

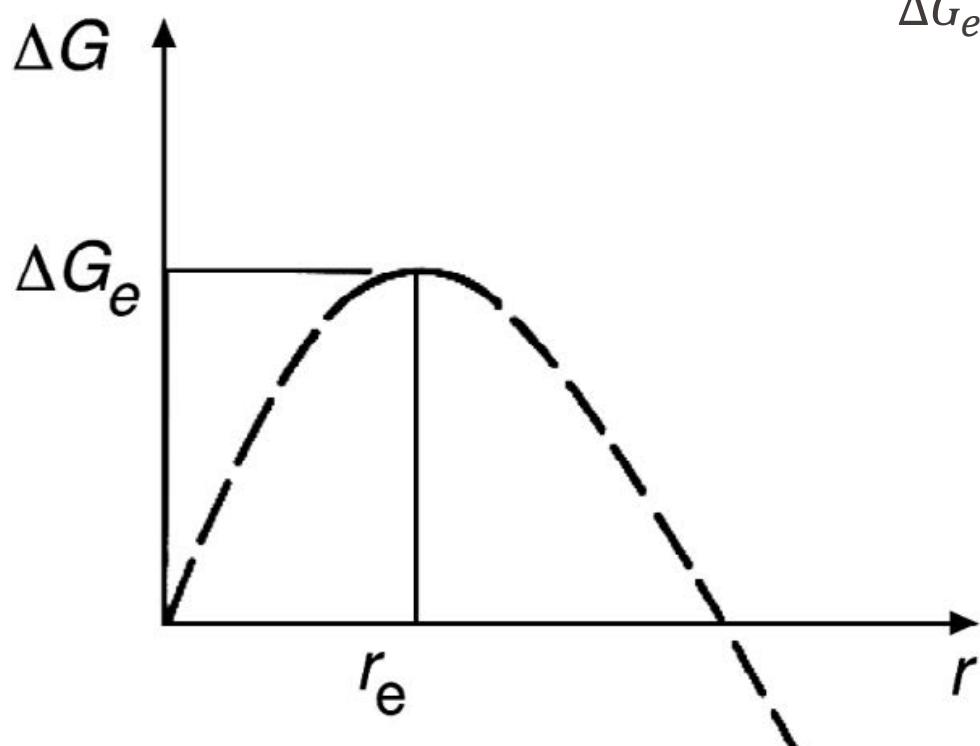


Zhengmao Lu
Energy Transport Advances
Laboratory
EPFL Mechanical Engineering

2024 Fall Semester

Photo Credit: Trougnouf

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



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

When $\theta = 180^\circ$, $F(\theta) = 0$

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

When $\theta = 0^\circ$, $F(\theta) = 1$

Same as homogeneous nucleation

Figure 5.9 in Carey

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 [$\text{m}^{-2}\text{s}^{-1}$]

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 \rightarrow $n+1$ molecule embryos through evaporation is the same as $n+1$ molecule embryos \rightarrow 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 \rightarrow $n+1$ molecule

Embryo Size Distribution

Embryo Size Distribution

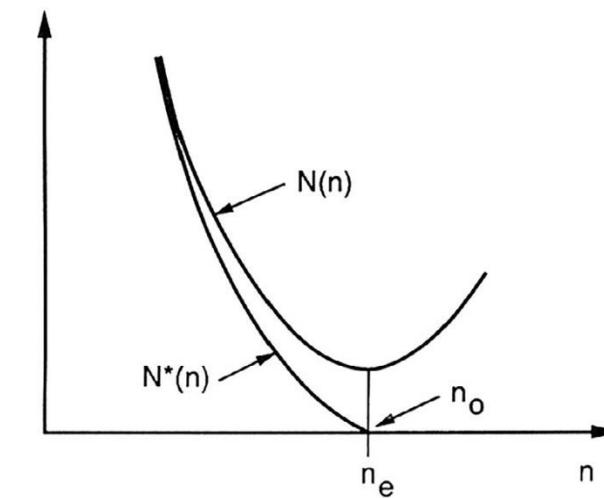


FIGURE 5.10 Carey

Embryo Size Distribution

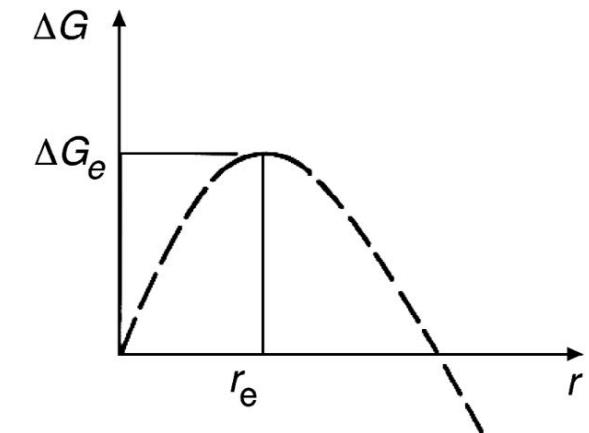
$$J = -N_n A_n j_{ne} \frac{\partial \left(\frac{N^*}{N} \right)}{\partial n}$$

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

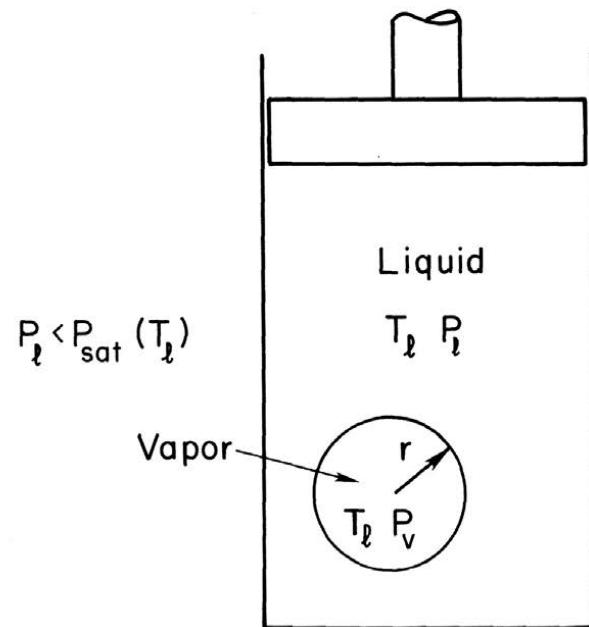
$[N(n)A(n)j_e(n)]^{-1}$ is only significantly greater than zero near $n = n_e$



