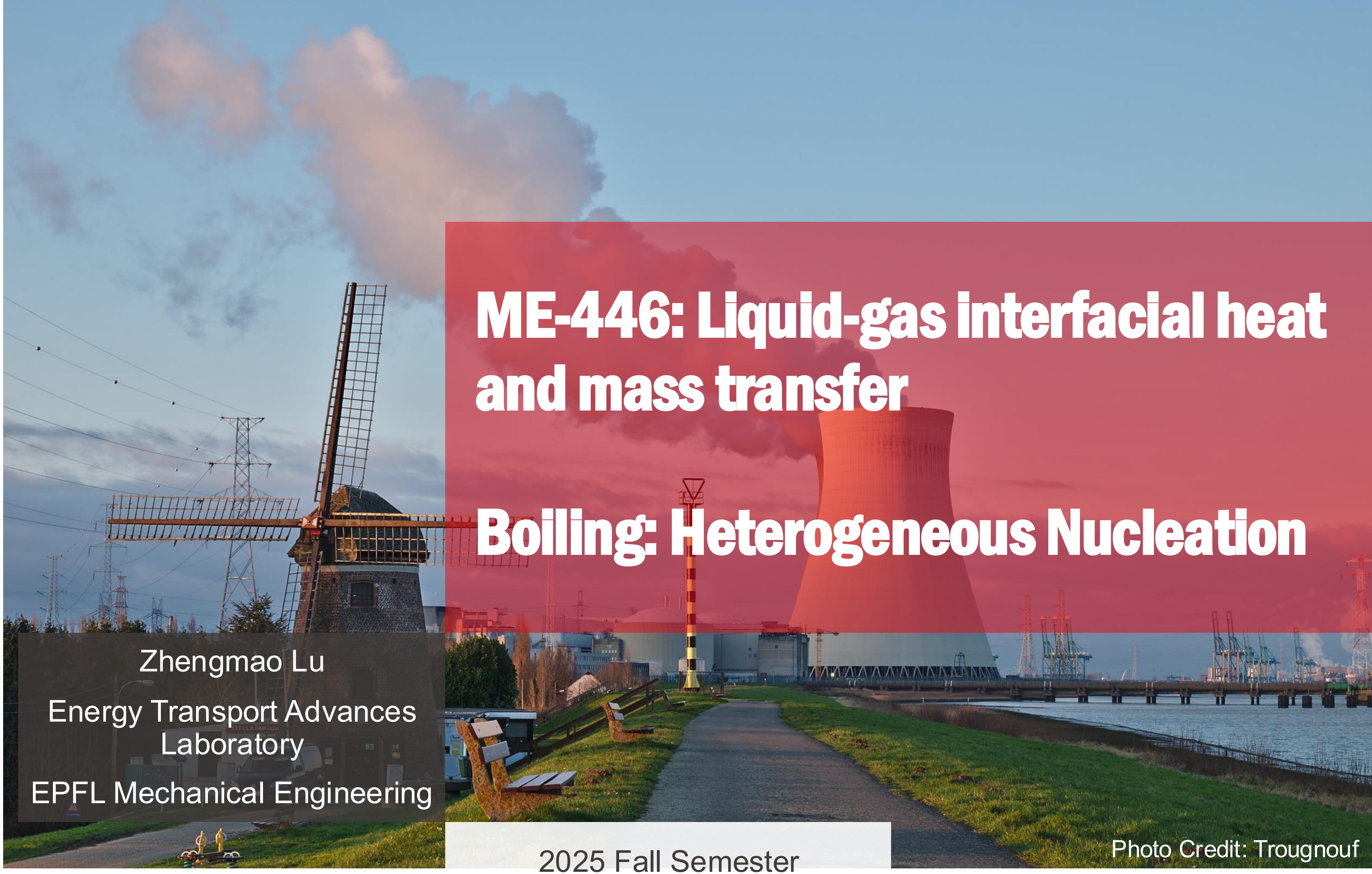


ME-446: Liquid-gas interfacial heat and mass transfer

Boiling: Heterogeneous Nucleation

Zhengmao Lu

Energy Transport Advances Laboratory

EPFL Mechanical Engineering

2025 Fall Semester

Photo Credit: Trougnouf

Last Time

- Analyze the free energy of vapor embryo (Thermodynamics)
- Understand the derivation of bubble growth kinetics and the implication for homogeneous nucleation

