## Heat and Mass Transfer



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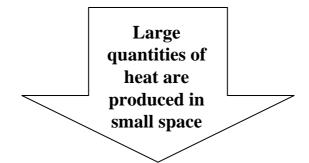
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# **Boiling and Condensation**

### **Heat Transfer with Phase Change**

- -Phase changes: Boiling & Condensation
- -Phase change gives high heat flux

Boiling gives high heat flux  $q_{boil} \sim 50,000,000~Btu/(h)(ft^2)$ 

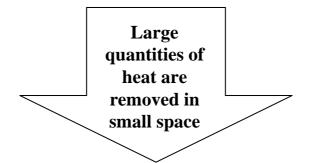


- **☑** Nuclear reactor design
- ☑ Rocket technology

### **Heat Transfer with Phase Change**

- -Phase changes: Boiling & Condensation
- -Phase change gives high heat flux

Condensation gives high heat flux  $h_{condensation} \sim 20,000 \; Btu/(h)(ft^2)(^oF)$ 



Condenser design

# Boiling

## Paradoxical quenching behavior

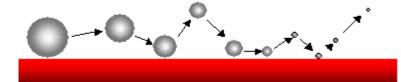
In quenching of very hot metals in liquids, the heat transfer rate often increases as the temperature difference between the metal and liquid decreases.

### Leidenfrost Phenomenon

#### Leidenfrost Phenomenon

Liquid drop bounces vigorously on the surface

Several seconds to evaporate

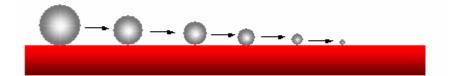


Very very Hot Surface

#### No Liquid drop bounce

No Liquid drop bounces on the surface

Several seconds to evaporate



Very Hot Surface

#### **Drop** wet the surface

Drop spread out on the surface A second or less to evaporate



# **Boiling Heat Transfer Mechanism**

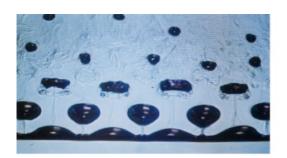
The explanation for both the paradoxical quenching behavior and the Leidenfrost phenomenon lies in the fact that

boiling heat transfer occurs by several difference mechanisms and that

the mechanism is often more important in determining heat flux than the temperature-difference driving force.

### Ordered & Chaotic Bubble Departure Behavior During Film Boiling

Hong, You, Ammerman and Chan



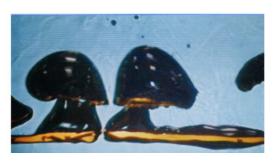


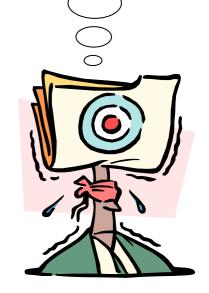
Among the various heat transfer mechanisms, boiling is perhaps the most complex.





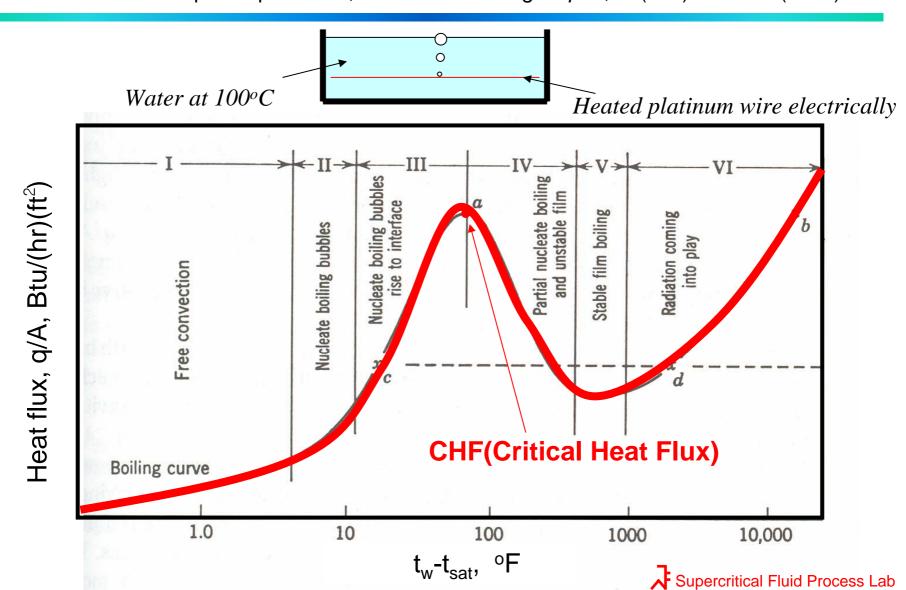






### **Boiling Mechanisms**

**Shiro Nukiyama**, "Maximum and minimum values of heat transmitted from metal to boiling Water under atmospheric pressure", *J. Soc. Mech. Eng. Japan*, **37**(206):367-374 (1934)



Bubble condenses before reaching the free liquid surface

Vapor film forms around the wire and portions of the film break off and rise The film collapse and reformation vapor film provides a considerable resistance to heat transfer

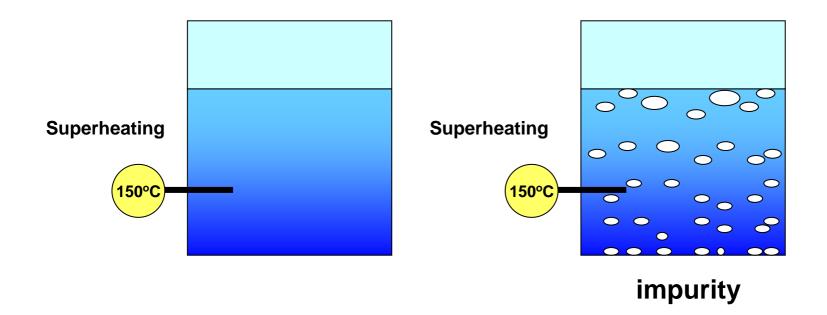
Supercritical Fluid Process Lab

# **Superheating**

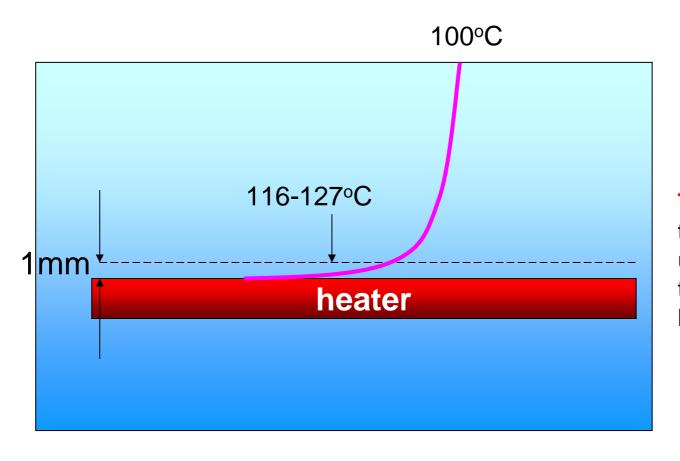
Superheating in excess of 100°F can be obtained if care is taken to use pure liquids and clean glassware. However, this state of supersaturation can be quickly ended, and violent ebullition of vapor occurs if impurities are added to the system.

