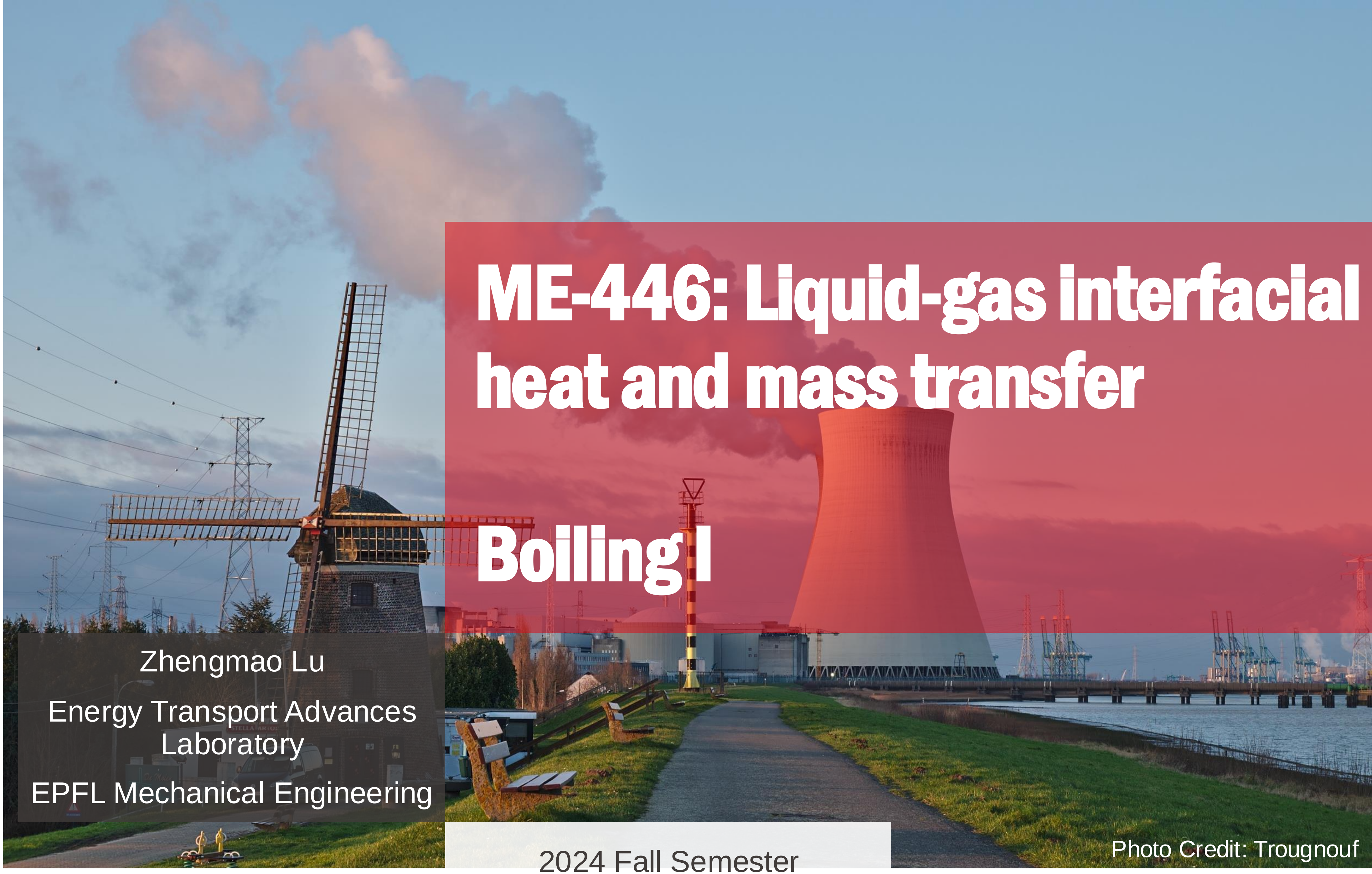

ME-446: Liquid-gas interfacial heat and mass transfer

Boiling I

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Energy Transport Advances Laboratory

