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

Evaporation II

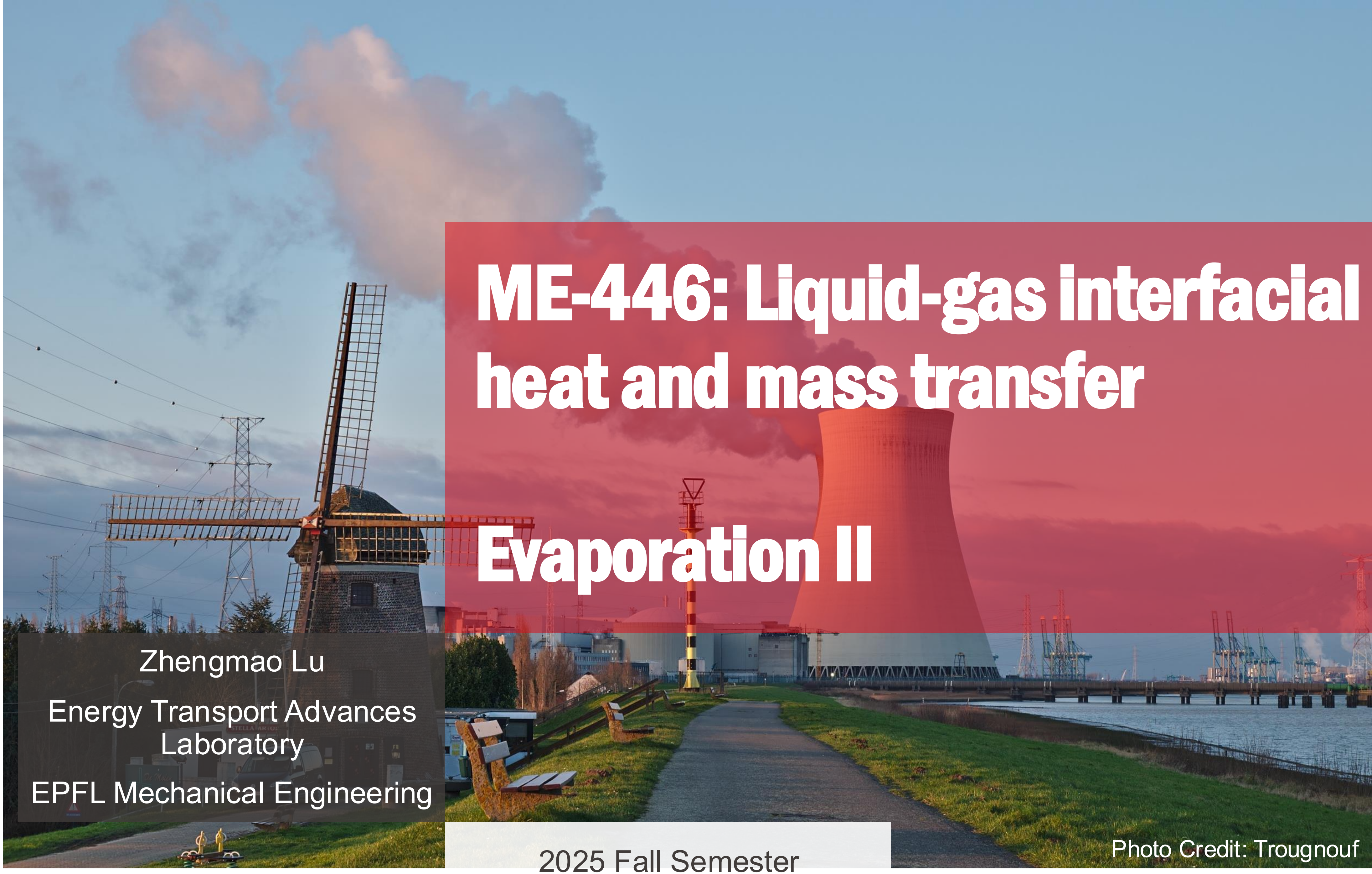

Photo Credit: Trougnouf

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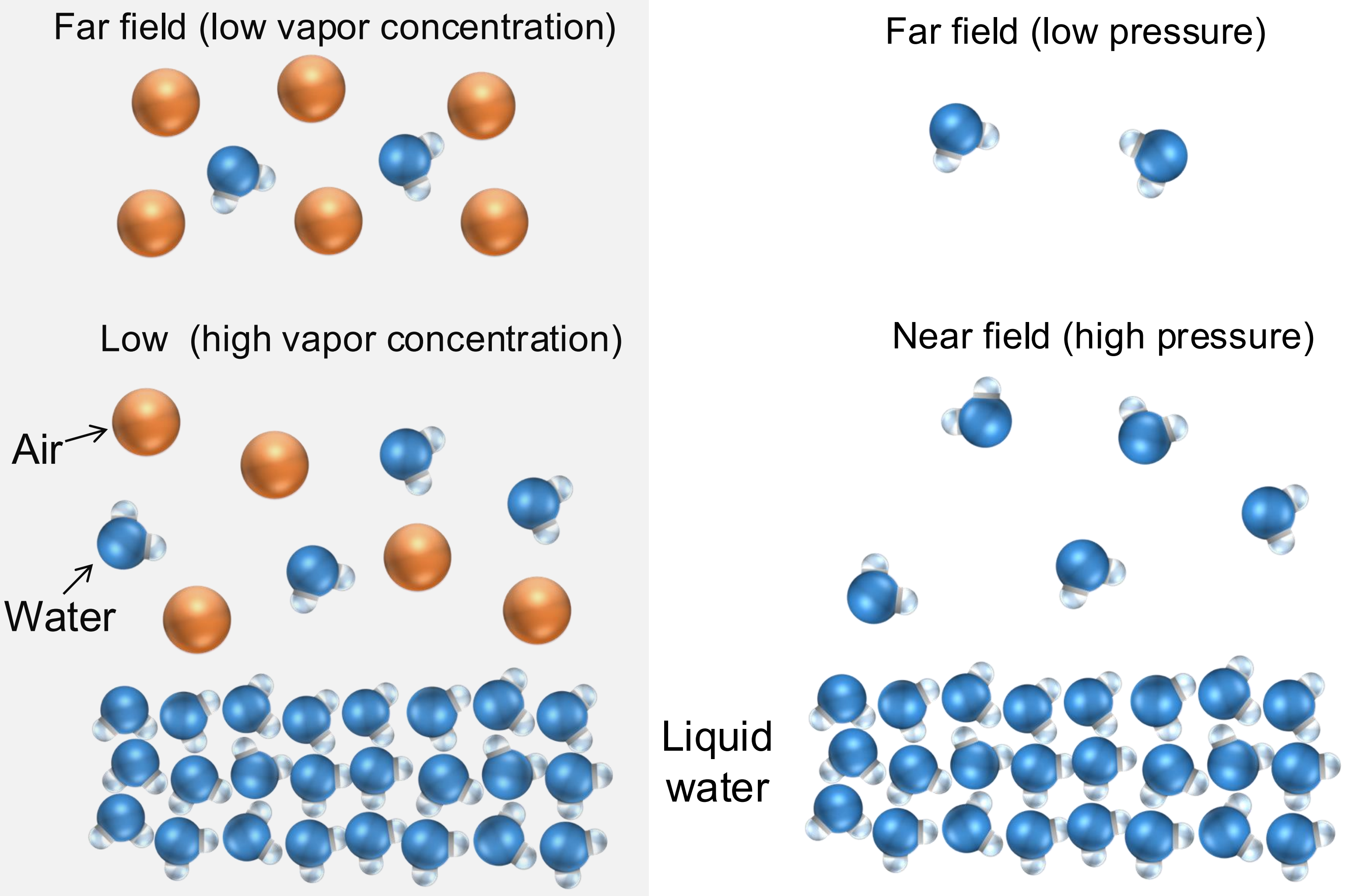
EPFL Mechanical Engineering