clean glassware, pure liquid

Violent ebullition of vapor



## **Superheating**



Thin zone: most of temperature drop usually occurs less than 1mm from the heater

Why the presence of superheat in boiling systems?

## How to explain for presence of superheat

 $t_{sat}$ ,  $P_{sat}$  ordinarily used by engineers apply to equilibrium at a flat interface between vapor and liquid. However, if a force balance is written at the equator of a spherical vapor bubble of radius r,  $P_g > P_l$ .

$$p_{g}(\pi r^{2}) = p_{l}(\pi r^{2}) + 2\pi r \sigma$$
Effect of the surface force, which tends to contact the bubble 
$$p_{g} - p_{l} = \frac{2\sigma}{r}$$
bubble

For small bubble,  $\Delta P$  is very high: Temperature of liquid must be much higher than the flat-surface saturation temperature to from the vapor nucleus

## How to explain for presence of superheat

If nuclei with large radii of curvature are available, the required excess pressure will be smaller and boiling will commence at a low superheat.

$$p_g - p_l = \frac{2\sigma}{r}$$

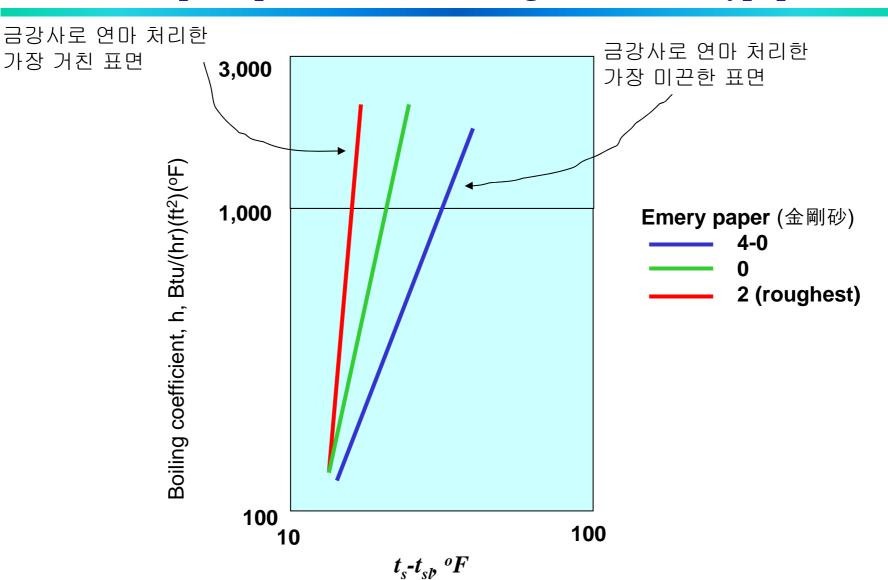
A perfect pure liquid in contact with a flat heated surface would, in theory, require an infinite amount of superheat.

A liquid is not, however, a continuum, and clusters of molecules could serve as nuclei. Furthermore, the conditions of perfect purity and flatness are unobtainable, so that the highest superheats recorded are of the order of 100 to 200°F (55 to 110°C).

However, it is likely that boiling does not require the presence of foreign matter, but can be initiate on the heating surface.

