EPFL

ETA-Lab
Energy Transport Advances

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

Boiling II

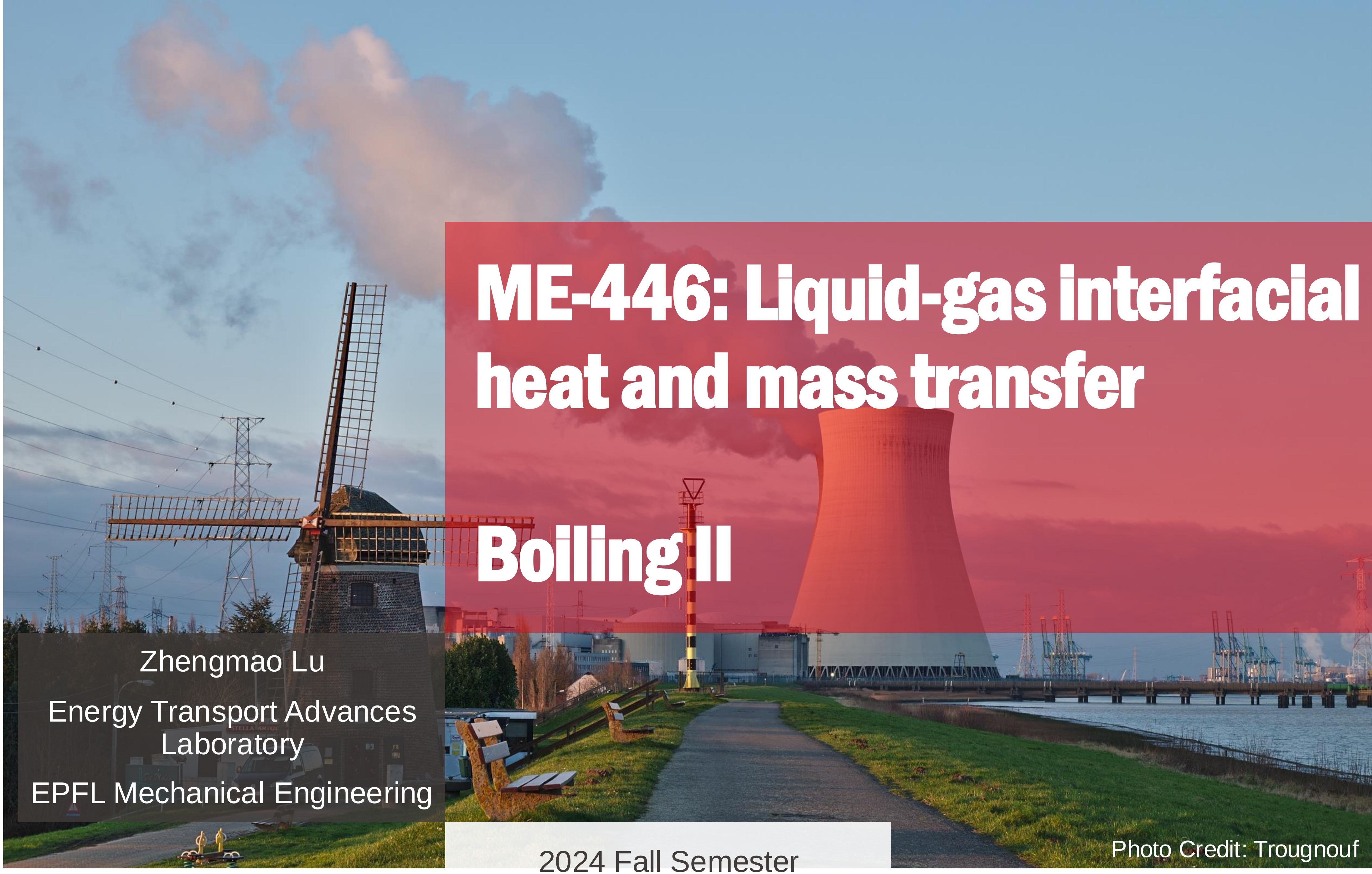

Photo Credit: Trougnouf

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2024 Fall Semester

Last Time

- Analyze the free energy of vapor embryo (Thermodynamics)
- Understand the derivation of bubble growth kinetics at small sizes