EPFL Mechanical Engineering

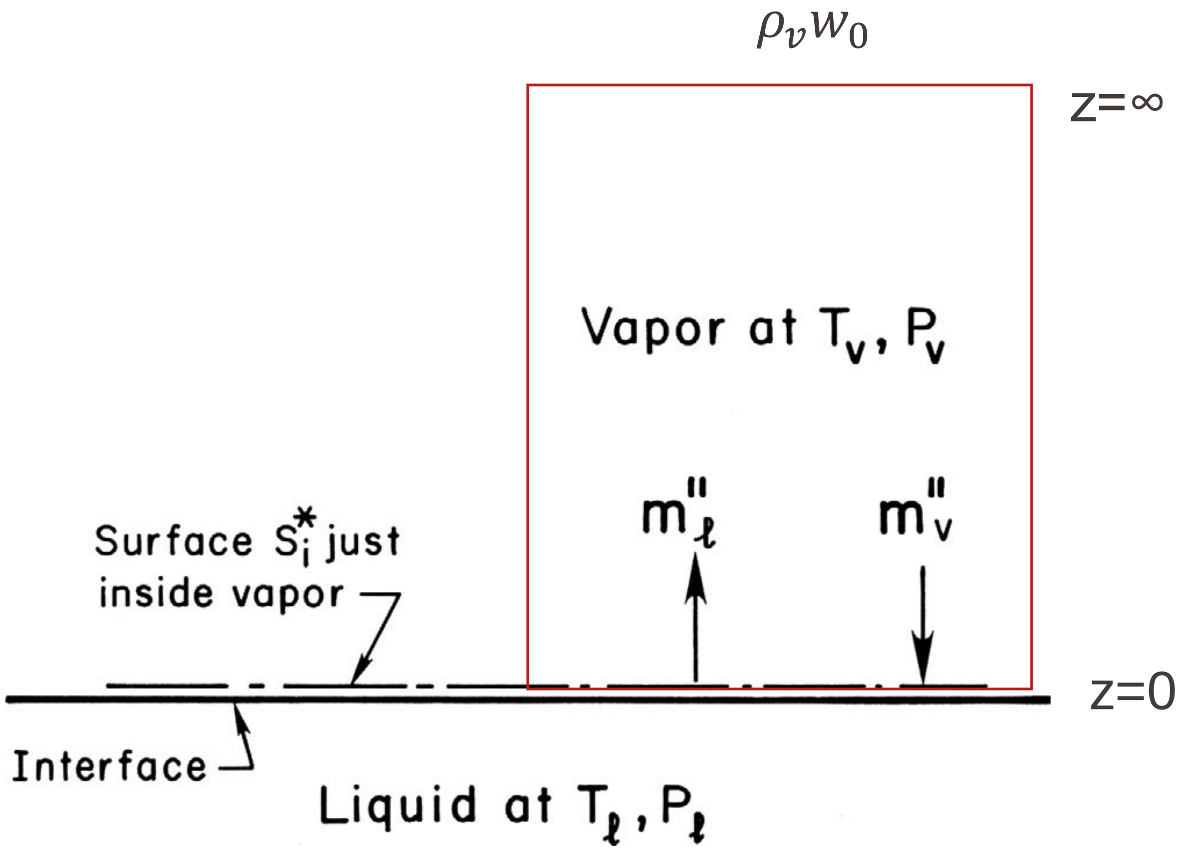
2024 Fall Semester

Photo Credit: Trougnouf

Last Time

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

Mass Balance



Mass balance

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

$$m_l'' = \hat{\sigma} m_e'' + (1-\hat{\sigma}) m_v''$$

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

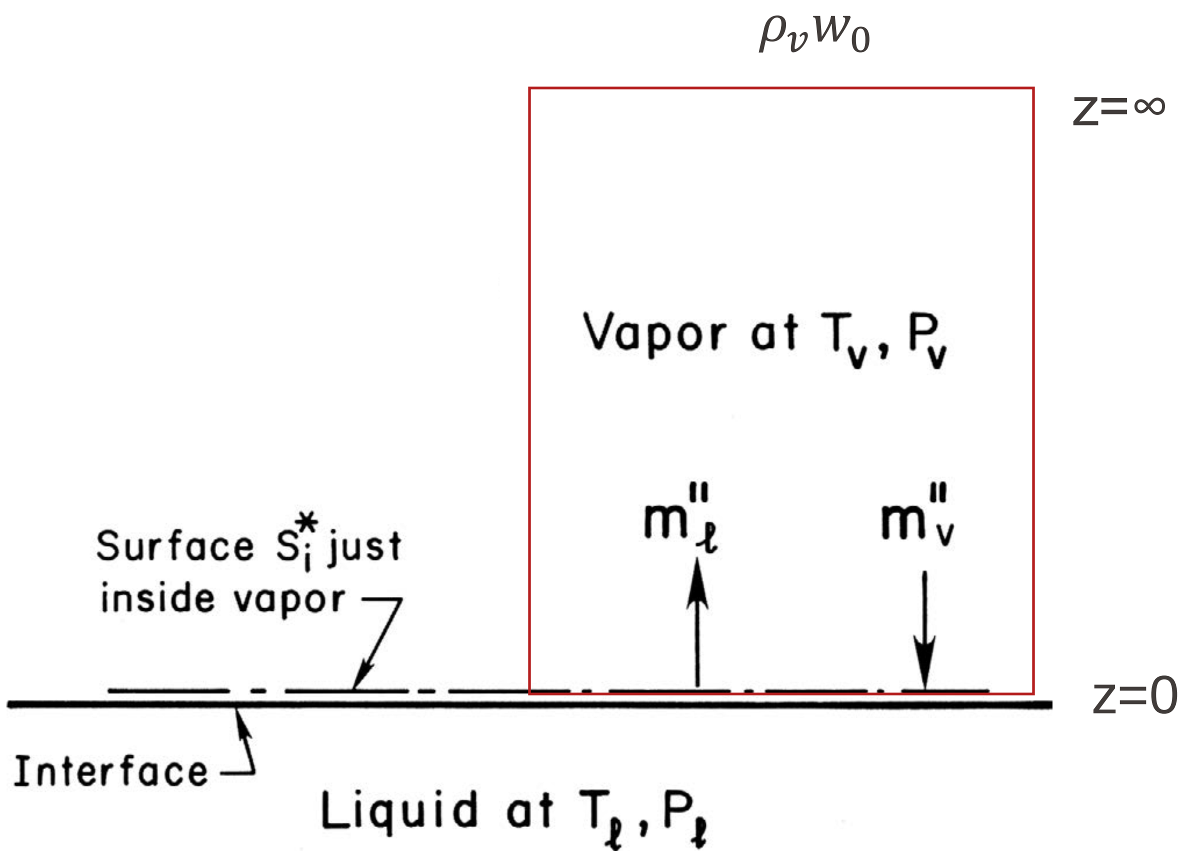
$$\hat{\sigma} \frac{P_l}{RT_l} \left(\frac{k_B T_l}{2\pi m}\right)^{\frac{1}{2}} - \hat{\sigma} m_v''(w_0) = \rho_v w_0$$