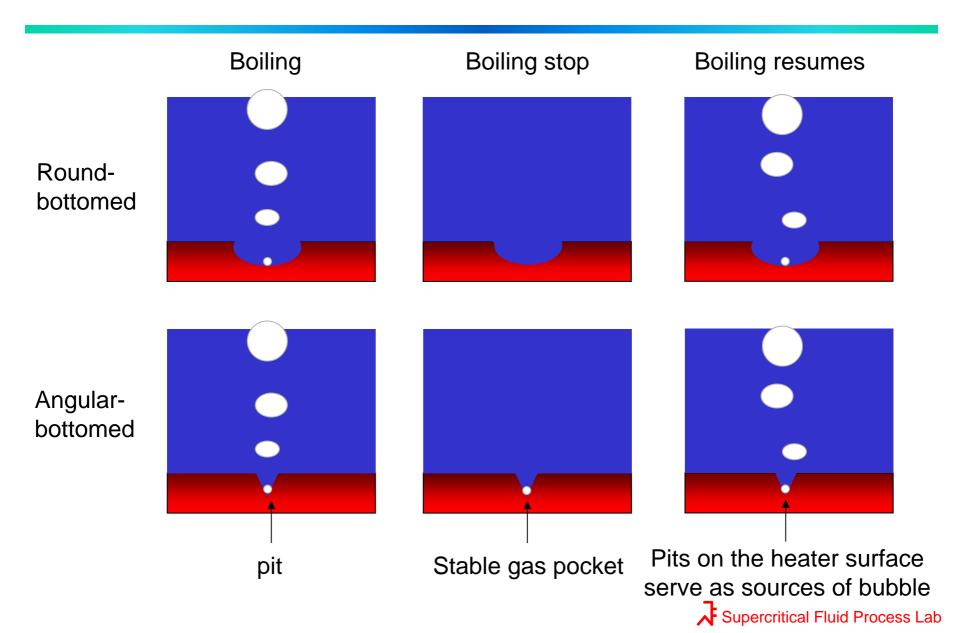
#### **Nucleate boiling**

# Heat Transfer Coefficient for n-hexane boiling on a flat plate polished with three grades of emerypaper

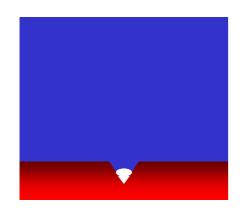


#### **Nucleate boiling**

# Surface roughness affects boiling



# Surface roughness affects boiling



Stable gas pocket

$$p_{l}(\pi r^{2}) = p_{g}(\pi r^{2}) - 2\pi r \sigma$$

$$p_l = p_g - \frac{2\sigma}{r}$$

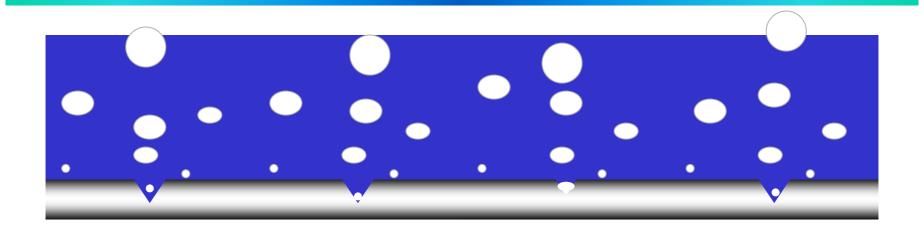
Negative (-) radius of curvature of the interface

Pits on the heater surface serve as sources of bubble

- -The liquid-vapor interface will bulge downward into the pit. The surface forces act with the pressure in the vapor space to balance the liquid pressure.
- -The liquid advances only until the radius of curvature of the interface is small enough so that  $\Delta P$  ( $P_l$ - $P_a$ ) is equal to  $2\sigma/r$  and a stable gas pocket remain.

#### **Nucleate boiling**

## Heat Transfer Coefficient for boiling

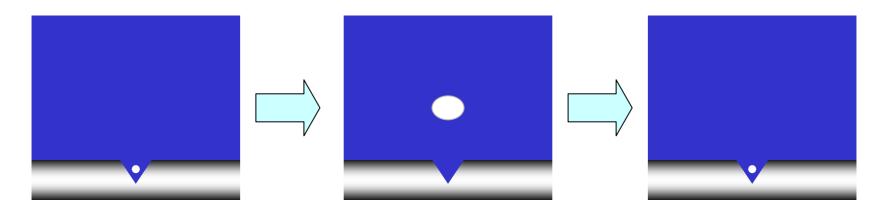


- -Experiments have shown that the heat transfer coefficient is proportional to some power of the concentration of bubble site ranging from 0.25 to 0.46.
- -The number of sites on a heater surface increases with an increase of superheat. The number of sites depends on the roughness of the surface and the physical properties of the boiling fluid.
- -The accurate prediction of boiling coefficients may be possible when these two mechanisms are understood.

### **Bubble behavior**

The formation, growth, and release of bubbles is an extremely rapid sequence of events.

J.B. Roll, *AIChE J.*, **10**:530 (1964)



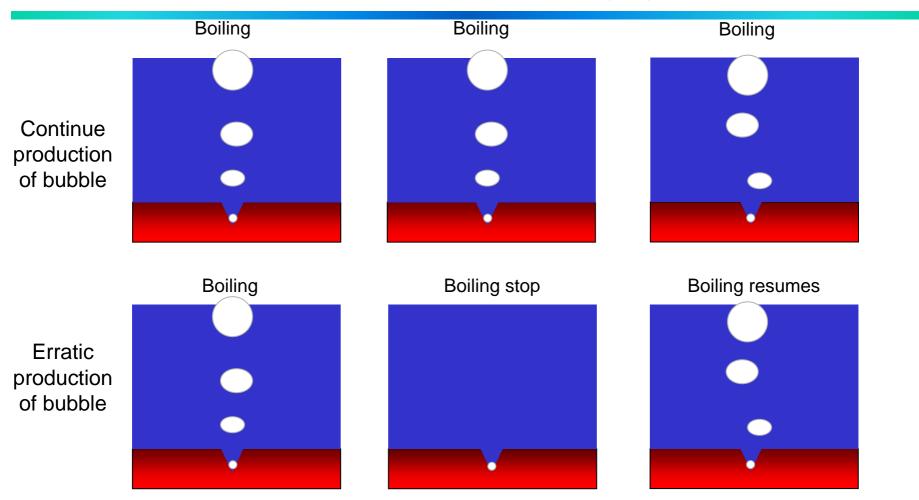
**0.01s**Growth time for the bubble at a nucleation site

0.01-0.06s

Following departure of the bubble from the site, there is a delay time of 0.01 to 0.06s before new bubble appears and repeats growth cycle.

#### **Erratic Bubble behavior**

F.D. Moore and R.B. Mesler, *AIChE J.*, **7**:620 (1961)



Fluctuating surface Temperature: Moore and Mesler showed that the surface temperature beneath a bubble site was lower than the surrounding surface temperature. They suggested that vaporization of a thin layer of liquid between the growing bubble and the heating surface caused removal of heat from the surface, thus lowing the surface temperature at that site.

Supercritical Fluid Process Lab

#### Correlations of nuclear boiling heat transfer coefficients

**Rohsenow and Forster-Zuber** 

$$Nu = a \operatorname{Re}^b \operatorname{Pr}^c$$

$$Re_b = \frac{D_b u \rho}{\mu}$$

u=Characteristic velocity

#### Rohsenow

$$u = fnV_b \quad [m/s]$$

f: the frequency of bubble formation at a site, [bubble/s/site]

n: the number of active sites per unit area[site/m<sup>2</sup>]

 $V_b$ : the volume of a bubble [m<sup>3</sup>/bubble]

#### Forster and Zuber

u = the radial velocity of the interface of the growing bubble [m/s]

u x 
$$r_b$$
=constant  $\implies$  Re $_b$ =constant  $\neq$  function of time

# Correlations of nuclear boiling heat transfer coefficients Westwater

The effect of surface tension

$$h = \text{constant} \cdot \sigma^n \tag{25-4}$$

The effect of degree of superheat

$$h = \text{constant } (\Delta t)^n$$
 (25-4)

n = 2.5 for many commercial surfaces

n = 1.4 for copper tube

n = 25 for flat surface polished with coarse emery paper

$$\Delta t = t_{\text{heater surface}} - t_{\text{saturated liquid}}$$

#### Correlations of nuclear boiling heat transfer coefficients

$$Nu = a \operatorname{Re}^b \operatorname{Pr}^c$$

$$Nu_b = \frac{h_b D_b}{k_l}$$

$$\frac{q}{A} = h_b \left( t_s - t_{sat} \right)$$

 $Re_b = \frac{D_b G_b}{\mu_l}$  (bubble Reynolds number)

 $G_b$ : average mass velocity

 $D_b = C_d \beta \sqrt{2\sigma / g(\rho_l - \rho_v)}$ 

 $C_d$ : constant (= 0.0148 for water)

 $\sigma$ : surface tension

 $\beta$ : bubble contact angle

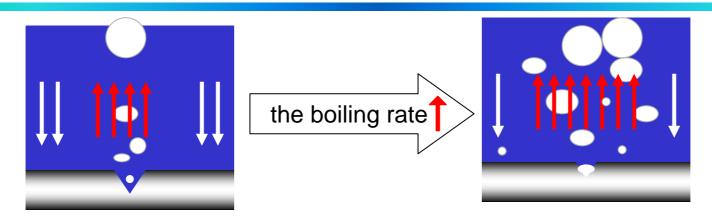
 $D_h$ : max. bubble diameter at the free surface.

