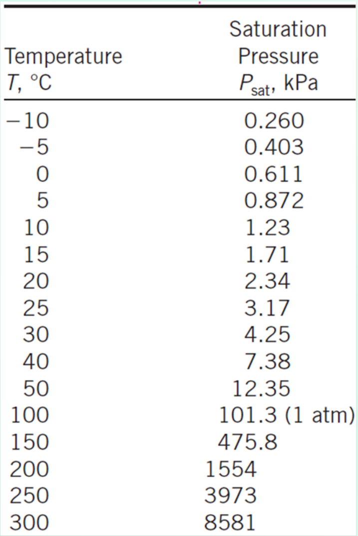
Vapor Pressure

- At a given pressure, the temperature at which a pure substance changes phase is T_{sat}.
- At a given temperature, the pressure at which a pure substance changes phase is P_{sat}.
- Vapor Pressure (P_v) of a pure substance is defined as the pressure exerted by its vapor in phase equilibrium with its liquid at a given temperature.
- For a pure substance, P_v is a Property and $P_v = P_{sat}$.



Temperature T, °C	Saturation Pressure P_{sat}, kPa
−10	0.260
−5	0.403
0	0.611
5	0.872
10	1.23
15	1.71
20	2.34
25	3.17
30	4.25
40	7.38
50	12.35
100	101.3 (1 atm)
150	475.8
200	1554
250	3973
300	8581

Saturation/vapor pressure of water

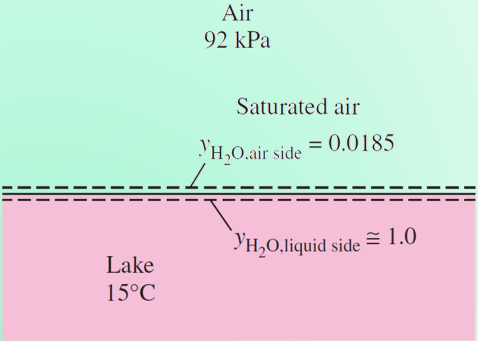
Problem

Determine the mole fraction of the water vapor at the surface of a lake whose temperature is 15°C. The atmospheric pressure at lake level is 92 kPa.

At phase equilibrium: $P_v = P_{\text{sat@15°C}} = 1.7057$ kPa

Mole fraction of water vapor in air:

$$x_v = \frac{n_i}{n} = \frac{n_i RT/V}{nRT/V} = \frac{P_v}{P} = \frac{1.7057}{92} = 0.0185$$



Henry’s Law

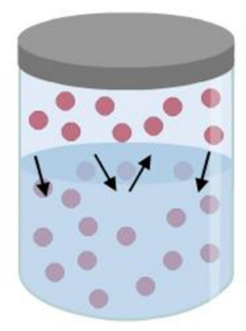
Statement

The amount of a gas that dissolves in a liquid is directly proportional to the partial pressure of that gas (Pi, g) in equilibrium with that liquid.

Mole fraction of species, i on liquid side,

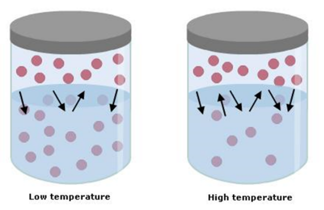
$$x_{i,l} = \frac{P_{i,g}}{H}$$

Henry’s constant in pressure units (Pa)

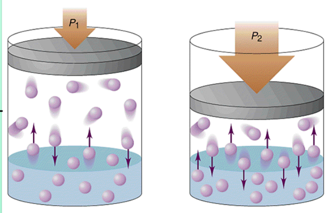


Henry’s Law

1. The concentration of a gas dissolved is $\propto H^{-1}$
2. $H \uparrow$ with $T \uparrow$
3. $x_{i,l} \uparrow$ with $P_i \uparrow$

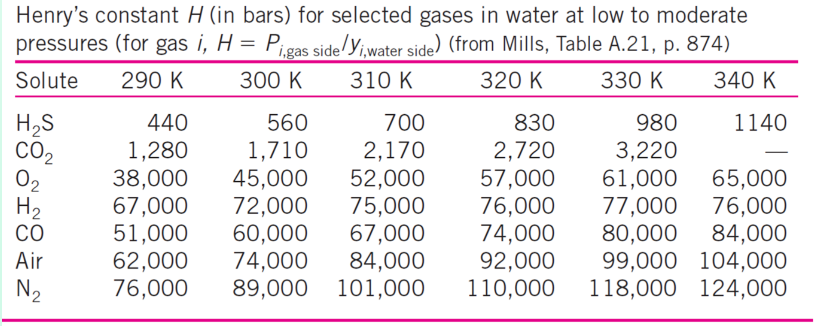


$$x_{i,l} = \frac{P_{i,g}}{H}$$



Henry's Law

$$x_{i,l} = \frac{P_{i,g}}{H}$$



Henry's constant *H* (in bars) for selected gases in water at low to moderate pressures (for gas *i*, $H = P_{i,\text{gas side}}/y_{i,\text{water side}}$) (from Mills, Table A.21, p. 874)

Solute	290 K	300 K	310 K	320 K	330 K	340 K
H_2S	440	560	700	830	980	1140
CO_2	1,280	1,710	2,170	2,720	3,220	—
O_2	38,000	45,000	52,000	57,000	61,000	65,000
H_2	67,000	72,000	75,000	76,000	77,000	76,000
CO	51,000	60,000	67,000	74,000	80,000	84,000
Air	62,000	74,000	84,000	92,000	99,000	104,000
N_2	76,000	89,000	101,000	110,000	118,000	124,000

Problem

Determine the concentration of dissolved air in water at ambient conditions. $H_{\mathsf{N_2}} = 9.2 \times 10^9$ Pa, $H_{\mathsf{O_2}} = 4.3 \times 10^9$ Pa

At phase equilibrium: $P_v = P_{\text{sat@30°C}} = 4.25$ kPa

$$\begin{aligned} P_{\text{total}} &= P_v + P_{\text{dry-air}} \\ P_{\text{dry-air}} &= 101.42 + 4.25 = 97.17 \text{ kPa} \\ P_{\text{dry-air}} &= P_{\mathsf{N_2}} + P_{\mathsf{O_2}} \\ P_{\mathsf{N_2}} &= 79\% P_{\text{dry-air}} = 76.7643 \text{ kPa} \end{aligned}$$

Mole fraction of $\mathsf{N}_{2,l}$, $x_{\mathsf{N}_{2,l}} = \frac{P_{\mathsf{N_2}}}{H} = \frac{76.7643 \times 10^3}{9.2 \times 10^9} = 8.34 \times 10^{-6}$

Mass fraction of $\mathsf{N}_{2,l}$, $y_{\mathsf{N}_{2,l}} = x_{\mathsf{N}_{2,l}} \times \frac{M_{\mathsf{N_2}}}{M_{\mathsf{H_2O}}}$

$$= 8.34 \times 10^{-6} \times \frac{28}{18} = 13 \times 10^{-6}$$

Solubility of $\mathsf{N_2}$ in water, $\mathsf{S}_{\mathsf{N_2}} = 13 \times 10^{-3}$ g/kg

i.e., 13 ppm of dissolved $\mathsf{N_2}$ in water.