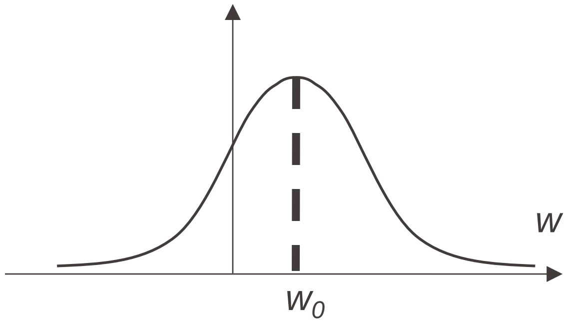
$$m_v''(w_0) = \rho_v \int_{-\infty}^{0} \left(\frac{m}{2\pi k_B T_v}\right)^{\frac{1}{2}} \exp\left(-\frac{m(w-w_0)^2}{2k_B T_v}\right) w\,dw$$

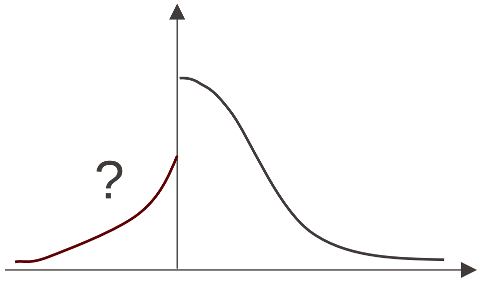
Solve for w_0

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

General Governing Equation

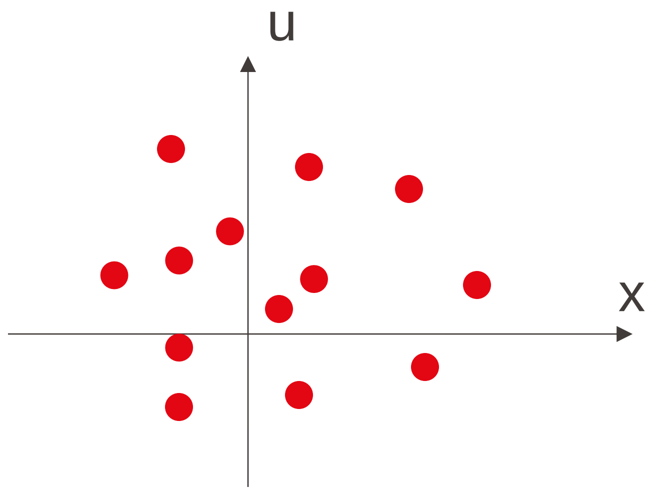






Define $\xi(u,v,w)dudvdw = nf(u,v,w)dudvdw$ which represent the number of molecules one expect to find in the ranges u to u + du, v to v + dv, w to w + dw in a unit volume

One-Dimensional Case



$$\frac{\partial \xi}{\partial t} = \frac{\partial \xi}{\partial x} \cdot \frac{\partial x}{\partial t} + \frac{\partial \xi}{\partial u} \cdot \frac{\partial u}{\partial t} + \Omega(\xi, \xi)$$

$$\frac{\partial \xi}{\partial t} = \frac{\partial \xi}{\partial x} \cdot u + \frac{\partial \xi}{\partial u} \cdot g_x + \Omega(\xi, \xi)$$

Evolution of F caused by streaming of molecules, external forces, and collisions between two molecules

Boltzmann Equation

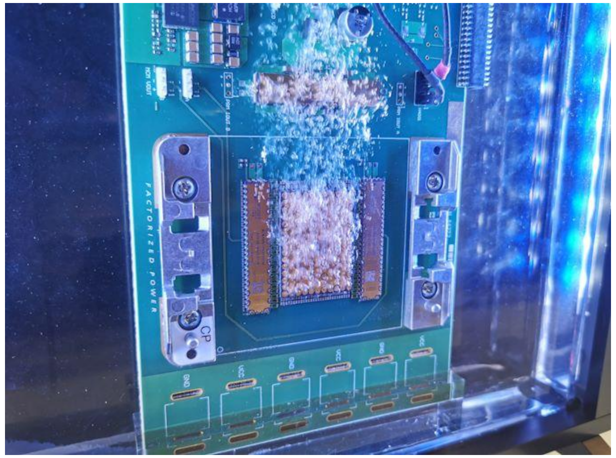
$$\frac{\partial \xi}{\partial t} = \frac{\partial \xi}{\partial x} \cdot u + \frac{\partial \xi}{\partial y} \cdot v + \frac{\partial \xi}{\partial z} \cdot w$$
$$+ \frac{\partial \xi}{\partial u} \cdot \frac{\partial u}{\partial t} + \frac{\partial \xi}{\partial v} \cdot \frac{\partial v}{\partial t} + \frac{\partial \xi}{\partial w} \cdot \frac{\partial w}{\partial t} + \Omega(\xi, \xi)$$