Embryo Size Distribution

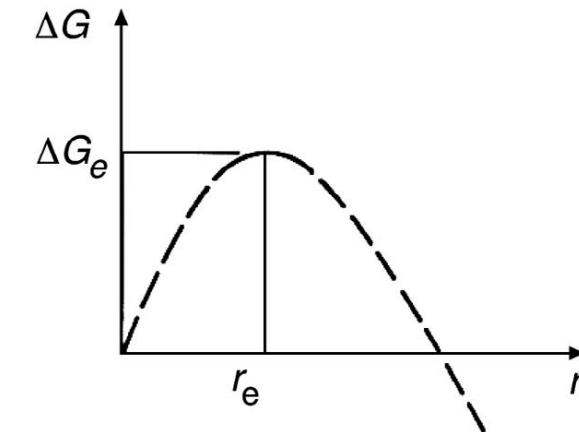
$$J \approx \frac{P_{ve}}{\sqrt{2\pi m k_B T_l}} \left(\int_0^{\infty} [N(n)A(n)]^{-1} dn \right)^{-1}$$

After Embryo Formation



Embryo Size Distribution

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



Physical Meaning of J

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

Physical Meaning of J

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

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)

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

increases sharply with temperature

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

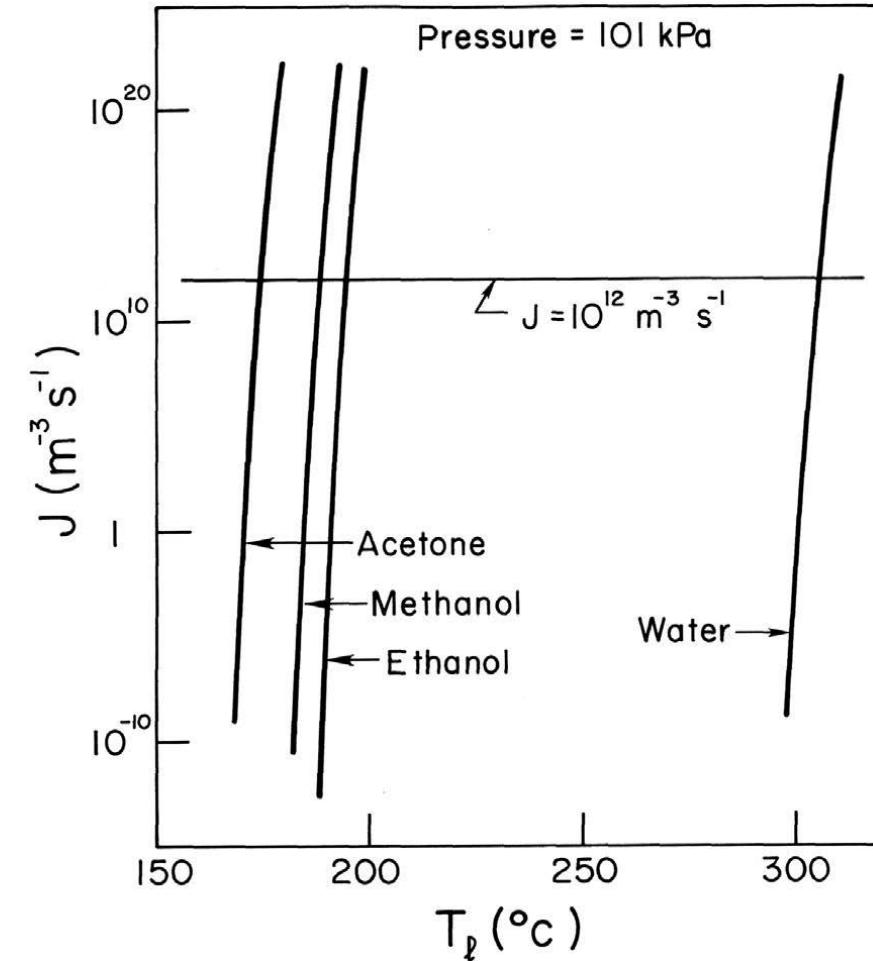
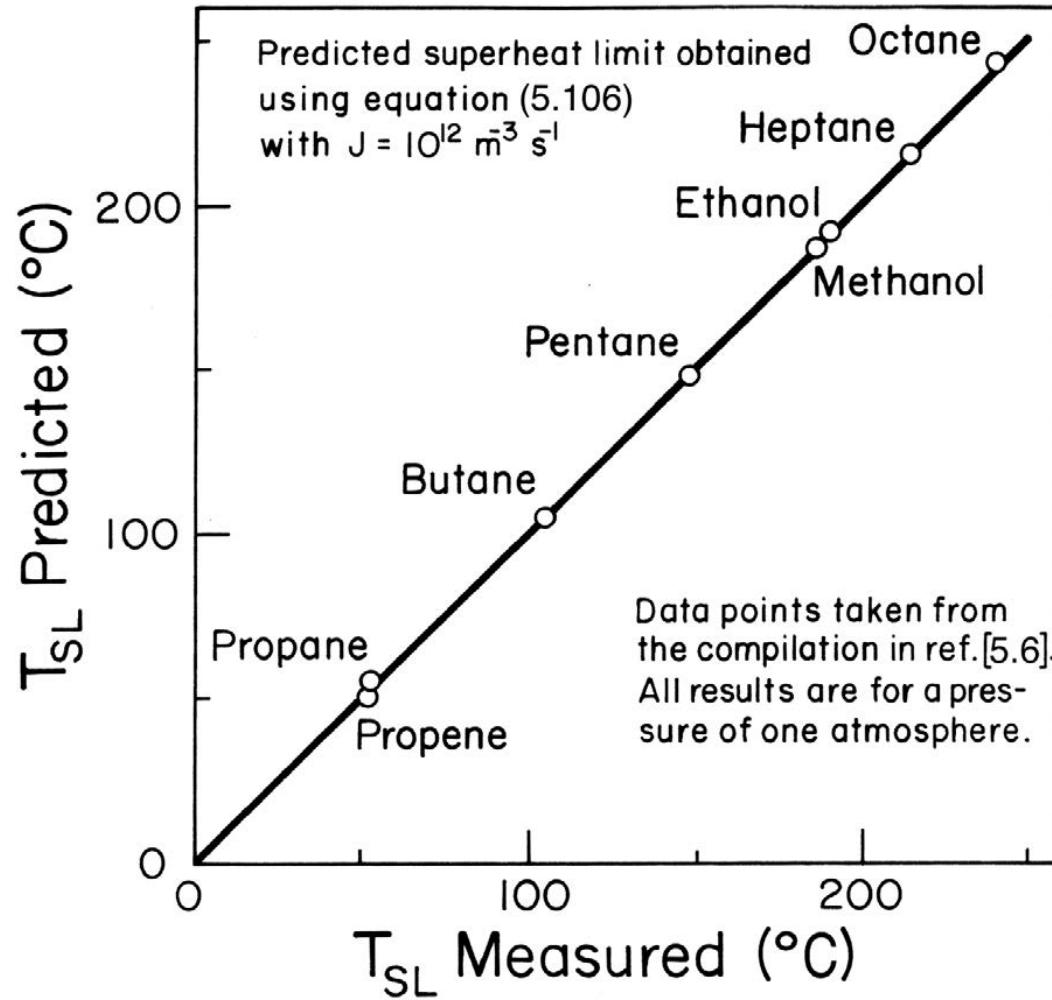


