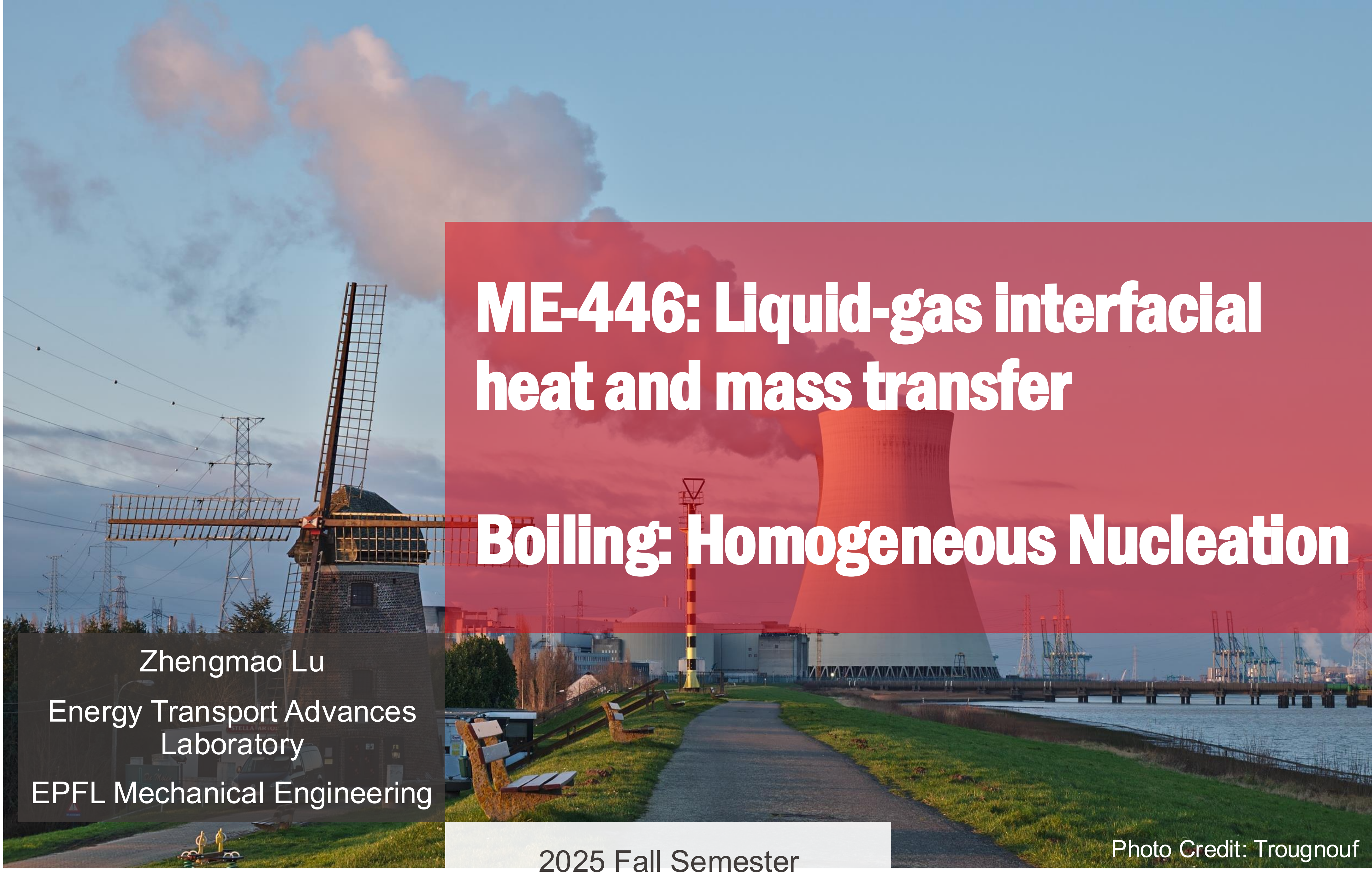


ME-446: Liquid-gas interfacial heat and mass transfer

Boiling: Homogeneous Nucleation

Zhengmao Lu

Energy Transport Advances Laboratory

EPFL Mechanical Engineering

2025 Fall Semester

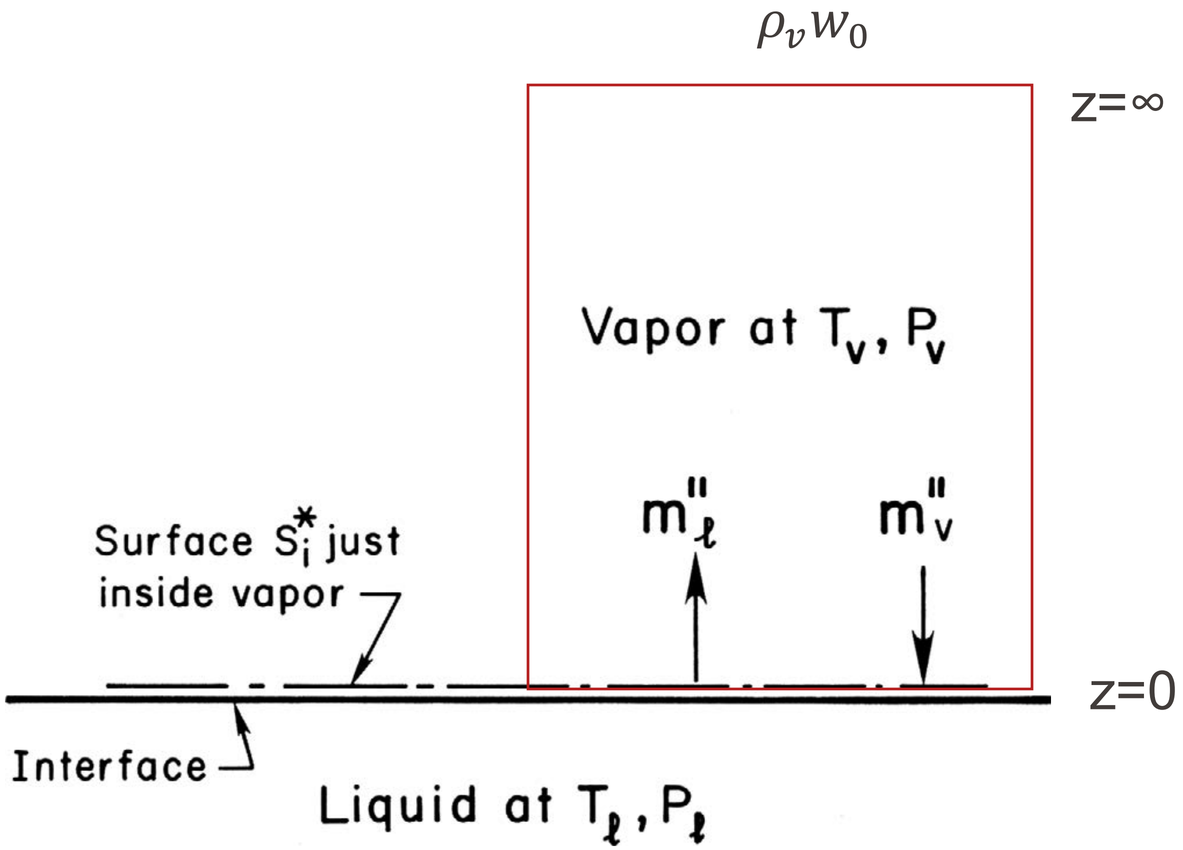
Photo Credit: Trougnouf

Last Time

- Velocity distribution function
- Relationship between macroscopic properties and velocity distribution
- Evaporation kinetics (Schrage equation)

$$q''_{evap} = \left(\frac{2\hat{\sigma}}{2-\hat{\sigma}}\right) h_{lv} (2\pi R)^{-\frac{1}{2}} \left(\frac{P_l}{\sqrt{T_l}} - \frac{P_v}{\sqrt{T_v}}\right) \approx \left(\frac{2\hat{\sigma}}{2-\hat{\sigma}}\right) \frac{h_{lv}}{\sqrt{2\pi R T_l}} (P_l - P_v)$$

Mass Balance



Mass balance

$$m_l'' - m_v'' = \rho_v w_0$$

$$m_l'' = \hat{\sigma} m_e'' + (1-\hat{\sigma}) m_v''$$
$$= \hat{\sigma} \frac{P_l}{RT_l}\left(\frac{k_B T_l}{2\pi m}\right)^{\frac{1}{2}} + (1-\hat{\sigma}) m_v''(w_0)$$

$$\hat{\sigma} \frac{P_l}{RT_l}\left(\frac{k_B T_l}{2\pi m}\right)^{\frac{1}{2}} - \hat{\sigma} m_v''(w_0) = \rho_v w_0$$

$$m_v''(w_0) = \rho_v \int_{-\infty}^{0} \left(\frac{m}{2\pi k_B T_v}\right)^{\frac{1}{2}} \exp\left(-\frac{m(w-w_0)^2}{2k_B T_v}\right) w dw$$

