

# Modern Thin Film Deposition Technologies

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**Course Objective:**

To prepare students with a solid knowledge of the physics behind majority of modern vapor phase thin film deposition technologies.

**Text book:**

<Thin Film Deposition: Principles & Practice> by Donald L. Smith; McGraw-Hill,  
ISBN 0-07-058502-4

**Materials covered:**

Chapters 1-7 & 9.

**Optional reading:** <Thin Film Processes II> John L. Vossen, and Werner Kern,  
Academic Press Inc., ISBN: 0-12-728251-3

Date	Sequence	Content
06/27/2017	1	Ch.1: introduction; Ch.2: Gas kinetics
06/27/2017	2	Ch.3: Vacuum Technology
06/27/2017	3	Ch.4: Evaporation;
06/29/2017	4	Ch.5: Deposition
06/29/2017	5	Ch.5: Deposition
06/29/2017	6	Ch.6: Epitaxy
06/30/2017	7	Ch.7: CVD
06/30/2017	8	Ch.7: CVD
06/30/2017	9	Ch.9: Plasma

### 1.3 Process Steps (see Fig. 1.1)

- a) **Source**: solid, liquid, vapor or gas; (**flux**)
- b) **Transport**: in vacuum or in gas phase (**uniformity**)
- c) **Deposition**: absorption, surface migration and reaction (**morphology**)
- d) **Analysis**

**The logic flow followed by this course**

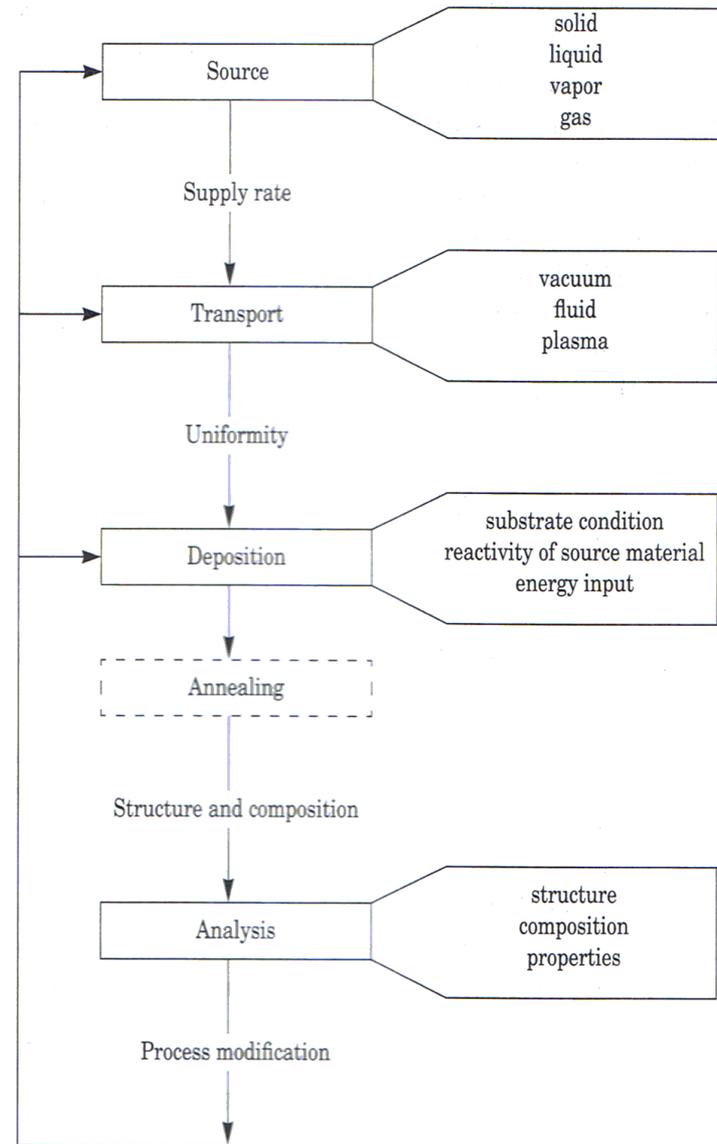


Figure 1.1 Thin-film process steps. In all steps, process monitoring is valuable, and contamination is a concern.