FIGURE 5.12, Carey

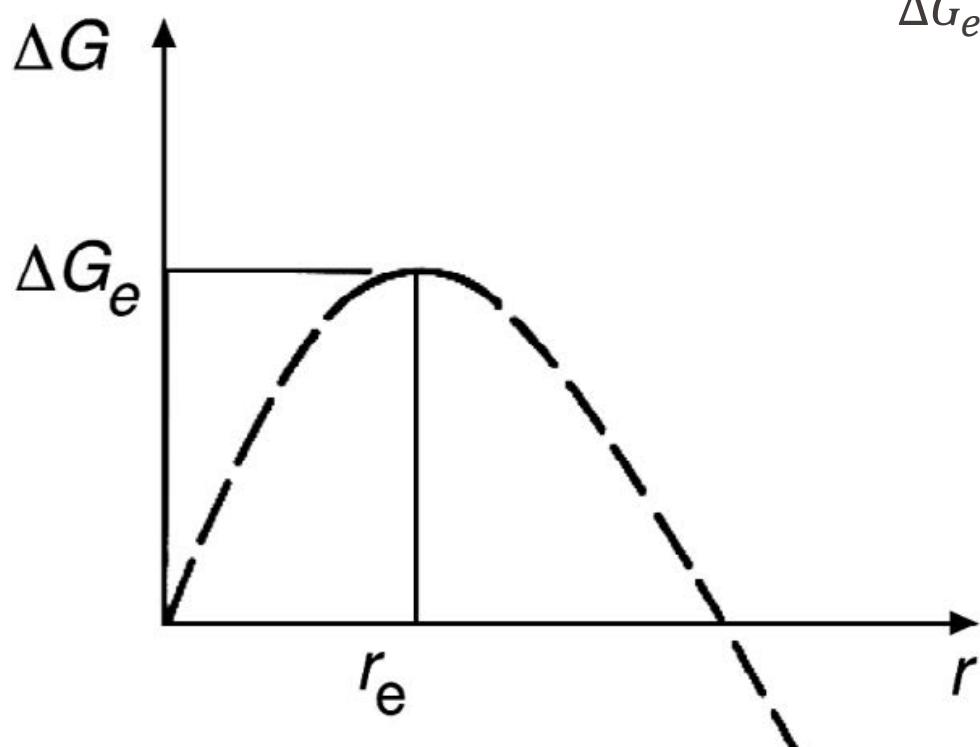
Measured Superheat Limit Data



Great agreement was found for low surface tension liquids

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

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



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

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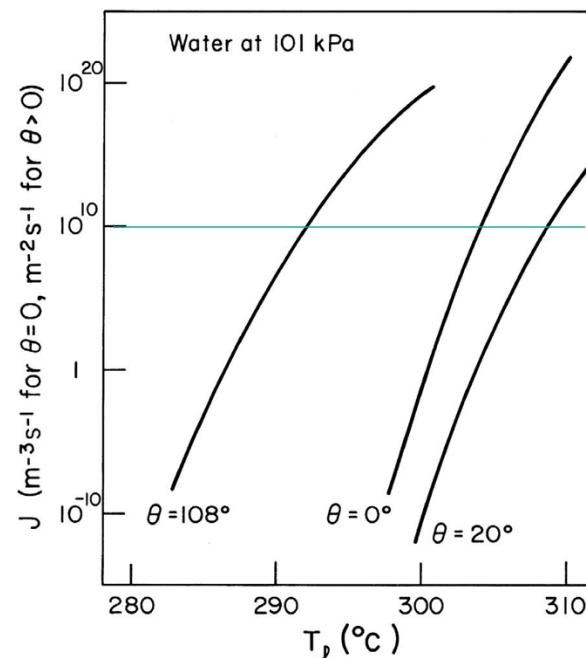
Same as homogeneous nucleation

Figure 5.9 in Carey

Heterogenous Critical Embryo Generation Rate

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

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



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

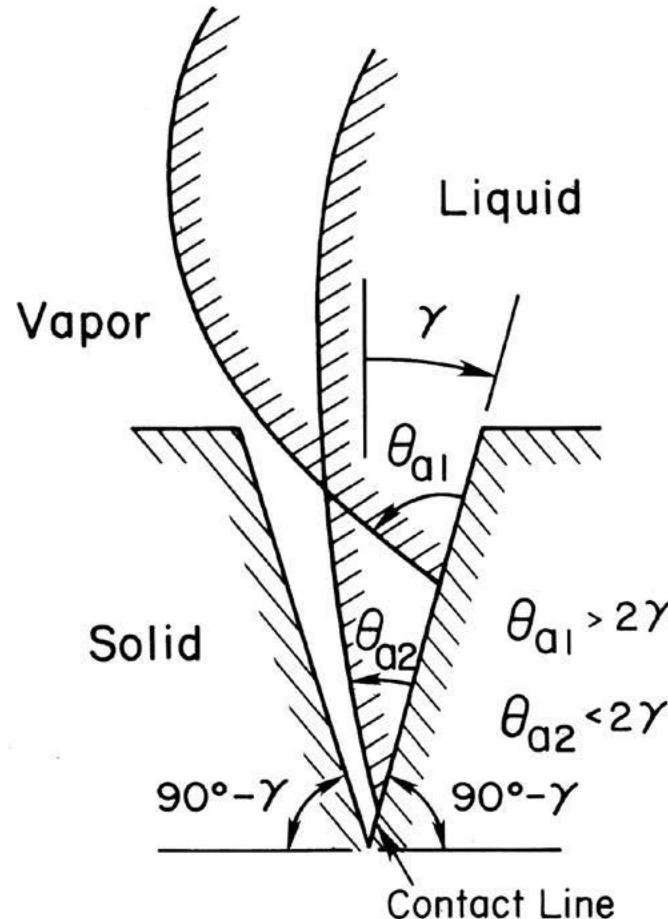
This limiting superheat temperature is clearly a function of the contact angle

However, according to this model, heterogeneous nucleation occurs at ~ 300 °C 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