Solve for w_0

$$q''_{evap} = \rho_v w_0 h_{lv}$$

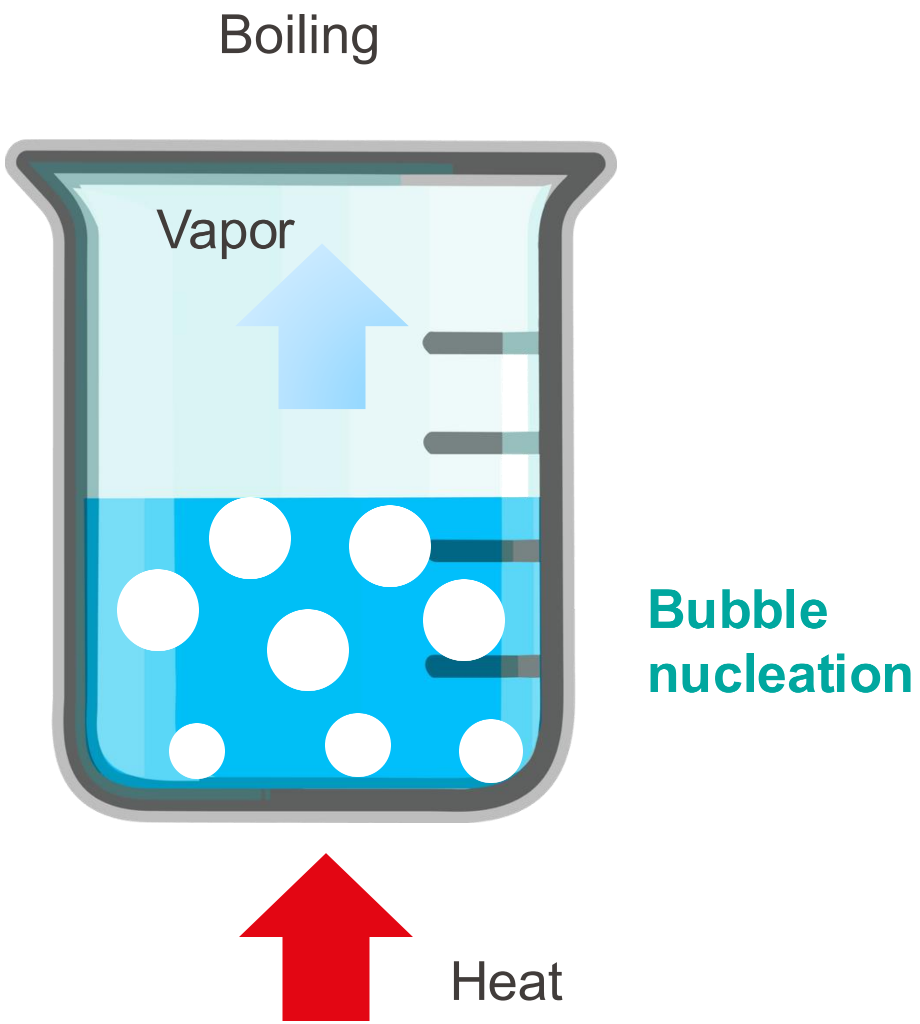
Boilling

cooking

(nuclear) power plant

immersion cooling

Evaporation vs Boiling



Intended Learning Objectives Today

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

  - Reading materials: **Carey**, Chapter 5.2, 5.3

Formation of a Vapor Embryo (Homogeneous Nucleation)