Problem

Determine the concentration of dissolved air in water at ambient conditions. $H_{\mathsf{N_2}} = 9.2 \times 10^9$ Pa, $H_{\mathsf{O_2}} = 4.3 \times 10^9$ Pa

At phase equilibrium: $P_v = P_{\text{sat@30°C}} = 4.25$ kPa

$$\begin{aligned} P_{\text{total}} &= P_v + P_{\text{dry-air}} \\ P_{\text{dry-air}} &= 101.42 + 4.25 = 97.17 \text{ kPa} \\ P_{\text{dry-air}} &= P_{\mathsf{N_2}} + P_{\mathsf{O_2}} \\ P_{\mathsf{O_2}} &= 21\% P_{\text{dry-air}} = 20.4057 \text{ kPa} \end{aligned}$$

Mole fraction of $\mathsf{O}_{2,l}, x_{\mathsf{O}_{2,l}} = \frac{P_{\mathsf{O_2}}}{H} = \frac{20.4057 \times 10^3}{4.3 \times 10^9} = 4.75 \times 10^{-6}$

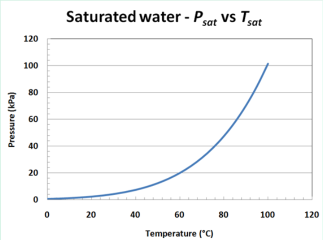
Mass fraction of $\mathsf{O}_{2,l}, y_{\mathsf{O}_{2,l}} = x_{\mathsf{O}_{2,l}} \times \frac{M_{\mathsf{O_2}}}{M_{\mathsf{H_2}O}} = 8.5 \times 10^{-6}$

Solubility of O_2 in water, $S_{O_2} = 8.5 \times 10^{-3}$ g/kg

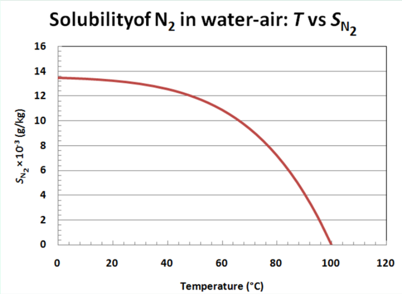
i.e., 8.5 ppm of dissolved O_2 in water.

Solubility with Temperature

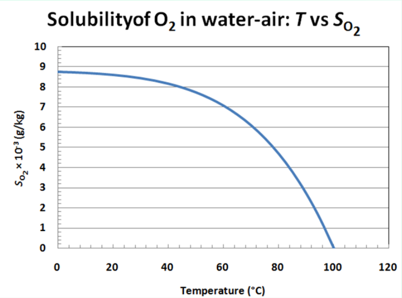
T (°C)	P_{sat} (kPa)	S_{N_2} (g/kg)	S_{O_2} (g/kg)
30	4.247	13×10^{-3}	8.4×10^{-3}
50	12.325	12×10^{-3}	7.7×10^{-3}
70	31.202	9.4×10^{-3}	6.1×10^{-3}
80	47.416	7.2×10^{-3}	4.7×10^{-3}
90	70.183	4.2×10^{-3}	2.7×10^{-3}
100	101.42	0	0



Solubility of air at Water-Air Interface



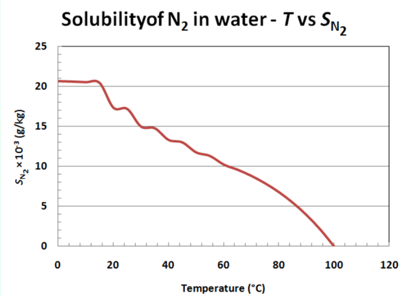
Solubilityof N_2 in water-air: T vs S_{N_2}

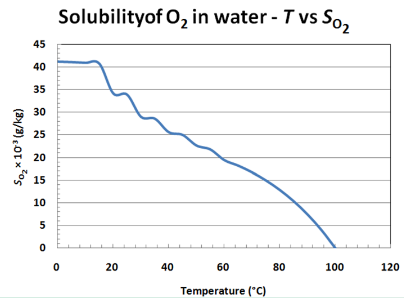


Solubilityof O_2 in water-air: T vs S_{O_2}

Henry's constant is considered not to vary with temperature

Solubility of air at Water-Air Interface


Solubilityof N_2 in water - T vs S_{N_2}


Solubilityof O_2 in water - T vs S_{O_2}

Henry's constant is considered to vary with temperature

Degassing Techniques

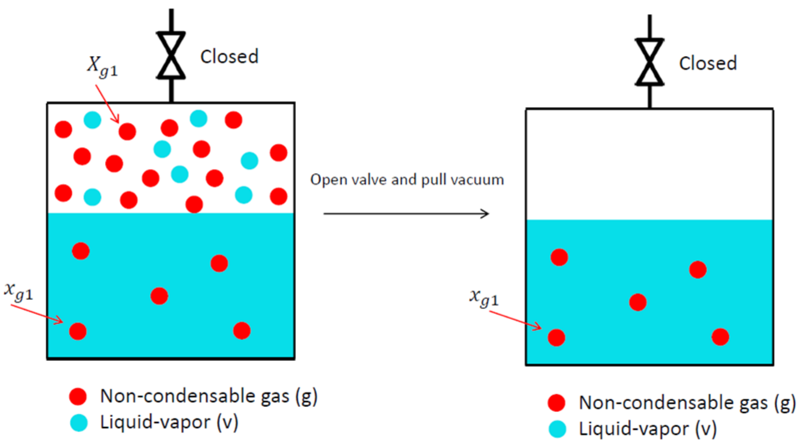
1. By boiling or superheating
2. Vacuum degasification
3. Freeze-pump-thaw cycling
4. Membrane degasification

Degassing Techniques

1. **By boiling or superheating**
   - Low purity limits
   - Significant fluid is lost while pulling vacuum

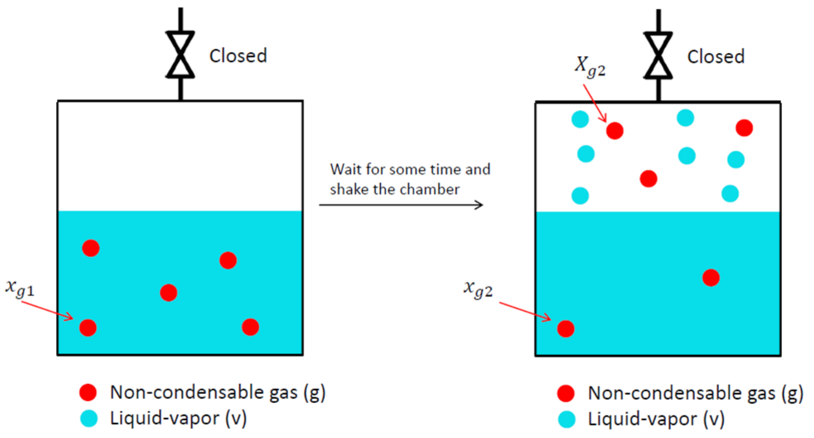
Degassing Techniques

2. **Vacuum degasification** (Assuming only v & g are evacuated)

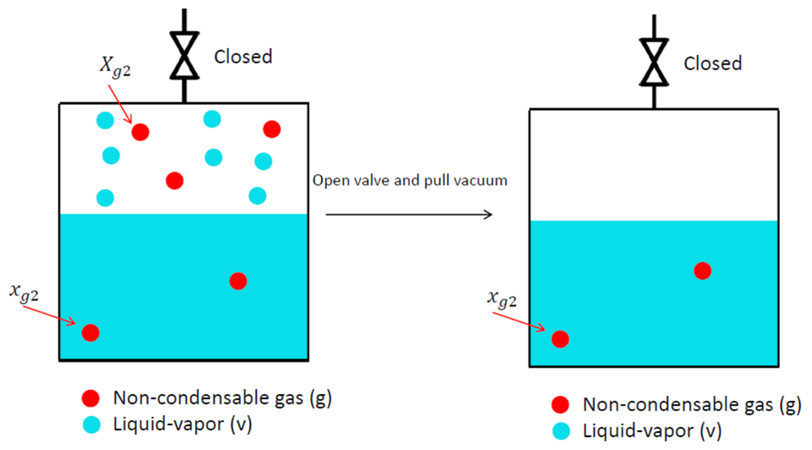


Degassing Techniques

2. Vacuum degasification

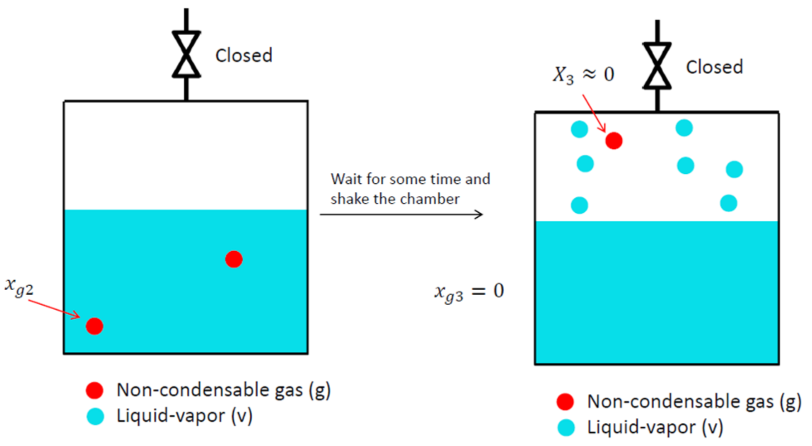


2. Vacuum degasification



Degassing Techniques

2. Vacuum degasification

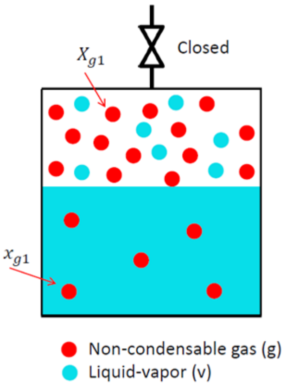


Problem

Imagine an insulated chamber with negligible thermal mass where the volume of the vapor and nitrogen space is equal to the volume of the liquid space (1 liter). Start with 70°C, and 101.325 kPa total pressure. Compute the number of moles of N_2 dissolved in the chamber after 3 cycles of vacuum degasification.