- 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

Figure 6.4 in Carey

Entrapped Gas/Vapor Theory

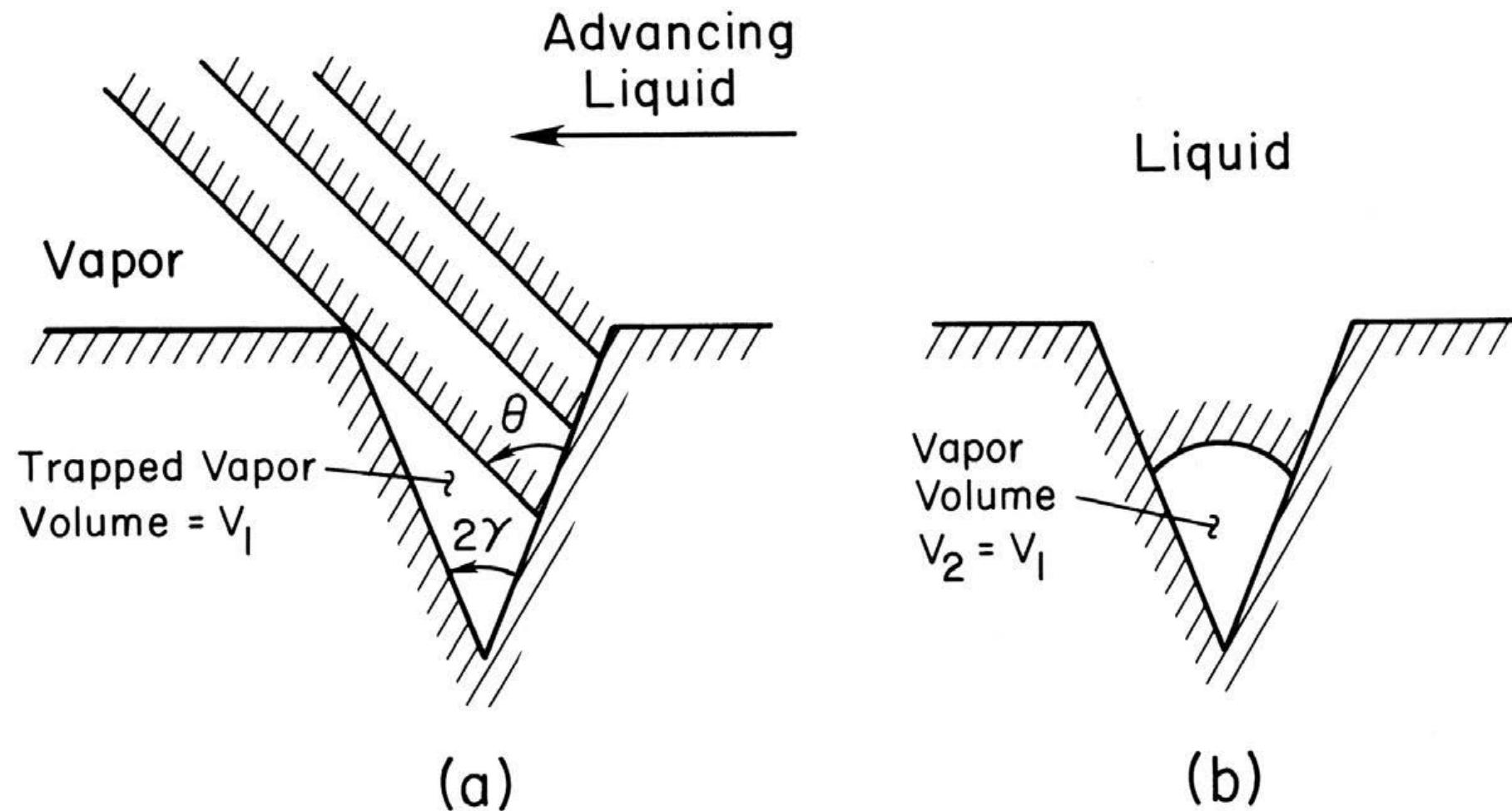
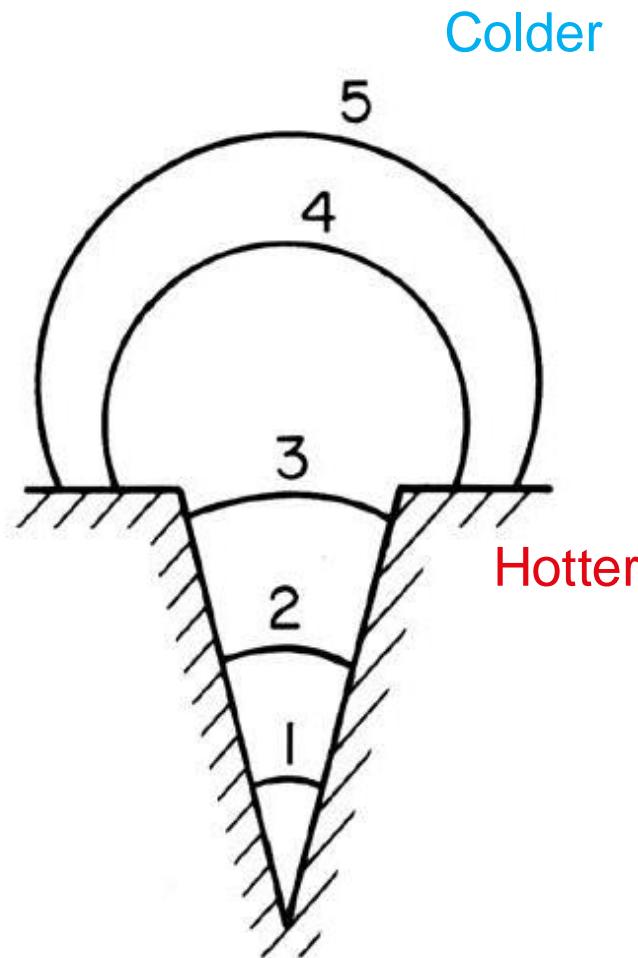