Heterogeneous Nucleation

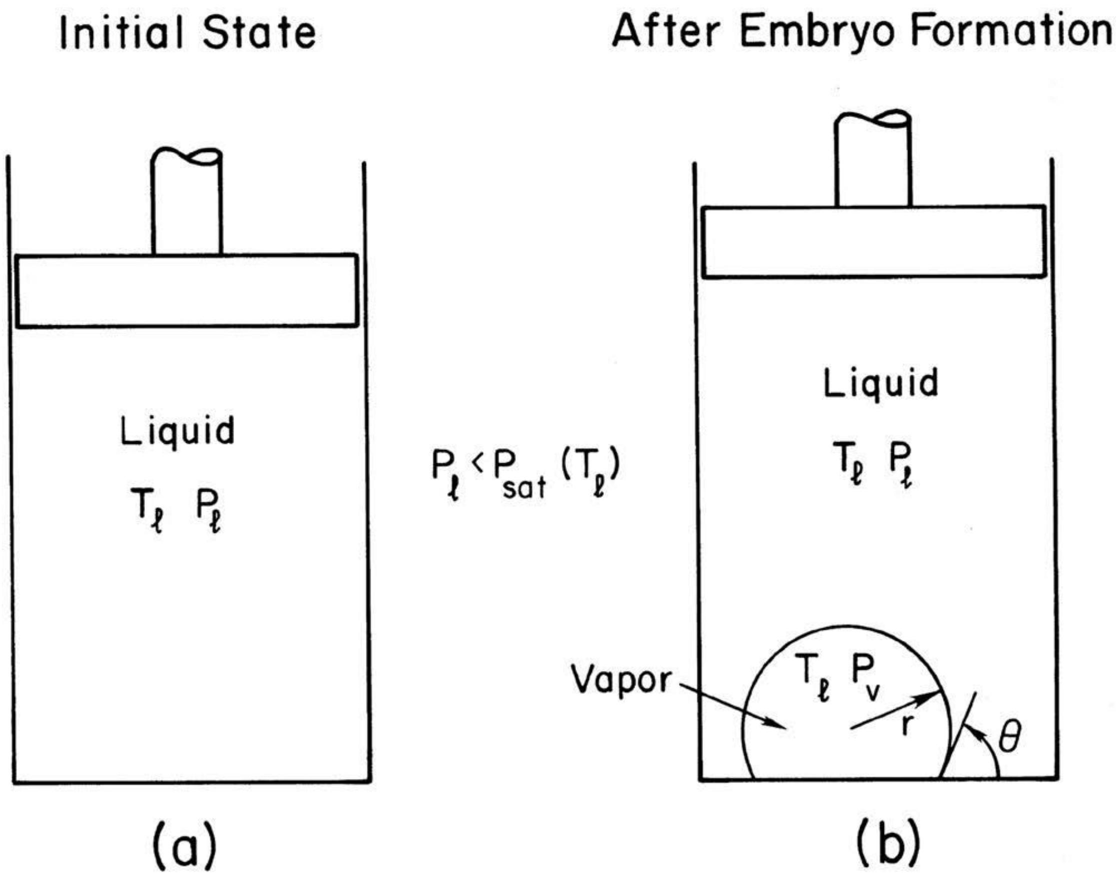


Figure 6.2 in Carey

Constant pressure constant temperature

Gibbs free energy analysis

$$G = G_l + G_v + G_i$$

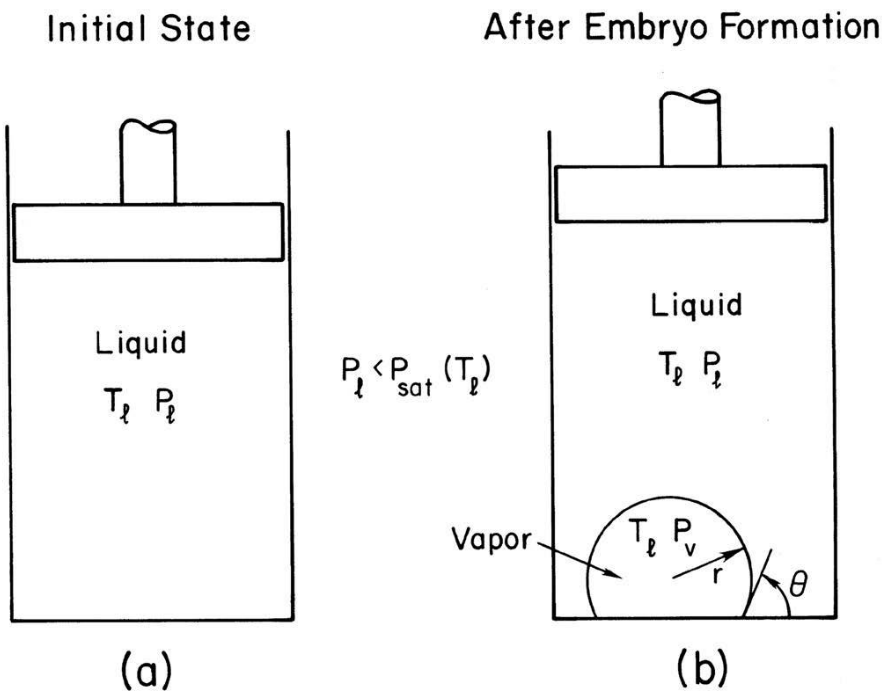
(b) – (a)

$$\Delta G_l = -\widehat{N}_v\, \hat{g}_l$$

$$\Delta G_v = \widehat{N}_v \hat{g}_v + (P_l - P_v)V_v$$

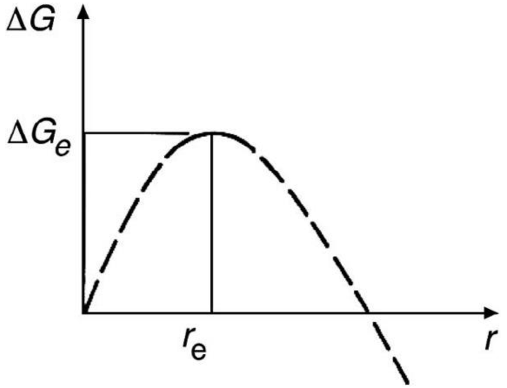
$$\begin{aligned}\Delta G_i &= \sigma_{lv}A_{lv} + \sigma_{sv}A_{sv} - \sigma_{sl}A_{sv} \\ &= \sigma_{lv}A_{lv} + \sigma_{lv}\cos\theta\, A_{sv} \\ &= \sigma_{lv}(A_{lv} + A_{sv}\cos\theta)\end{aligned}$$

Gibbs Free Energy Change



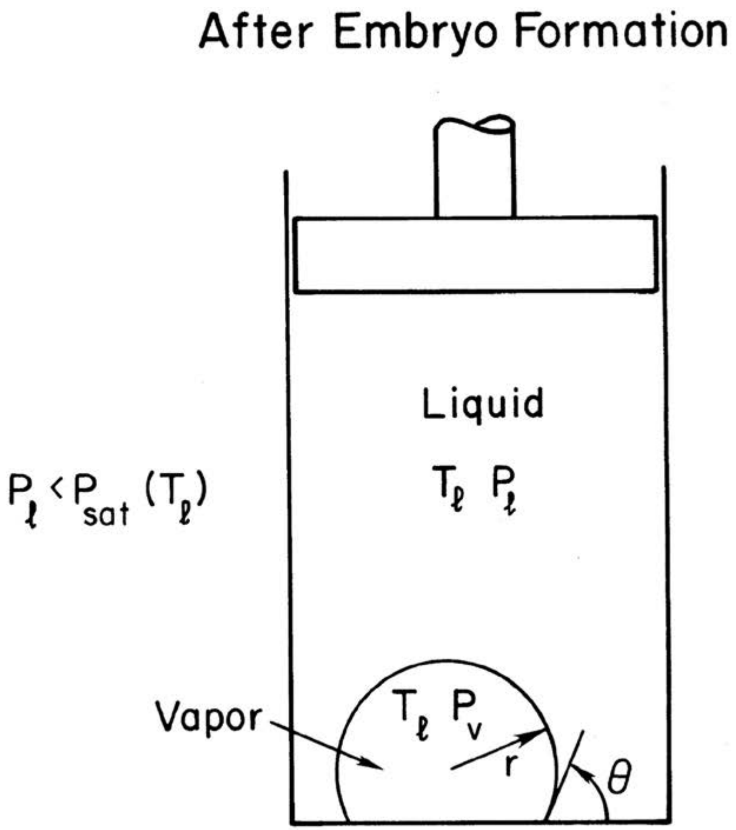
$$\Delta G = \hat{N}_v(\hat{g}_v - \hat{g}_l) + (P_l - P_v)V_v$$
$$+\sigma_{lv}[2\pi r^2(1 + \cos\theta) + \pi r^2 \cos\theta(1 - \cos^2\theta)]$$

$$\Delta G_e = \frac{4}{3}\pi r_e^2 \sigma_{lv}\left[\frac{1}{2} + \frac{3}{4}\cos\theta - \frac{1}{4}\cos^3\theta\right] = \frac{4}{3}\pi r_e^2 \sigma_{lv} F(\theta)$$



$$\Delta G = \Delta G_e - \left(\frac{4\pi\sigma_{lv}F}{3}\right)\left(2 + \frac{P_l}{P_{ve}}\right)(r - r_e)^2 + \cdots$$

Equilibrium Bubble Radius



$$g_{sat,l}(T_l, P_{sat}) = g_{sat,v}(T_l, P_{sat}) = g_{sat}$$

$$dg = vdP - SdT$$

$$g_v - g_{sat} = \int_{P_{sat}}^{P_v} v_v dP = \int_{P_{sat}}^{P_v} \frac{RT_l}{P} dP = RT_l \ln\left(\frac{P_v}{P_{sat}}\right)$$

$$g_l - g_{sat} = \int_{P_{sat}}^{P_l} v_l dP = v_l(P_l - P_{sat})$$

In equilibrium $g_v = g_l$

$$\Rightarrow P_{ve} = P_{sat} \exp\left[\frac{v_l(P_l - P_{sat})}{RT_l}\right]$$

$$r_e = \frac{2\sigma}{P_{ve} - P_l} = \frac{2\sigma}{P_{sat} \exp\left[\frac{v_l(P_l - P_{sat})}{RT_l}\right] - P_l}$$