Gibbs Free Energy Barrier

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

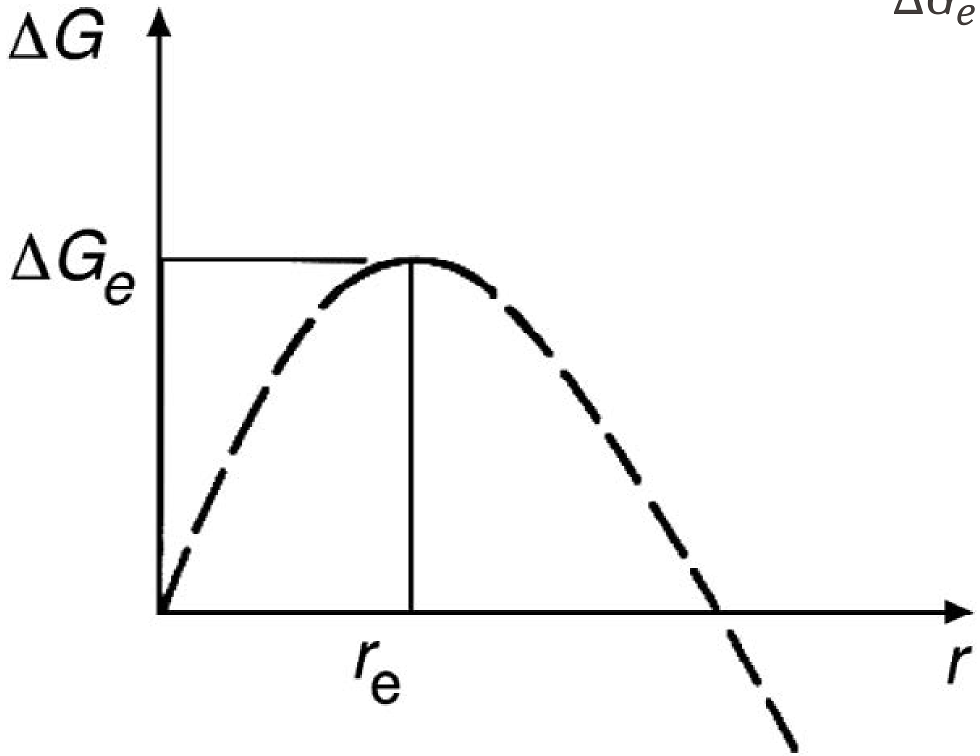


Figure 5.9 in Carey

When $\theta = 180°$, $F(\theta) = 0$

When $\theta = 90°$, $F(\theta) = \frac{1}{2}$

When $\theta = 0°$, $F(\theta) = 1$

Same as homogeneous nucleation

Embryo Size Distribution

Let's assume the number of embryos consisting of n molecules per unit volume N_n follows

$$N_n = \rho_{N,l} \exp\left[-\frac{\Delta G(r)}{k_B T_l}\right]$$

$\rho_{N,L}$ can be understood as the number of liquid molecules per unit volume ($\Delta G = 0$ corresponds to the liquid phase)

For an embryo of size n, define j_{ne} as the evaporating molecular flux and j_{nc} as the condensing molecular flux [m^{-2}s^{-1}]

For equilibrium distribution of N_n

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

A_n and A_{n+1} are the interfacial areas of n and n+1 molecule embryos, respectively

Embryo Size Distribution

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

The rate at which n molecule embryos → n+1 molecule embryos through evaporation is the same as n+1 molecule embryos → n molecule embryos through condensation
No net exchange between two size groups

In superheated liquid, equilibrium is not necessarily satisfied

Consider the excess rate of n molecule embryos → n+1 molecule

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

$$J_n = N_n A_n j_{ne} \left(\frac{N_n^*}{N_n} - \frac{N_{n+1}^*}{N_{n+1}} \right) = -N_n A_n j_{ne} \frac{\partial \left(\frac{N^*}{N} \right)}{\partial n}$$

Treating n as a continuous variable

Embryo Size Distribution

$$\frac{\partial N_n^*}{\partial t} = J_{n-1} - J_n$$

$$J_n = -N_n A_n j_{ne} \frac{\partial \left(\frac{N^*}{N}\right)}{\partial n}$$

Assuming a steady non-equilibrium condition $\frac{\partial N_n^*}{\partial t} = 0$

$\frac{\partial N_n^*}{\partial t} = 0 \Rightarrow J = \mathrm{const}$ Steady stream of embryos growing progressively in size

Embryo Size Distribution

Consider the case where no embryos have *r* > r_e

$N_n^* \to 0$ as $n \to n_e$ $\quad n_e \hat{v}_v = \frac{4}{3}\pi r_e^3$

when *r* > r_e, bubbles grow spontaneously

For very small bubbles, phase change barely occurs, so things are near-equilibrium

$N^*/N \to 1$ as $n \to 0$

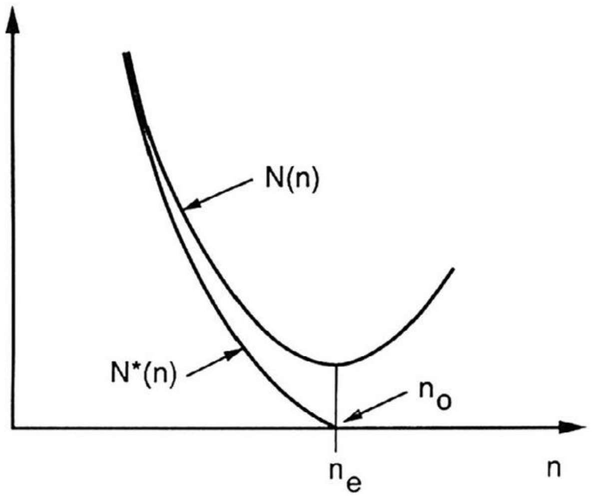


FIGURE 5.10 Carey

Embryo Size Distribution

$$J = -N_n A_n j_{ne} \frac{\partial \left(\frac{N^*}{N}\right)}{\partial n}$$

$$\frac{\partial}{\partial n}\left(\frac{N^*(n)}{N(n)}\right) = -J[N(n)A(n)j_e(n)]^{-1}$$

$$\frac{N^*(n)}{N(n)} = -J\int_{n_e}^{n}[N(n')A(n')j_e(n')]^{-1}\,dn'$$

$N^*/N \rightarrow 0$ as $n \rightarrow n_e$

$$J = \frac{N^*(n)}{N(n)}\left(\int_{n}^{n_e}[N(n')A(n')j_e(n')]^{-1}\,dn'\right)^{-1}$$

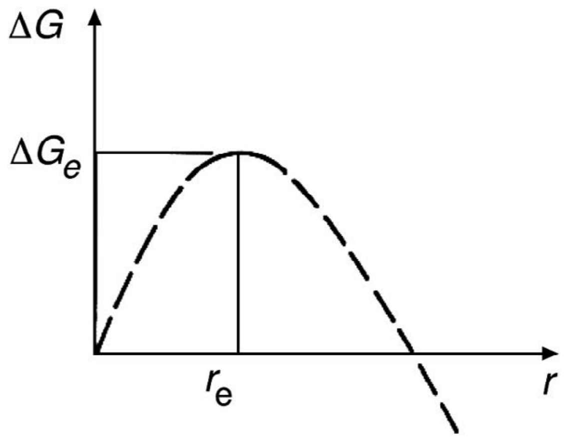
True for any n

$$J = \left(\int_{0}^{n_e}[N(n)A(n)j_e(n)]^{-1}\,dn\right)^{-1}$$

$N^*/N \rightarrow 1$ as $n \rightarrow 0$

Embryo Size Distribution

$$J = \left(\int_0^{n_e} [N(n)A(n)j_e(n)]^{-1}\, dn \right)^{-1}$$



$$N(n) = \rho_{N,l} \exp\left[-\frac{\Delta G(r)}{k_B T_l} \right]$$ has a sharp minimum at r_e or n_e