 $t_s$ - $t_{sat}$ : temp. difference between surface and sat'd liquid temp.

 $k_1$ : thermal conductivity of liquid.

#### **Nucleate boiling**

### **Maximum Heat Flux**



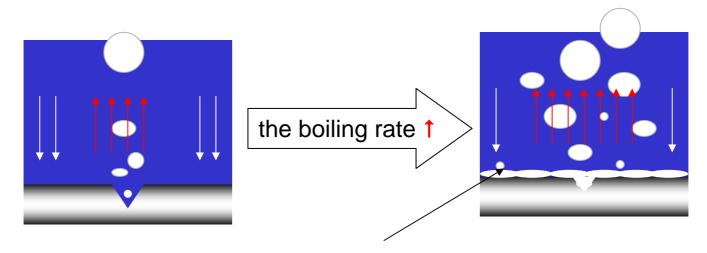
At steady state, the mass rate of the vapor rising from the surface = The mass rate of liquid proceeding toward the surface

the boiling rate ↑, rate of liquid influx ↑, the area of available for liquid flow ↓, the liquid velocity must increase very sharply.

A limiting condition is reached because the drag exerted by each phase on the other prevents indefinite increases in velocity. At this limiting condition, the liquid flow toward the heated surface cannot increase and the surface becomes largely blanketed with vapor.

Electrical heater (constant heat flux): t<sub>s</sub> rises quickly becoming film boiling Steam-heated tube (constant temp.): becoming transition zone Supercritical Fluid Process Lab

## Film Boiling



- Heater surface completely blankets with vapor (Film)
- Heat transfer by conduction, convection and radiation.
- t<sub>high</sub>: radiation dominant (high heat flux)

Film boiling is important in rocket technology when liquefied gases such as  $H_2$  and  $O_2$  are used to cool the rocket engine. Extremely high superheats occur in these systems, causing heat to be transferred by film boiling.

## Film Boiling

Stable film boiling (V)

On the surface of horizontal tubes and vertical plates

Bromley eq.:

$$h = 0.62 \left[ \frac{k v^{2} \rho_{v} (\rho_{l} - \rho_{v}) g (h_{fg} + 0.4 C_{pv} \Delta t)}{D_{0} \mu_{v} (t_{s} - t_{sat})} \right]^{\frac{1}{4}}$$

Film boiling (VI)

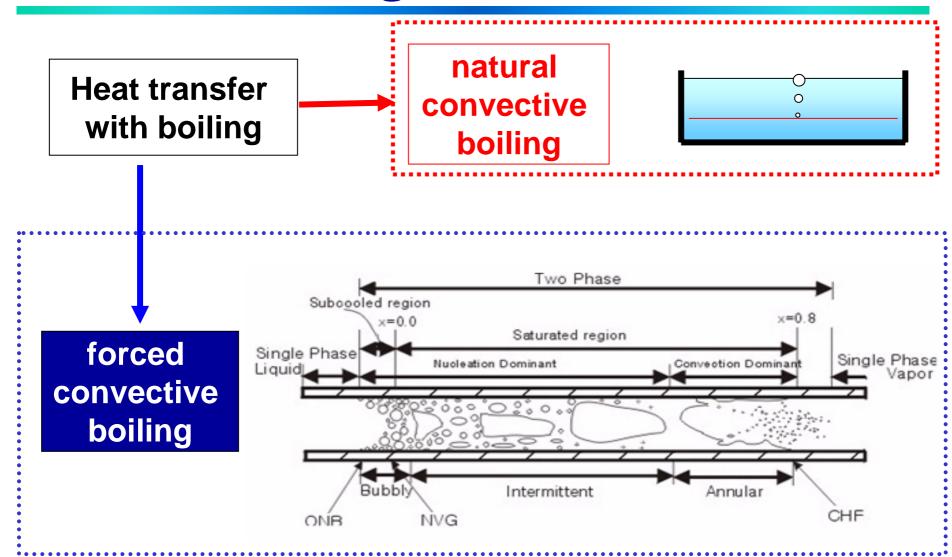
$$h = h_c \left(\frac{h_c}{h}\right)^{1/2} + h_r$$

h: total heat transfer coefficient

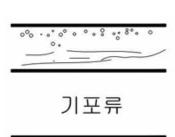
h<sub>c</sub>:coefficient

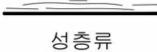
h<sub>r</sub>:radiant heat transfer coefficient

## **Boiling Mechanisms**



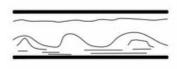
# Patterns of two phase flow







파형류



파형-환상류



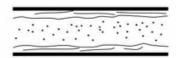
플러그류



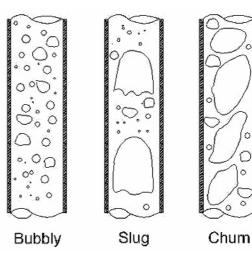
슬러그류



환상류



환상-분무류



Annular

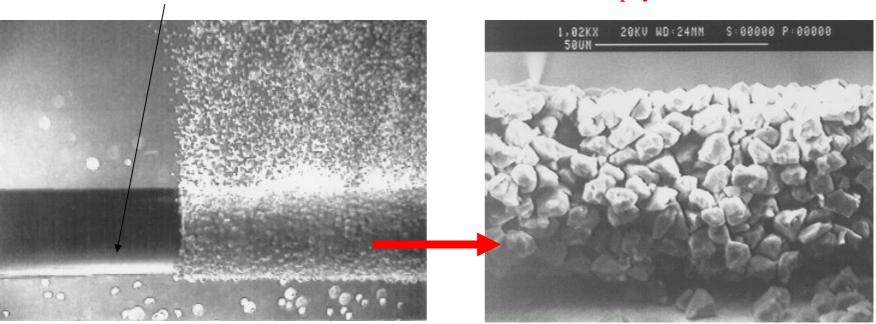
### 2상 유동양식 판별법

- 가시화 기법
- 정압 측정법
- 압력강하 측정법
- X선 감쇠법
- 전기전도도 측정법

## **Applications for coated surface**

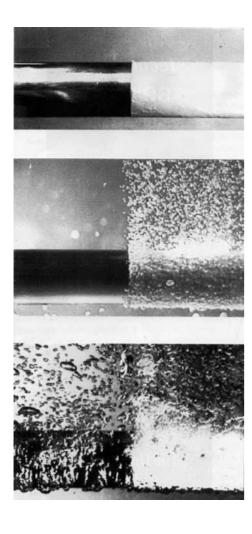
1/2-inch-diameter copper tube.
Only the **right half** of the copper tube has been coated.