Physical Meaning of *J*

$$J_n = N_n^* A_n j_{ne} - N_{n+1}^* A_{n+1} j_{(n+1)c}$$

J_n : the rate at which embryo bubbles grow from n to n + 1 molecules per unit volume [$m^{-3}s^{-1}$], which is a constant at a steady state

This includes the rate at which bubbles of the critical size are generated

Higher J implies higher probability of nucleation

Heterogenous Critical Embryo Generation Rate

$$J = \frac{\rho_{N,l}^{\frac{2}{3}}(1+\cos\theta)}{2F}\left(\frac{3F\sigma_{lv}}{\pi m}\right)^{\frac{1}{2}}\exp\left(-\frac{\Delta G_e}{k_B T_l}\right) \qquad [m^{-2}s^{-1}]$$

$\rho_{N,l}^{\frac{2}{3}}$ replaces $\rho_{N,L}$ because we consider nucleation from the surface

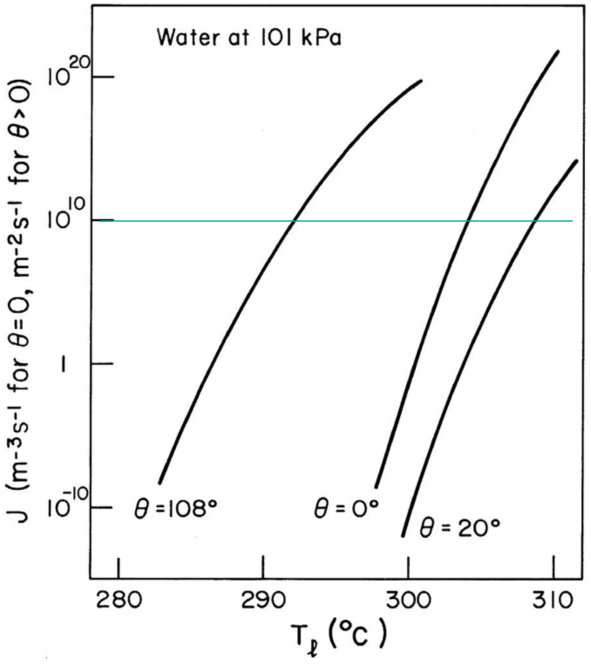


FIGURE 6.3

Given a threshold J (e.g., 10^{10} $m^{-2}s^{-1}$), one can determine the limiting liquid temperature beyond which rapid spontaneous nucleation occurs

This limiting superheat temperature is clearly a function of the contact angle

However, according to this model, heterogeneous nucleation occurs at ~300 ℃ on most common surfaces (**which is not what we observe**)

Intended Learning Objectives Today

- Understand the mechanism for heterogeneous nucleation in practical systems (entrapped gas/vapor theory)
- Understand Hsu's criteria for nucleation site activation
- Analyze the timescales in the bubble cycle to evaluate bubble departure frequency

  - Reading materials: Carey 6.2, 6.3;
    Zhang et al, 2021 (https://doi.org/10.1016/j.ijheatmasstransfer.2020.120640)

Entrapped Gas/Vapor Theory

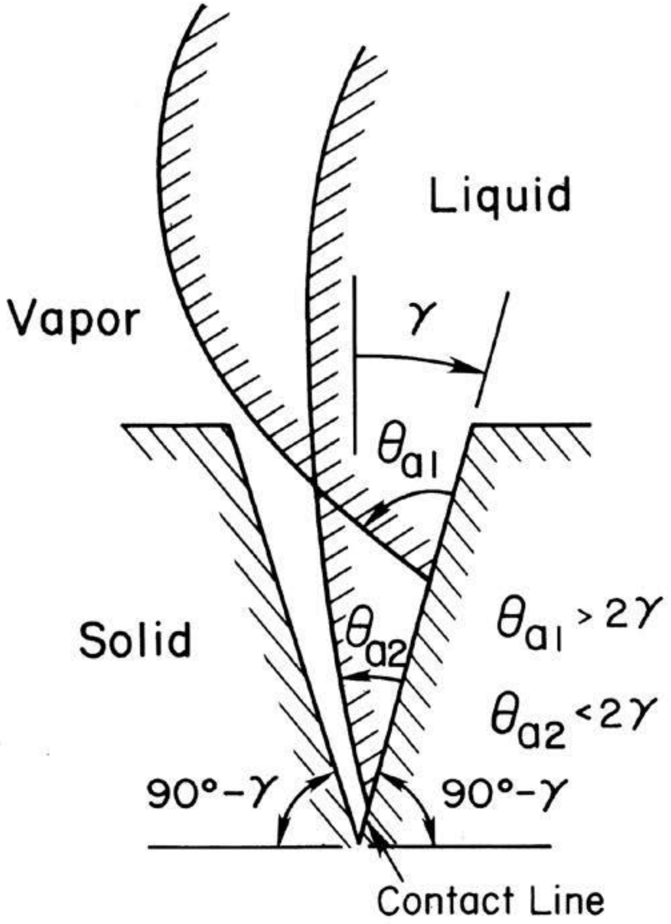


Figure 6.4 in Carey

- Most real solid surfaces contain pits, scratches, or other irregularities
- When liquid passes over a gas-filled groove, advancing CA θ_a is maintained during filling process
- Gas entrapped if $\theta_a > 2\gamma$ ("nose" of liquid striking the opposite wall)
- This initial gas core, entrapped or from outgassing of heated liquid, can facilitate nucleation