2025 Fall Semester

Last Week

Air → Diffusion Limited

Vapor → Kinetically Limited

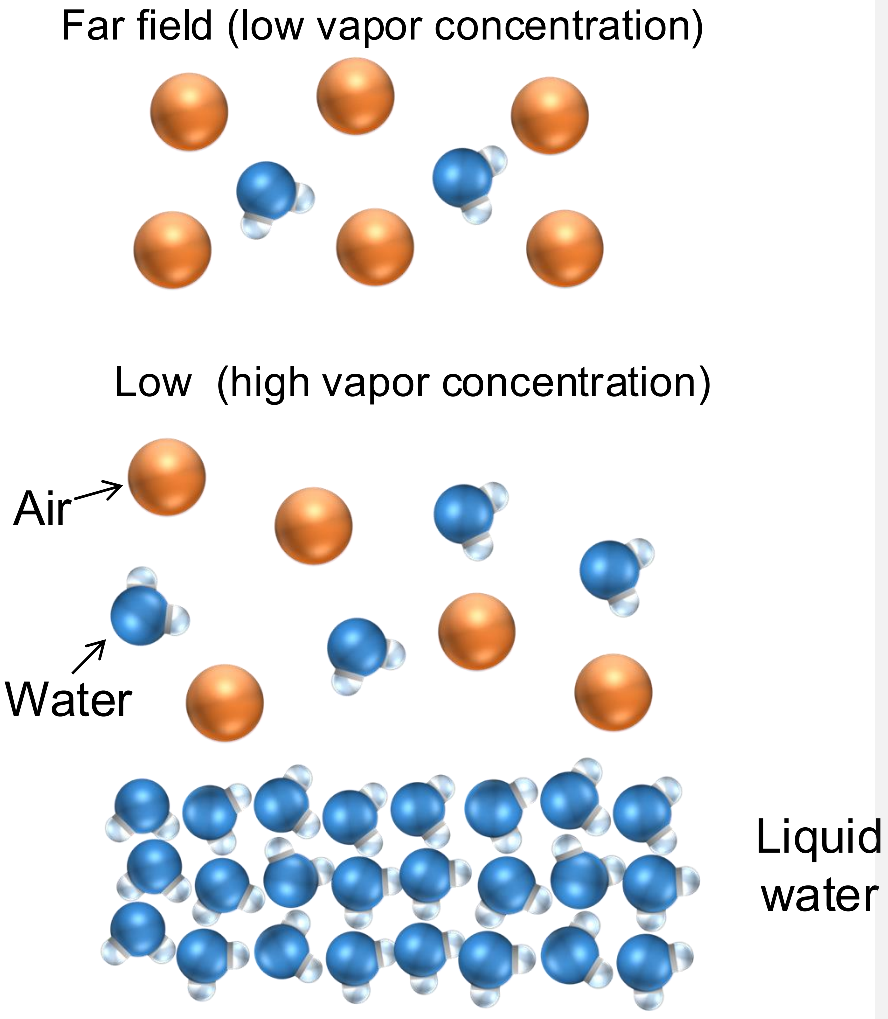


Last Week

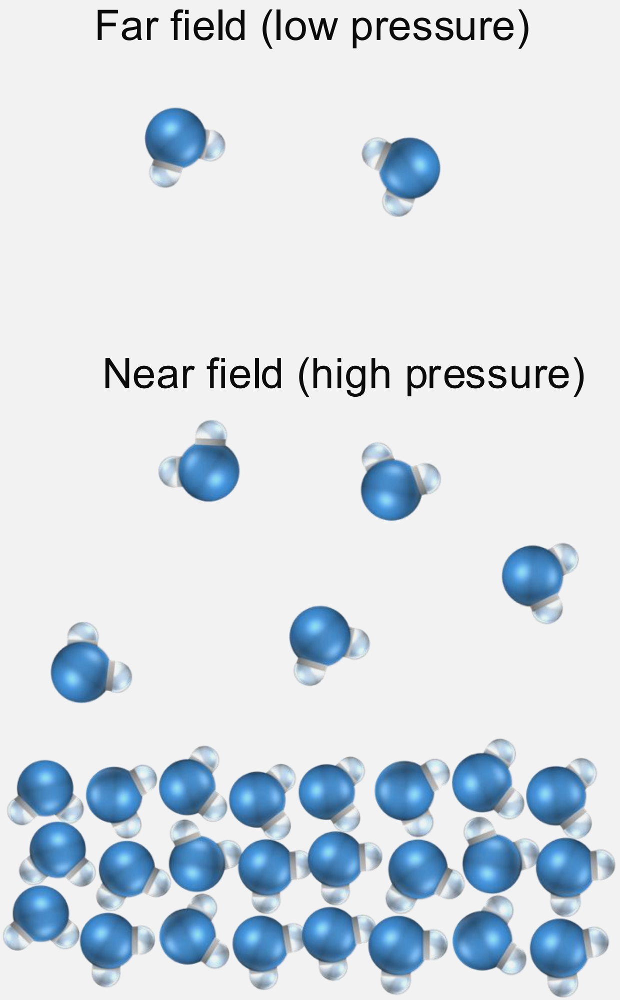
- Fick’s Law of Diffusion
  - Physical meaning of gradient and divergence operators
- Heat and mass transfer analogy
- Coffee ring effects