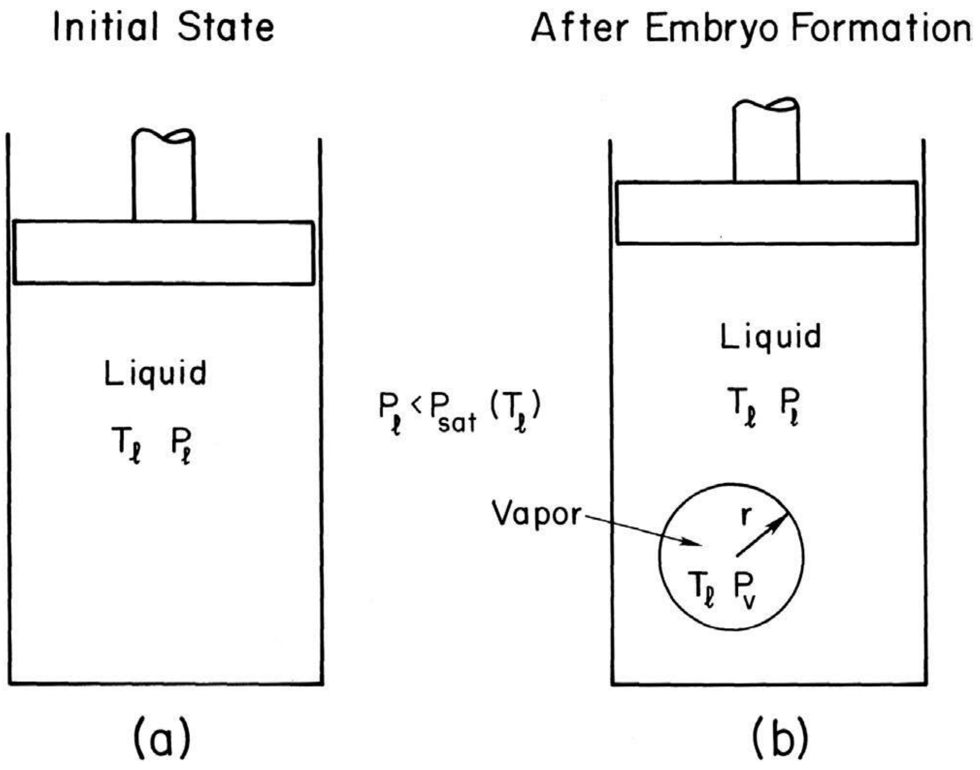


Figure 5.7 in Carey

Vapor bubble in bulk liquid at constant temperature and pressure

Gibbs free energy analysis

$$G = G_l + G_v + G_i$$

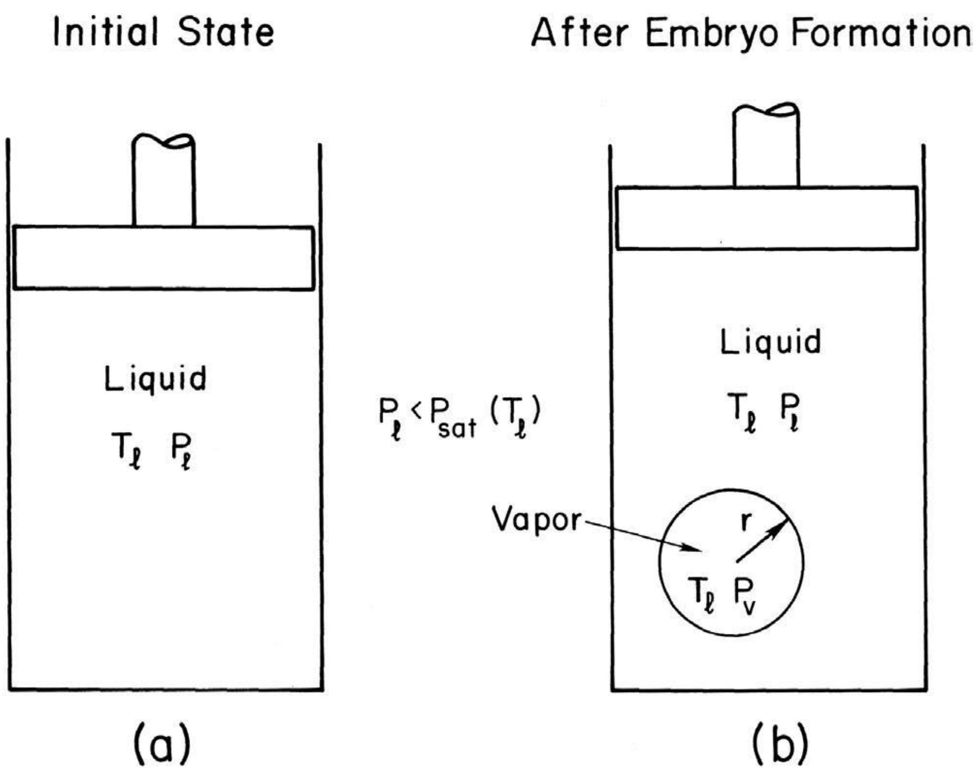
(b) – (a)

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

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

$$\Delta G_i = 4\pi r^2 \sigma_{lv}$$

Homogeneous Nucleation



$$\Delta G = \hat{N}_v(\hat{g}_v - \hat{g}_l) + (P_l - P_v)V_v + 4\pi r^2 \sigma_{lv}$$

Assuming the system reaches equilibrium when $r = r_e$

$$\hat{g}_v = \hat{g}_l$$

$$P_v - P_l = 2\sigma_{lv}/r_e$$

$$\Delta G_e = \frac{4}{3}\pi r_e^2 \sigma_{lv}$$

Gibbs Free Energy Change

$$\Delta G = \hat{N}_v(\hat{g}_v - \hat{g}_l) + (P_l - P_v)V_v + 4\pi r^2 \sigma_{lv}$$