Entrapped Gas/Vapor Theory

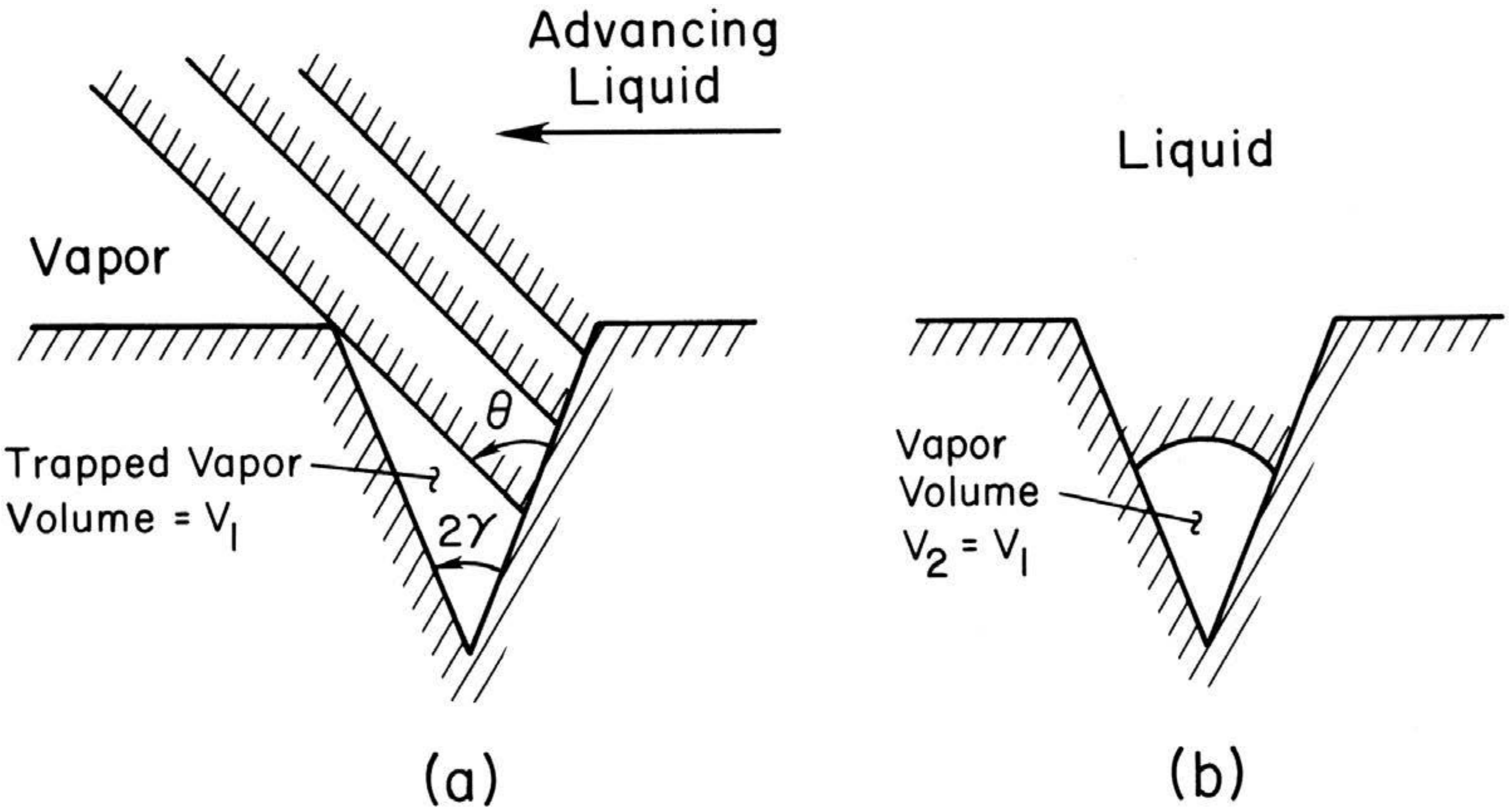


FIGURE 6.7

Entrapped Gas/Vapor Theory

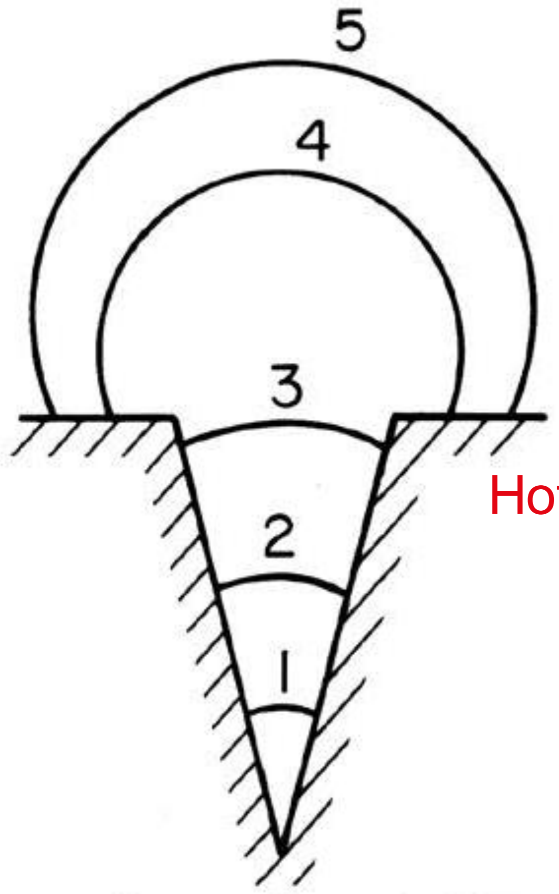
- Clear correlation between locations of surface cavities and and those of bubble nucleation sites has been documented in literature

- When liquid is pressurized to dissolve entrapped gases before being heated, the required superheat to initiate nucleation is similar to the homogeneous case

- After the initial nucleation, surface cavities can be refilled with vapor to sustain nucleation

- During boiling, bubbles released from surface cavities carry away entrapped gases; when the system is subsequently cooled down, the cavities may no longer contain entrapped gas

Criteria for Nucleation Site Activation



- Whether bubble can grow out of the cavity overcoming capillary pressure?
- Whether bubble can keep growing as it gets closer to the bulk fluid which is colder than the heated wall

Hsu's Model

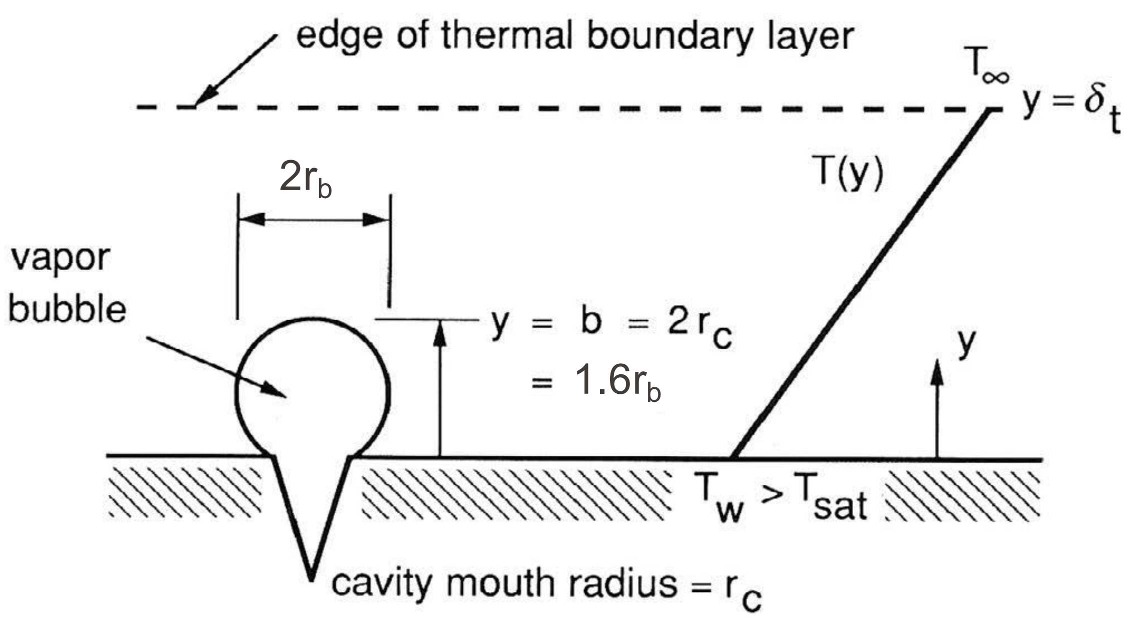


Figure 6.11 in Carey

A thermal boundary layer of fixed thickness δ_t is assumed to be adjacent to the wall