$H_{N_2} = 9.2 \times 10^9$ Pa, $P_{sat@70^\circ C} = 31.176$ kPa.

Hint: Calculate the number of moles of N_2 and water on gas side and also on liquid side for each cycle. Assume that no other gas exists other than N_2 and H_2O.



On Gas/vapor Side

At phase equilibrium:

$P_v = P_{\text{sat@70°C}} = 31.176$ kPa

$P_{\text{total}} = P_v + P_{\text{N}_2}$

$P_{\text{N}_2} = 101.325 - 31.176 = 70.146$ kPa

By definition P_{N_2} is the pressure exerted if the whole volume is filled with N_2. Here the volume is 1 liter = 0.001 m^3.

$$n_{\text{N}_2,v} = \frac{P_{\text{N}_2}V}{RT} = \frac{70149 \times 0.001}{8.314 \times 343.14} = 0.0246 \text{ moles}$$

Similarly for water in vapor state:

$$n_{\text{H}_2\text{O},v} = \frac{P_{\text{H}_2\text{O}}V}{RT} = \frac{31176 \times 0.001}{8.314 \times 343.14} = 0.0109 \text{ moles}$$

On Liquid Side

Number of moles of H_2O in 1 liter of volume:

$$n_{\mathsf{H_2O},l} = \frac{V_{\mathsf{H_2O},l}}{\mathsf{M}_{\mathsf{H_2O},l}} = \frac{1 \text{ kg}}{18 \ \frac{\text{g}}{\text{mol}}} = 55.55 \text{ moles}$$

From Henry's law, mole fraction of N_2 in liquid water:

$$x_{\mathsf{N_2},l} = \frac{P_{\mathsf{N_2}}}{H_{\mathsf{N_2}}} = \frac{70149}{9.2 \times 10^9} = 7.62 \times 10^{-6}$$

By the definition of mole fraction:

$$x_{\mathsf{N_2},l} = \frac{n_{\mathsf{N_2},l}}{n_{\mathsf{H_2O},l} + n_{\mathsf{N_2},l}}$$

$$\implies n_{\mathsf{N_2},l} = n_{\mathsf{H_2O},l} \times x_{\mathsf{N_2},l} = 0.424 \times 10^{-3} \text{ moles}$$

We started with a Chamber Containing

$n_{\mathsf{H_2O},l} = 55.55$ moles $\qquad n_{\mathsf{N_2},l} = 0.424 \times 10^{-3}$ moles

$n_{\mathsf{H_2O},v} = 0.0109$ moles $\qquad n_{\mathsf{N_2},,v} = 0.0246$ moles

During the first cycle of vacuum degasification, we removed all the vapor, *i.e.*, 0.0109 moles of H_2O and 0.0246 moles of N_2 from the chamber.

Number of molecules left in the chamber are:

55.55 moles of H_2O and 0.424×10^{-3} moles of N_2

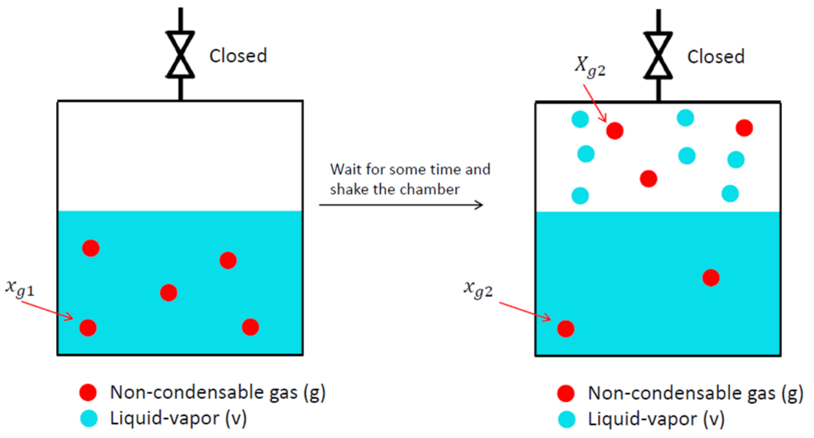
The chamber is now allowed to settle:

Phase equilibrium: Part of H_2O (l) evaporates

Dissolved N_2 in H_2O (l) comes-out following Henry's law.

After First Cycle

The molecules in the liquid have to be distributed in liquid and gas.



After First Cycle

At phase equilibrium: $P_v = P_{\text{sat@70°C}} = 31.176$ kPa

55.55 moles of H_2O has be distributed as $n_{H_2O,l}$ and $n_{H_2O,v}$

$\because n_{H_2O,l} \gg n_{H_2O,v}$, change in volume of H_2O (l) is negligible,
i.e., $V_{H_2O,v} = 1$ liter $= 1$ kg $= 0.001$ m^3.

$\implies n_{H_2O,l} = 55.55$ moles

Similar to previous calculations, $n_{H_2O,v} = 0.0109$ moles

In a strict sense, they should be computed iteratively.

P_{N_2} and P_{total} are not known as this stage.

After First Cycle

$$x_{\mathsf{N_2},l} = \frac{P_{\mathsf{N_2}}}{H_{\mathsf{N_2}}} = \frac{n_{\mathsf{N_2},v} RT}{V} \frac{1}{H_{\mathsf{N_2}}}$$

Also, $x_{\mathsf{N_2},l} = \dfrac{n_{\mathsf{N_2},l}}{n_{\mathsf{H_2O},l} + \cancelto{0}{n_{\mathsf{N_2},l}}}$

$$\Longrightarrow \boxed{n_{\mathsf{N_2},l} = \frac{n_{\mathsf{H_2O},l} RT}{H_{\mathsf{N_2}} V} \; n_{\mathsf{N_2},v}}$$

0.424×10^{-3} moles of N_2 is distributed as $n_{\mathsf{N_2},l}$ and $n_{\mathsf{N_2},v}$

$$\boxed{n_{\mathsf{N_2},l} + n_{\mathsf{N_2},v} = 0.424 \times 10^{-3}}$$

End of First Cycle

$$n_{\mathsf{H_2O},l} = 55.55 \text{ moles} \qquad n_{\mathsf{N_2},l} = 7.18 \times 10^{-6} \text{ moles}$$

$$n_{\mathsf{H_2O},v} = 0.0109 \text{ moles} \qquad n_{\mathsf{N_2},,v} = 0.0004168 \text{ moles}$$

We started with

$$n_{\mathsf{N_2},l} = 0.424 \times 10^{-3} \text{ moles}$$

$$n_{\mathsf{N_2},,v} = 0.0246 \text{ moles}$$

In one cycle of vacuum degasification, we observe reduction by 59 times of dissolved N_2 in liquid H_2O.

End of Second Cycle

$$n_{\mathsf{H_2O},l} = 55.55 \text{ moles}$$
$$n_{\mathsf{H_2O},v} = 0.0109 \text{ moles}$$

$$n_{\mathsf{N_2},l} = ??? \text{ moles}$$
$$n_{\mathsf{N_2},,v} = ??? \text{ moles}$$

We started with

$$n_{\mathsf{N_2},l} = 0.424 \times 10^{-3} \text{ moles}$$
$$n_{\mathsf{N_2},,v} = 0.0246 \text{ moles}$$

In two cycles of vacuum degasification, we observe reduction by ??? times of dissolved N_2 in liquid H_2O.