Fundamental Picture of Evaporation

Air → Diffusion Limited



Vapor → Kinetically Limited



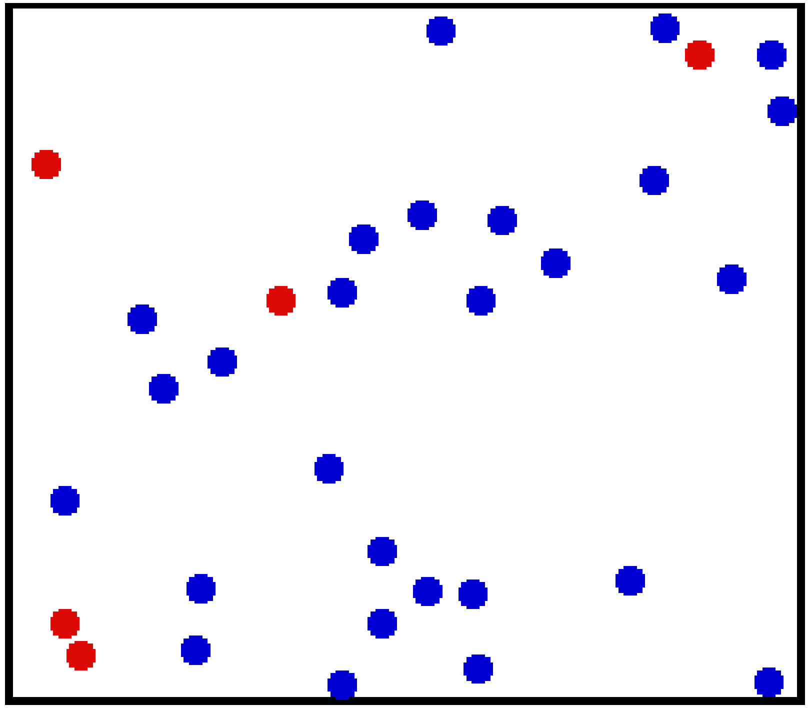
Intended Learning Objectives Today

- Understand basic assumptions of the **kinetic theory of gases**
- Relate **macroscopic quantities** to microscopic molecular motion
- Derive and understand the limit of **Schrage equation** for evaporation

Reading materials: **Carey** Chapter 4.5, Appendix I

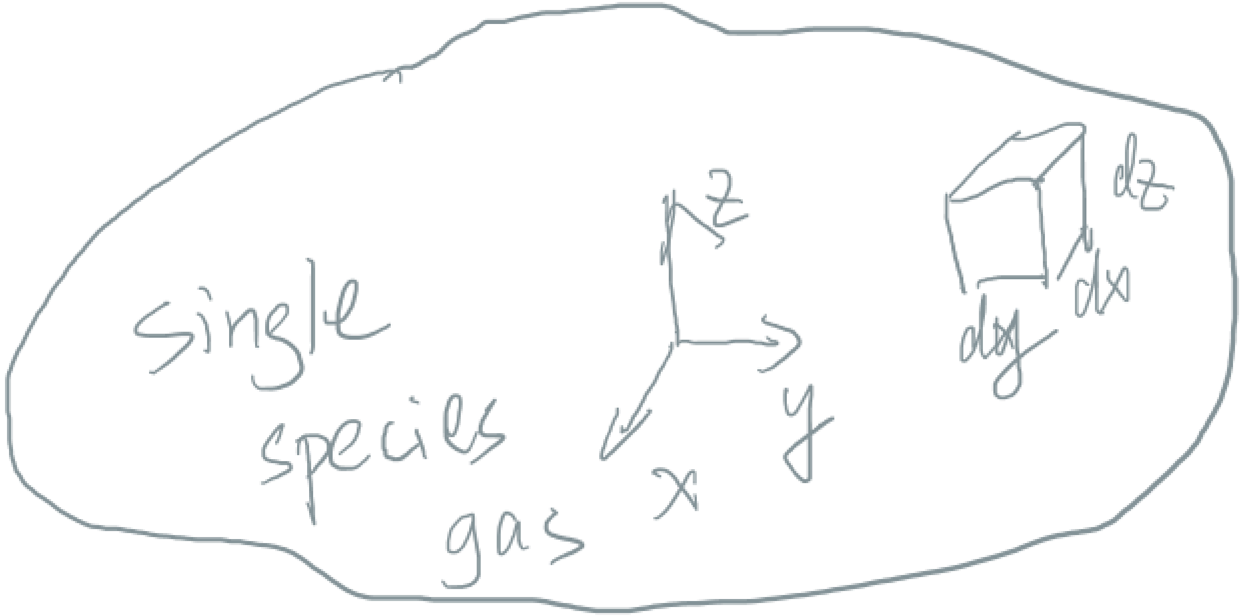
Crash Course on Kinetic Theory of Gases

- Consider gas as **a large number of randomly moving particles** that collide with one another every now and then
- Collisions are elastic: **kinetic energy is conserved** before and after
- Between collisions, particles are not affected by any force field



Credit: A. Greg

Velocity Distribution Function



The fraction of (or the probability of finding) molecules with Cartesian velocities (u, v, w) in the ranges *u* to *u* + d*u*, v to *v* + d*v*, *w* to *w* + d*w* in a unit volume is

$$\frac{dn_{uvw}}{n} = f(u, v, w)dudvdw$$

n: number density

$n = \rho/m$, where *m* is molecular mass

Velocity Distribution Function

$$\int f(u,v,w)dudvdw = \int \frac{dn_{uvw}}{n} dudvdw = 1$$

f can be seen as a probability density function

Marginal distribution $\quad f_x(u) = \int dv \int dw\, f(u,v,w)$

$f_x(u)$ is the probability density function for u $\quad \int f_x du = 1$

We can define $f_y(v)$, $f_z(w)$ similarly

Average Properties

Average velocity in x-direction $u_0 = \int fudud vdw = \int f_x udu$

Similarly, we can define average velocity in y- and z- direction: v_0, w_0

Average kinetic energy $\bar{e}_k = \int f \frac{m}{2}(u^2 + v^2 + w^2)dudvdw$

$$\bar{e}_k = \int f \frac{m}{2}[(u_r + u_0)^2 + (v_r + v_0)^2 + (w_r + w_0)^2]dudvdw$$

u_r, v_r, w_r are velocities relative to the bulk for each molecule in x-, y-, and z-directions

$$\bar{e}_k = \frac{m}{2}(u_0^2 + v_0^2 + w_0^2) + \int f \frac{m}{2}(u_r^2 + v_r^2 + w_r^2)dudvdw = e_{kb} + \bar{e}_{kr}$$