Hsu postulated the height of the embryo bubble b, the bubble radius r_b and the cavity mouth radius r_c follow

$$b = 2r_c = 1.6r_b$$

Not quite justified, should be seen as order of magnitude estimation

Hsu's Model

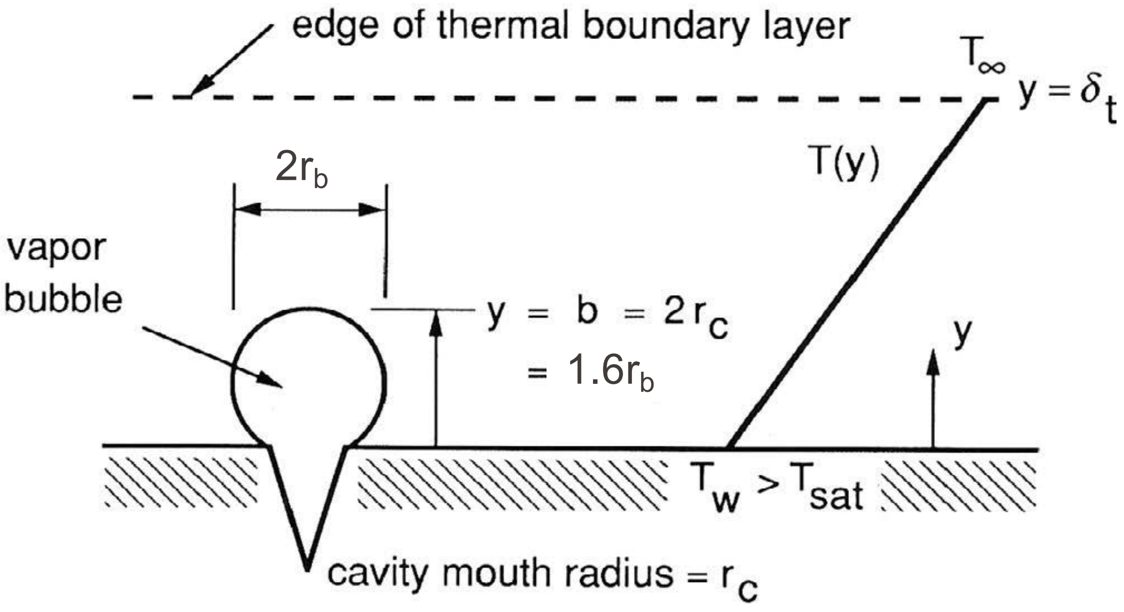


Figure 6.11 in Carey

$$\frac{\partial T}{\partial t} = \alpha_l \left(\frac{\partial^2 T}{\partial y^2} \right)$$

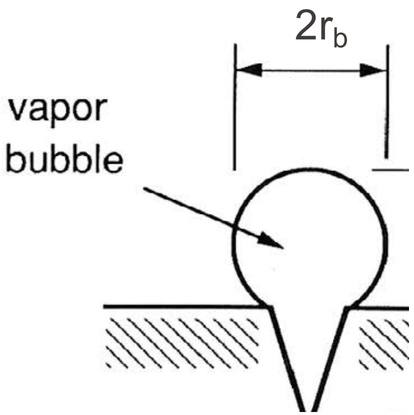
Steady-state temperature profile in the thermal boundary layer is linear

Coldest point on bubble surface at y = b

$$T_{top} = T_\infty + (T_w - T_\infty)\left(1 - \frac{b}{\delta_t}\right)$$

What is the required equilibrium temperature given a bubble size?

Clausius-Clapeyron Relation



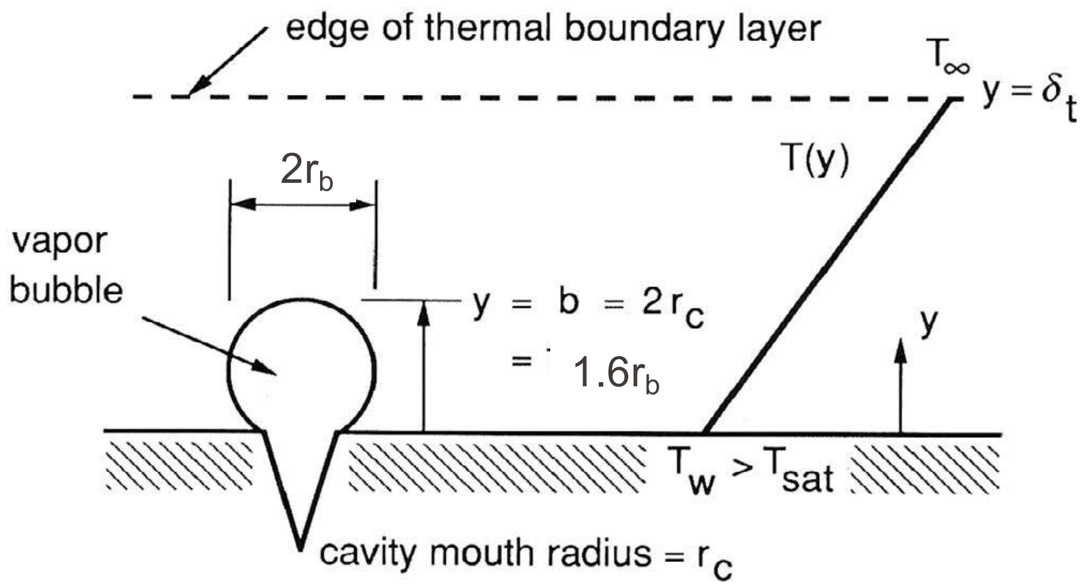
Along the liquid-vapor saturation curve

$$\frac{dP}{dT} = \frac{h_{lv}}{T(v_v - v_l)} \approx \frac{h_{lv}}{Tv_v} = \frac{\rho_v h_{lv}}{T}$$

$$P_{sat}(T_{le}) - P_l = P_{sat}(T_{le}) - P_{sat}\big(T_{sat}(P_l)\big) \approx \frac{\rho_v h_{lv}}{T_{sat}(P_l)}(T_{le} - T_{sat}(P_l))$$

$$P_{sat}(T_{le}) - P_l = \frac{2\sigma}{r_b} \qquad \Rightarrow T_{le} = T_{sat}(P_l) + \frac{2\sigma T_{sat}(P_l)}{\rho_v h_{lv} r_b}$$