Considering T_l and P_l as fixed values, assuming mechanical equilibrium is always satisfied

$P_v = P_l + \frac{2\sigma_{lv}}{r}$ is a function of r

With ideal gas law, $\hat{N}_v = P_v V_v / k_B T_l$ is also a function of r

ΔG can be considered as a function of r, to which we can apply Taylor expansion near r_e

$$\frac{d\Delta G}{dr} = \hat{N}_v \left(\frac{\partial \hat{g}_v}{\partial P_v}\right)_{T_l} \frac{dP_v}{dr} + \frac{d\hat{N}_v}{dr}(\hat{g}_v - \hat{g}_l) - \frac{dP_v}{dr} V_v + 4\pi r^2 (P_l - P_v) + 8\pi r \sigma_{lv}$$

$$= \hat{N}_v \hat{v}_v \frac{dP_v}{dr} + \frac{d\hat{N}_v}{dr}(\hat{g}_v - \hat{g}_l) - \frac{dP_v}{dr} V_v + 4\pi r^2 \left(\frac{2\sigma_{lv}}{r} + P_l - P_v\right)$$

At $r = r_e$, $\frac{d\Delta G}{dr} = 0$

Gibbs Free Energy Change

$$\frac{d\Delta G}{dr} = \frac{d\widehat{N}_v}{dr}(\hat{g}_v - \hat{g}_l) + 4\pi r^2\left(\frac{2\sigma_{lv}}{r} + P_l - P_v\right)$$

At $r = r_e$, $$\frac{d^2\Delta G}{dr^2} = -\frac{8\pi\sigma_{lv}}{3}\left(2 + \frac{1}{1 + \frac{2\sigma_{lv}}{r_e P_l}}\right)$$ Homework

$$\Delta G = \Delta G_e - \frac{8\pi\sigma_{lv}}{3}\left(2 + \frac{1}{1 + \frac{2\sigma_{lv}}{r_e P_l}}\right)(r - r_e)^2 + \cdots$$