Homework

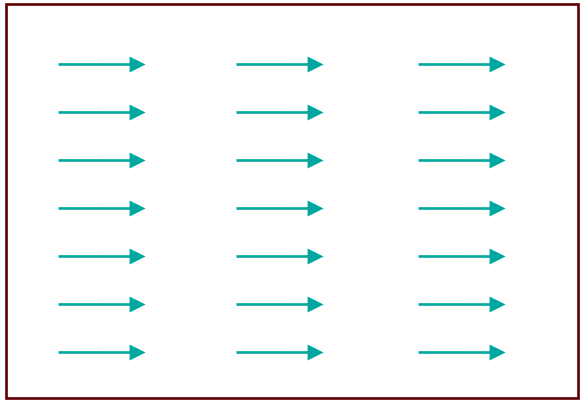
Temperature in Kinetic Theory

$$\frac{3}{2}k_BT = \bar{e}_{kr} = \int f\frac{m}{2}(u_r^2 + v_r^2 + w_r^2)dudvdw$$

k_B: Boltzmann constant 1.38×10^{-23} [J/K]

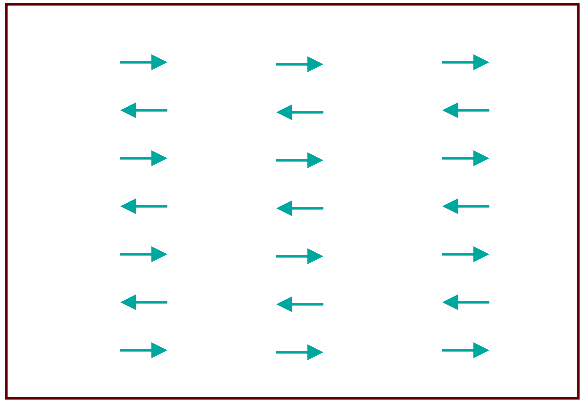
Pop quiz

Situation A



All molecules moving in the same direction at 10 m/s

Situation B



Half of the molecules moving in one direction 5 m/s and the other half moving in the opposite direction at 5 m/s

Scan the QR code with your device
Or go to **echo360poll.eu**

Enter Code

luepfl

In which case is the temperature higher

A. $T_A > T_B$

B. $T_A < T_B$

C. $T_A = T_B$

D. I don’t really know

Maxwell-Boltzmann Distribution

$$\frac{dn_{uvw}}{n} = f(u, v, w)dudvdw$$

In equilibrium, f takes a Gaussian form $\quad f \propto \exp\left(-\frac{e_k}{k_B T}\right)$

Kinetic energy of each molecule $\quad e_k = \frac{1}{2}m(u^2 + v^2 + w^2)$

$$\int f dudvdw = 1 \Rightarrow \int C \exp\left(-\frac{m}{2k_B T}(u^2 + v^2 + w^2)\right) dudvdw = 1$$

$$\Rightarrow C = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}}$$

Check the Gaussian integral $\int e^{-x^2} dx = \sqrt{\pi}$

Maxwell-Boltzmann Distribution

$$f_{MB}(u,v,w) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left[-\frac{m}{2k_B T}(u^2+v^2+w^2)\right]$$

Marginal M-B distribution in x-direction

$$f_{MBx}(u) = \int dv \int dw\, f_{MB}(u,v,w) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{mu^2}{2k_B T}\right)$$

Similarly, we can obtain $f_{MBy}(v)$, $f_{MBz}(w)$

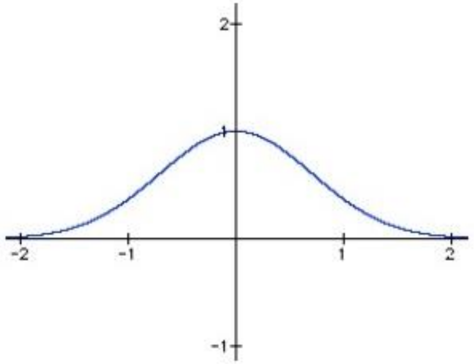
$$f_{MB} = f_{MBx}(u)\, f_{MBy}(v)\, f_{MBz}(w)$$

Maxwell-Boltzmann Distribution

In standard M-B distribution

Average velocity in x-direction $$u_0 = \int f_{MBx} u du = \int \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{mu^2}{2k_B T}\right) u du = 0$$

Odd function times even function



Similarly, $v_0 = 0, w_0 = 0$

$$\bar{e}_{kr} = \bar{e}_k = \int f_{MB} \frac{m}{2}(u^2 + v^2 + w^2) du dv dw = \frac{3}{2} k_B T$$

The parameter *T* we put in the M-B distribution happens to represent temperature

Drifted M-B Distribution

In the case that the vapor is moving at a bulk velocity (u_0, v_0, w_0), but otherwise is in equilibrium, we can take the frame of reference that moves at the bulk vapor velocity.

In this reference frame, the bulk vapor is static and M-B applies

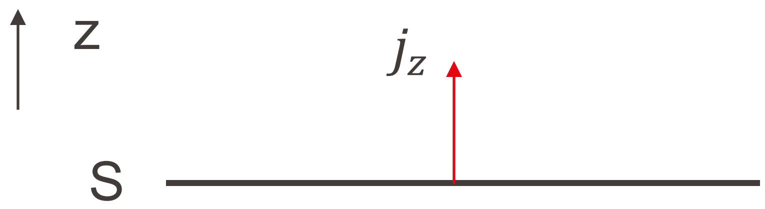
$$f(u,v,w) = f_{MB}(u-u_0, v-v_0, w-w_0)$$

$$= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left[-\frac{m}{2k_B T}\left((u-u_0)^2 + (v-v_0)^2 + (w-w_0)^2\right)\right]$$

Marginal distribution $$f_x(u) = \int dv \int dw\, f(u,v,w) = f_{MBx}(u-u_0)$$

$$u_0 = \int f_x u du = \int u f_{MBx}(u-u_0)\, du$$ Consistent

Mass Flux Across a Surface



How to determine the molecular flux across a surface if the velocity distribution function is known

j_z : the rate at which molecules pass through surface S per unit area

What matters is velocity distribution in the direction perpendicular to the surface $f_z(w)dw$