The major complexities are buried in $\Omega(F, F)$

Boiling

cooking

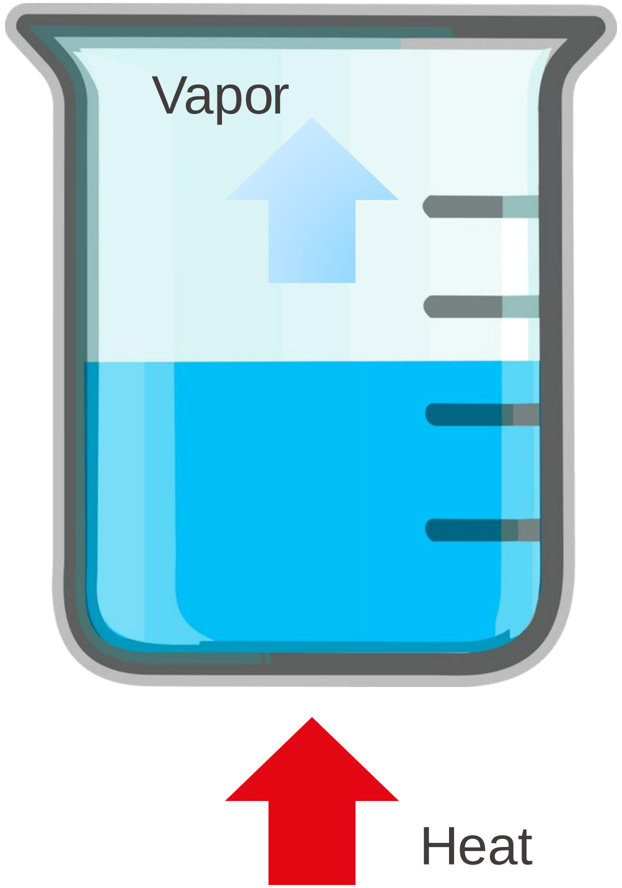
(nuclear) power plant



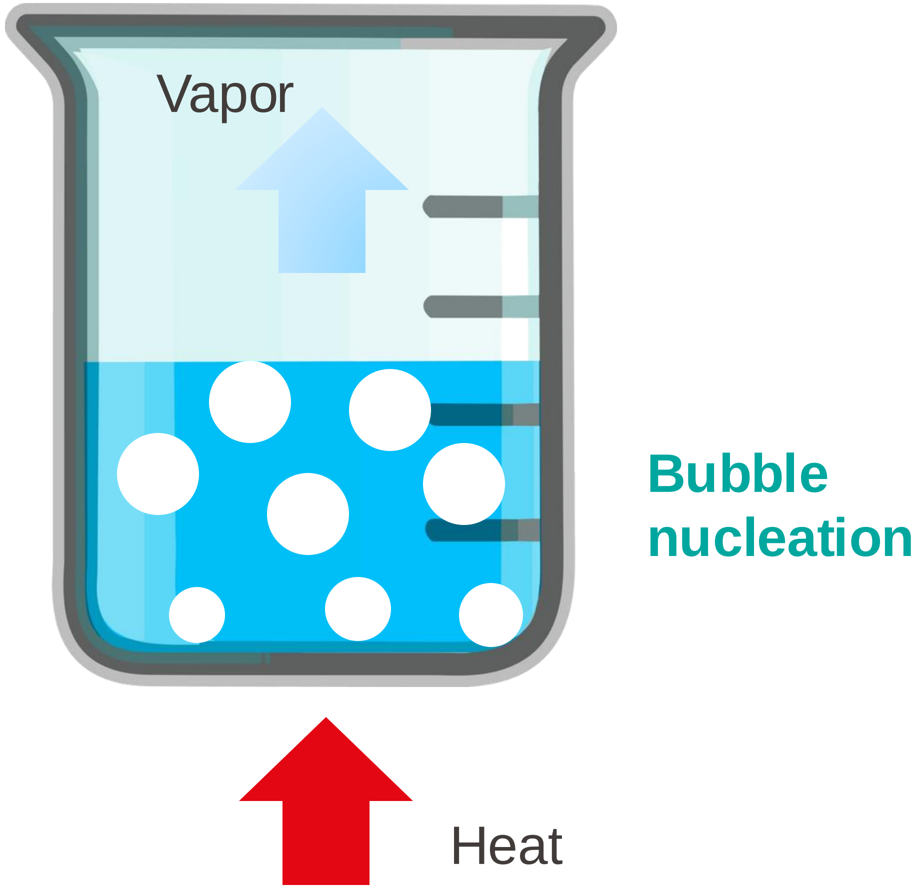
immersion cooling

Evaporation vs Boiling

Evaporation



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, 6.1

Formation of a Vapor Embryo (Homogeneous Nucleation)

