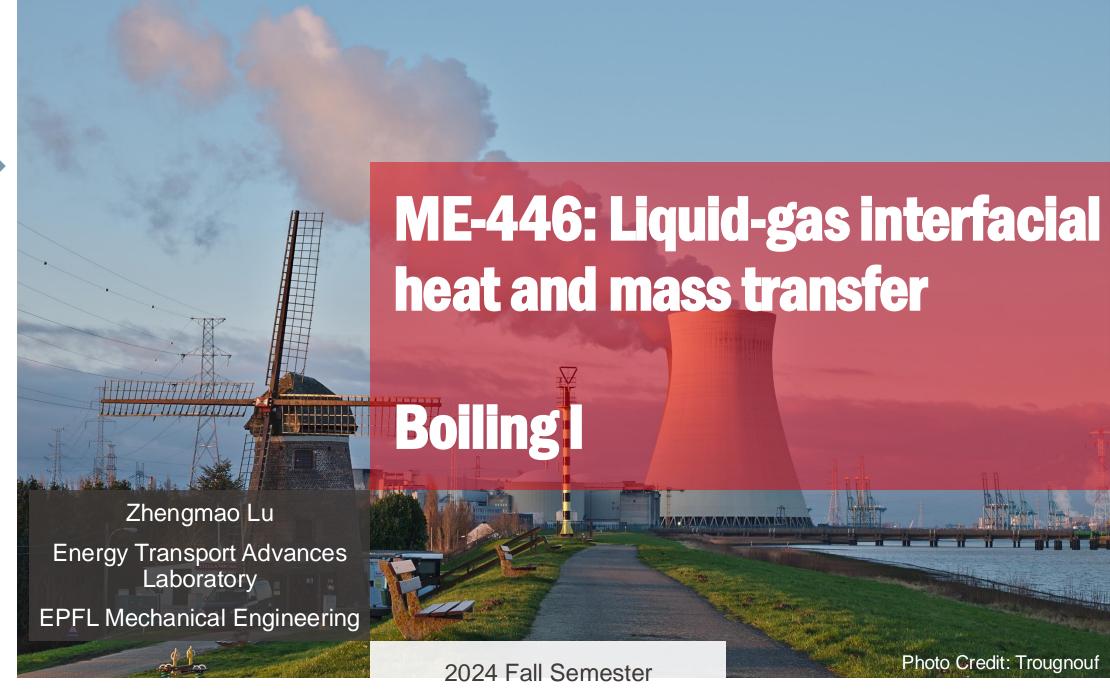
EPFL





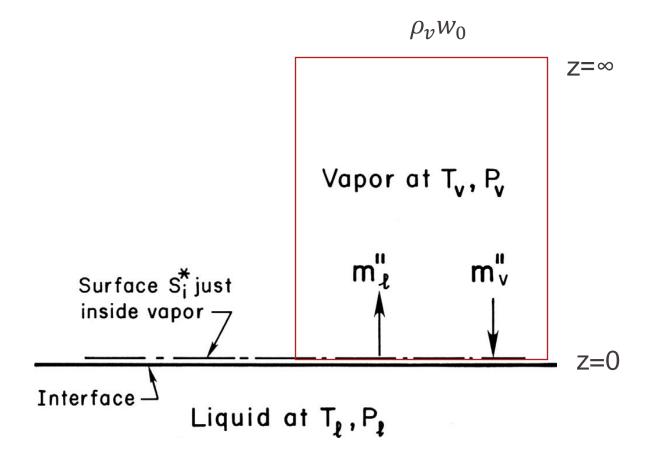


Last Time

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

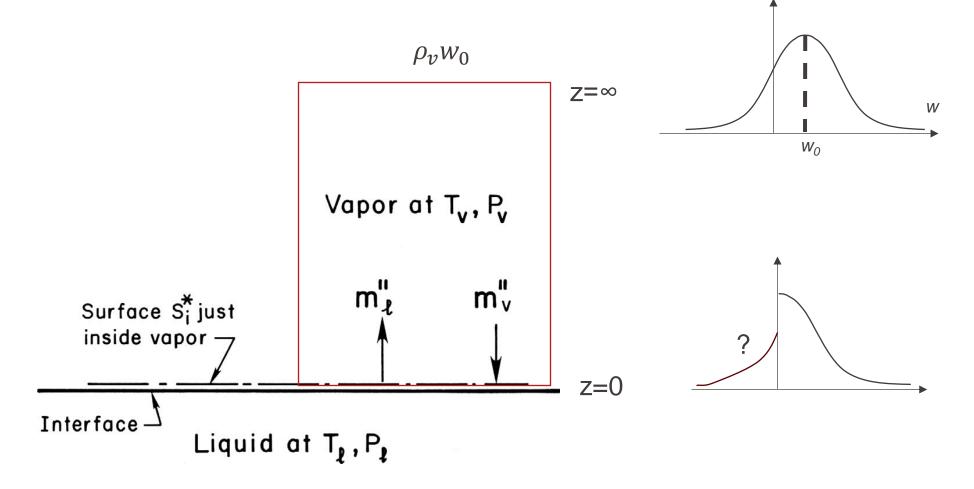


Mass Balance

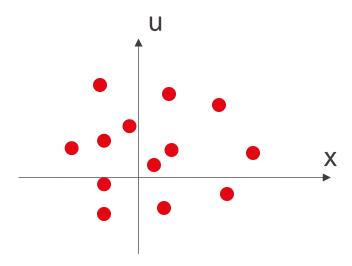




General Governing Equation



One-Dimensional Case





Boltzmann Equation