$[N(n)A(n)j_e(n)]^{-1}$ is only significantly greater than zero near n = n_e

Therefore, we approximate $j_e(n) = j_e(n_e) = \frac{P_{ve}}{\sqrt{2\pi m k_B T_l}}$ One-way M-B flux from last week

$$J \approx \frac{P_{ve}}{\sqrt{2\pi m k_B T_l}} \left(\int_0^{n_e} [N(n)A(n)]^{-1}\, dn \right)^{-1} \approx \frac{P_{ve}}{\sqrt{2\pi m k_B T_l}} \left(\int_0^{\infty} [N(n)A(n)]^{-1}\, dn \right)^{-1}$$

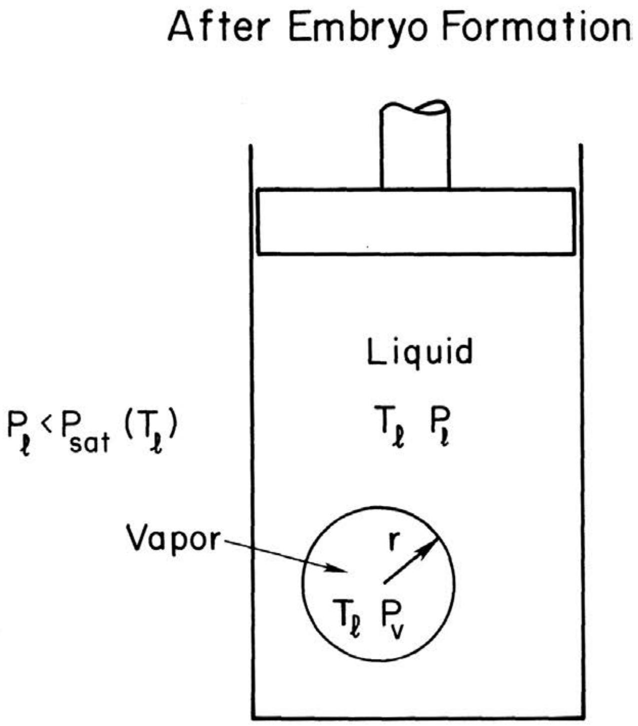
Embryo Size Distribution

$$J \approx \frac{P_{ve}}{\sqrt{2\pi m k_B T_l}} \left(\int_0^{\infty} [N(n)A(n)]^{-1}\, dn \right)^{-1}$$

$$N(n) = \rho_{N,l} \exp\left[-\frac{\Delta G(r)}{k_B T_l} \right] \qquad A(n) = 4\pi r^2$$

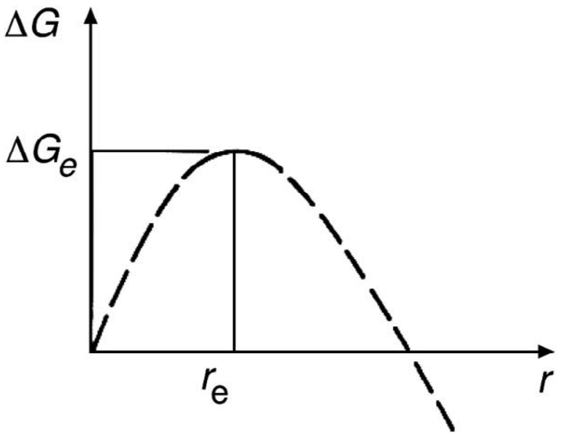
$$n\hat{v}_v = \frac{4}{3}\pi r^3 \qquad \frac{dn}{dr} = \frac{4}{3}\pi r^2 \left(\frac{P_{ve}}{k_B T_l} \right) \left(2 - \frac{P_l}{P_{ve}} \right) dr$$

$$J \approx \frac{3\rho_{N,l}}{2 - P_l/P_{ve}} \left(\frac{k_B T_l}{2\pi m} \right)^{1/2} \left(\int_0^{\infty} \exp\left[\frac{\Delta G(r)}{k_B T_l} \right] dr \right)^{-1}$$



Embryo Size Distribution

$$J \approx \frac{3\rho_{N,l}}{2 - P_l/P_{ve}} \left(\frac{k_B T_l}{2\pi m}\right)^{1/2} \left(\int_0^\infty \exp\left[\frac{\Delta G(r)}{k_B T_l}\right] dr\right)^{-1}$$



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

For homogeneous case, $$J = \rho_{N,l}\left[\frac{6\sigma_{lv}}{\pi m\left(2 - \frac{P_l}{P_{ve}}\right)}\right]^{1/2} \exp\left(-\frac{4\pi r_e^2 \sigma_{lv}}{3k_B T_l}\right)$$

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

Physical Meaning of *J*

J represents the rate at which embryo bubbles grow from n to n + 1 molecules per unit volume [$m^{-3}s^{-1}$]

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

Higher J implies higher probability of nucleation

Physical Meaning of J

$$J = \rho_{N,l}\left[\frac{6\sigma_{lv}}{\pi m\left(2-\frac{P_l}{P_{ve}}\right)}\right]^{1/2}\exp\left(-\frac{4\pi r_e^2\sigma_{lv}}{3k_BT_l}\right)$$ increases sharply with temperature

A change of 1°C can change J by as much as three or four orders of magnitude

We expect that there will exist a narrow range of temperature below which homogeneous nucleation does not occur, and above which it occurs almost immediately.