The molecular flux due to molecules with z-velocity between w and w+dw is $nf_z(w)dw \cdot w$

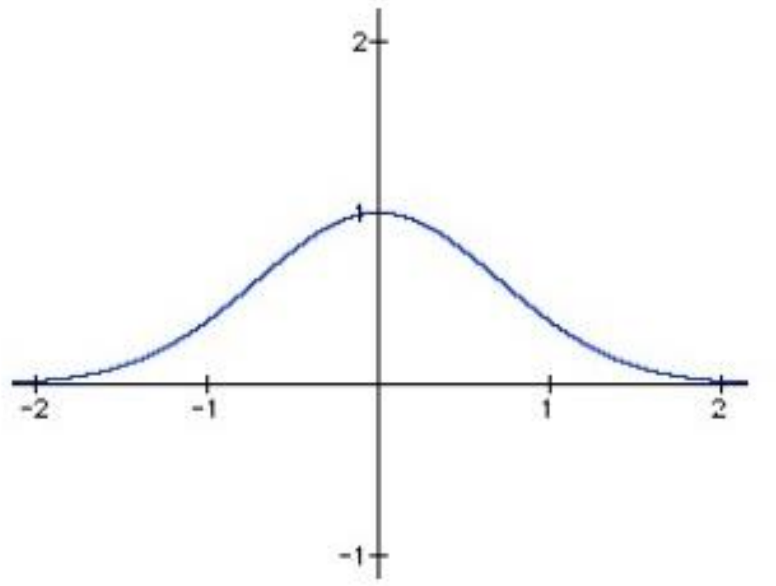
$$j_z = n\int f_z(w)wdw$$

Mass flux $m_z'' = mj_z = \rho\int f_z(w)wdw$

For standard M-B, $m_z'' = 0$

For drifted M-B, $m_z'' = \rho w_0$

One Way Mass Flux



With symmetric velocity distribution such as M-B, although the net molecular flux is zero is zero, there are two one-way molecular fluxes negating each other.

For standard M-B

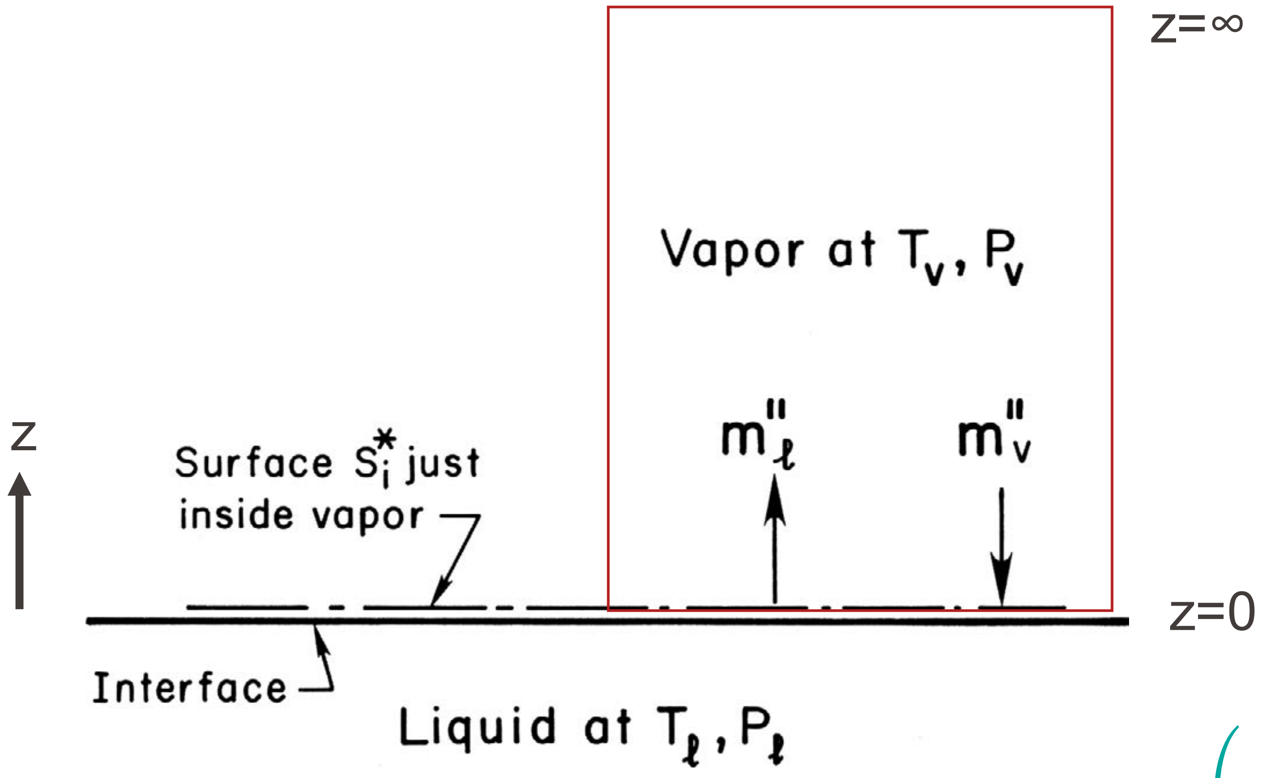
$$j_{z^+} = \int_0^\infty n f_{MBz} w dw = \int_0^\infty n \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{mw^2}{2k_B T}\right) w dw = n \left(\frac{k_B T}{2\pi m}\right)^{\frac{1}{2}}$$