1.4. The difference between vapor and gas:

*vapor should be condensable whereas gas is not.*

*For this course, we will focus on vapor and gas phase transport.*

*Physical vapor deposition (PVD): vapor phase transport;*

*Chemical vapor deposition (CVD): gas phase transport;*

## Chapter 2. Gas Kinetics

- The distribution function of gas molecules;
- The impingement rate of gas molecules on surfaces;
- Transport properties: diffusion, viscosity, and heat transfer;

## 2.2 Maxwell-Boltzmann Distribution (see Fig. 2.4):

Now we shift our attention to the behavior of the evaporants after they become “airborne”;

The molecular speed distribution as functions of the mass and the temperature (macroscopic parameters)

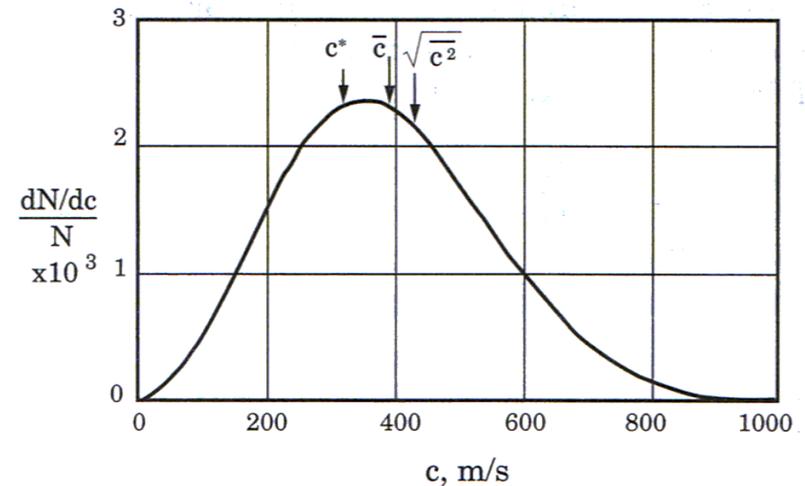
$$\frac{dN/dc}{N} = 4\pi c^2 \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{\frac{1}{2} m c^2}{k_B T} \right)$$

$N$  – total # of molecules in the ensemble

$c$  – molecular speed

$m$  – molecular mass

$T$  – absolute temperature



$N$  = number of atoms in the distribution

$\bar{c}$  = mean speed

$\sqrt{c^2}$  = root-mean-square (rms) speed

$c^*$  = speed of sound

**Figure 2.4** Maxwell-Boltzmann distribution of molecular speeds for Ar at room T.

2.4 Average speeds: Knowing the speed distribution (MB and Fig.2.4) several statistical measures of the molecular motion can be derived.

$$\bar{c} \equiv \int_{c=0}^{c=\infty} c \frac{dN/dc}{N} dc = \sqrt{\frac{8RT}{\pi M}}$$

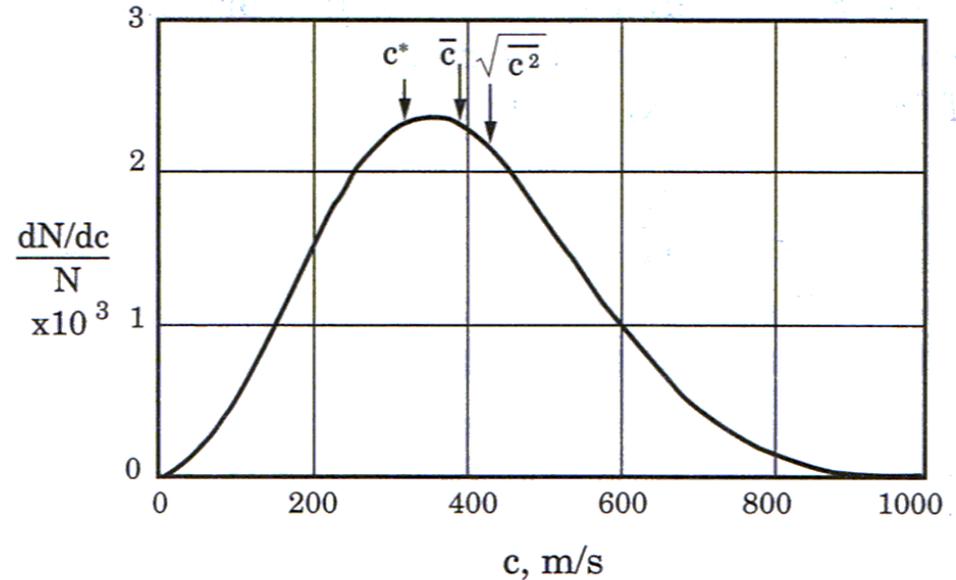
$$R = k_B N_A$$

$$M = m N_A$$

$$\sqrt{\overline{c^2}} \equiv \sqrt{\int_{c=0}^{c=\infty} c^2 \frac{dN/dc}{N} dc} = \sqrt{\frac{3RT}{M}}$$

$$c_m \equiv c \left| \frac{d}{dc} \left( \frac{dN}{dc} \right) \right|_{=0}$$

where  $N_A$  is Avogadro's number,  
 $6.02 \times 10^{23}$  mc/mol;