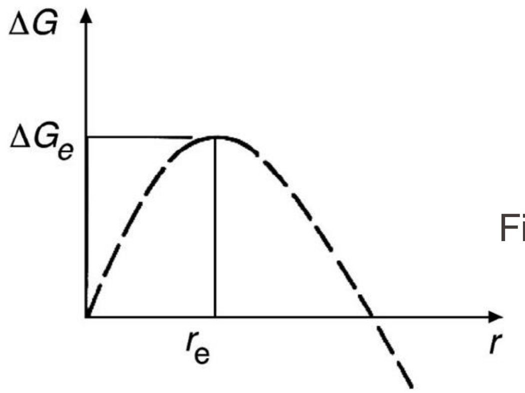


Figure 5.9 in Carey

Gibbs Free Energy Change

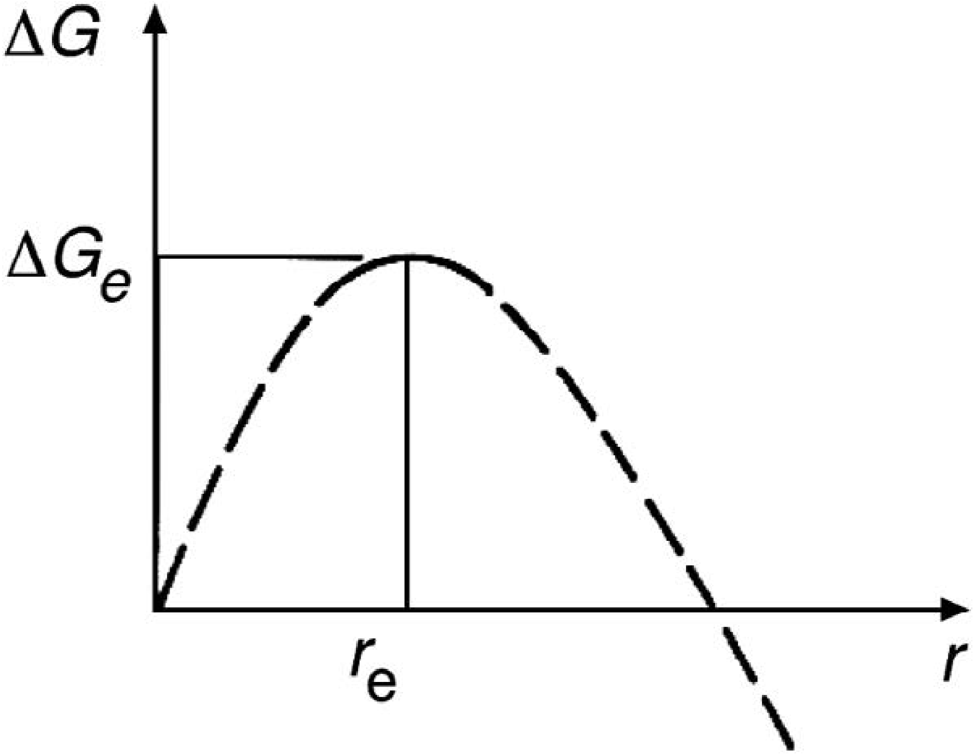


Figure 5.9 in Carey

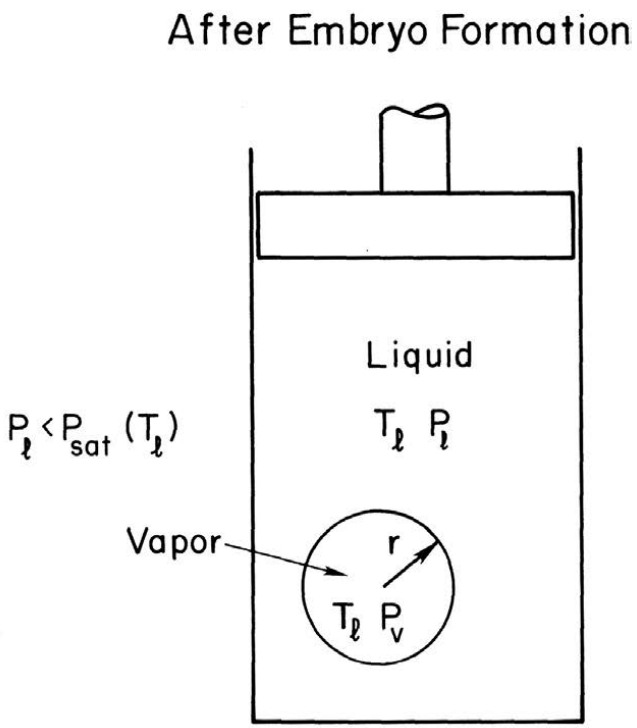
Density fluctuation in superheated liquid produces bubbles of random r

If $r < r_e$, the bubble collapses
If $r > r_e$, the bubble grows

How do we determine r_e

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 $g_v = g_l$

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

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

Embryo Size Distribution

Consider the number of embryos consisting of n molecules per unit volume N_n

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

$\rho_{N,L}$ 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

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

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

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 $\frac{\partial N_n^*}{\partial t} = 0$

$$\frac{\partial N_n^*}{\partial t} = 0 \Rightarrow J = \text{const}$$

Steady stream of embryos growing progressively in size

Embryo Size Distribution

At equilibrium, when $r > r_e$, bubbles grow exponentially, so no embryos for $r > r_e$