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

EPFL

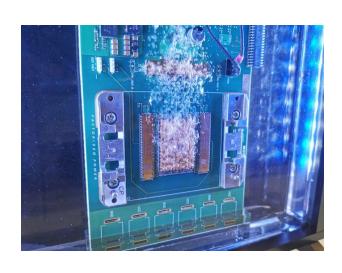
Boiling



cooking



(nuclear) power plant



immersion cooling

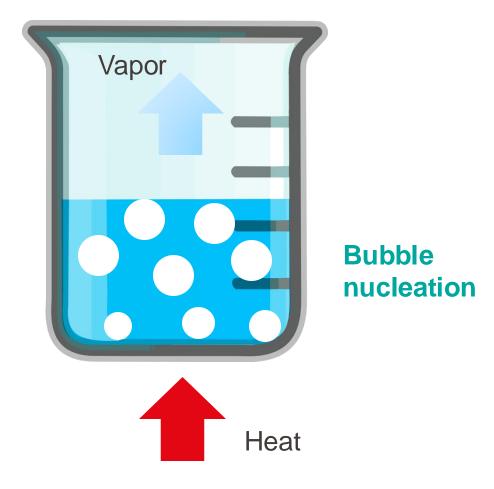
EPFL

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)

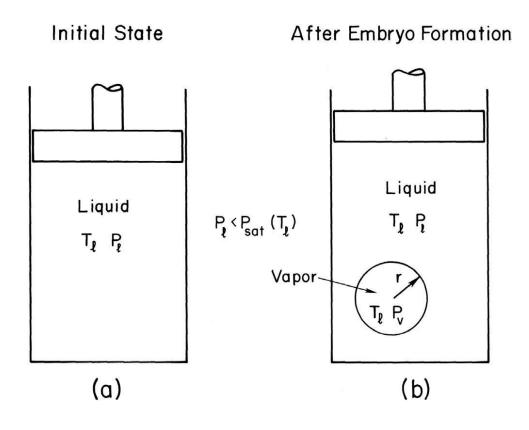
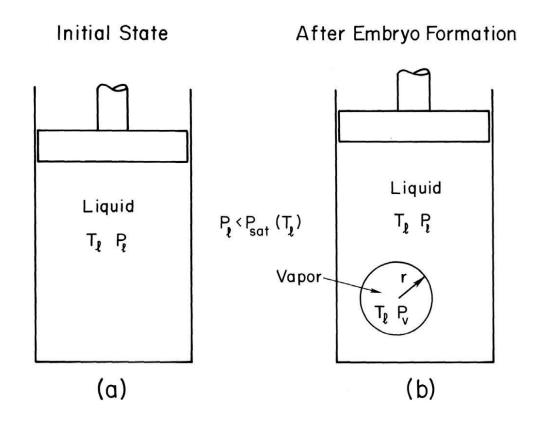