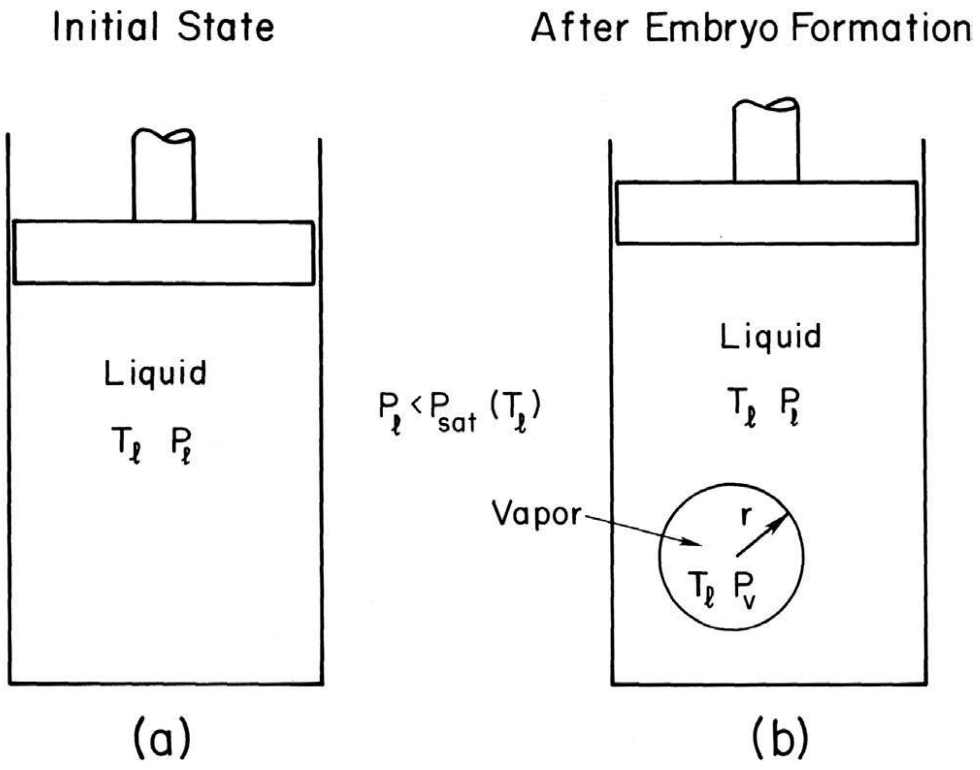


Figure 5.7 in Carey

Vapor bubble in bulk liquid at constant temperature and pressure

Gibbs free energy analysis

$$G = G_l + G_v + G_i$$

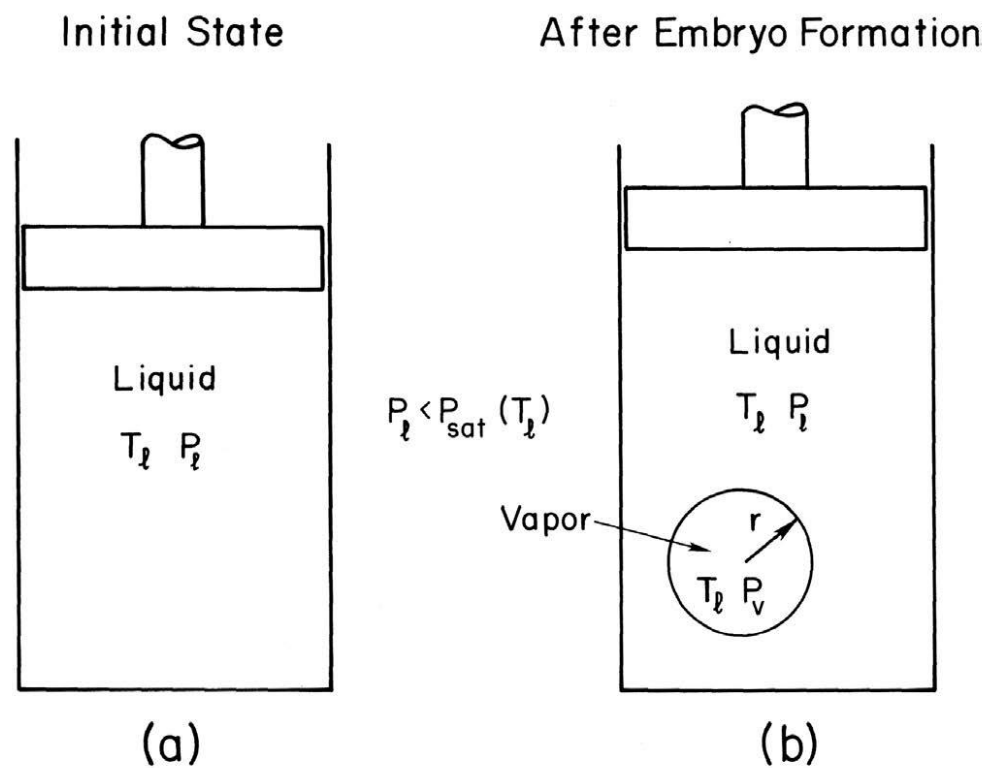
(b) – (a)

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

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

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

Homogeneous Nucleation



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

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

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

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, $\widehat{N}_v = P_v V_v / k_B T_l$ 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