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

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

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

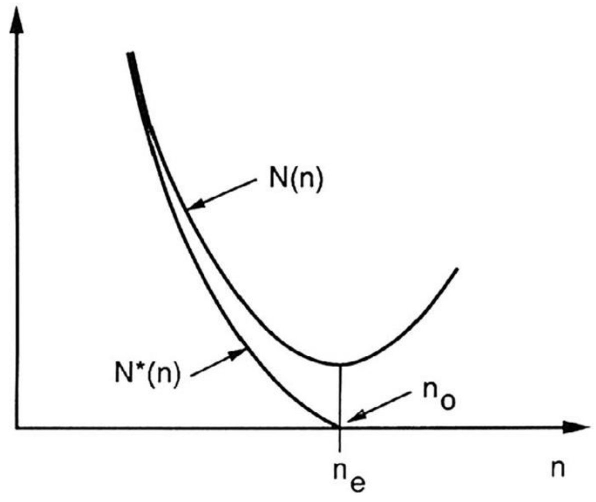


FIGURE 5.10 Carey

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 $n \rightarrow n_e$

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

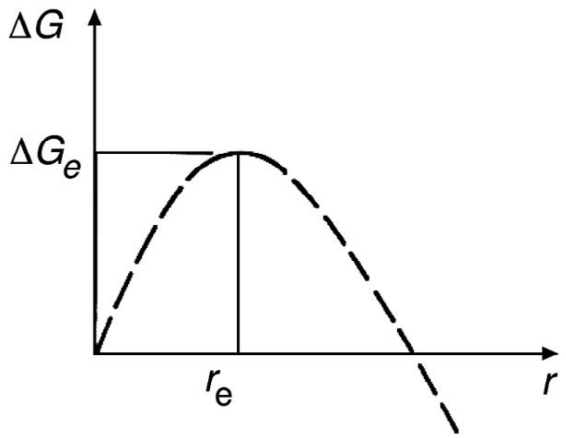
True for any n

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

$N^*/N \rightarrow 1$ 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

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

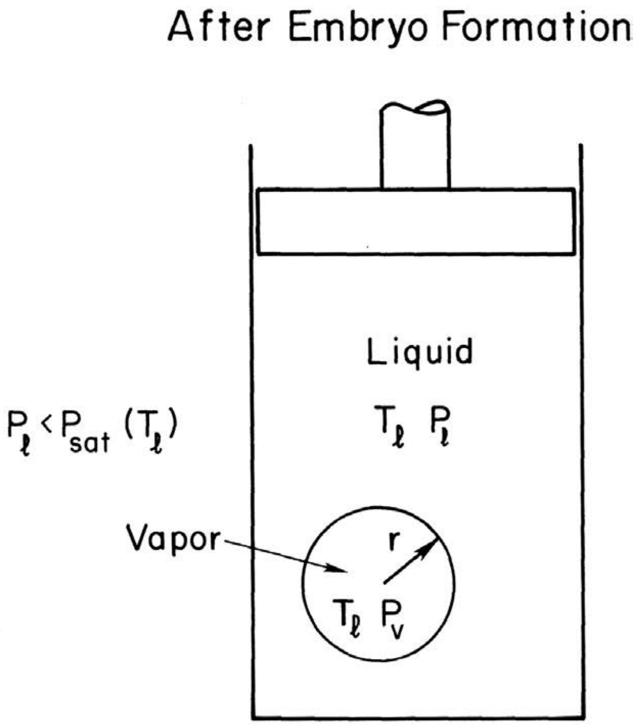
Embryo Size Distribution

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

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

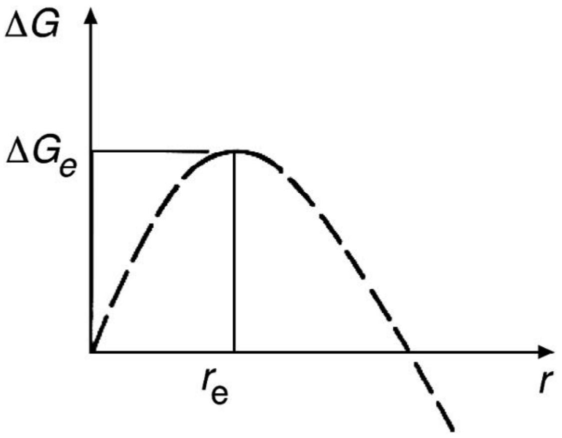
$$n k_B T_l = \left(P_l + \frac{2\sigma_{lv}}{r} \right) \frac{4}{3} \pi r^3$$

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



Embryo Size Distribution

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



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

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

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

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

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.