Generation Rate of Bubble of Critical Size

(Homogeneous case)

$$J = \rho_{N,l}\left[\frac{6\sigma_{lv}}{\pi m\left(2-\frac{P_l}{P_{ve}}\right)}\right]^{1/2}\exp\left(-\frac{4\pi r_e^2\sigma_{lv}}{3k_BT_l}\right)$$

increases sharply with temperature

There exists narrow range of temperature below which nucleation does not occur, and above which it occurs almost immediately.

$$10^{12}\ \mathrm{m^{-3}s^{-1}} = 10^{-6}\mu\mathrm{m^{-3}s^{-1}}$$

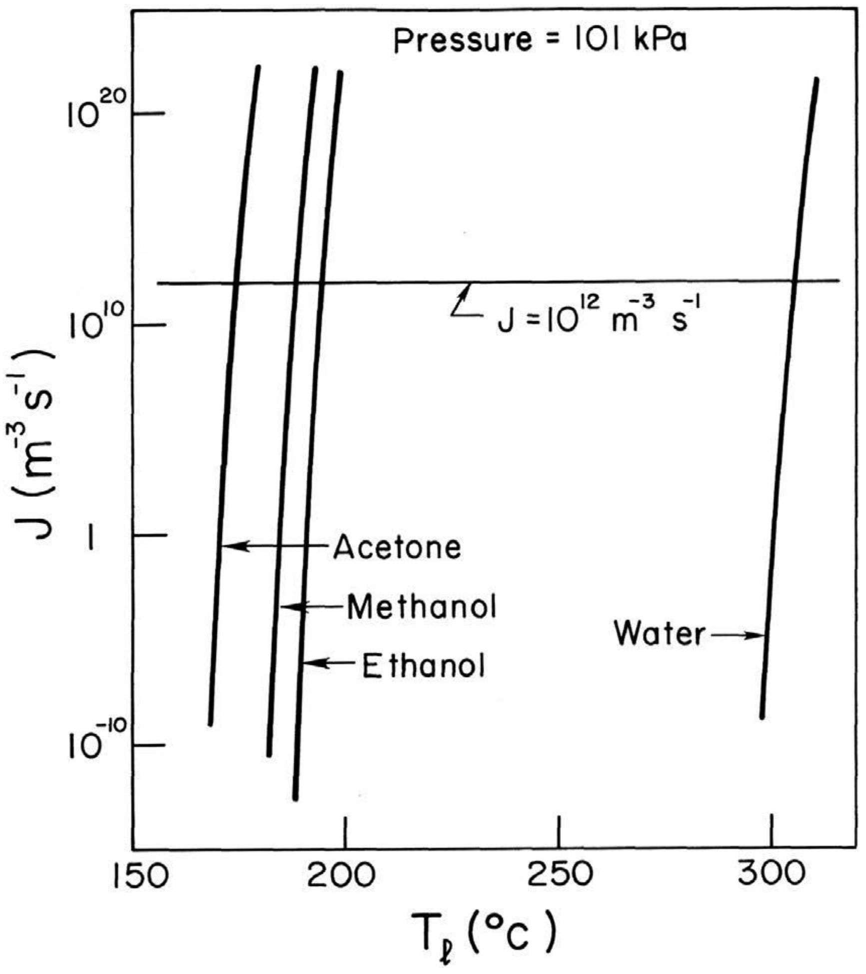


FIGURE 5.12, Carey

Measured Superheat Limit Data

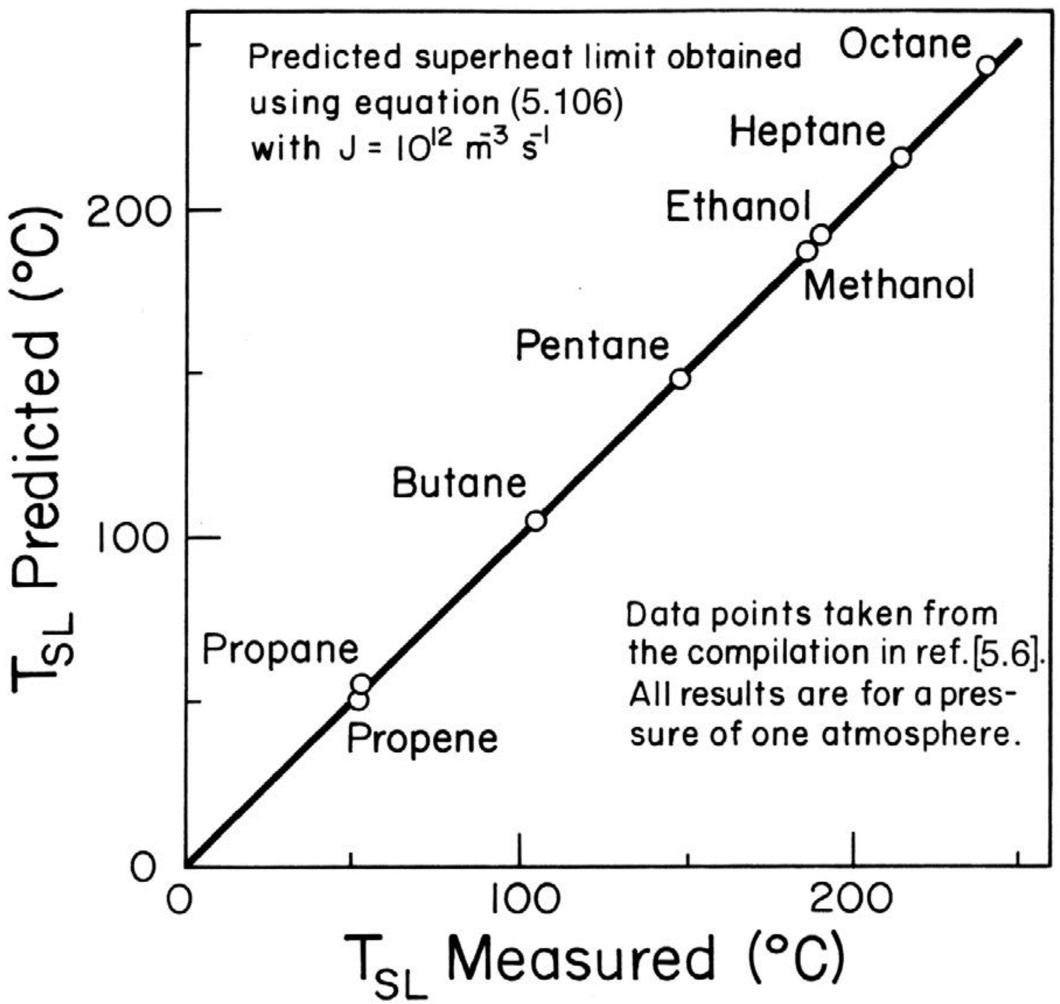


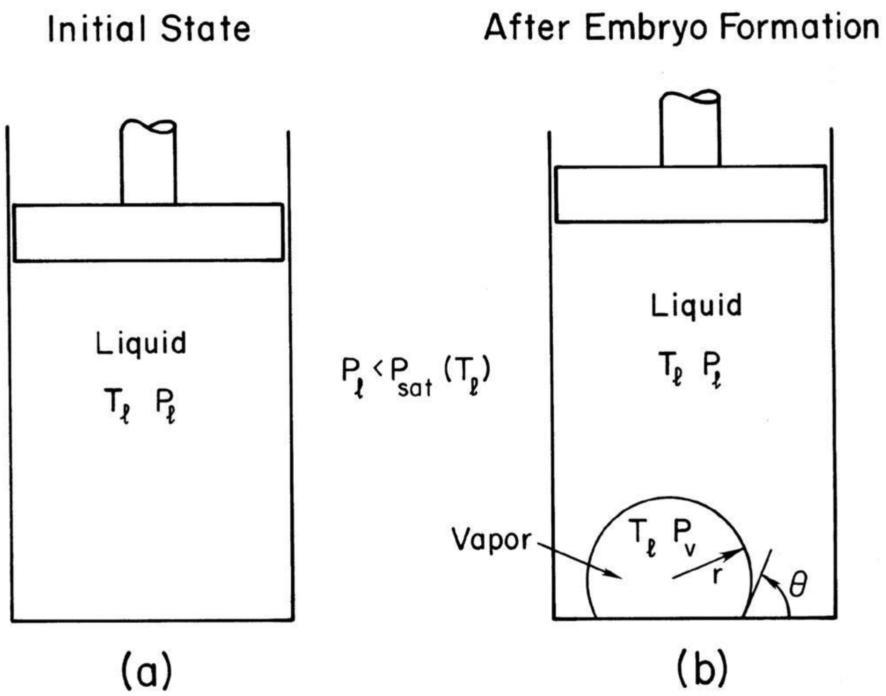
FIGURE 5.13

Great agreement was found for low surface tension liquids

For water, the predicted superheat limit is about 300 ℃ while the measured one is 250-280 ℃

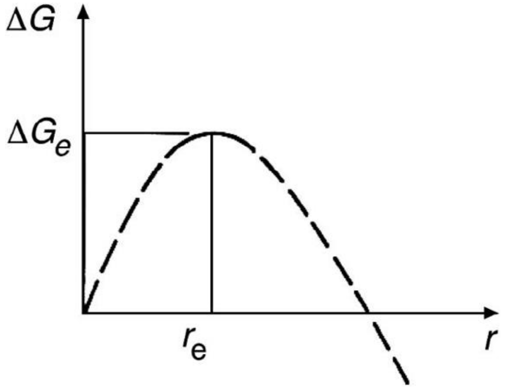
When homogeneous nucleation does occur, vapor is generated at an extremely rapid rate