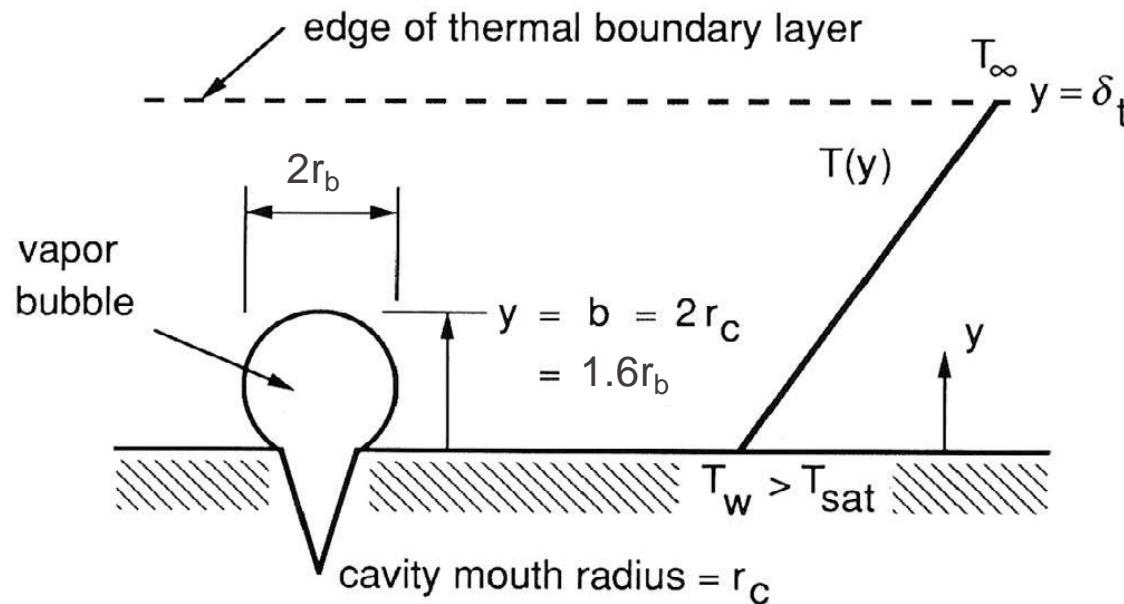
FIGURE 6.7

Entrapped Gas/Vapor Theory

- Clear correlation between locations of surface cavities 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





- 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

Figure 6.11 in Carey

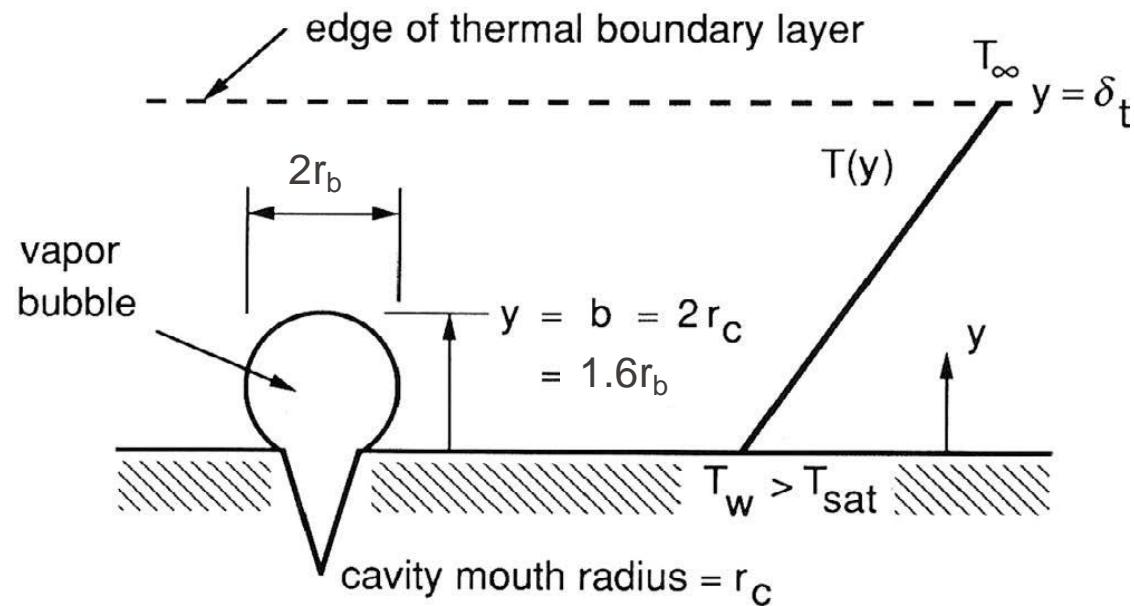
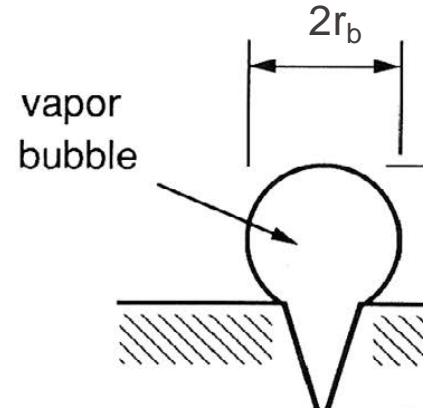
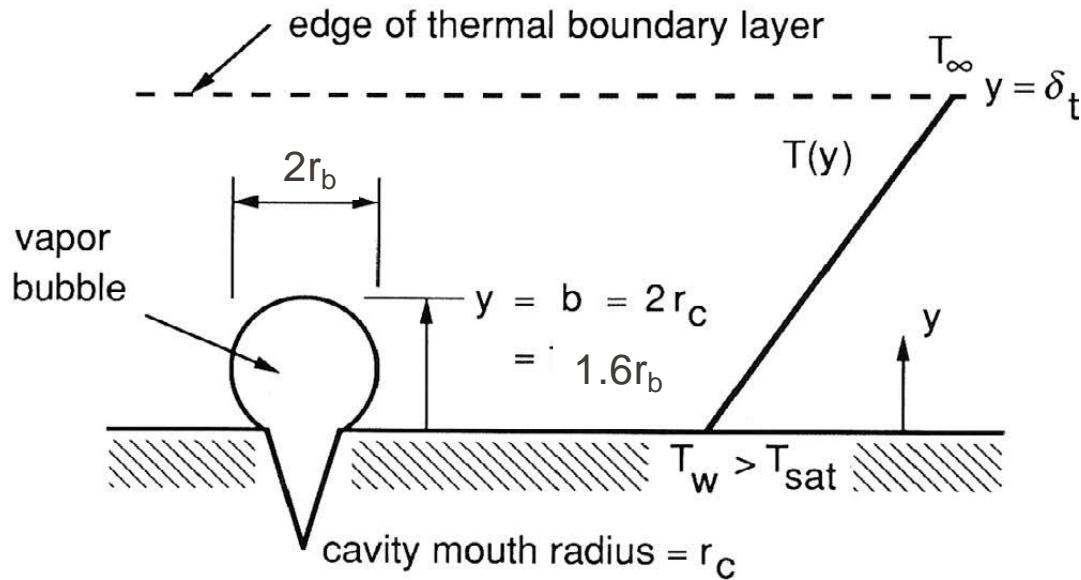