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

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

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

Gibbs Free Energy Change

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

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

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

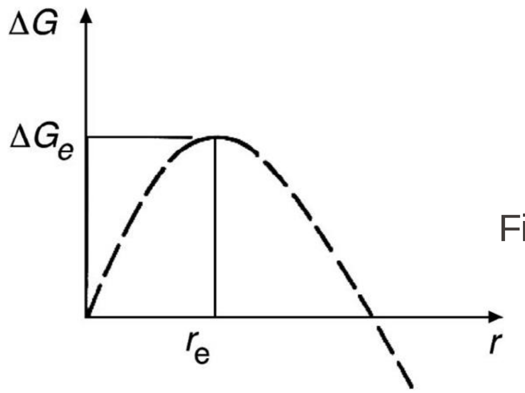


Figure 5.9 in Carey

Gibbs Free Energy Change

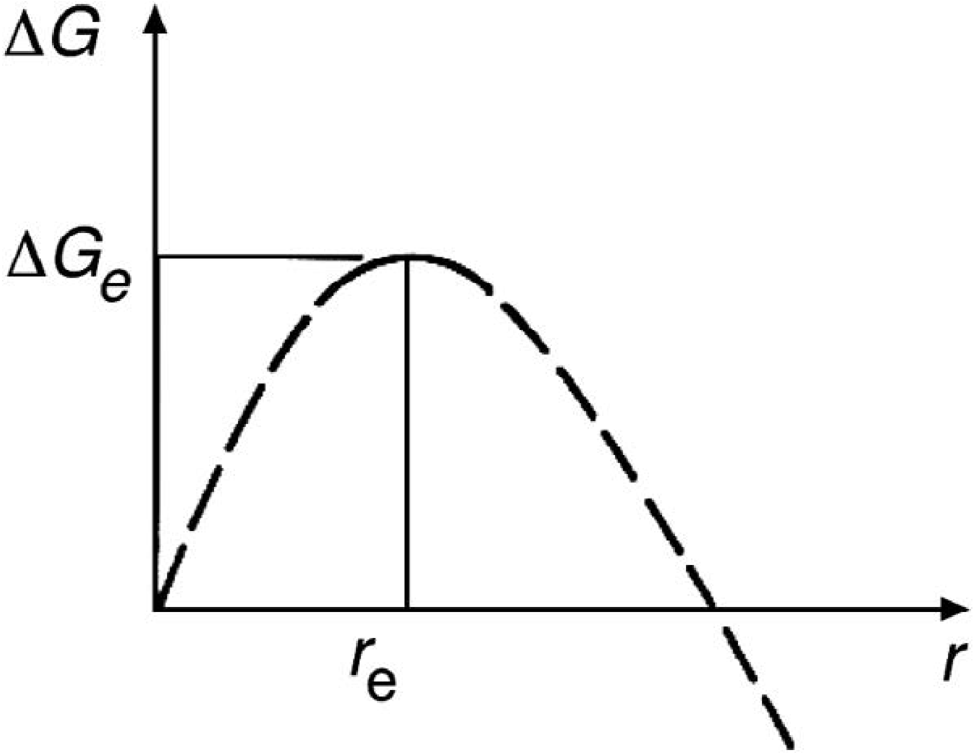