[m/s]

$$j_{z^-} = -j_{z^+}$$

$$m''_{z^+} = \rho \left(\frac{k_B T}{2\pi m}\right)^{\frac{1}{2}}$$

Liquid-Vapor Interfacial Transport



z-direction opposite to Figure 4.10 in Carey

Far away from the surface (P_v, T_v)

$$\rho_v = \frac{P_v}{RT_v}$$

R: specific gas constant

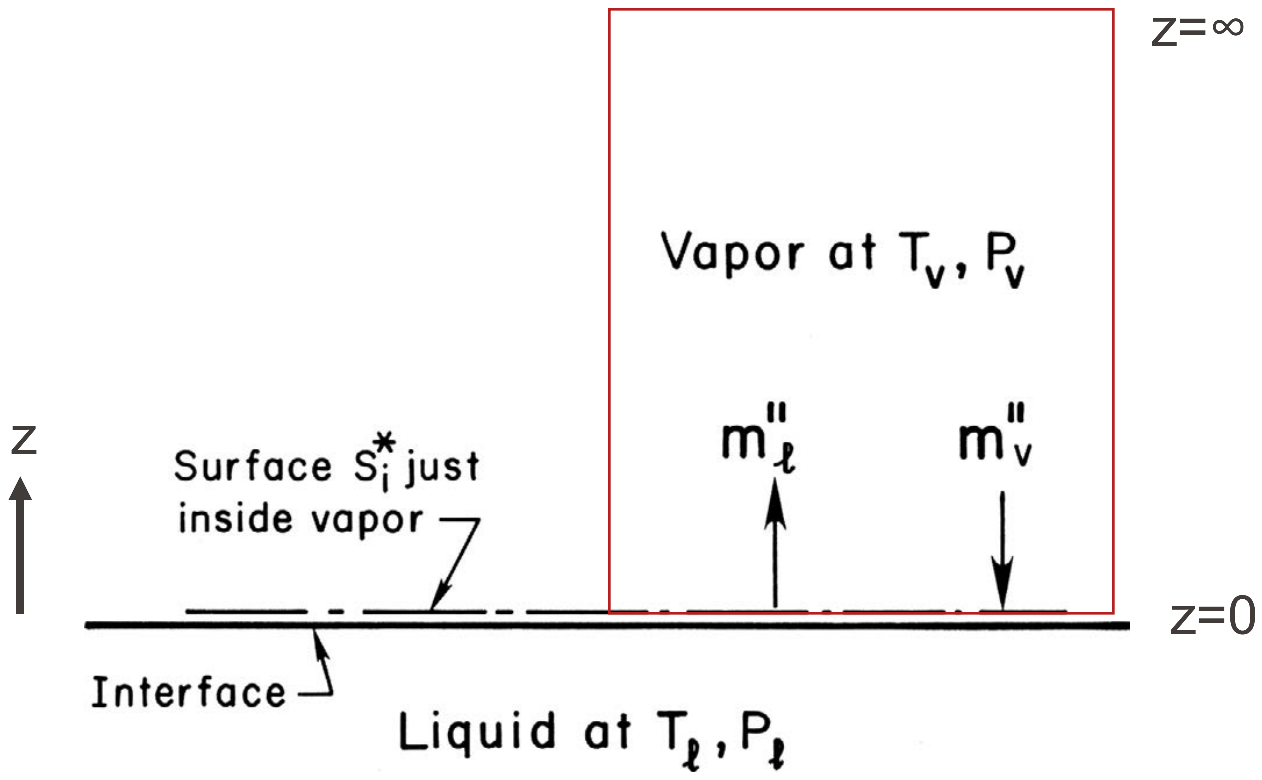
$$R = \frac{k_B}{m};\ R = \frac{\bar{R}}{M};\ \bar{R} = k_B N_A$$

$$f_\infty = f_{MB}(u, v, w - w_0)\Big|_{T_v}$$

$$= \left(\frac{m}{2\pi k_B T_v}\right)^{\frac{3}{2}} \exp\left[-\frac{m}{2k_B T_v}\left(u^2 + v^2 + (w - w_0)^2\right)\right]$$

w_0 unknown bulk vapor velocity at z=∞; mass flux in the system $\rho_v w_0$

Liquid-Vapor Interfacial Transport



At surface S_i^*, m_l'' is due to

1) molecules emitted from liquid surface

$$m_e'' = \hat{\sigma}_e \rho_e \left(\frac{k_B T_l}{2\pi m}\right)^{\frac{1}{2}}$$

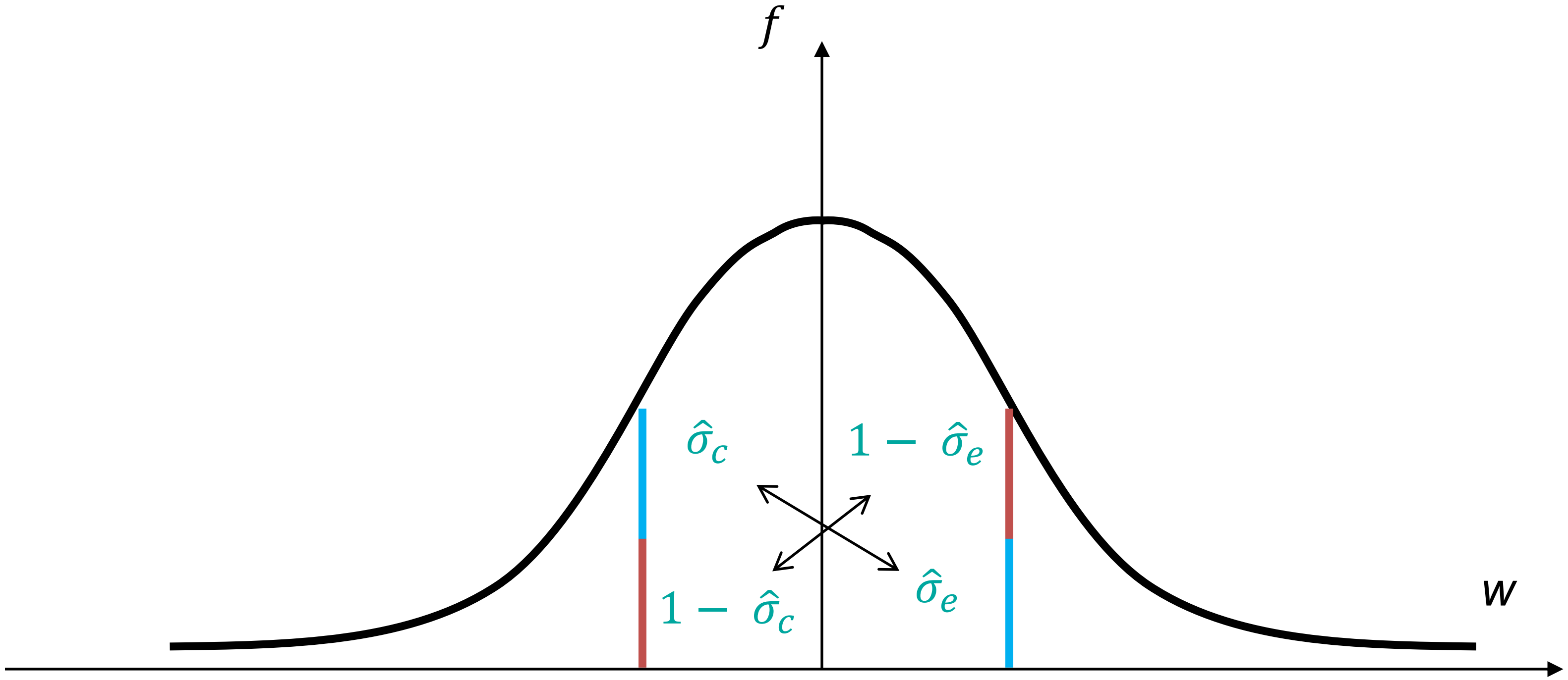
$$\rho_e = P_l / R T_l$$

(one-way flux from equilibrium vapor at z = 0, with evaporation coefficient $\hat{\sigma}_e$ for non-ideality)