Figure 6.11 in Carey

Clausius-Clapeyron Relation



Bubble Nucleation Criteria



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

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

Bubble Nucleation Criteria

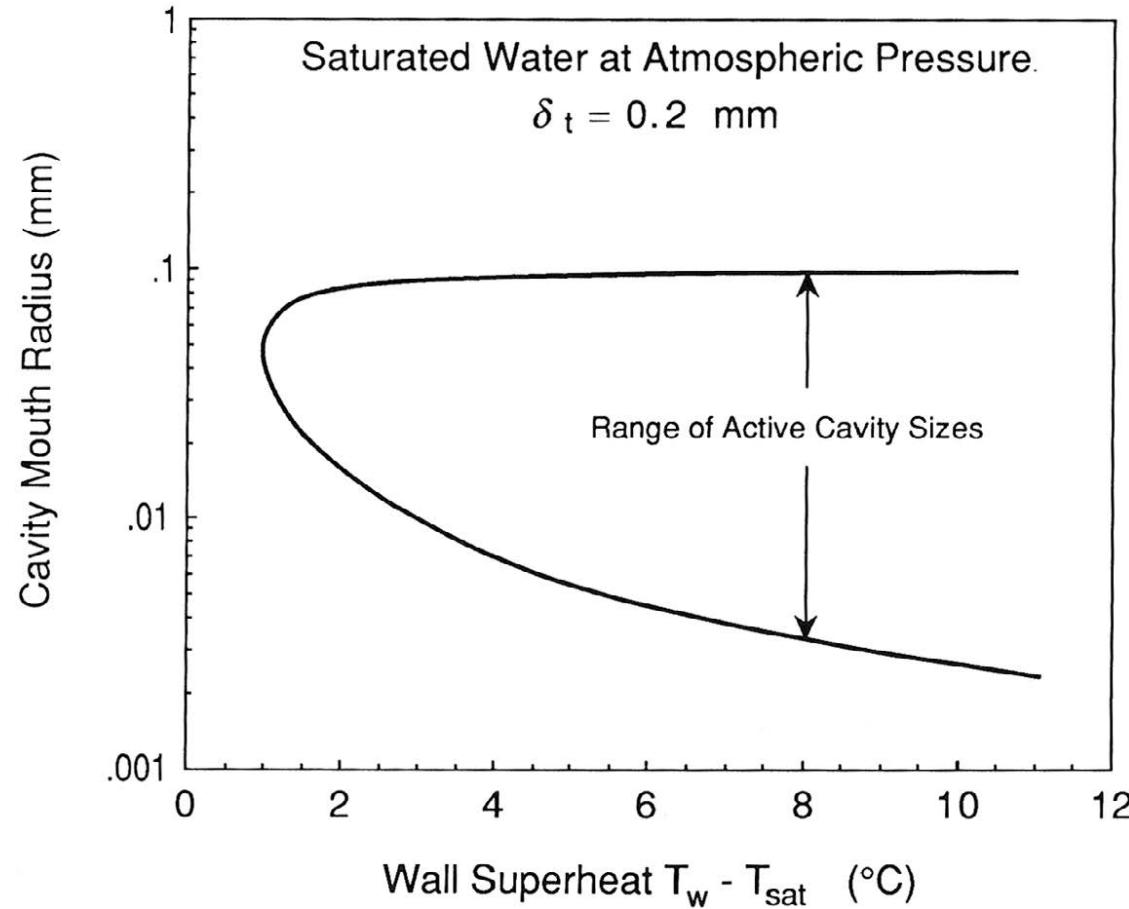
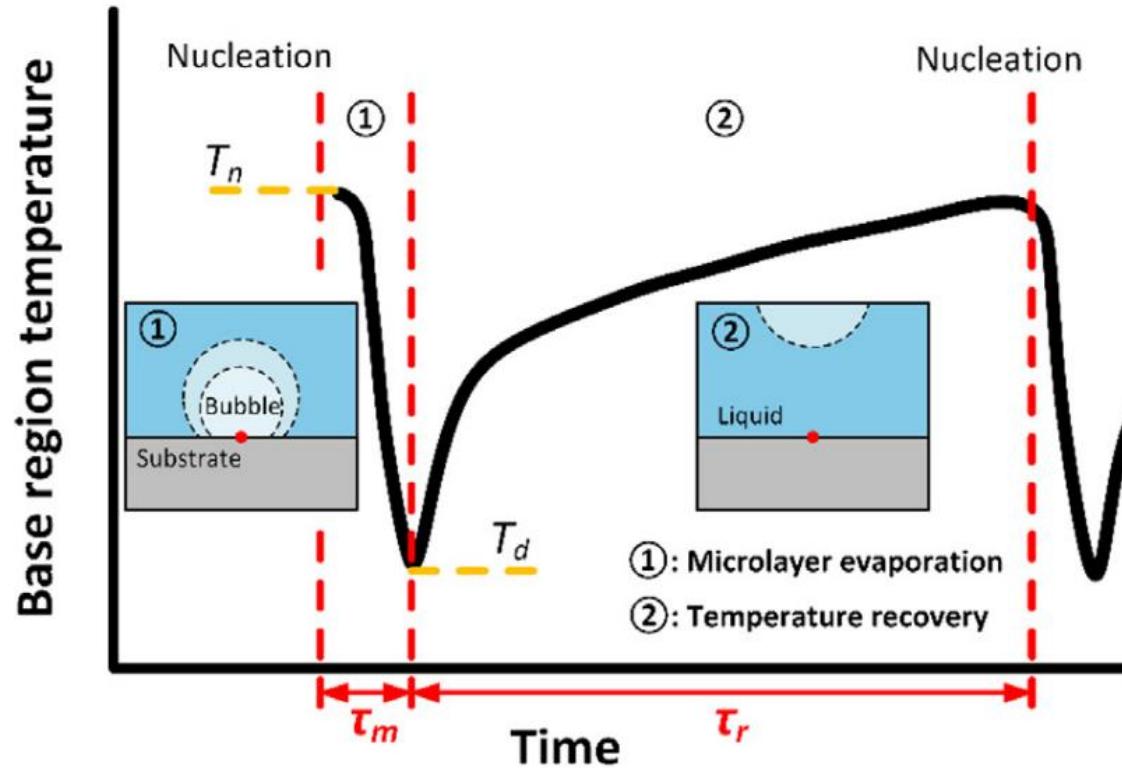