Heterogeneous Nucleation



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

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



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

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

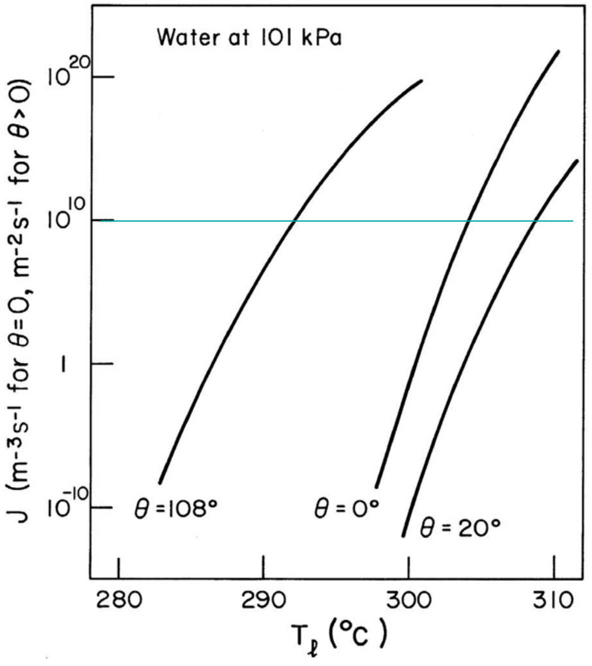


FIGURE 6.3

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

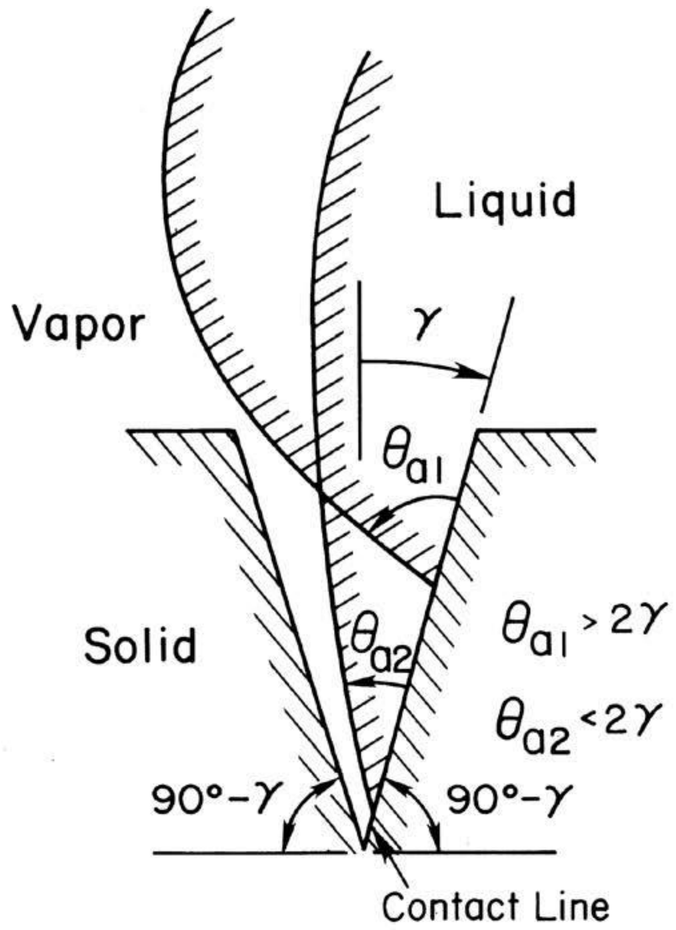


Figure 6.4 in Carey

Most real solid surfaces contain pits, scratches, or other irregularities

When liquid passes over a gas-filled groove, advancing CA θ_a maintained during the 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

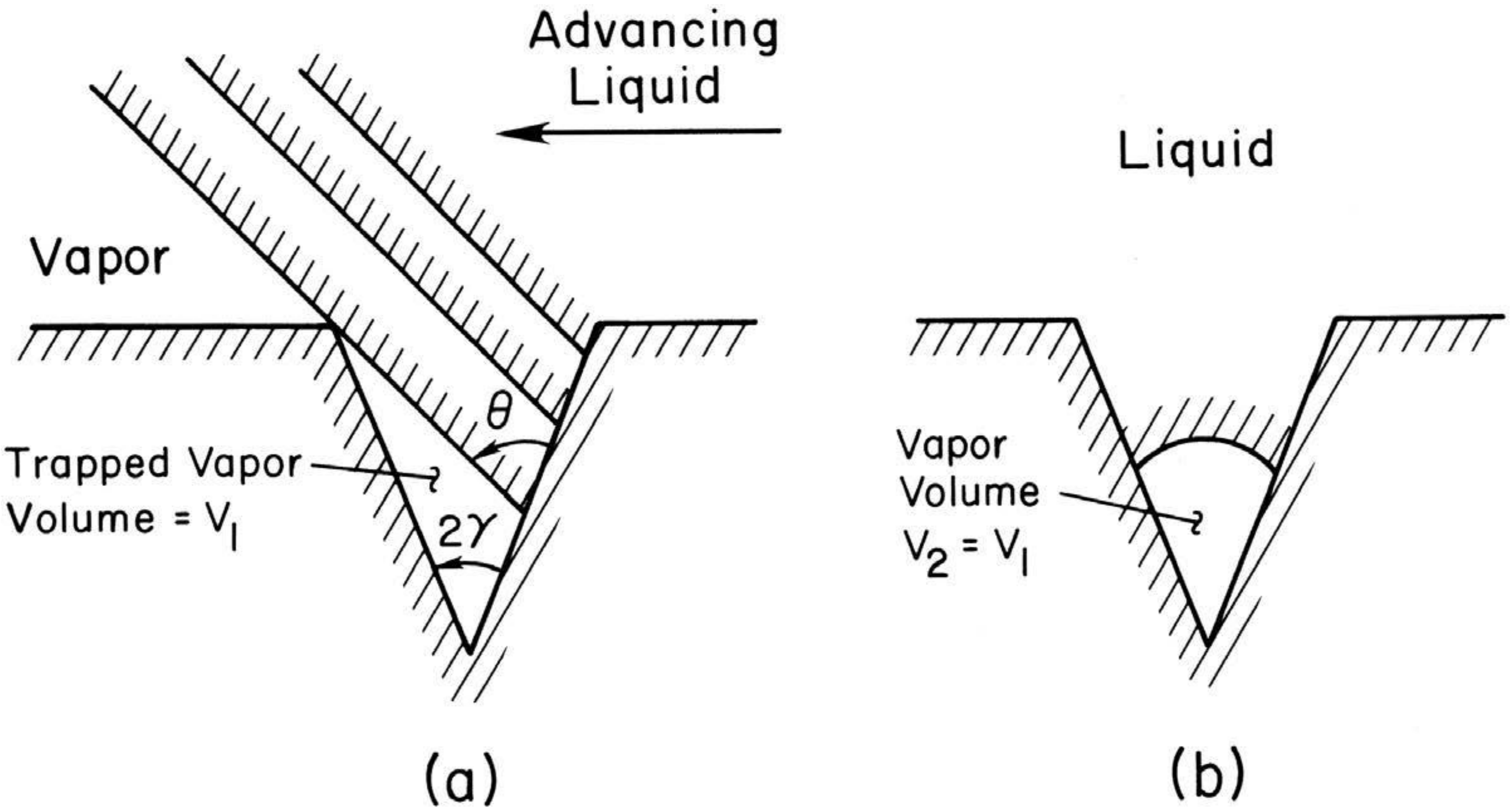


FIGURE 6.7

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 on the same order of the homogeneous case