#### Spayed alumina

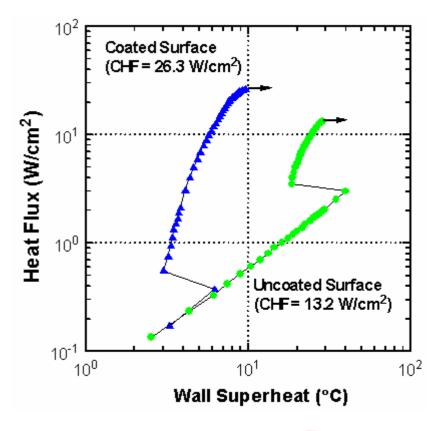


- Phase-Change Heat Exchangers
- Electronics Cooling (Electrically Non-Conducting Composition)
- Refrigeration Evaporators
- Chemical Processing

### Forming microscale cavities on the surface



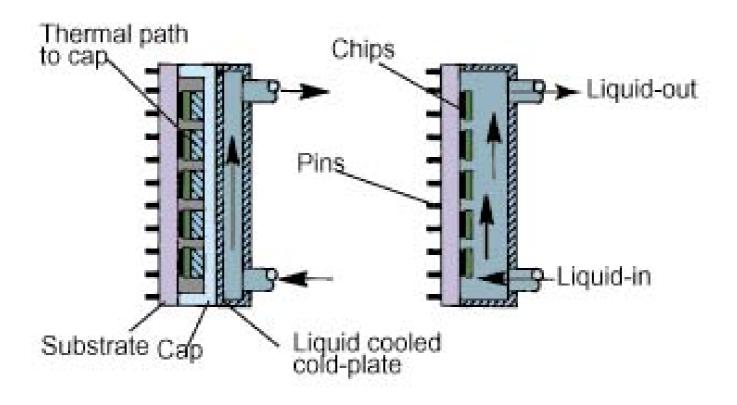
- •minimum impact to existing hardware
- •low wall superheats at boiling incipience
- •high heat transfer coefficients in nucleate boiling
- •increased critical heat flux



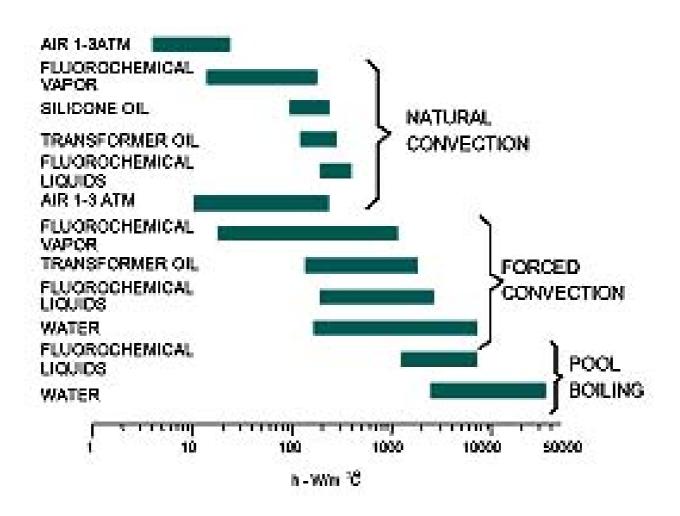
#### **Bubble radii for difference surface**

Surface	Incipience Superheat (°C.)	Embryonic Bubble Radius (µm)
Reference	20 to 27	0.10 to 0.15
Sprayed Alumina (0.3–5 $\mu$ m)	9 to 18	0.16 to 0.42
Painted Diamand (1–3 $\mu$ m)	4 to 10	0.40 to 1.44
Painted Diamond (8–12 $\mu$ m)	3 to 8	0.54 to 2.07

# Indirect and direct liquid immersion cooling for a multi-chip module package



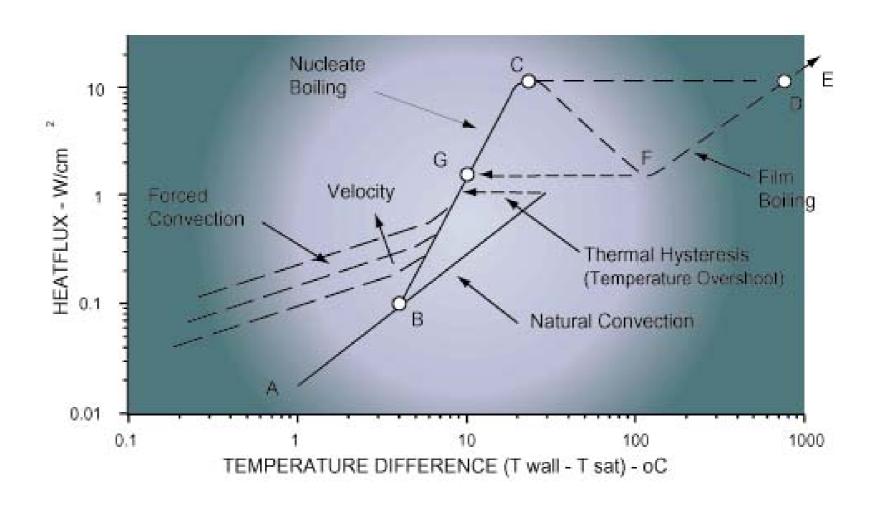
# Relative magnitude of heat transfer coefficients for various coolants and modes of convection