End of Third Cycle

$$n_{\mathsf{H_2O},l} = 55.55 \text{ moles} \qquad n_{\mathsf{N_2},l} = ??? \text{ moles}$$

$$n_{\mathsf{H_2O},v} = 0.0109 \text{ moles} \qquad n_{\mathsf{N_2},,v} = ??? \text{ moles}$$

We started with

$$n_{\mathsf{N_2},l} = 0.424 \times 10^{-3} \text{ moles}$$

$$n_{\mathsf{N_2},,v} = 0.0246 \text{ moles}$$

In three cycles of vacuum degasification, we observe reduction by ??? times of dissolved N_2 in liquid H_2O.

Degassing Techniques

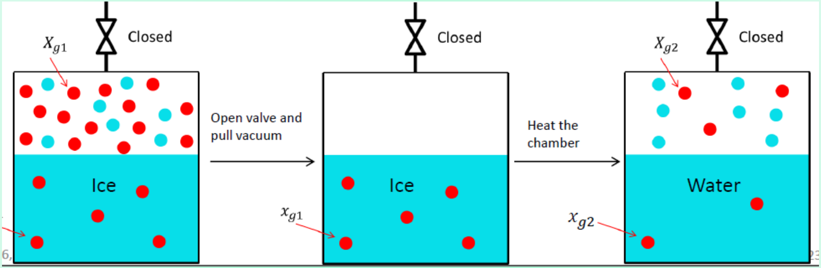
2. Vacuum degasification

- Some liquid is lost while pulling vacuum
- The chamber temperature needs to be controlled
- Needs 3 cycles to get high purity limits

Degassing Techniques

3. Freeze-pump-thaw cycling

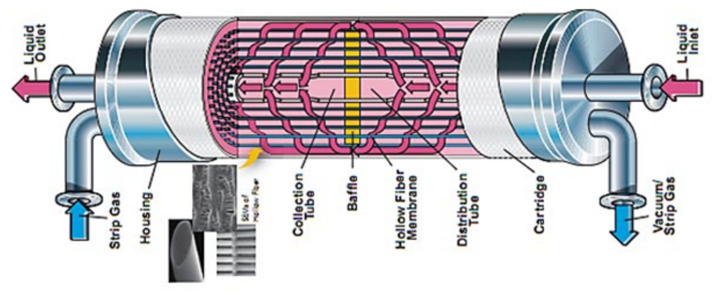
- Very small amount of fluid is lost
- Needs 3 cycles to get high purity limits
- Less hazardous



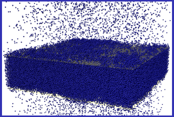
Degassing Techniques

4. Membrane degasification

Pull vacuum through a membrane such as Gore-Tex



Multiphase Flow and Heat Transfer



Liquid-Vapor Interface

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Liquid-Vapor Interface

In Macroscopic view, the boundary between the bulk phases

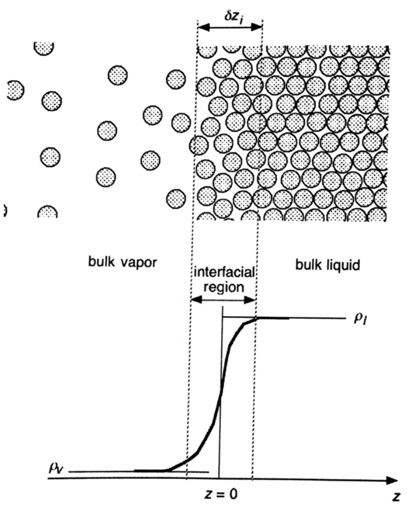
- Idealized as a surface
- Discontinuity in properties
- Net conversion of one phase into the other - Phase change

In Nanoscale view, the boundary between the bulk phases

- Actually a region
- A transition of mean molecular density exists
- This transition affects the thermo-physics and transport in this region

Easy for analysis as a surface, but Nanoscale perspective gives better understanding.

Liquid-Vapor Interface



Variation of the molecular density

Interacting Forces between Two Molecules

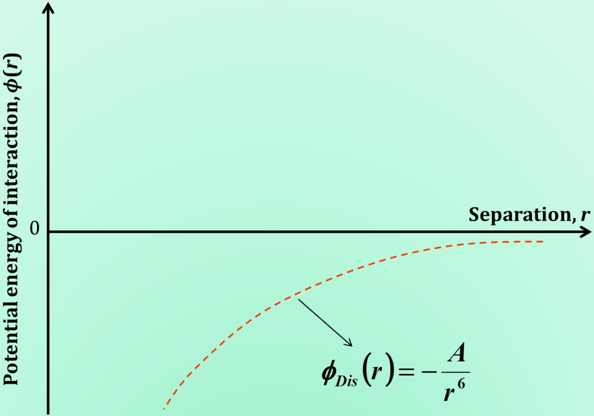
At longer range, two molecules exert attractive force.

- Dipole-dipole forces or Electrostatic forces
    - Opposite sides of the molecule have opposite charges
- Dipole-induced forces
    - Permanently charged particle induces a dipole in a nearby neutral molecule
    - Strength depends on easy of polarization
- London interactions or Dispersion forces
    - Stronger interactions allow solid and liquid states to persist to higher temperatures.
    - Non-polar molecules show similar behavior, indicating that there are some types of intermolecular interactions that cannot be attributed to simple electrostatic attractions.

$$\phi_{Dis}(r) = -\frac{A_{Dis}}{r^6}$$

Interacting Forces between Two Molecules

The potential function (ϕ) is the energy that must be input to bring two molecules from infinite distance apart to center-to-center spacing



r.

A is a constant varies with the type of molecule, polarizability of the molecules.

Interacting Forces between Two Molecules

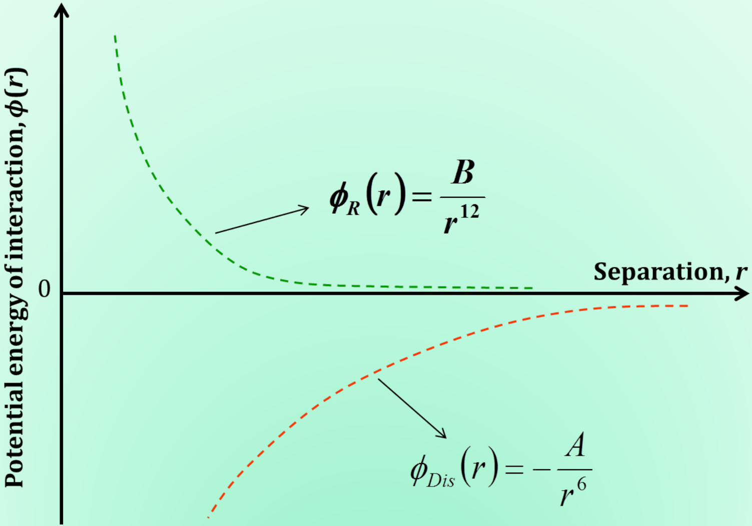
At very short range, two molecules exert a repulsive force

- Interference of the electron orbits of one molecule with those of the other.
- The energy required to bring two molecules from infinite distance apart to center-to-center spacing, r

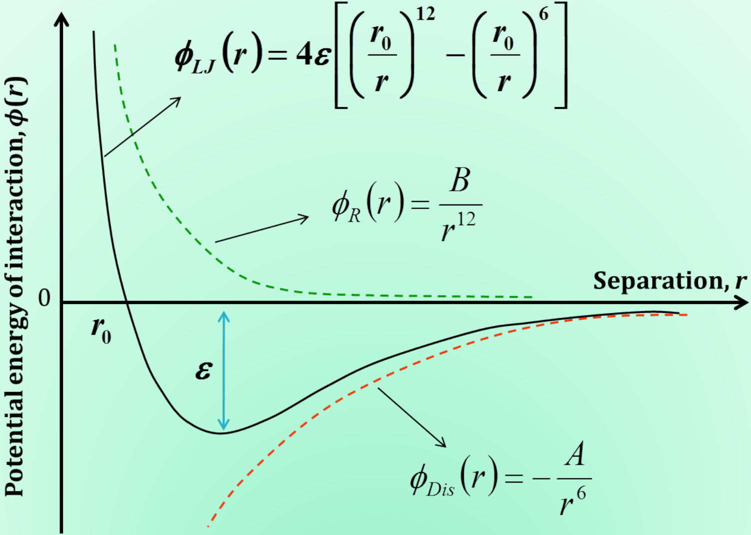
$$\phi_R(r) = \frac{B}{r^k}, 9 \leq k \leq 15$$

where B is a constant depending on the type of molecule.