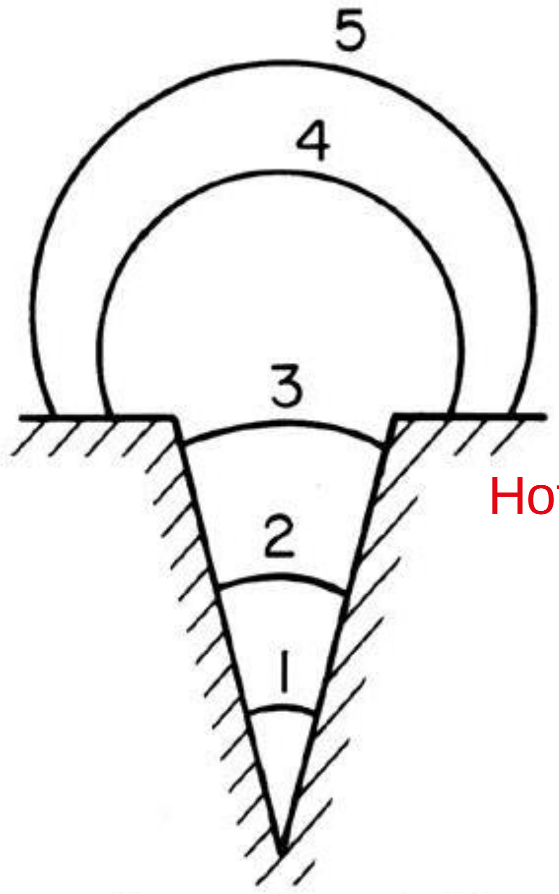
After the initial nucleation, surface cavities can be refilled with vapor to sustain nucleation

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

Not a satisfactory explanation for heterogeneous nucleation of low surface tension liquids

Criteria for Nucleation Site Activation

Colder



Hotter

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

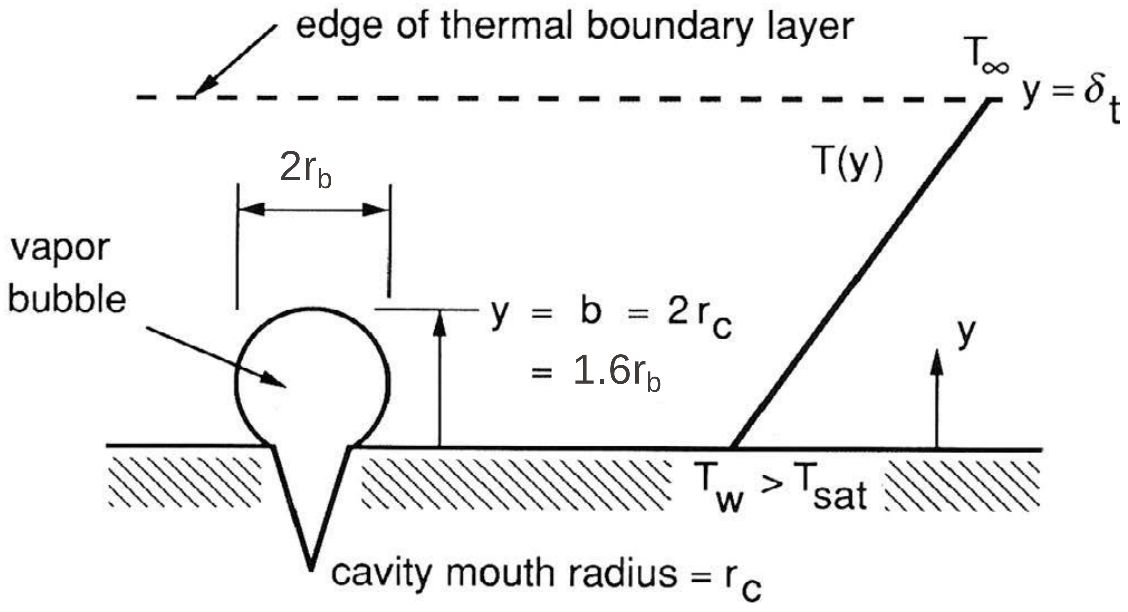


Figure 6.11 in Carey

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

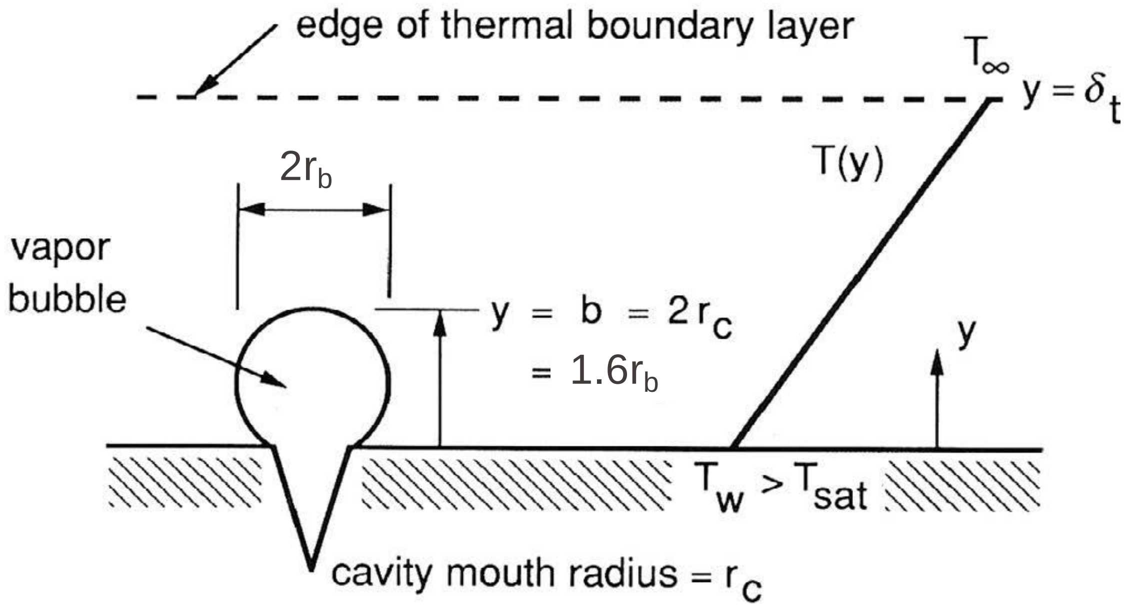


Figure 6.11 in Carey

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

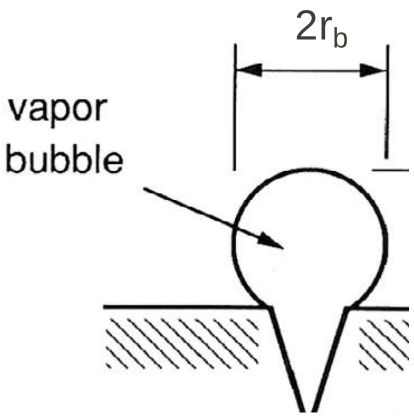
Steady-state temperature profile in the thermal boundary layer is linear