$N$  = number of atoms in the distribution

$\bar{c}$  = mean speed

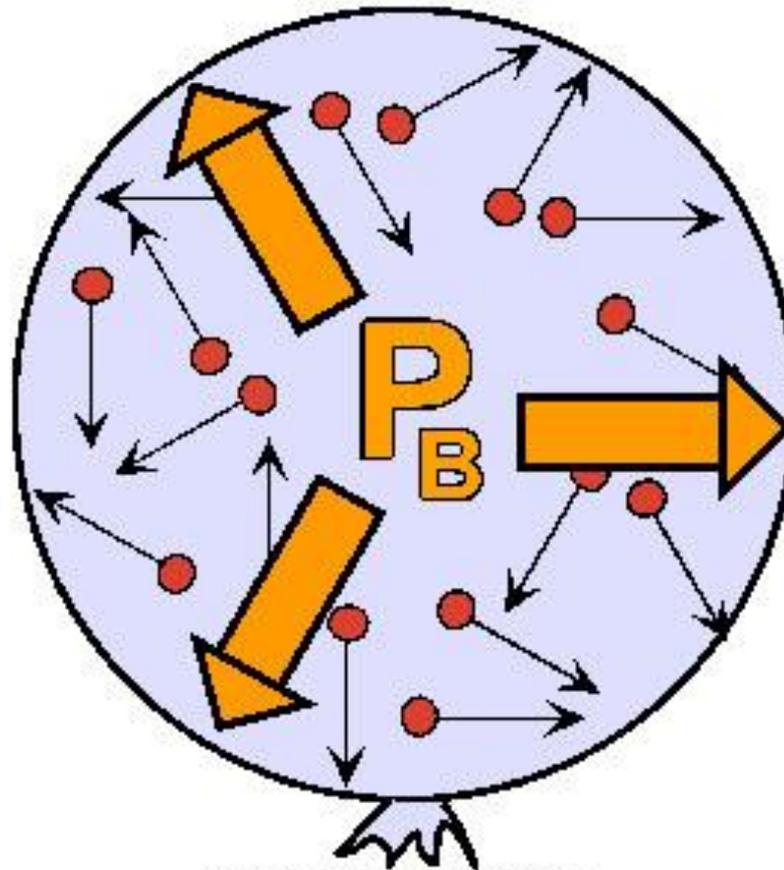
$\sqrt{\overline{c^2}}$  = root-mean-square (rms) speed

$c^*$  = speed of sound

**Figure 2.4** Maxwell-Boltzmann distribution of molecular speeds for Ar at room T.

# Pressure of A Body of Gas Molecules

**Figure 5.1.1** Internal pressure in a balloon.



<http://www.indiana.edu>

## 2.5 Molecular Impingement Flux (see Fig. 2.5)

This is a quantity that is fundamental to the film deposition rate to the zeroth order.

2.5.1 Consider a gas molecule at A;

2.5.2 Consider the case in which there is no bulk flow, which is always true when one gets close to a stationary surface. As a result, the direction of motion is completely random.

2.5.3 Focusing on molecules with velocity  $v$ ;

2.5.4 A molecule has 50% chance to have the velocity pointing downward and will hit the surface of interest

$$J_i = \frac{1}{2} n v_x$$

where  $n$  is the density of molecules at point A.

Starting from this slide, we shift our attention to how the evaporants strike a surface after they arrive at the vicinity of the substrate surface;