2) vapor molecules reflected from liquid surface $(1 - \hat{\sigma}_c)|m_v''|$

$\hat{\sigma}_c$: condensation coefficient/probability

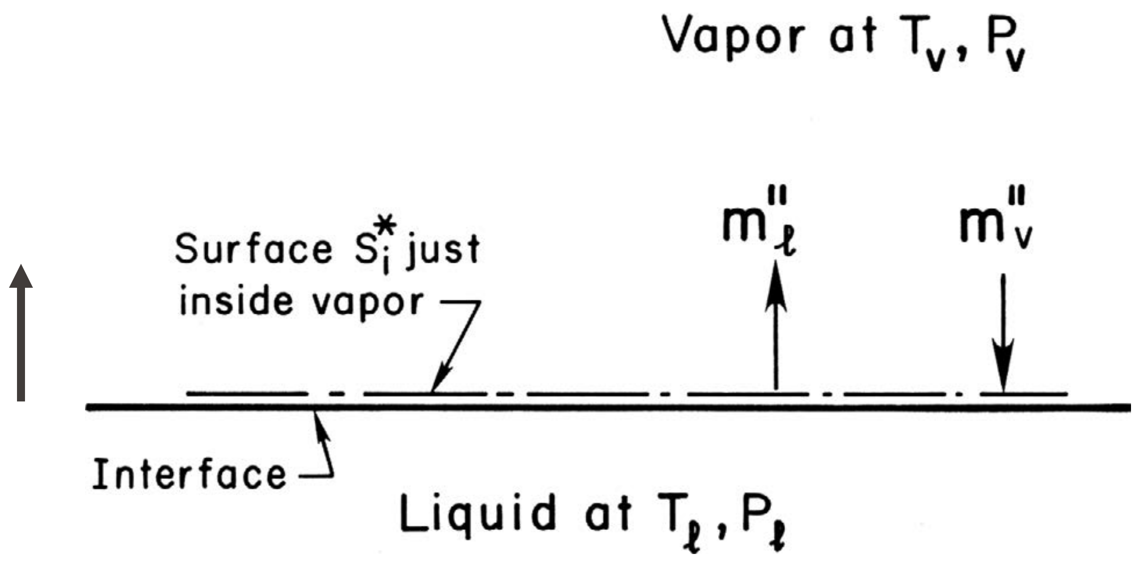
Evaporation/Condensation Coefficient



In equilibrium, $\hat{\sigma}_c = \hat{\sigma}_e = \hat{\sigma}$ Accommodation coefficient

Analogous to Kirchhoff's law, emissivity = absorptivity

Hertz-Knudsen Equation



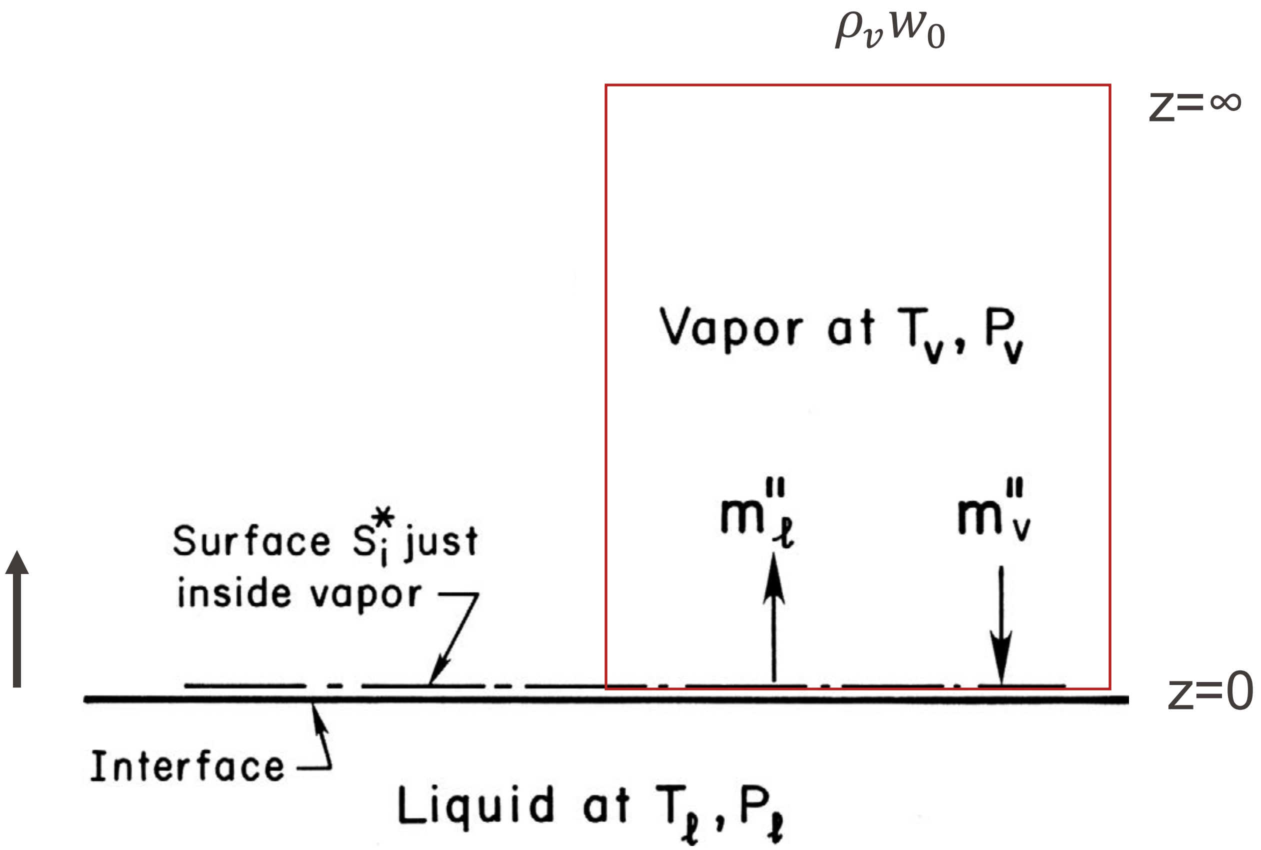
$$|m_v''| = \rho_v \left(\frac{k_B T_v}{2\pi m}\right)^{\frac{1}{2}}$$