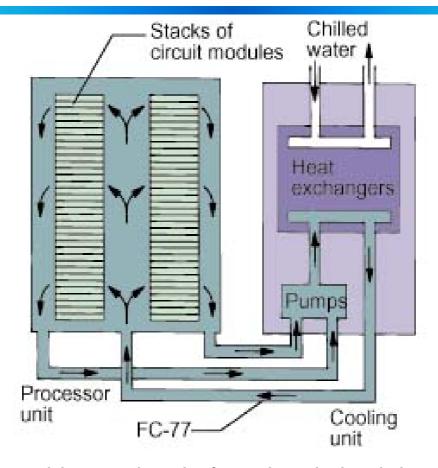
# Comparison of thermophysical properties of some fluorocarbon coolants and water

PROPERTY	FC-87	FC-72	FC-77	H <sub>2</sub> O
Boiling Point @ 1 Atm (°C)		56	97	100
Density x 10 <sup>-3</sup> (kg/m <sup>3</sup> )	1.633	1.680	1.780	0.997
Specific Heat x 10 <sup>-3</sup> (w-s/kg-K)	1.088	1.088	1.172	4.179
Thermal Conductivity (w/m-K)	0.0551	0.0545	0.057	0.613
Dynamic Viscosity x104 (kg/m-s)		4.50	4.50	8.55
Heat of Vaporization x10 <sub>L</sub> -4 (w-s/kg)		8.79	8.37	243.8
Surface Tension x10 <sup>3</sup> (N/m)		8.50	8.00	58.9
Thermal Coefficient of Expansion $\times$ 10 <sup>3</sup> (K <sup>-1</sup> )	1.60	1.60	1.40	0.20
Dielectric Constant	1.71	1.72	1.75	78.0

# Typical heat transfer regimes for immersion cooling with a fluorocarbon liquid



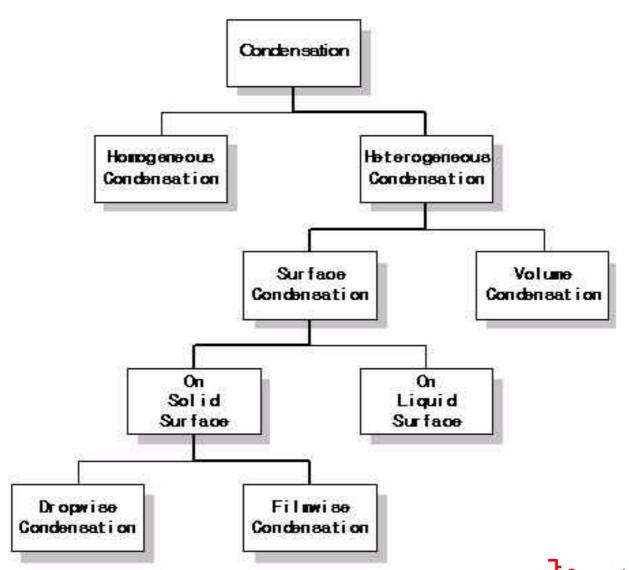
#### **CRAY-2** liquid immersion cooling system



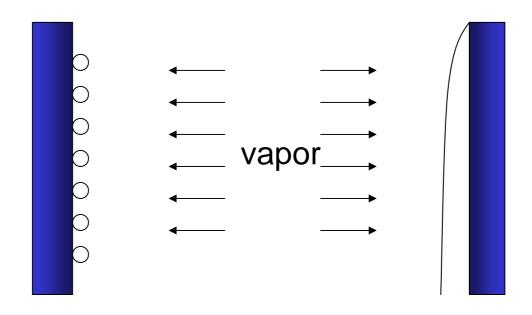
Each module assembly consisted of 8 printed circuit boards on which were mounted arrays of single chip carriers. A total flow rate of 70 gpm was used to cool 14 stacks containing 24 module assemblies each. The power dissipated by a module assembly was reported to be 600 to 700 watts.

# Condensation

#### **Condensation**



### **Condensation Mechanism**



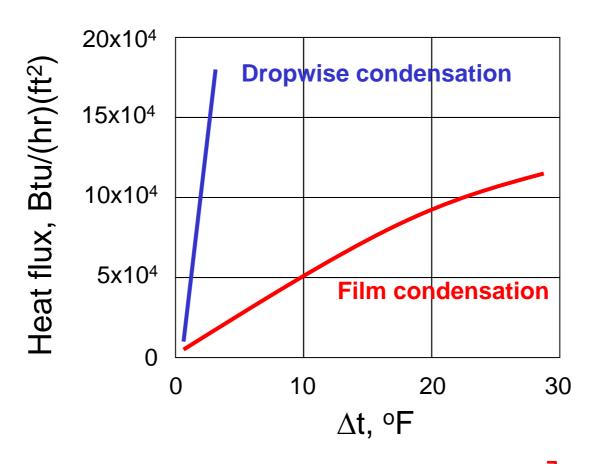
Dropwise condensation

Film condensation

Higher heat transfer coefficient!

## Condensation: Dropwise vs. Film

D. West group, Int. J. Heat and Mass Transfer, 8, 419 (1965)

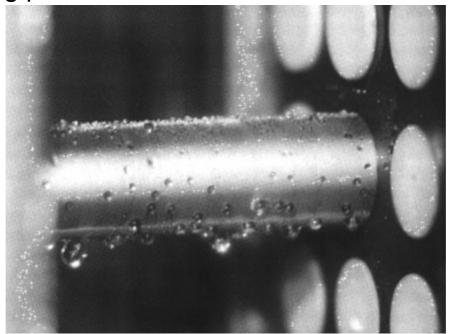


## **Dropwise Condensation**



### **Promoting Dropwise Condensation (DWC)**

To generate the low surface energy, hydrophobic surface required to promote dropwise condensation, the surfaces are treated using a plasma coating process.



promoting dropwise condensation (DWC) of organo-silicon polymer films deposited by plasma enhanced chemical vapor deposition (PECVD) on steam condenser tube materials

#### **Film Condensation**

액적응축에 관하여는 막응축의 경우에 비해 큰 열전달 성능이 기대되어 많은 연구가 이루어졌으나, 실제로 이를 구현하는 데에는 큰 어려움이 있는 관계로, 아직도 실용화가 되지 않고 있다.

액적응축을 구현하려면 열교환 표면의 wettability를 조절할 수 있어야하는데, 현실적으로 이를 구현할 만한 신뢰성 있는 방법이 알려져 있지 않다.