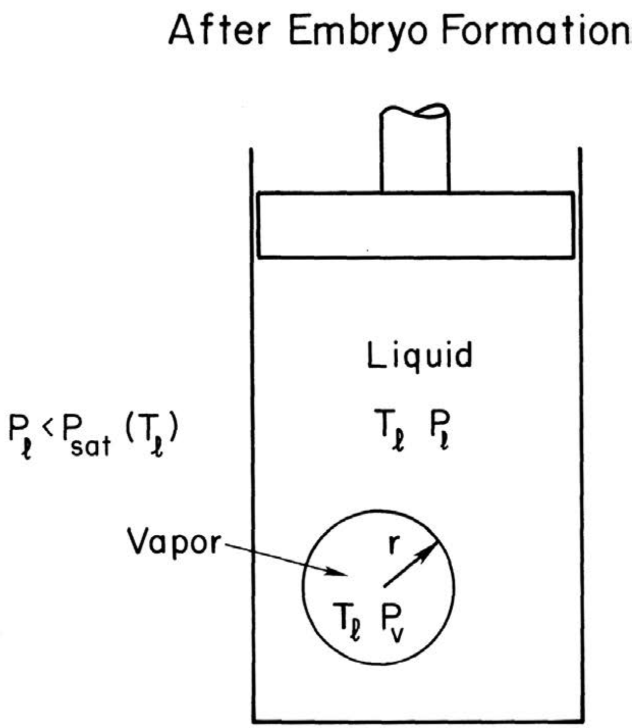
Figure 5.9 in Carey

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 $\quad g_v = g_l$

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

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

Heterogeneous Nucleation

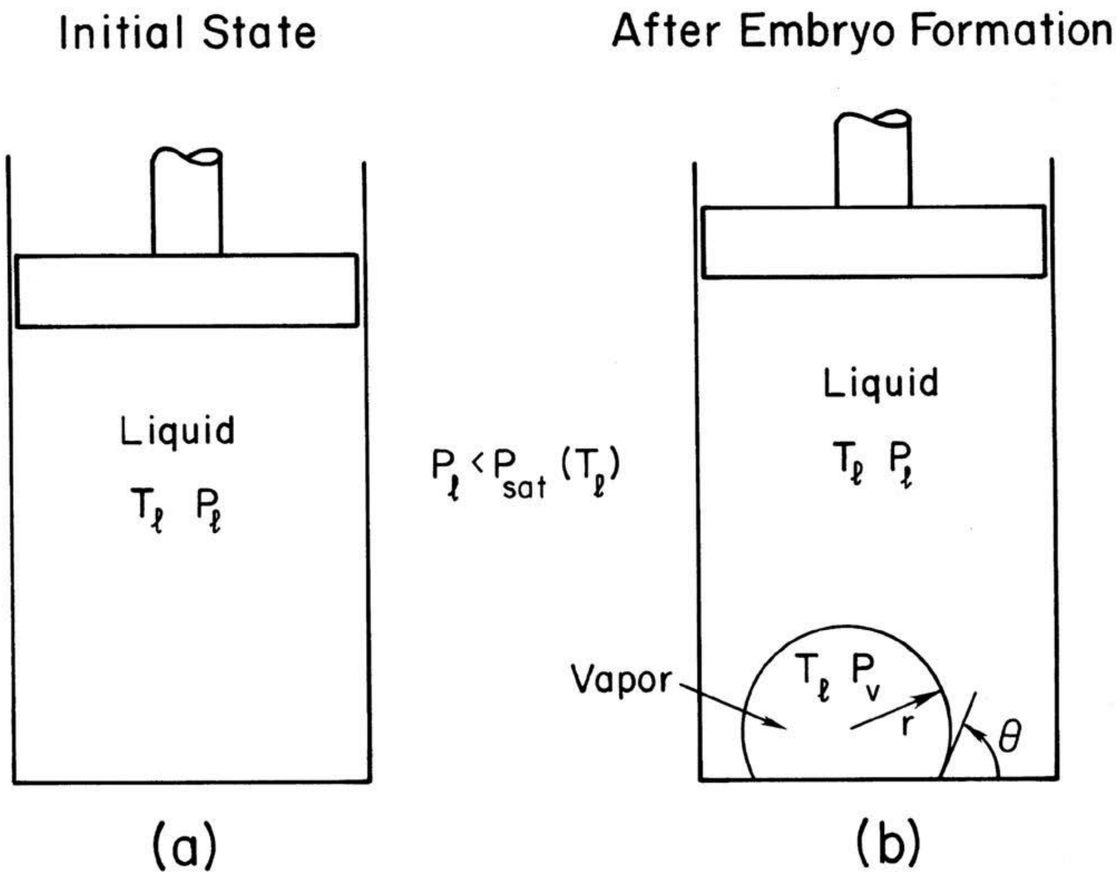


Figure 6.2 in Carey

Constant pressure constant temperature

Gibbs free energy analysis

$$G = G_l + G_v + G_i$$

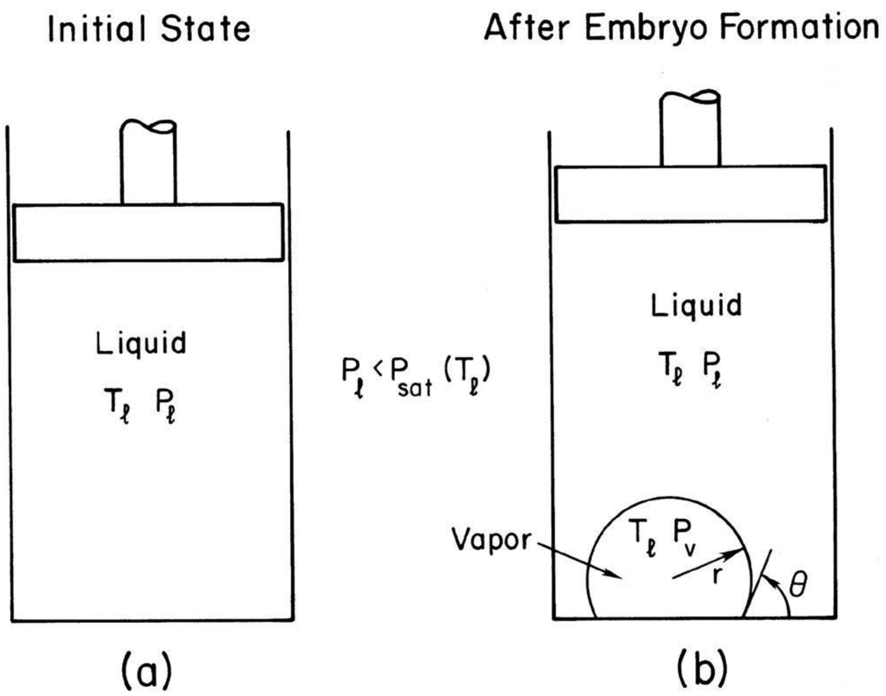
(b) – (a)