Figure 6.13 in Carey

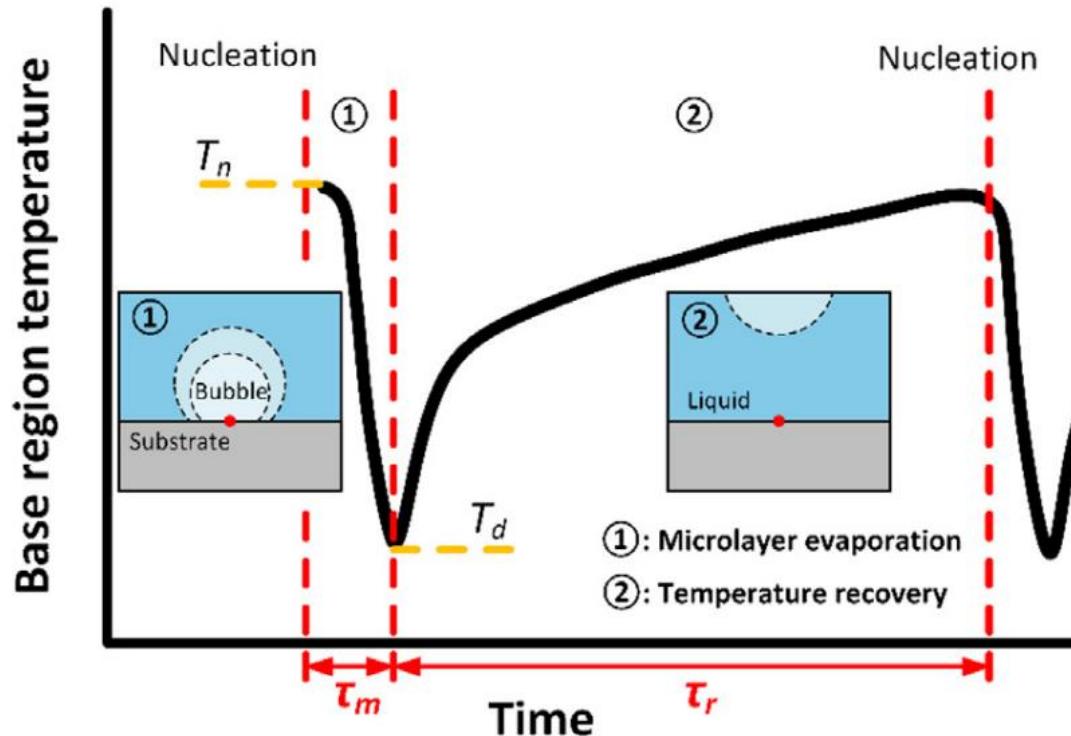
Beyond Nucleation



- 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

Zhang et al., 2021

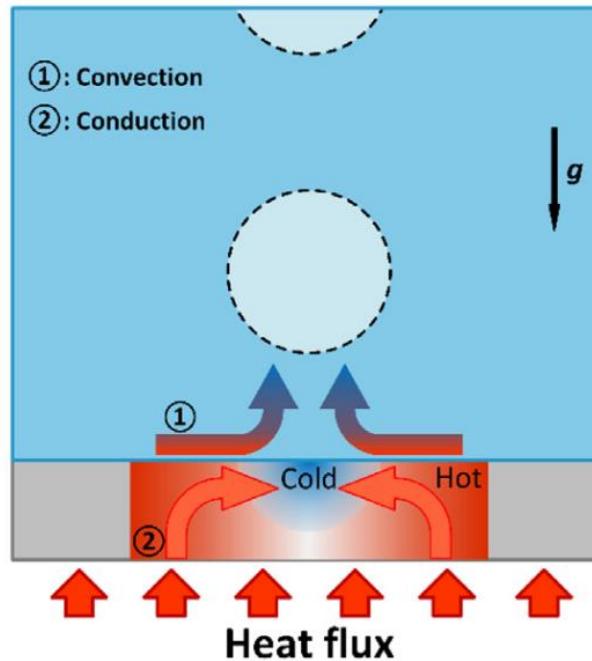
<https://doi.org/10.1016/j.ijheatmasstransfer.2020.120640>