즉, 표면의 wettability를 방지하는 여러 가지 방법들이 제안되고는 있으나, 사용 기간이 오래 지나거나 벽면의 과냉도가 커지는 경우에는 액적응축이 막응축으로 변화해 가므로 실제 응축장치는 열전달 성능이 낮은 막응축을 기준으로 설계되고 있다.

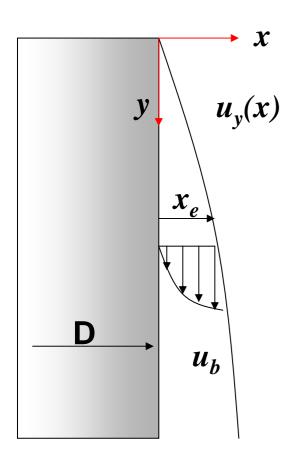
## **Dropwise Condensation**

막응축에 관해서는 1916년에 Nusselt에 의해서 제안된 모델이 기본이 되어 현재까지 꾸준히 개선되고 사용되어 오고 있다.

즉, 당초의 Nusselt의 모델에서는 층류 액막, 일정한 물성치, 전도 만에 의한 열전달 등의 가정들과 함께, 액막내의 과냉도 및 운동량 변화 무시, 그리고 액막과 기체 경계면에서의 전단력 무시등 여러 가지 가정들을 전제하고 있다.

그러나, 좀더 실제적이고 넓은 범위에서 적용이 가능하도록 위의 가정을 제거하고 모델을 개선하는 과정을 거쳐 오고 있다

#### **Condensation on Vertical Tubes**



Assumption: (Laminar flow, Re<sub>I</sub> < 2000)

- 1. The flow of liquid is entirely viscous.
- 2. There is negligible drag at the v- $\ell$  interface
- 3. The contribution of inertia forces to the downward flow of liquid is negligible.

$$Re_L = \frac{4x_e u_b \rho}{\mu} = \frac{4\Gamma}{\mu}$$

$$\Gamma = x_e u_b \rho$$

(mass flow rate per unit of tube perimeter)

mass flow rate =  $\pi D\Gamma$ 

#### **Condensation on Vertical Tubes**

D>> $x_e$ : cylindrical system can be described by rectangular coordinate Steady state incompressible & Newtonian, Laminar (Re<sub>L</sub> < 2000) kinematics:  $u_v = u_v(x)$ ,  $u_x = u_z = 0$ : continuity is satisfied.

$$x - comp: 0 = -\frac{\partial P}{\partial x}$$

$$y - comp: 0 = -\frac{\partial P}{\partial y} + \mu \frac{\partial^{2} u_{y}}{\partial x^{2}}$$

$$P = P(y)$$

$$z - comp: 0 = -\frac{\partial P}{\partial z}$$

$$P = p + \rho g y - \frac{1}{3} \mu \sqrt{v}$$
 From continuity

#### Navier-Stokes equation

$$y_{x} \frac{\partial u_{y}}{\partial x} + u_{y} \frac{\partial u_{y}}{\partial y} + u_{z} \frac{\partial u_{y}}{\partial z} + u_{x} \frac{\partial u_{y}}{\partial z} + u_{x} \frac{\partial u_{y}}{\partial \theta} = g_{c}Y - \frac{g_{c}}{\rho} \frac{\partial p}{\partial y} + v \left( \frac{\partial^{2} u_{y}}{\partial x^{2}} + \frac{\partial^{2} u_{y}}{\partial y^{2}} + \frac{\partial^{2} u_{y}}{\partial z^{2}} \right)$$

$$\frac{\partial^2 u_y}{\partial x^2} = -\frac{\rho g}{\mu} = -\frac{g}{\nu} \qquad (Y = g / g_c)$$
 (25-9)

BCs: at 
$$x = 0$$
,  $u_y = 0$   
at  $x = x_e$ ,  $\frac{du_y}{dx} = 0$ 

$$u_y = \frac{g}{v} \left( x_e x - \frac{x^2}{2} \right)$$

(25-11)



$$u_b = \frac{\int_0^{x_e} u_y dx}{x_e} + \frac{g}{v} \frac{x_e^2}{3}$$

$$w = \pi D\Gamma = \pi D \cdot x_e u_b \rho = \frac{\rho \pi Dg}{v} \frac{x_e^3}{3}$$

$$\Gamma = \frac{\rho g x_e^3}{3\nu} \qquad x_e = \sqrt[3]{\left(\frac{3\nu\Gamma}{\rho g}\right)} \tag{25-13}$$

To find mean heat-transfer coefficient, a heat balance on a differential length of tube dy located at a distance y from the top of the tube.

$$dq = h_{y}\pi D dy (t_{sv} - t_{s}) = k\pi D dy \frac{(t_{sv} - t_{s})}{x_{e}}$$

$$convection$$

$$conduction$$

$$(25-15)$$

$$h_{y} = \frac{k}{x}$$

All heat of condensation released at the v-l interface is conducted horizontally to the tube surface

$$h_{y} = \frac{dq}{dA(t_{sv} - t_{s})} = \frac{\lambda dw}{dA(t_{sv} - t_{s})} \quad \lambda : \text{latent heat of vaporization}$$

$$\frac{dw}{dA} = \frac{dw}{\pi D dy} = \frac{d\Gamma}{dy} \qquad w = \pi D\Gamma$$
 (25-18)

$$h_{y} = \frac{k}{x_{e}} = \frac{\lambda}{\left(t_{sv} - t_{s}\right)} \frac{d\Gamma}{dy}$$

$$(t_{sv} - t_s) = \frac{x_e \lambda}{k} \frac{d\Gamma}{dv}$$

(25-20)

Supercritical Fluid Process Lab

For the entire length L of the tube on which laminar flow exists, we write

$$q = h_{m}A(t_{sv} - t_{s}) = \lambda w_{L} \qquad (t_{sv} - t_{s}) = \frac{\lambda w_{L}}{h_{m}A} = \frac{\lambda \Gamma_{L}}{h_{m}L} \qquad (25-21, 22)$$

$$(25-22) \rightarrow (25-20)$$

$$dy = \frac{x_{e}h_{m}L}{k\Gamma_{L}}d\Gamma = \left(\frac{3v\Gamma}{\rho g}\right)^{1/3} \frac{h_{m}L}{k\Gamma_{L}}d\Gamma = \frac{h_{m}L}{k\Gamma_{L}} \left(\frac{3v}{\rho g}\right)^{1/3} \Gamma^{1/3}d\Gamma \qquad (25-23)$$

$$at \quad y = 0, \quad \Gamma = 0$$

$$at \quad y = L, \quad \Gamma = \Gamma_{L}$$

$$\Gamma = \frac{\rho g x_{e}^{3}}{3v} \qquad x_{e} = \sqrt[3]{\left(\frac{3v\Gamma}{\rho g}\right)}$$