Interacting Forces between Two Molecules



Lennard-Jones 6-12 Potential

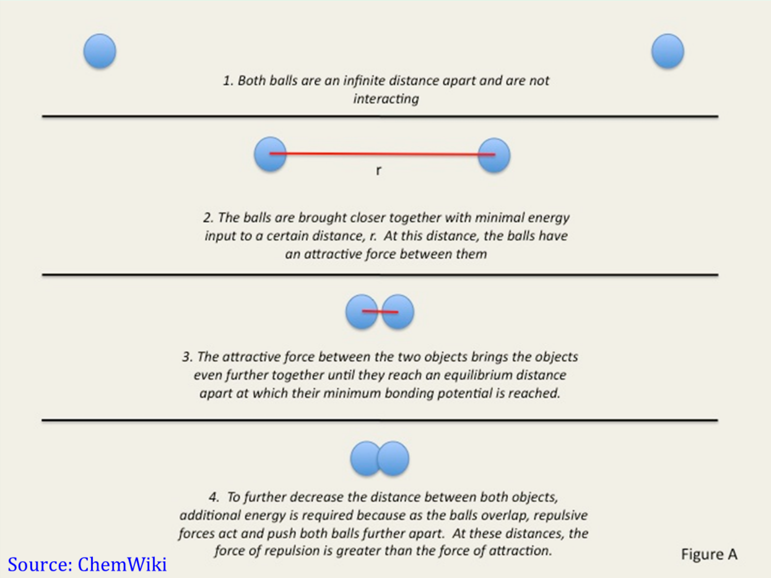


$$\phi_{LJ}(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right]$$

$$\phi_R(r) = \frac{B}{r^{12}}$$

$$\phi_{Dis}(r) = -\frac{A}{r^6}$$

Liquid-Vapor Interfacial Region (Nanoscale)



1. Both balls are an infinite distance apart and are not interacting

2. The balls are brought closer together with minimal energy input to a certain distance, r. At this distance, the balls have an attractive force between them

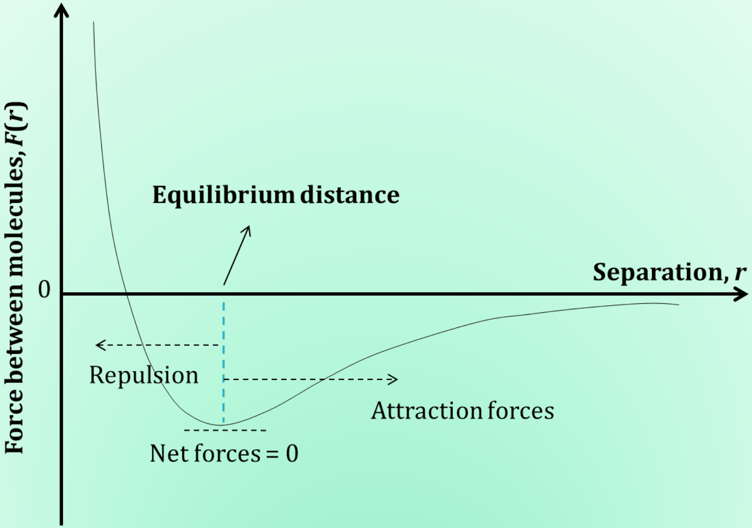
3. The attractive force between the two objects brings the objects even further together until they reach an equilibrium distance apart at which their minimum bonding potential is reached.

4. To further decrease the distance between both objects, additional energy is required because as the balls overlap, repulsive forces act and push both balls further apart. At these distances, the force of repulsion is greater than the force of attraction.

Figure A

Source: ChemWiki

Interacting Forces between Two Molecules



Lennard-Jones 6-12 Potential

$$\phi_{LJ}(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right]$$

- To bring two molecules that are initially very far apart into closer proximity, we must remove energy - **Condensation**
- If two molecules are close enough to feel attractive forces, but not so close that repulsive forces come into play, then energy must be supplied to increase the spacing of the molecules - **Vaporization**

Lennard-Jones 6-12 Potential

$$\phi_{LJ}(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right]$$

ε is the depth of potential well (J):

$$\phi_{LJ} = -\varepsilon\big|_{r=2^{1/6}r_0}$$

- Energy that must be input for one molecule to escape the attractive pull of another.
- In a two-phase system, escape of molecules from a liquid phase into a vapor phase at the interface is more probable if the translational kinetic energy is larger than ε.

r_0 is the distance at which potential energy is zero (nm).

Maxwell-Boltzmann Distribution

The number of molecules with seed in the interval c to $c + dc$:

$$dN_c = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} c^2 e^{\frac{-mc^2}{2k_B T}} dc$$

N is the number of molecules
c is the speed of the molecule, m/s
m is the mass of the molecule, kg
k_B is the Boltzmann constant, 1.38×10^{-23} $\text{m}^2\text{kg/s}^2$ K
T is the absolute temperature, K

Maxwell-Boltzmann Distribution

We are interested in knowing the number of molecules that would have kinetic energy more that the minimum potential (depth of the potential well).

Convert speed distribution to kinetic energy of a molecule:

$$K = \frac{1}{2} m c^2$$

$$c = \sqrt{\frac{2K}{m}} \qquad dc = \frac{1}{\sqrt{2mK}} dK$$

$$dN_K = 2\pi N \left(\frac{1}{\pi k_B T} \right)^{\frac{3}{2}} K^{\frac{1}{2}} e^{\frac{-K}{k_B T}} dK$$

Maxwell-Boltzmann Distribution

The number of molecules in the gas with energies above ε:

$$N_{>\varepsilon} = \int_{\varepsilon}^{\infty} dN_K$$

The fraction of molecules with energies above ε is:

$$\boxed{\frac{N_{>\varepsilon}}{N} = \left(\frac{4\varepsilon}{\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{\varepsilon}{k_B T}} + \text{erfc}\left(\sqrt{\frac{\varepsilon}{k_B T}}\right)}$$

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

Error function term can be neglected if $\varepsilon \gg k_B T$.

Equilibrium Vapor Pressure

- Molecules having energies above the threshold value (ε) increase rapidly with temperature.
- This determines chemical reaction rates and the equilibrium conditions in two-phase systems.
- Even at low temperatures some fraction of the molecules in the liquid will have sufficient energy to escape the cohesive forces of other liquid molecules at the liquid-vapor interface.
- The fraction capable of escaping in this manner will increase rapidly with temperature.

Vapor Pressure & Latent Heat of Vaporization

- A liquid with a small cohesive energy will have a higher vapor pressure than one with a large cohesive energy.
- In general, cohesive energy $\propto \varepsilon$ (Lennard-Jones potential).
- $H_{lv} \cong$ cohesive energy of the liquid
- At same temperature, a liquid with a high H_{lv} should have a lower vapor pressure than a liquid with a smaller H_{lv}.