Bubble Nucleation Criteria



$$T_{top} = T_\infty + (T_w - T_\infty)\left(1 - \frac{b}{\delta_t}\right)$$

$$T_{le} = T_{sat}(P_l) + \frac{2\sigma T_{sat}(P_l)}{\rho_v h_{lv} r_b}$$

$T_{top} > T_{le} \Rightarrow$ Eq. (6.47) in Carey

Bubble Nucleation Criteria

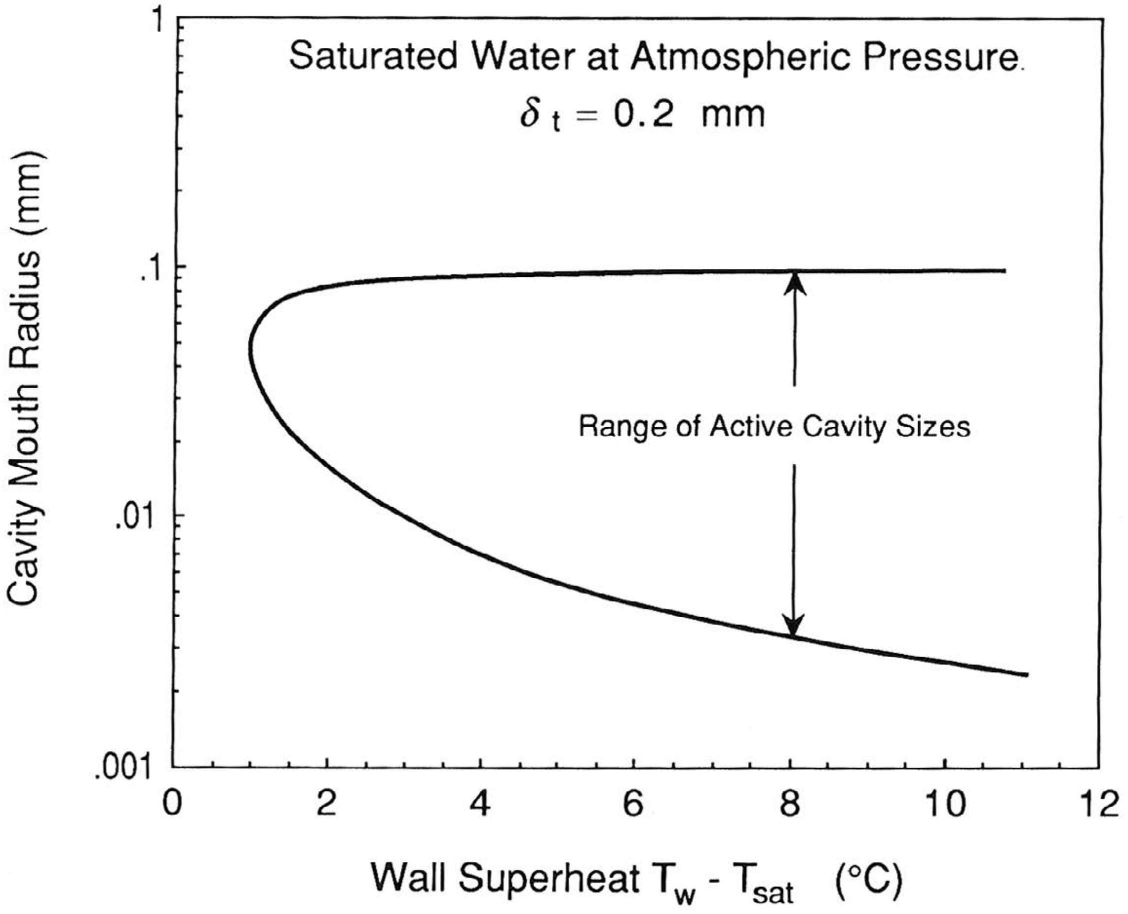
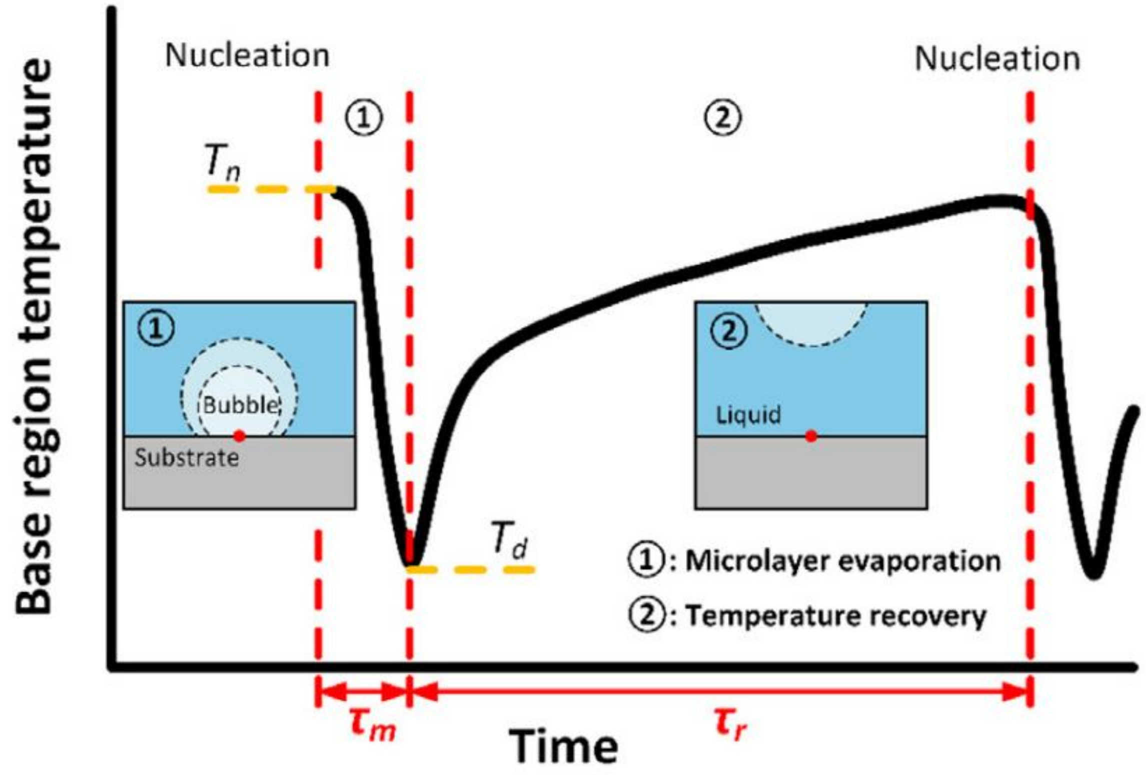


Figure 6.13 in Carey

- If the bubble is too small, the Laplace pressure will be too large for nucleation to occur
- If the bubble is too large, the top of the bubble may be surrounded by liquid of not-high-enough temperature