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



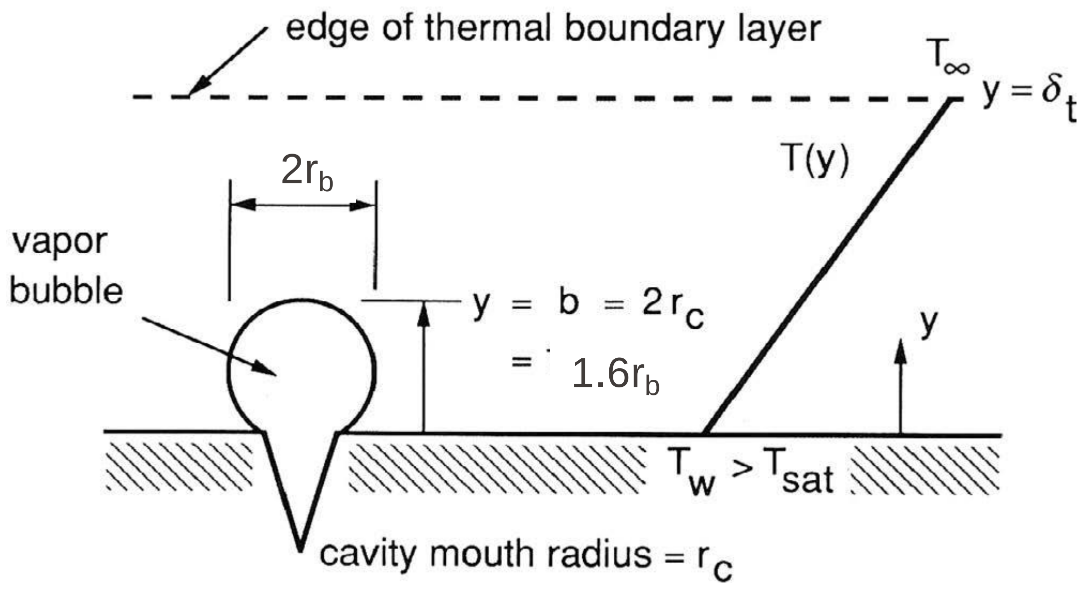
Along the liquid-vapor saturation curve

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

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

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

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

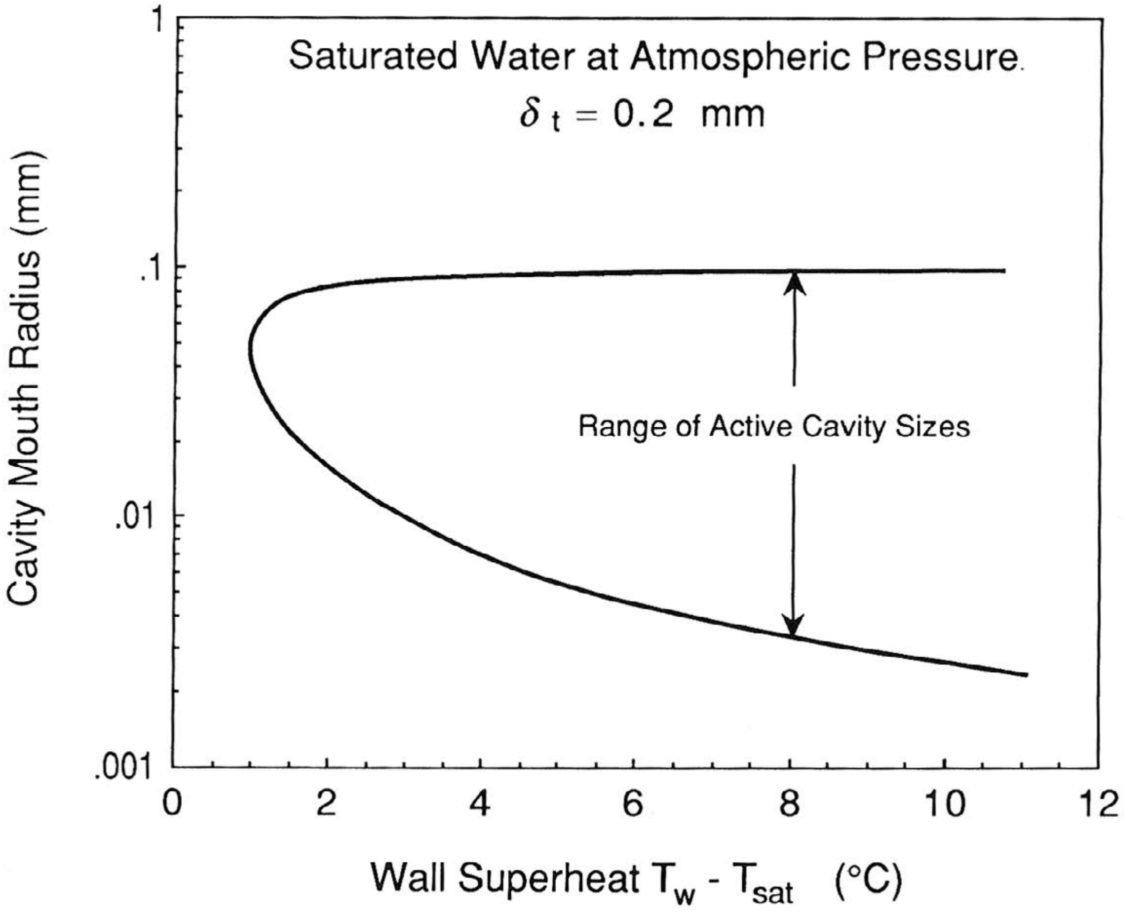


Figure 6.13 in Carey

- 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