- At 20°C, Water:

$$P_{\text{sat}} = 2.34 \text{ kPa and } H_{lv} = 2454 \text{ kJ/kg}$$

- At 20°C, Saturated refrigerant-134a:

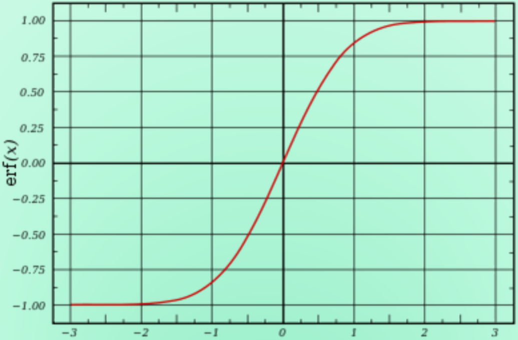
$$P_{\text{sat}} = 572.1 \text{ kPa and } H_{lv} = 182.3 \text{ kJ/kg}$$

Problem

For saturated nitrogen at 77 K, estimate the fraction of the molecules that have translational kinetic energies larger than, $\varepsilon = 1.31 \times 10^{-21}$ J.

$$\frac{N_{>\varepsilon}}{N} = \left(\frac{4\varepsilon}{\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{\varepsilon}{k_B T}} + \text{erfc}\left(\sqrt{\frac{\varepsilon}{k_B T}}\right)$$

$$k_B = 1.38 \times 10^{-23} \text{ m}^2\text{kg/s}^2 \text{ K}$$



Problem

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$$\frac{N_{>\varepsilon}}{N} = \left(\frac{4\varepsilon}{\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{\varepsilon}{k_B T}} + \mathsf{erfc}\left(\sqrt{\frac{\varepsilon}{k_B T}}\right)$$

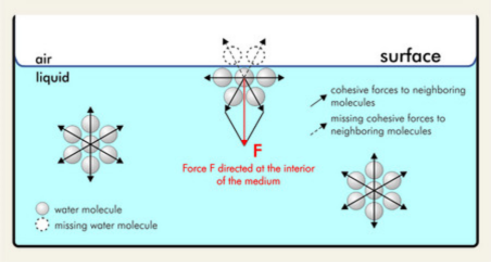
$$\frac{\varepsilon}{k_B T} = 1.23$$

$$\boxed{\frac{N_{>\varepsilon}}{N} = \left(\frac{4 \times 1.23}{\pi}\right)^{\frac{1}{2}} e^{-1.23} + \mathsf{erfc}\left(\sqrt{1.23}\right) = 0.483}$$

Thus, the Boltzmann distribution predicts that almost half the molecules have translation energy values greater than $\varepsilon = 1.31 \times 10^{-21}$ J.

Surface Tension

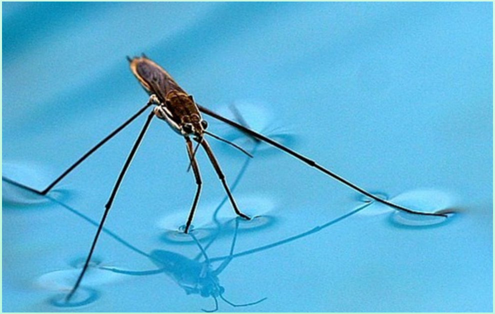
The net attractive force causes the liquid surface to contract inwards until repulsion from other surrounding molecules start dominating.



- If there are no external forces, spherical interface is formed.
- Intermolecular attraction - Interfacial Tension.

Surface Tension

Practically, the phenomenon is comparable to a thin layer surrounding the liquid and making it hard to dip an object in and to pull it out of the liquid.



Water strider

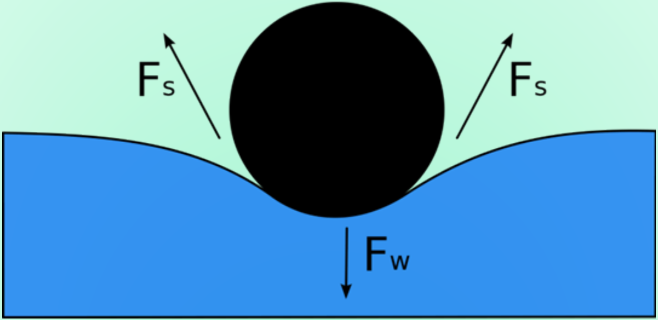
Surface Tension

Practically, the phenomenon is comparable to a thin layer surrounding the liquid and making it hard to dip an object in and to pull it out of the liquid.

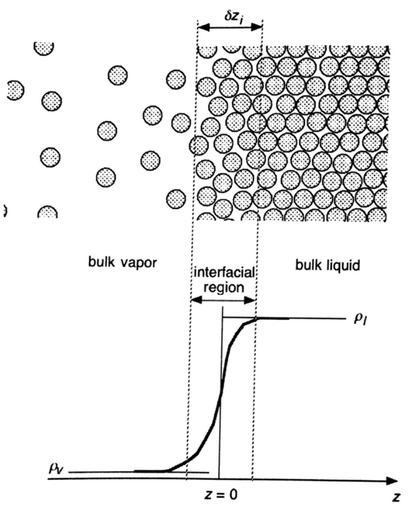
Green Basilisk Lizard - The Jesus Christ Lizard

Surface Tension

- Against force (F) work has to be performed to move something through this layer or to expand its surface.
- Hence, σ is the amount of force (Nm) necessary to expand the surface (m^2) of a liquid by one unit.



Van der Waals (Molecular) Theory of Capillarity



Variation of the molecular density

Normal to the Interface

- The mean spacing of the molecules in the liquid near the interface is greater than in the bulk liquid.
- The repulsive force varies more rapidly with spacing than the longer-range attractive forces.
- In the direction normal to the interface, this combination of effects would produce a force imbalance that would draw the molecules towards the bulk liquid.
- The mean spacing of the molecules in the direction normal to the interface could decrease slightly to establish a balance between long-range attractive forces and repulsion from close neighboring molecules.

Parallel to the Interface

- In the directions parallel to the interface, however, the decrease in repulsion force between molecules produced by the increases spacing does not create a force imbalance because of the radial symmetry of the force interactions.
- Consequently, there is no impetus to decrease the mean spacing in this direction.
- The decrease in repulsive forces between immediate neighbors, with littel change in the longer-range attractive forces may thus produce a net tension force among molecules in the interface region acting equally in all directions parallel to the interface.

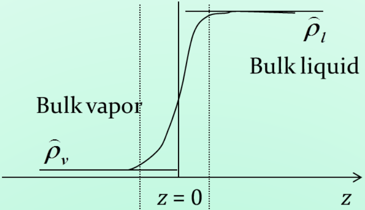
Van der Waals (Molecular) Theory of Capillarity

- **Postulate:** Postulate: The mean properties vary continuously across the transition region between the bulk phases. Mean molar density,

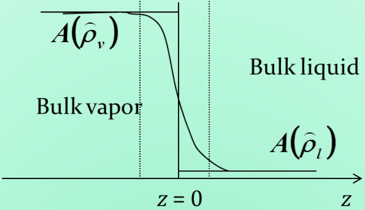
$$\hat{\rho} = \frac{\rho_n}{N_A}$$

- On the liquid side of the interfacial region, ρ is lower that that in the bulk liquid.
- Energy per molecule in the interfacial region $>$ in bulk liquid.
- The system has an additional free energy per unit area of interface due to the presence of the interface.
- Interfacial tension is due to the excess interfacial free energy per unit area.

Van der Waals (Molecular) Theory of Capillarity



Variation of mean molar density



Variation of the volumetric free energy

Van der Waals (Molecular) Theory of Capillarity

The interface surface is so chosen that the mass in the interfacial region with a distributed density profile is the same as would exist in the region with a discontinuous density step change at $z = 0$.

$$\int_{-\infty}^{0} (\hat{\rho} - \hat{\rho}_v) dz + \int_{0}^{\infty} (\hat{\rho} - \hat{\rho}_l) dz = 0$$

Van der Waals (Molecular) Theory of Capillarity

$$\boxed{\sigma = \int_{-\infty}^{0} \left[A - A(\hat{\rho}_v)\right] dz + \int_{0}^{\infty} \left[A - \psi(\hat{A}_l)\right] dz}$$

A is the Helmholtz free energy per unit volume

the max. work a system can do at constant $V \& T$.

- Apply a system held at constant T with a V that encompasses the interfacial region over a unit area of the interface.
- Equilibrium corresponds to a minimum in volumetric free energy (A).
- σ is the property nothing but this equilibrium free energy.

Van der Waals (Molecular) Theory of Capillarity

$$\boxed{\sigma = \int_{-\infty}^{0} \left[A - A(\hat{\rho}_v)\right] dz + \int_{0}^{\infty} \left[A - A(\hat{\rho}_l)\right] dz}$$

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the max. work a system can do at constant $V \& T$.