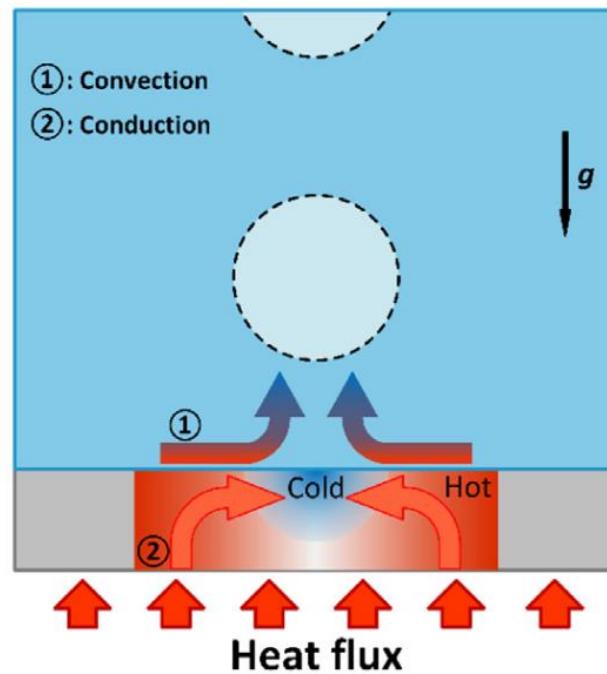


We are interested in departure frequency and the departure bubble size

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

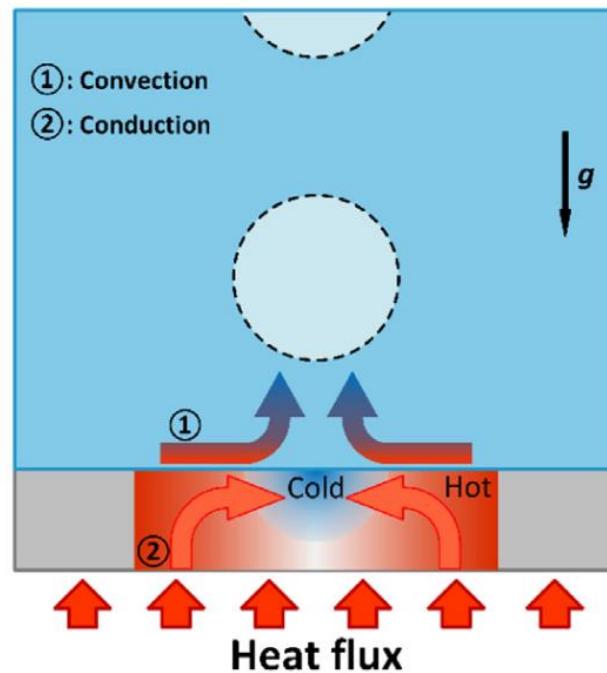
Temperature Recovery Mechanism





① Rewetting of surrounding superheated liquid

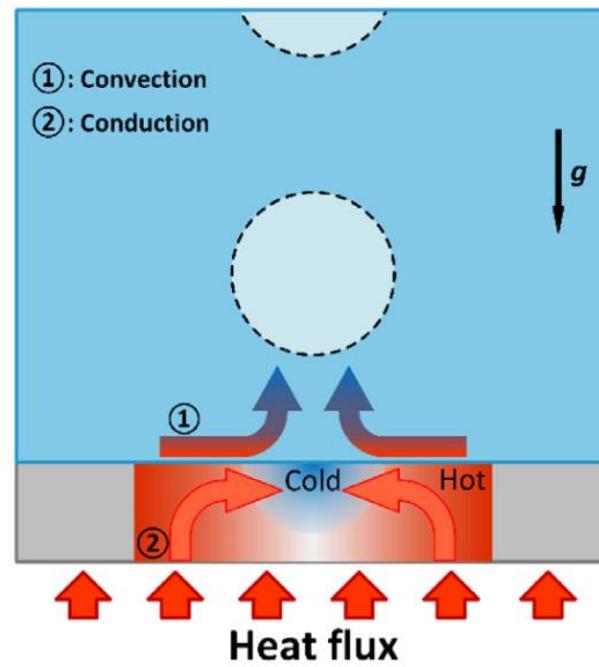
Transient heat conduction of a semi-infinite wall with a convective boundary condition



① Rewetting of surrounding superheated liquid

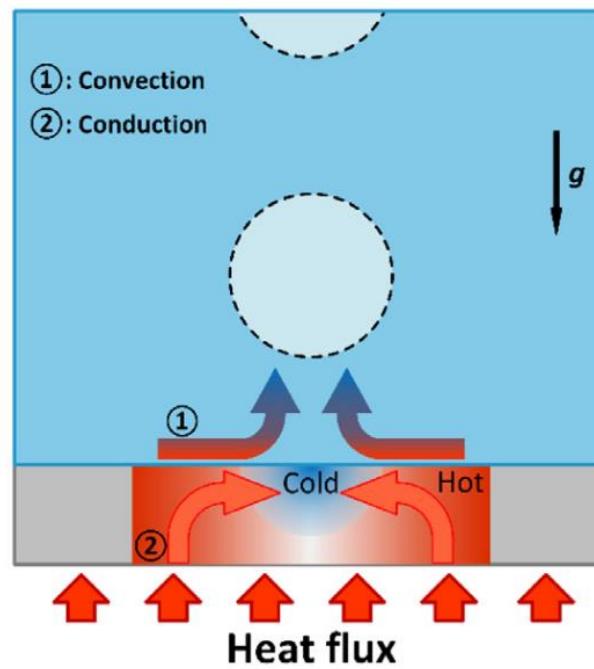
$$\tau_w = \frac{k_s^2}{h^2 \alpha_s}$$

How to determine h



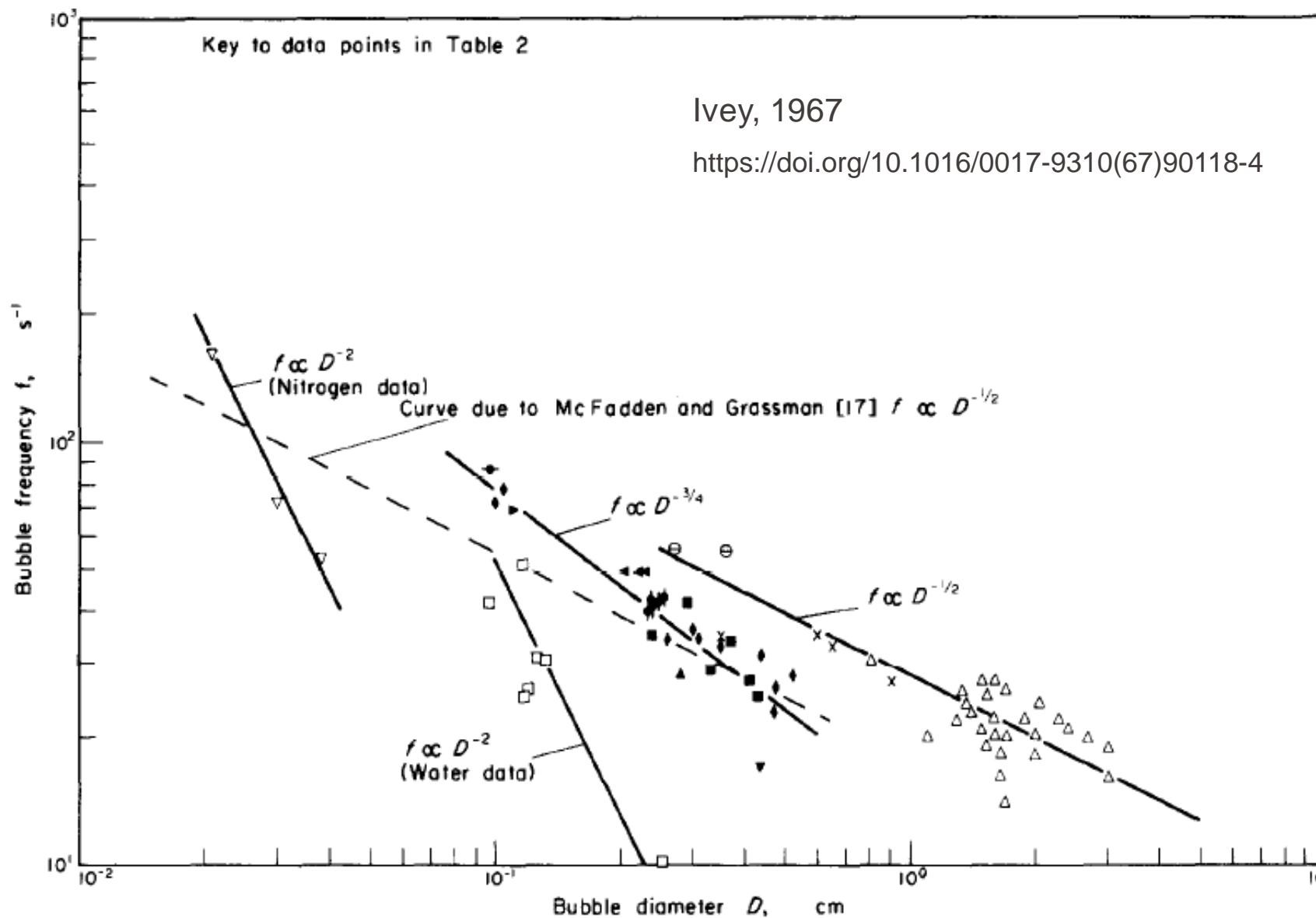
② Heat conduction from surrounding solid region

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



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

Comparison to Experiments



- Entrapped gas/vapor theory
- Onset of nucleation coupled with thermal boundary layer
- Timescale analysis for bubble growth and departure cycle