Integration gives the mean heat-transfer coefficient for the entire laminar region

$$h_{m} = 0.925 \left(\frac{k^{3} \rho g}{\nu \Gamma_{L}}\right)^{1/3} = 0.925 \left(\frac{k^{3} \rho g \lambda}{\nu h_{m} L(t_{sv} - t_{s})}\right)^{1/3}$$
(25-28)

Solving  $h_m$ 

$$h_m = 0.942 \left( \frac{k^3 \rho g \lambda}{\nu L(t_m - t_s)} \right)^{1/4} \qquad \Gamma_L = \frac{h_m L(t_{sv} - t_s)}{\lambda}$$

$$\Gamma_L = \frac{h_m L (t_{sv} - t_s)}{\lambda}$$

(25-29)

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$$h_m = 0.942 \left( \frac{k^3 \rho g \lambda}{\nu L(t_{sv} - t_s)} \right)^{1/4} \quad \text{Re}_L = \frac{4\Gamma}{\mu}$$

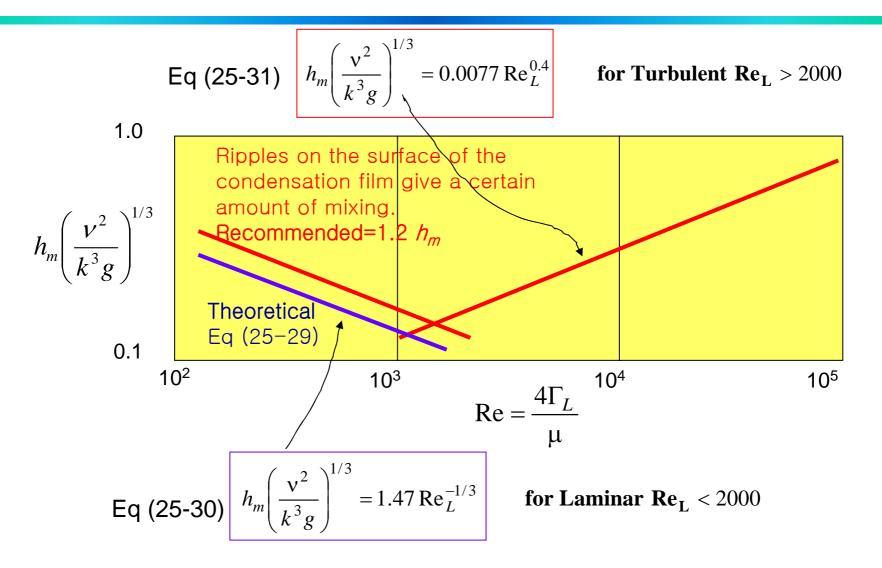
$$Re_L = \frac{4\Gamma}{\mu}$$

$$h_m \left(\frac{v^2}{k^3 g}\right)^{1/3} = 1.47 \,\text{Re}_L^{-1/3}$$
 for Laminar Re<sub>L</sub> < 2000

$$h_m \left(\frac{v^2}{k^3 g}\right)^{1/3} = 0.0077 \,\text{Re}_L^{0.4}$$
 (25-31) for Turbulent  $\text{Re}_L > 2000$ 

If the tube is sufficiently long, the film thickness increases and the flow becomes turbulent. Empirical correlation is given as Eq. (25-31) which can be applied to the entire tube, i.e., Both the laminar and turbulent portion.

#### Condensing coefficients on a vertical tube



#### Condensing coefficients on horizontal tubes

#### Nusselt's derivation

$$h_m = 0.725 \left( \frac{k^3 \rho g \lambda}{\nu D(t_{sv} - t_s)} \right)^{1/4}$$

$$h_m \left(\frac{v^2}{k^3 g}\right)^{1/3} = 1.20 \,\mathrm{Re}_L^{-1/3}$$

Vapor may cause ripples to occur ⇒ higher than (25-32)

(25-32)

(25-33)

Highest *h*(thinnest film)

Lowest **h** (thick film)

Hydraulic radius=Thickness of the film at any point

Re = 
$$\frac{(4)(\text{hydaulic radius})(u_b\rho)}{\mu}$$
 =  $\frac{(4)(\mathbf{x_e})(u_b\rho)}{\mu}$  =  $\frac{4}{\mu}\frac{\Gamma_L}{2}$  =  $\frac{2\Gamma_L}{\mu}$ 

 $\Gamma_L$ : total rate of condensate formation on the tube per foot of length

 $\Gamma_L/2$ : the rate for each side

#### Condensing coefficients on banks of horizontal tubes Effect of N tubes in a vertical row

$$(h_m)_N = 0.725 \left(\frac{k^3 \rho g \lambda}{v N D(t_{sv} - t_s)}\right)^{1/4}$$
 Re<sub>L</sub> < 2000 (25-37)

(그림3 - 수평관 주위에 형성된 막응축의 여러가지 배출 모드)

The mean heat transfer coefficients on successive tubes diminish at  $Re_L$  <2100. There will always be a certain amount of turbulence on any tube below the top, because of the condensate dripping from the tube above. This has the effect of increasing  $(h_m)_N$ .

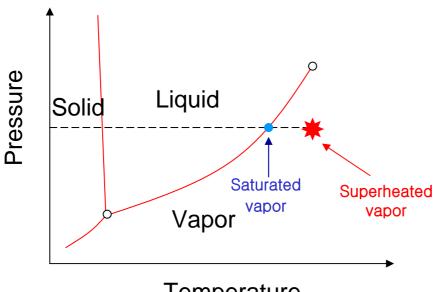
Supercritical Fluid Process Lab

## Superheated Vapor

Condensation of superheated vapor

De-superheating + Removal of latent heat

Resistance is negligible



t(°C)	P* (bar)
50	0.12
100	1.0
180	10.0
234	30.0

Temperature

#### **Effect of Non-condensable Gases**

Condensation of superheated vapor

Sensible heat + Removal of latent heat

Resistance is not negligible

Total condenser must contain provision for continuous or periodic venting; Otherwise the non-condensable gases will accumulate and the capacity of the condenser will diminish to zero.

#### Homework

25-1(a) 25-4