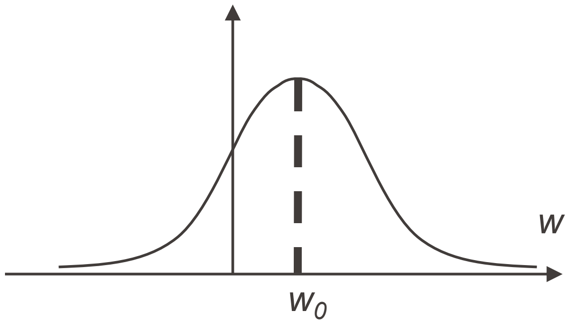
$$m_l'' = \hat{\sigma}_e m_e'' + (1 - \hat{\sigma}_c)|m_v''|$$

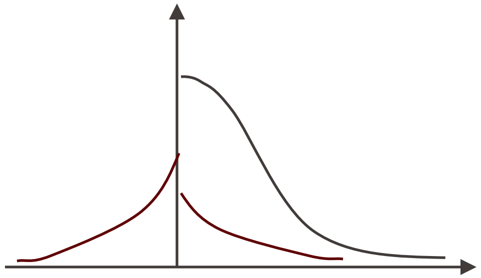
$$m_{net}'' = m_l'' - m_v'' = \hat{\sigma}_e m_e'' - \hat{\sigma}_c |m_v''|$$

$$[m_{net}'']_{\mathrm{HK}} = \hat{\sigma}_e \rho_e \left(\frac{k_B T_l}{2\pi m}\right)^{\frac{1}{2}} - \hat{\sigma}_c \rho_v \left(\frac{k_B T_v}{2\pi m}\right)^{\frac{1}{2}}$$

Schrage Equation



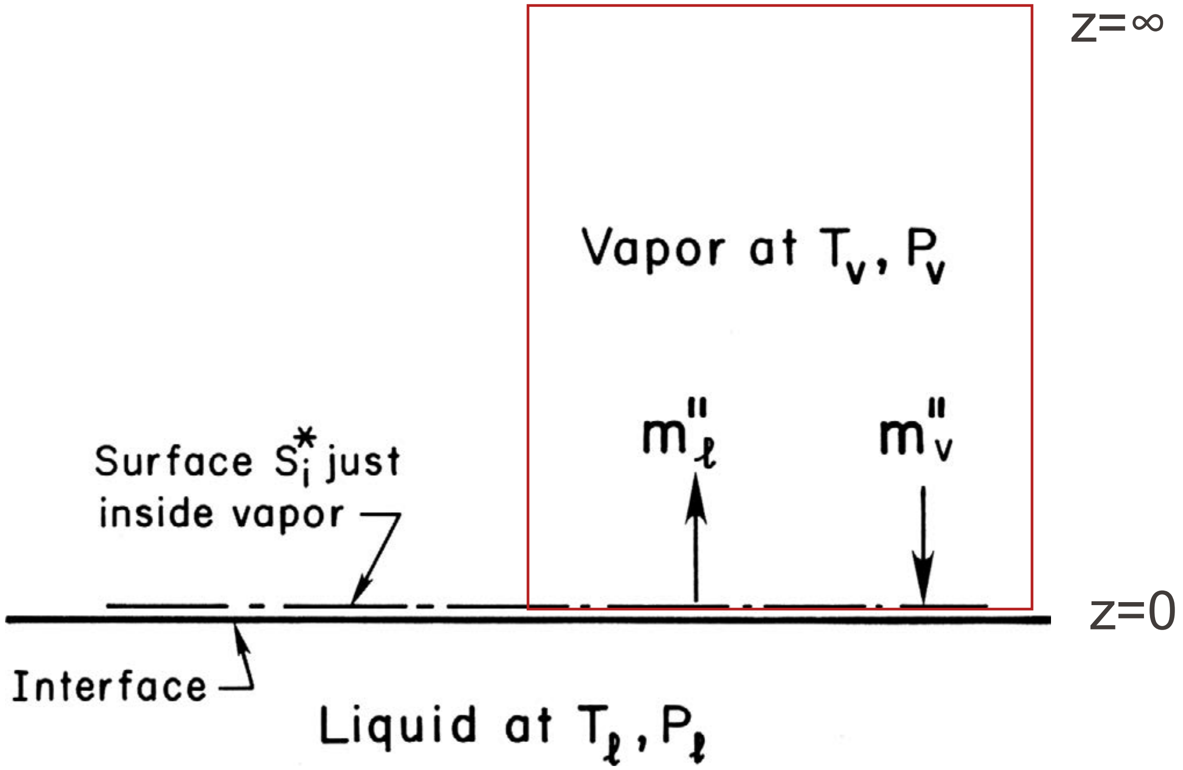




$$m_v'' = -m\int_{-\infty}^{0} n_\infty f_{\infty z} w dw = \rho_v \int_{-\infty}^{0}\left(\frac{m}{2\pi k_B T_v}\right)^{\frac{1}{2}} \exp\left(-\frac{m(w-w_0)^2}{2k_B T_v}\right) w dw = m_v''(w_0)$$

Mass Balance

$\rho_v w_0$



Mass balance

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

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

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

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

Solve for w_0

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

Schrage Equation

When $\frac{1}{2}mw_0^2 \ll k_B T_v$, the evaporation heat flux can be written in a closed form

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

z-direction defined differently from Carey

When $\hat{\sigma} = 0$, liquid surface is like an impermeable wall and there is no evaporation

Additional comment: Schrage's assumption about the velocity distribution has implications in energy and momentum balance/imbalance as well (which will result in three equations with one unknown, causing inconsistencies)

Summary

- Understand basic assumptions of the **kinetic theory of gases**
- Relate **macroscopic quantities** to microscopic molecular motion
- Derive and understand the limit of **Schrage equation** for evaporation

Reading materials: **Carey** Chapter 4.5, Appendix I