Beyond Nucleation

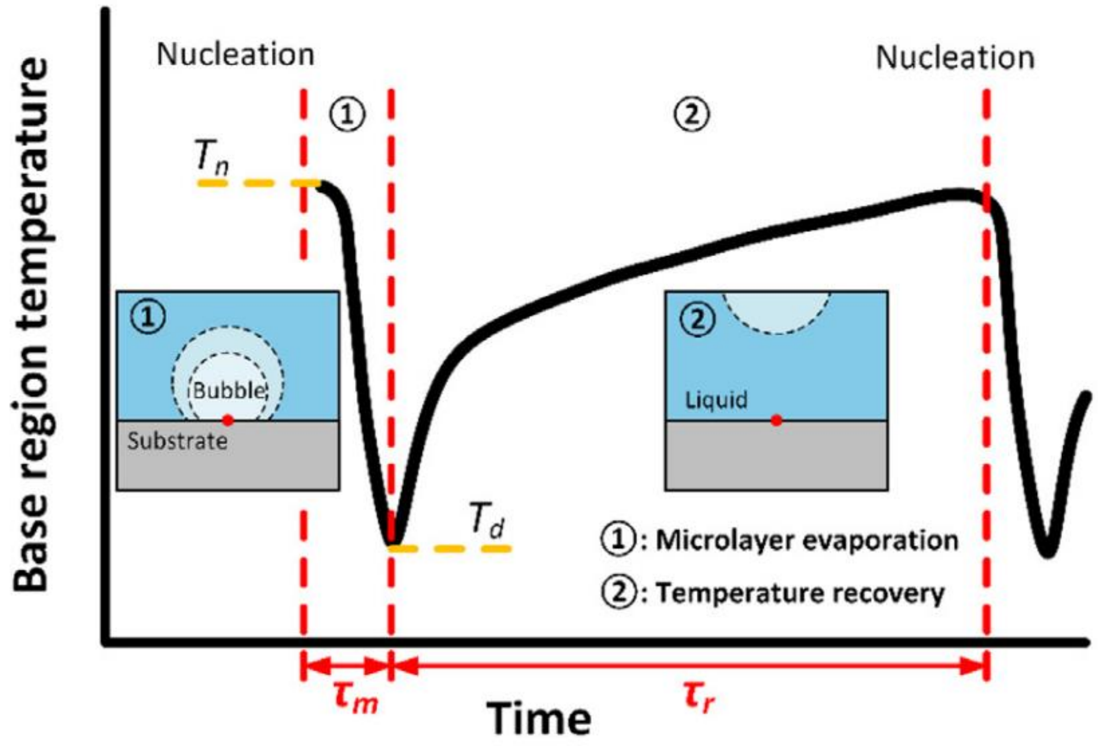


Zhang *et al.*, 2021

https://doi.org/10.1016/j.ijheatmasstransfer.2020.120640

- Right after nucleation, substrate temperature drops due to rapid evaporation
- After bubble departure, the substrate needs to be reheated through convection and conduction to reach nucleation temperature again

Timescale Analysis



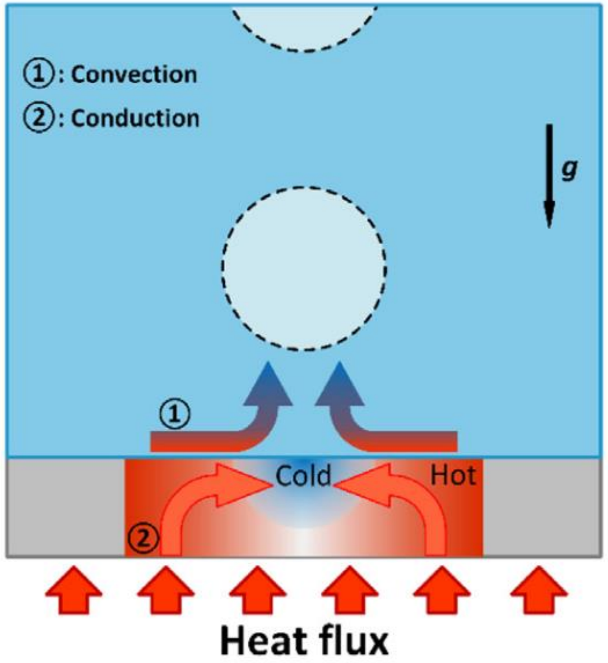
We are interested in bubble **departure frequency** and **departure size**

In isolated bubble regime, evaporation (cooling) much faster than temperature recovery (heating)

$\tau_m \ll \tau_r$

Bubble departure frequency $f = \frac{1}{\tau_m + \tau_r} \approx \frac{1}{\tau_r}$

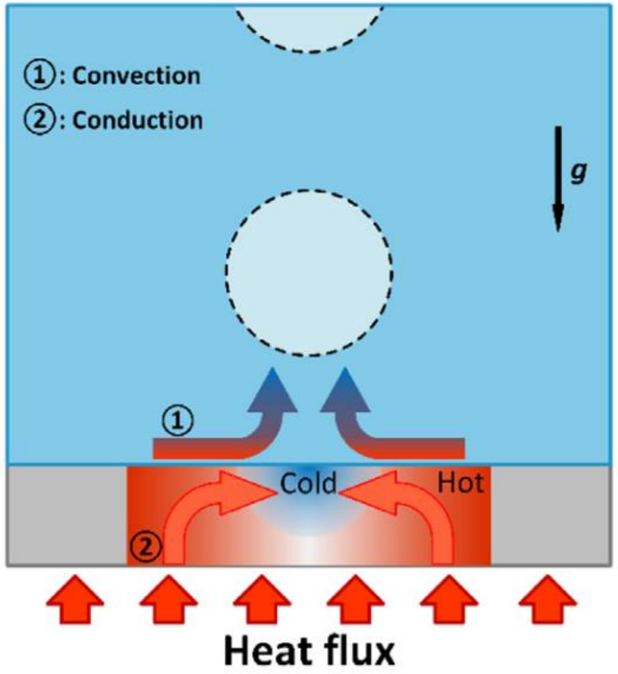
Temperature Recovery Mechanism



① Rewetting of surrounding superheated liquid

② Heat conduction from surrounding solid region

Timescale Analysis



① Rewetting of surrounding superheated liquid

Transient heat conduction of a semi-infinite wall with a convective boundary condition

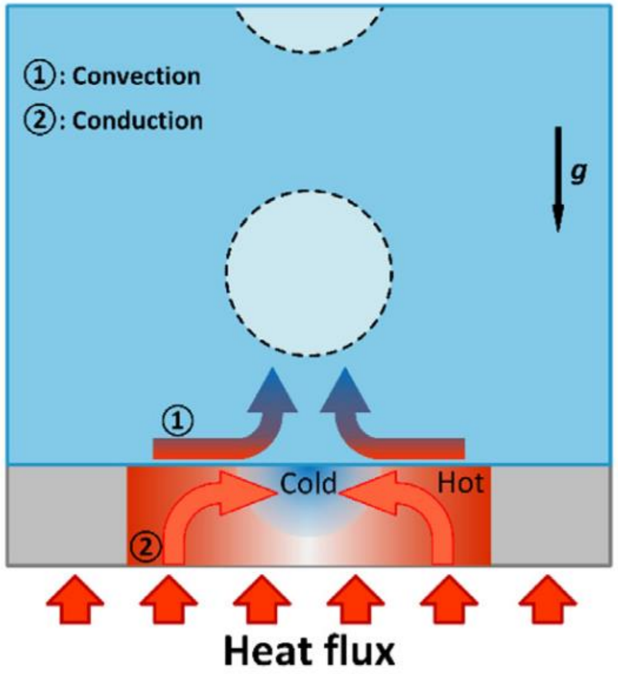
$$\frac{T_b(t) - T_d}{T_n - T_d} = 1 - e^{\frac{t}{\tau_w}}\left[1 - \mathrm{erf}\left(\sqrt{\frac{t}{\tau_w}}\right)\right]$$