Figure 5.7 in Carey



Homogeneous Nucleation





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

Considering T_I and P_I as fixed values, assuming mechanical equilibrium is always satisfied

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



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

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



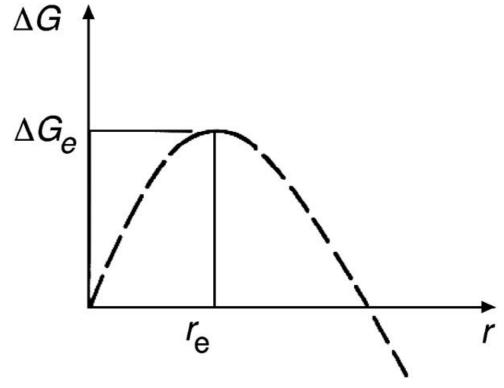


Figure 5.9 in Carey

Density fluctuation in superheated liquid produces bubbles of random r

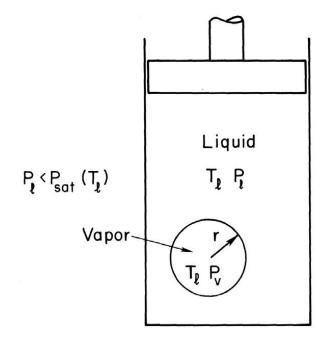
If $r < r_e$, the bubble collapses If $r > r_e$, the bubble grows

How do we determine r_e



Equilibrium Bubble Radius

After Embryo Formation





Heterogeneous Nucleation

Initial State

Liquid T, P,

After Embryo Formation

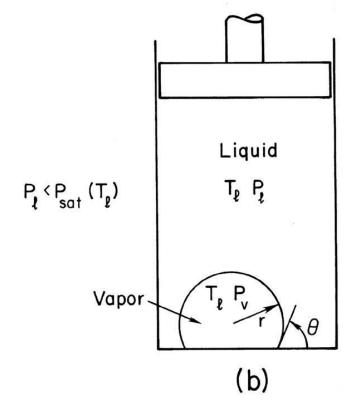
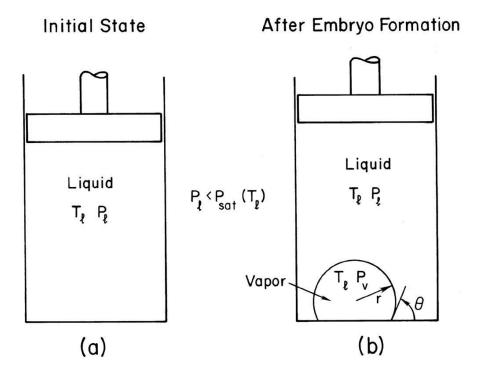
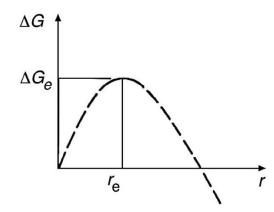


Figure 6.2 in Carey

(a)