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

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

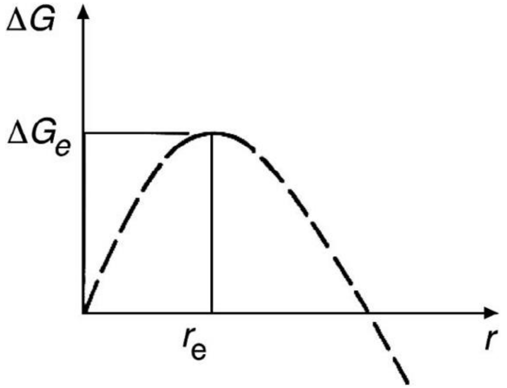
$$\begin{aligned}\Delta G_i &= \sigma_{lv}A_{lv} + \sigma_{sv}A_{sv} - \sigma_{sl}A_{sv}\\ &= \sigma_{lv}A_{lv} + \sigma_{lv}\cos\theta\, A_{sv}\\ &= \sigma_{lv}(A_{lv} + A_{sv}\cos\theta)\end{aligned}$$

Gibbs Free Energy Change



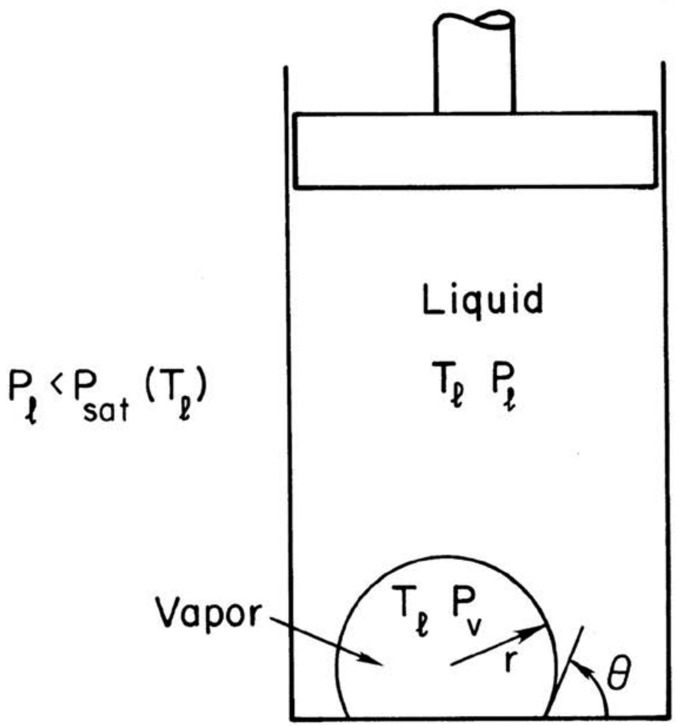
$$\Delta G = \hat{N}_v(\hat{g}_v - \hat{g}_l) + (P_l - P_v)V_v$$
$$+\sigma_{lv}[2\pi r^2(1+\cos\theta) + \pi r^2\cos\theta(1-\cos^2\theta)]$$

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



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

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 $g_v = g_l$

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

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

Gibbs Free Energy Barrier

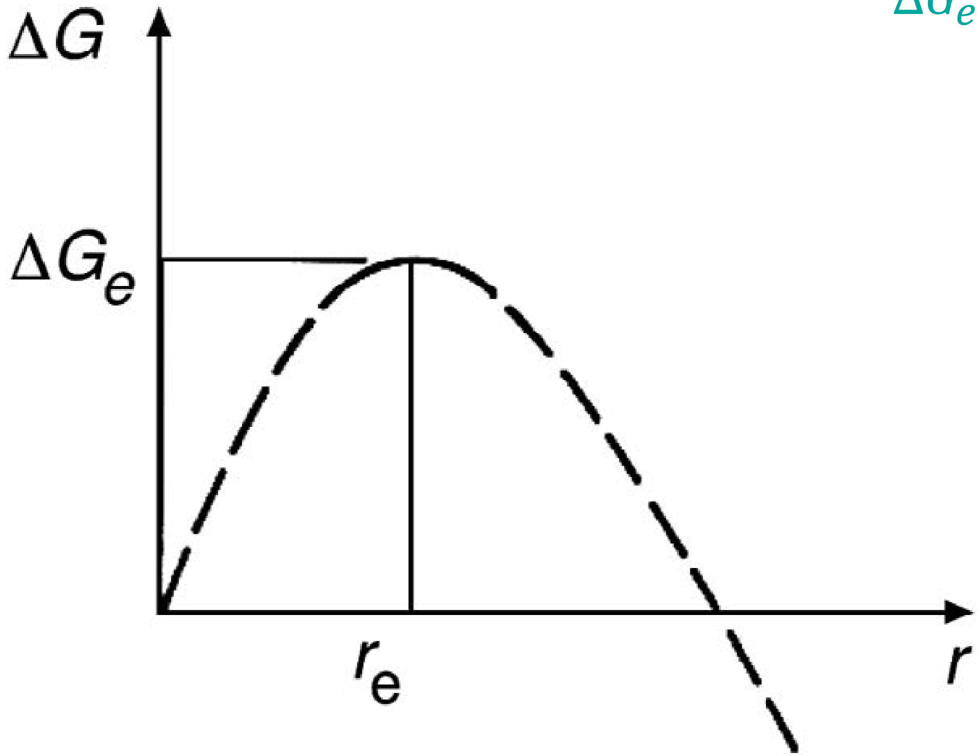


Figure 5.9 in Carey

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

When $\theta = 180°$, $F(\theta) = 0$

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

EPFL

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