- Apply a system held at constant T with a V that encompasses the interfacial region over a unit area of the interface.
- Equilibrium corresponds to a minimum in volumetric free energy (A).
- σ is the property nothing but this equilibrium free energy.

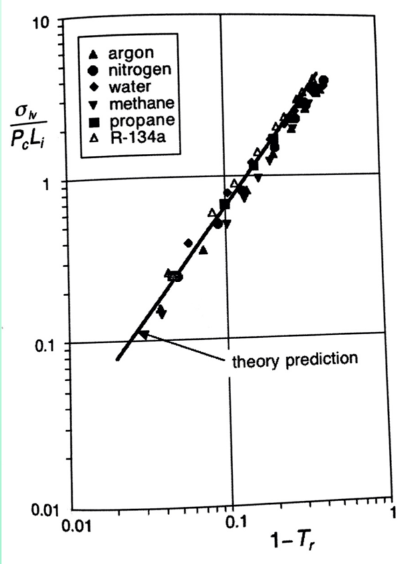
Dimensionless Surface Tension

Modified Redlich-Kwong model for dimensionless σ:

$$\frac{\sigma_{lv}}{P_c L_i} = 14.65 \left(1 - \frac{T}{T_c}\right)^{1.33}$$

L_i is a characteristic length associated with the size of the interfacial region:

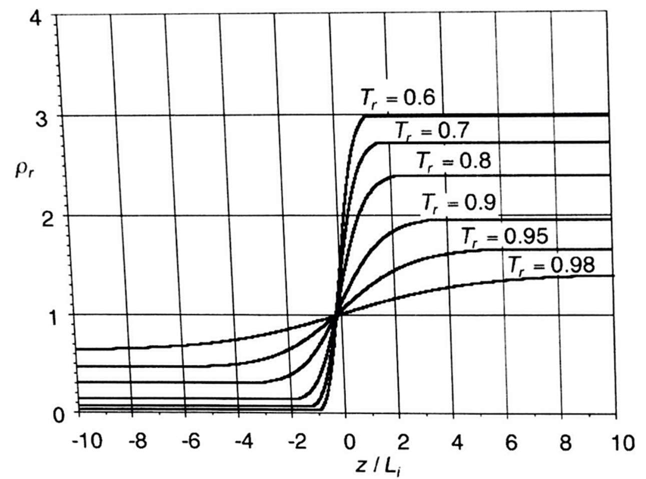
$$L_i = \left(\frac{k_B T_c}{P_c}\right)^{\frac{1}{3}}$$



Interface Properties

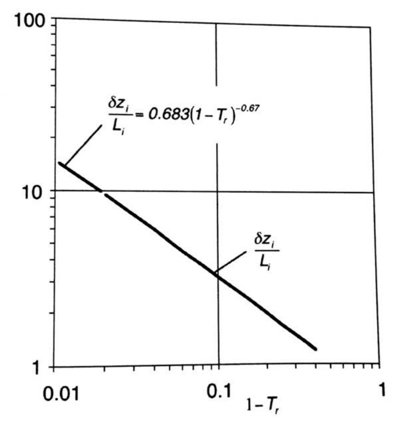
$$\rho_r = \frac{\rho}{\rho_c}$$

$$T_r = \frac{T}{T_c}$$



Reduced density profiles across the interfacial region predicted at various reduced temperatures

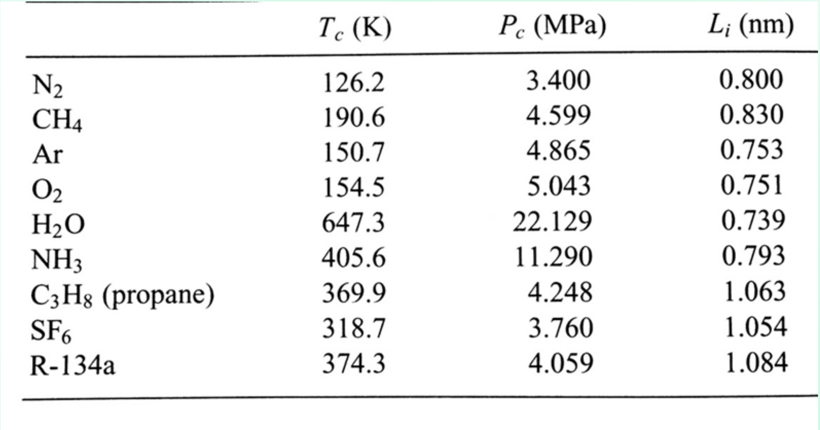
Dimensionless Interfacial Thickness



Dimensionless interfacial thickness:

$$\frac{\delta z_i}{L_i} = 0.683\left(1 - \frac{T}{T_c}\right)^{-.67}$$

Characteristic Length



	T_c (K)	P_c (MPa)	L_i (nm)
N_2	126.2	3.400	0.800
CH_4	190.6	4.599	0.830
Ar	150.7	4.865	0.753
O_2	154.5	5.043	0.751
H_2O	647.3	22.129	0.739
NH_3	405.6	11.290	0.793
C_3H_8 (propane)	369.9	4.248	1.063
SF_6	318.7	3.760	1.054
R-134a	374.3	4.059	1.084

$$L_i = \left(\frac{k_B T_c}{P_c}\right)^{\frac{1}{3}}$$

Problem

For water at atmospheric pressure, estimate the surface tension and the interfacial region thickness. $T_c = 647.3$ K, $P_c = 22.1$ MPa and $L_i = 0.739$ nm.

$$\frac{\sigma_{lv}}{P_c L_i} = 14.65 \left(1 - \frac{T}{T_c}\right)^{1.33}$$

$$L_i = \left(\frac{k_B T_c}{P_c}\right)^{\frac{1}{3}}$$

$$k_B = 1.38 \times 10^{-23} \text{ m}^2\text{kg/s}^2 \text{ K.}$$

$$\frac{\delta z_i}{L_i} = 0.683 \left(1 - \frac{T}{T_c}\right)^{-.67}$$

Problem: Solution

For water at atmospheric pressure, estimate the surface tension and the interfacial region thickness. $T_c = 647.3$ K, $P_c = 22.1$ MPa and $L_i = 0.739$ nm.

At $T = 300$ K

$$\sigma_{lv} = 0.105 \text{ N/m}$$
$$\delta z_i = 0.766 \text{ nm}$$

At $T = 373.14$ K

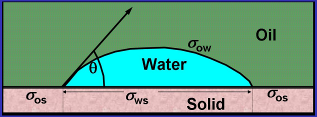
$$\sigma_{lv} = 0.07635 \text{ N/m}$$
$$\delta z_i = 0.898 \text{ nm}$$

Actual value, $\sigma = 0.0712$ N/m at T = 303.2 K

$\sigma = 0.0589$ N/m at T = 373.14 K

The effective diameter of a water molecule = 0.28 nm.

Multiphase Flow and Heat Transfer



Wettability

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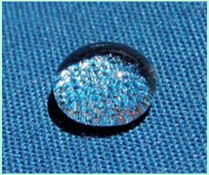
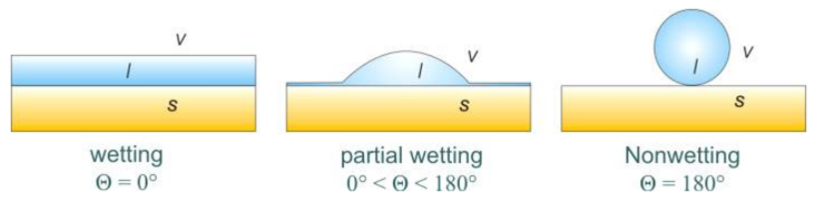
Wettability

- Usually, a liquid-vapor phase change is accomplished by transferring energy through the walls of a container or channel into or out of a two-phase system.
- The vaporization or condensation process ultimately takes place at the liquid-vapor interface.
- However, the contact through which the energy is transferred will strongly affect the resulting heat and mass transfer in the system.
- The performance of heat transfer equipment in which vaporization or condensation occurs may depend strongly on the way that the two phases contact the solid walls.