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

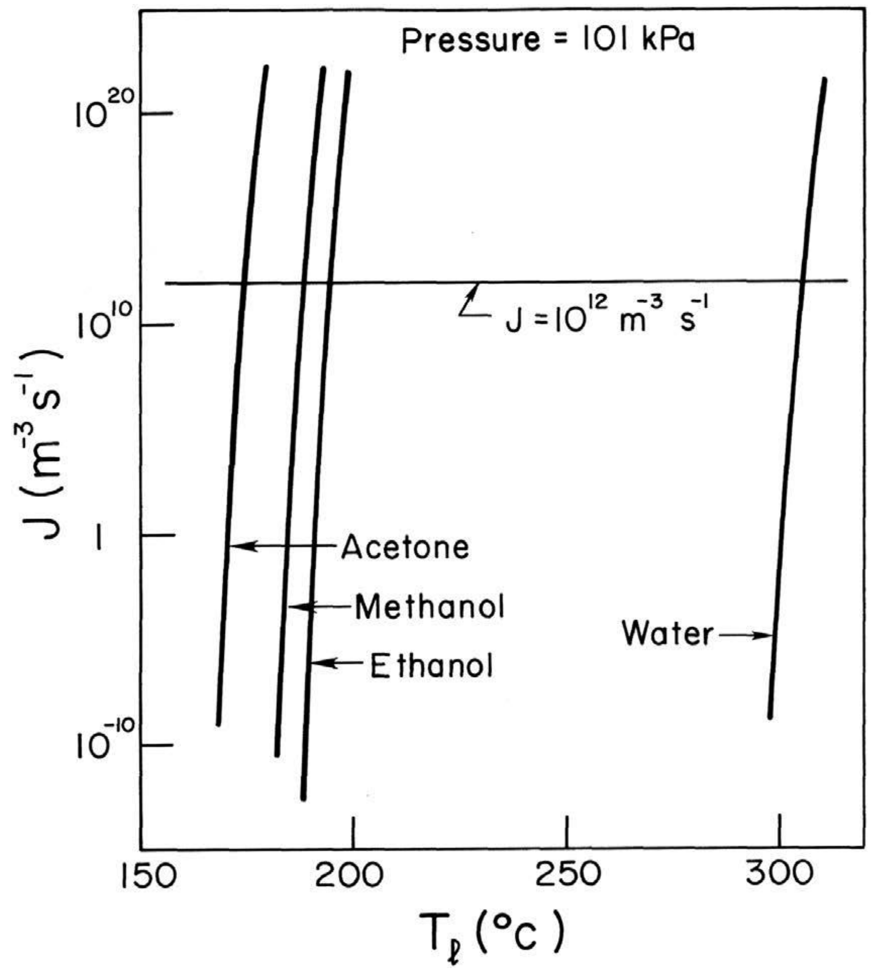


FIGURE 5.12, Carey

Measured Superheat Limit Data

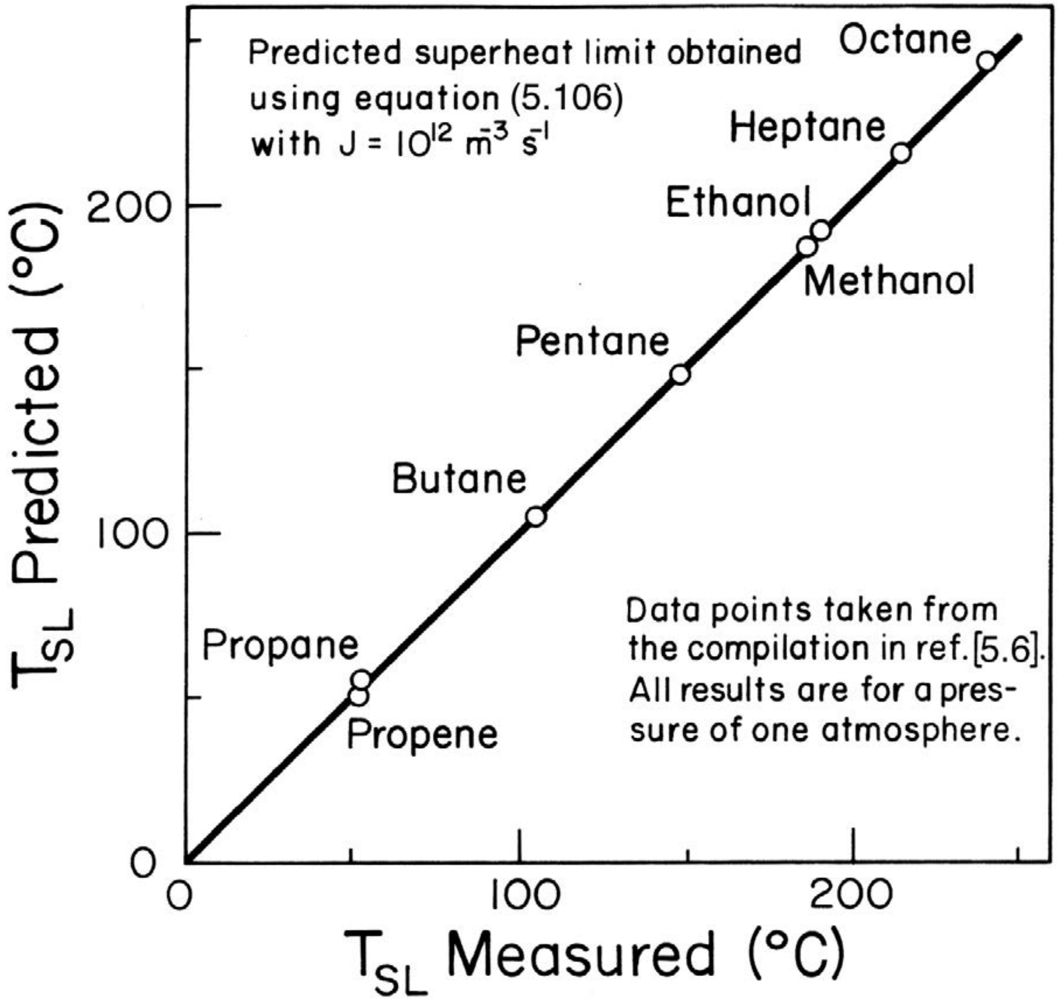


FIGURE 5.13

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

Intended Learning Objectives Today

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

  - Reading materials: **Carey**, Chapter 5.2, 5.3