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-x^2}\,dx$$

$$\tau_w = \frac{k_s^2}{h^2 \alpha_s}$$

Characteristic time for rewetting induced convection

Timescale Analysis



① Rewetting of surrounding superheated liquid

$$\tau_w = \frac{k_s^2}{h^2 \alpha_s}$$

How to determine *h*

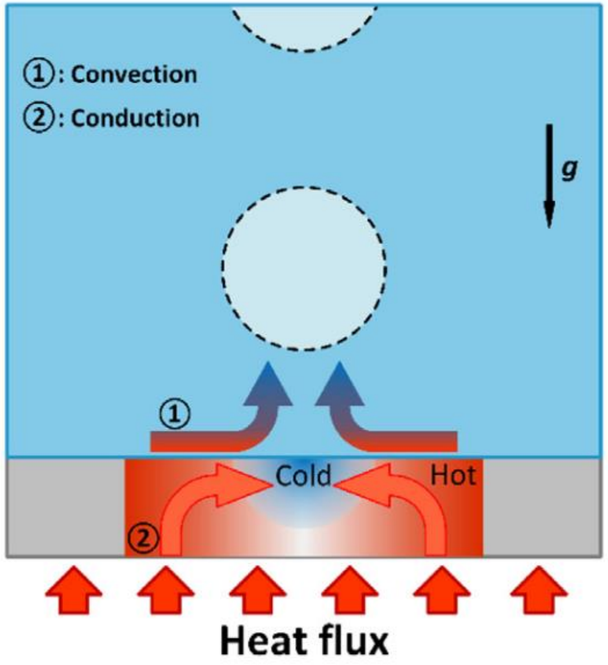
Rewetting flow is caused by density difference

$$\mathrm{Ra} = \frac{g \Delta\rho D^3}{\mu_l \alpha_l} \approx \frac{g D^3}{\nu_l \alpha_l}$$

$$\frac{hD}{k_l} = \mathrm{Nu} \propto \mathrm{Ra}^{1/4}$$

$$\tau_w \propto \frac{k_s^2}{k_l^2} \left(\frac{\nu_l \alpha_l}{g}\right)^{\frac{1}{2}} \alpha_s^{-1} D^{\frac{1}{2}}$$

Timescale Analysis

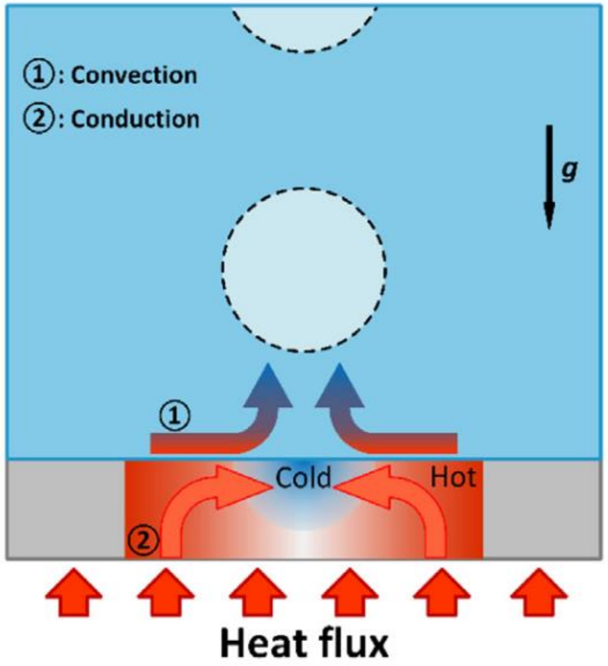


② Heat conduction from surrounding solid region

Characteristic timescale $\tau_d \propto \frac{D^2}{\alpha_s}$

$$\Rightarrow \frac{\tau_d}{\tau_w} \sim D^{1.5}$$

Timescale Analysis



- Rewetting and heat conduction are two competing mechanisms for temperature recovery

$$\frac{\tau_d}{\tau_w} \sim D^{1.5}$$

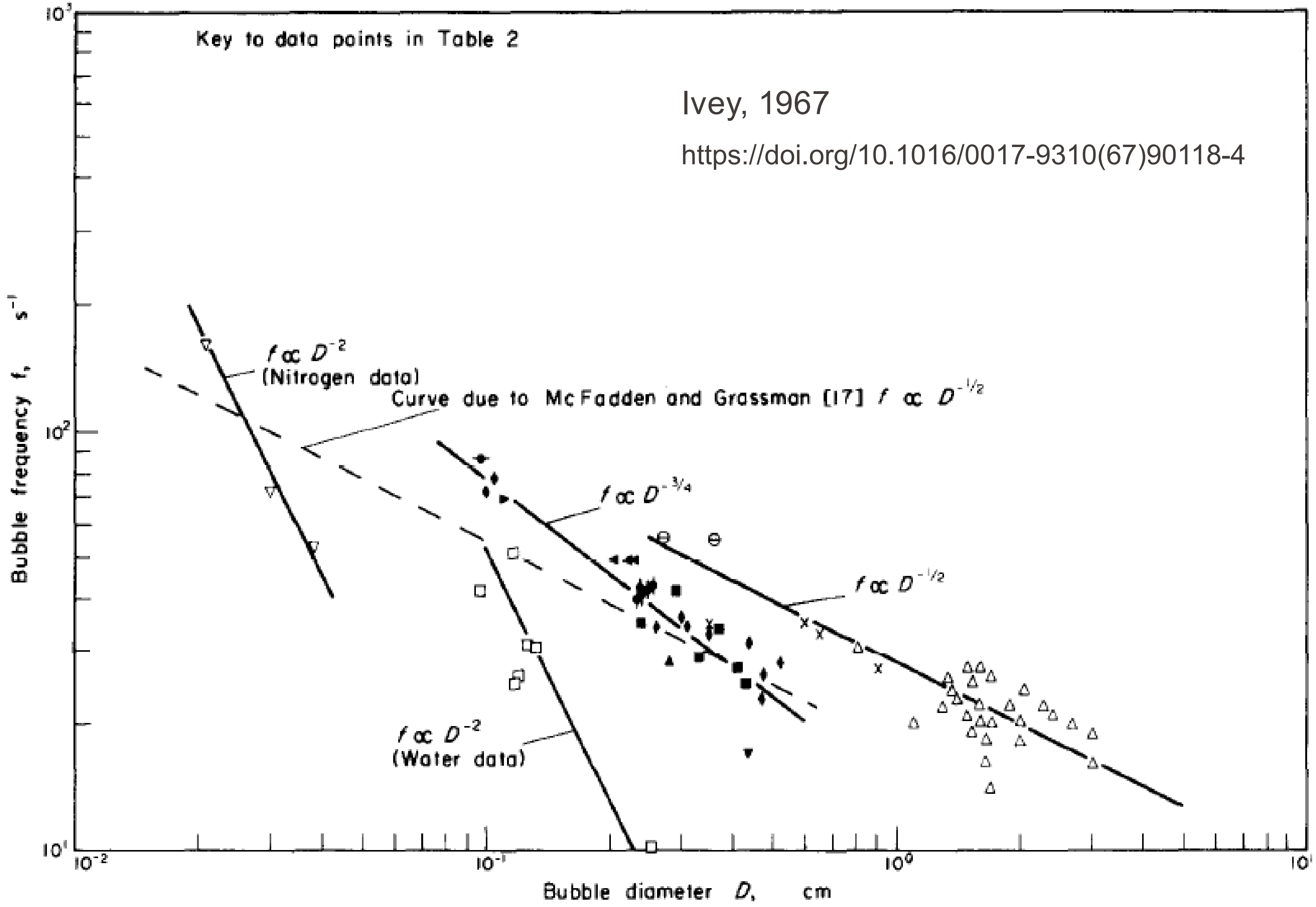
When *D* is relatively large, rewetting-induced convection dominates

$$f = \frac{1}{\tau_w} \sim g^{0.5} D^{-0.5}$$

When *D* is relatively small, conduction dominates

$$f = \frac{1}{\tau_d} \sim D^{-2}$$

Comparison to Experiments



Ivey, 1967

https://doi.org/10.1016/0017-9310(67)90118-4