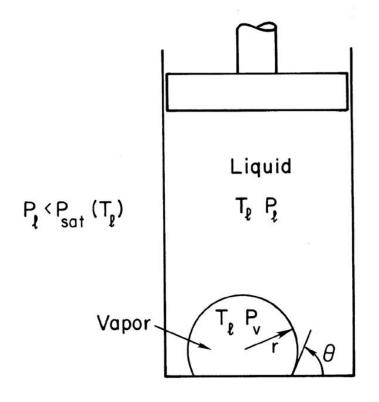






Equilibrium Bubble Radius

After Embryo Formation



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

$$dg = vdP - SdT$$

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

In equilibrium

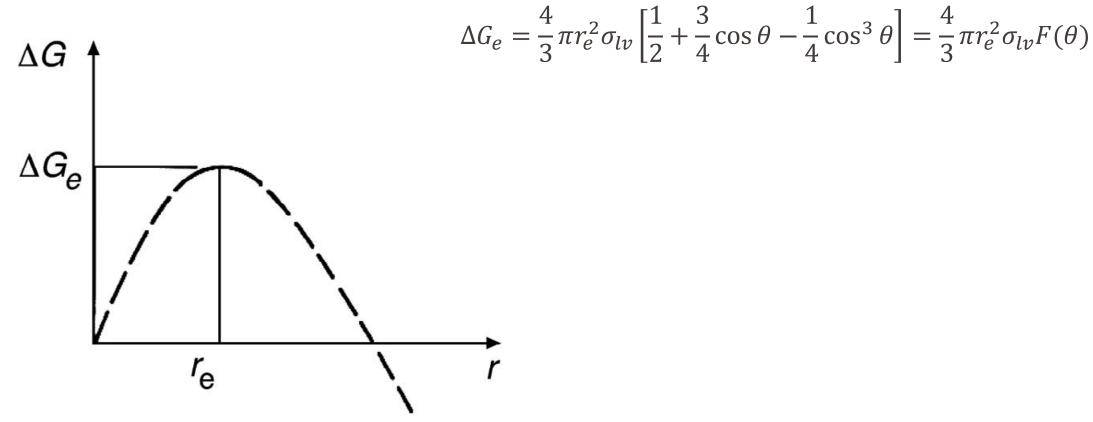
$$g_v = g_l$$

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

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



Gibbs Free Energy Barrier





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⁻²s⁻¹]



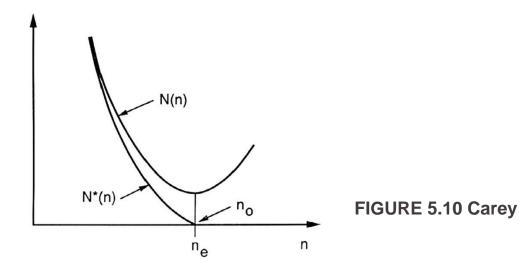
$$N_n A_n j_{ne} = N_{n+1} A_{n+1} j_{(n+1)c}$$

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

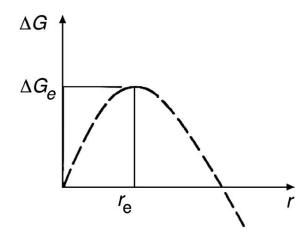
In superheated liquid, equilibrium is not necessarily satisfied

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





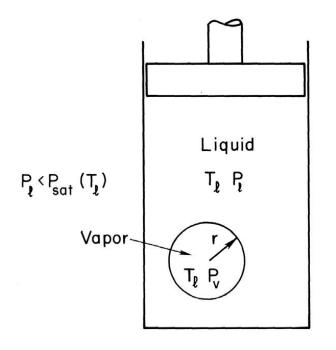






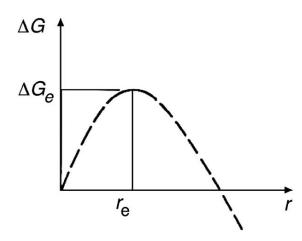
$$J \approx \frac{P_{ve}}{\sqrt{2\pi m k_B T_l}} \left(\int_0^\infty [N(n)A(n)]^{-1} dn \right)^{-1}$$

After Embryo Formation





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



EPFL

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

$$J = \rho_{N,l} \left[\frac{6\sigma_{lv}}{\pi m \left(2 - \frac{P_l}{P_{No}}\right)} \right]^{1/2} \exp\left(-\frac{4\pi r_e^2 \sigma_{lv}}{3k_B T_l}\right) \text{ increases sharply with temperature}$$

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.

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

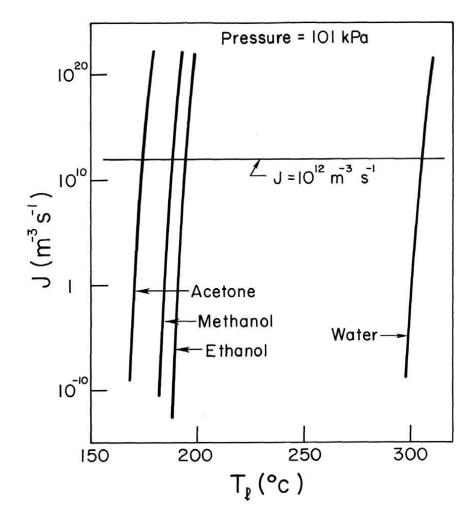


FIGURE 5.12, Carey



Intended Learning Objectives Today

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