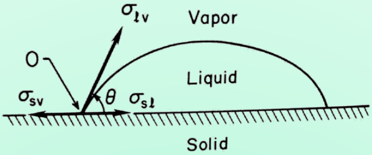
Wettability

- Liquids with weak affinities for a solid wall will collect themselves into beads while those with high affinities for solid will form film to maximize the liquid-solid contact area.
- The affinity of liquids for solids - **wettability of the fluid.**





Neumann's Formula or Young's Equation



$$\sigma_{sv} = \sigma_{sl} + \sigma_{lv} \cos\theta$$

Vertical force $\sigma_{lv} \sin\theta$ must be balanced by a vertical reaction force in the solid.

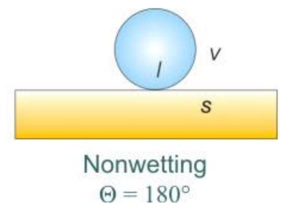
- Small and also modulus of elasticity of solid is high
- No deformation occurs

σ_{sl} and σ_{sv} are not available easily.

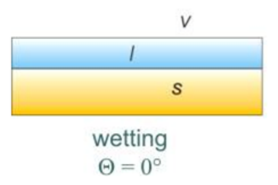
Neumann's Formula or Young's Equation

As $\theta \to 180^\circ$ (if g is negligible)

- Liquid droplet - sphere
- One point of contact on solid
- Completely non-wetting



Nonwetting
$\Theta = 180^\circ$



wetting
$\Theta = 0^\circ$

As $\theta \to 0^\circ$

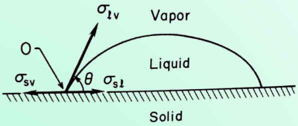
- A thin film configuration
- Completely wet the solid

- Wetting liquid: As $0^\circ < \theta < 90^\circ$
- Non-wetting liquid: As $90^\circ < \theta < 180^\circ$

  one point of contact on solid

Neumann's Formula or Young's Equation

$$\sigma_{sv} = \sigma_{sl} + \sigma_{lv}\cos\theta; \qquad |\cos\theta| \not> 1$$



At equilibrium:

$$\left|\frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}}\right| < 1$$

If $\dfrac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} < -1,\ \sigma_{sl}$ pulls the contact line, $\theta \to 180^\circ$

Never happens for a droplet surrounded by its vapor, but could happen for a liquid droplet in another immiscible liquid.

If $\dfrac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} > 1,\ \sigma_{sv}$ pulls the contact line, $\theta \to 0^\circ$

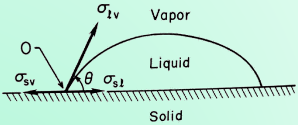
Until the film becomes so thin that molecular interactions come into play.

Spreading Coefficient

$$\mathsf{Sp}_{ls} = \sigma_{sv} - (\sigma_{lv} + \sigma_{sl})$$

Sp_{ls} measures the difference between the surface energy σ_{sv} and its value in the case of complete wetting.

$$\mathsf{Sp}_{ls} = \sigma_{lv} (\cos\theta - 1)$$



$\mathsf{Sp}_{ls} > 0$, the liquid will wet the solid and spontaneously spread into a thin film.

$\mathsf{Sp}_{ls} < 0$, the liquid will partially wet the solid and establish an equilibrium contact angle.

These results are theoretical and no lack of σ_{sv} and σ_{sl}.

Work of Adhesion

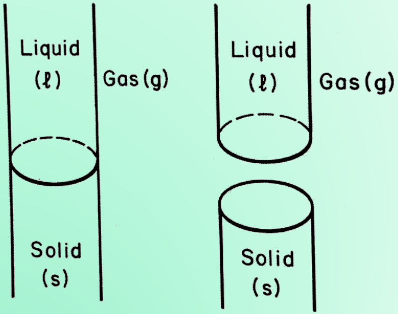
Cylindrical column formed by l, s and low density gas, g. The net reversible work required per unit of interface area:

$$w_{sl} = \sigma_{lg} + \sigma_{sg} - \sigma_{sl}$$

Essentially,

- Forming 2 new interfaces
- Breaking one interface

Adhesion: due to the minimum reversible work required to tear the liquid off the solid surface.



Work of Cohesion

Now consider, instead of solid-liquid column there is only one liquid column. To tear a single liquid column in half:

$$w_{ll} = 2\sigma_{lg}$$

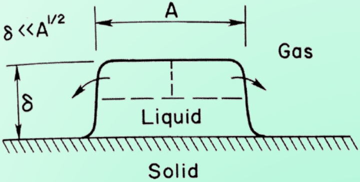
Essentially, two interfaces are formed without breaking any interface.

Cohesion: work required to break internal bonds of the material.

Adhesion - for dissimilar particles
Cohesion - for similar particles

Work per Unit Area Required for Spreading

Now lets march further. Lets say there is a liquid column of area A, and height δ. We are making it into a liquid column of area $2A$ and height of $\delta/2$.



$$w_{sp} = \sigma_{lg} + \sigma_{sl} - \sigma_{sg}$$

$$= -\mathrm{Sp}_{ls}$$

Work interaction is negative (Sp_{ls} is positive for spreading). Work could be extracted if we can ($= \mathrm{Sp}_{ls}$).

Adhesion and Cohesion

$$\mathsf{Sp}_{ls} = -w_{sp} = w_{sl} - w_{ll}$$

$$\text{Spreading coefficient} = \text{difference between} \begin{cases} \text{the work of adhesion} \\ \text{the work of cohesion} \end{cases}$$

Sp_{ls} indicates the tendency of the liquid to adhere to the solid relative to its internal cohesive forces.

Surface Tension of a Mixture

$$w_{sl} = \sigma_{lg} + \sigma_{sg} - \sigma_{sl}$$

Applying it to any two solid or liquid phases a and b, and a low density gas or vapor phase g,

$$w_{ab} = \sigma_{bg} + \sigma_{ag} - \sigma_{ab}$$

$$\sigma_{ab} = \sigma_{bg} + \sigma_{ag} - w_{ab}$$

The work of adhesion is approximately given as:

$$w_{ab} \cong 2\left(\sigma_{ag}\sigma_{bg}\right)^{\frac{1}{2}}$$

$$\boxed{\sigma_{ab} = \sigma_{bg} + \sigma_{ag} - 2\left(\sigma_{ag}\sigma_{bg}\right)^{\frac{1}{2}}}$$

Problem

For water and hexane in contact with air at 20°C, σ_{wg} is 0.0728 N/m and σ_{hg} is 0.0184 N/m respectively. Use these data to estimate the interfacial tension between hexane and water. Compare this value to experimentally determined value of $\sigma_{wh} = 0.0511$ N/m.

$$\sigma_{ab} = \sigma_{bg} + \sigma_{ag} - 2\left(\sigma_{ag}\sigma_{bg}\right)^{\frac{1}{2}}$$

$$\sigma_{wh} = 0.0180 \text{ N/m}$$

This is 65% accuracy or 35% of the actual value.

$$\mathrm{Sp}_{hw} = \sigma_{wg} - \sigma_{hg} - \sigma_{wh}$$

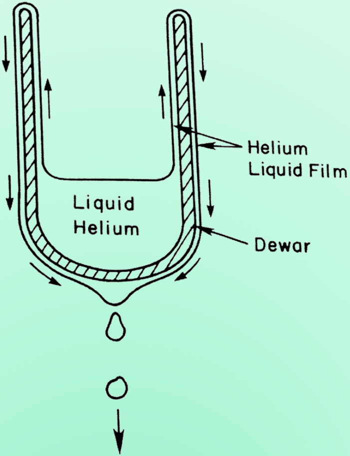
Problem

$$\text{Sp}_{hw} = \sigma_{wg} - \sigma_{hg} - \sigma_{wh} = 0.0033 \text{ N/m}$$

- $\text{Sp}_{hw} > 0$, hexane would spontaneously spread over the surface of water
- However, close to zero and so tendency is weak.
- Hexane is unlikely to form lens-shaped droplets.
- Spread out into a film, not aggressively covers the entire liquid surface.

Spread Thin Films

Spontaneous spreading of liquid helium over the walls of a Dewar



flask