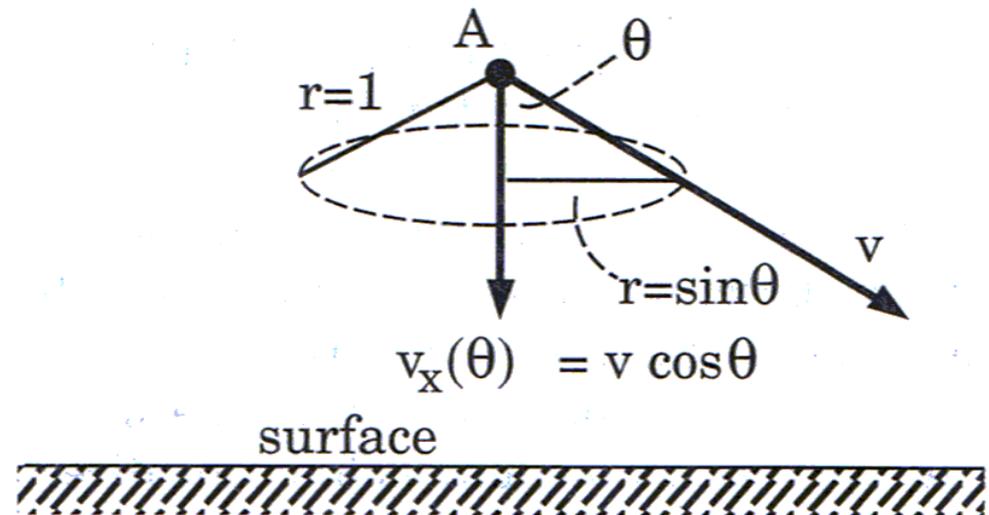


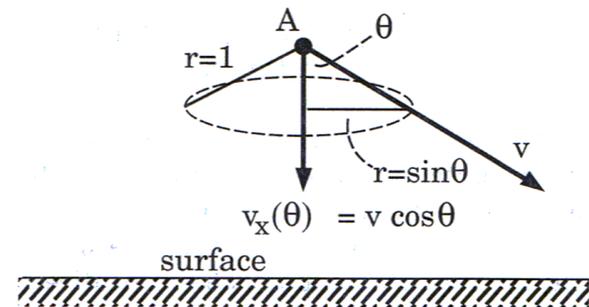
Figure 2.5 Geometry of molecular impingement.

2.5.5 Now we need to express  $J_i$  in terms of an average  $v_x$  that represents molecules with a given  $v$  but with directions varying from  $\theta = 0$  to  $\theta = 90^\circ$ . The average is carried out across a hemisphere surface of radius  $r = 1$  for simplicity. The flux continuity dictates that the flux is the same across the flat surface and across the fractional sphere:

$$\bar{v}_x = \frac{\int v_x dA}{\int dA} = \frac{1}{2\pi} \int_0^{\pi/2} (v \cos \theta) \cdot (2\pi \sin \theta) d\theta$$

where  $v \cos \theta$  is the x component of  $v$  over the ring band with an incremental area of  $(2\pi \sin \theta) d\theta$  [alternatively, if  $r \neq 1$ , then the ring band incremental area will be  $(2\pi r \cdot \sin \theta) r \cdot d\theta$ ]:

$$\therefore \bar{v}_x = \frac{1}{2} v$$



## 2.9 Knudsen Equation

Using  $J_i = \frac{1}{2} n \left( \frac{1}{2} v \right) = \frac{n}{4} v \Rightarrow \frac{n}{4} \bar{c}$  and  $\bar{c} = \sqrt{\frac{8RT}{\pi M}}$

Important for PVD

we have  $J_i = \frac{n}{4} \sqrt{\frac{8RT}{\pi M}}$   $\therefore n = \frac{p}{k_B T} = \frac{N_A p}{RT}$

$$\therefore J_i = \frac{1}{4} \frac{N_A p}{RT} \sqrt{\frac{8RT}{\pi M}} = \frac{N_A p}{\sqrt{2\pi MRT}} \left( \frac{mc}{m^2 \cdot \text{sec}} \right)$$

since  $R=8.31 \text{ Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$  and  $N_A=6.02\times 10^{23} \text{ mc/mol}$ ;

$$\therefore J_i \left( \frac{mc}{\text{cm}^2 \cdot \text{sec}} \right) = 2.63 \times 10^{20} \frac{p}{\sqrt{MT}}$$

This is the impingement rate on a unit surface when the units of  $p$ ,  $M$  and  $T$  are Pa, g, and K. For the unit of  $p$  in torr, the numerical factor changes to  $3.51 \times 10^{22}$ . A useful number to remember is that one monolayer equivalent of molecules strike a surface in one second at  $p \sim 10^{-6}$  torr.

## 2.9 Knudsen Equation

### Relating $J_i$ or $J_r$ to the film growth rate

At the substrate end,  $J_i$  is sometimes called  $J_r$ . Film growth rate,  $\frac{dh}{dt}$  is:

$$J_r = \frac{dh}{dt} \left( \rho_m \frac{N_A}{M} \right)$$

the quantity inside the bracket is the number of atoms per unit volume;  $J_r$  is the molecular deposition flux,  $\text{mc}/\text{m}^2\text{s}$ , and  $\rho_m$ =film density,  $\text{kg}/\text{m}^3$ .

### 2.10.3 Mean-free paths:

$$\ell_i = \frac{1}{\pi a^2 n}$$



Figure 2.6 Geometry for mean-free-path calculation showing a particle traveling into the plane of the drawing and encountering gas molecules of diameter  $a$ ; the particle is an electron in part (a) and an ion in (b).

As a homework assignment, please derive these expressions by yourselves

### 2.10.4 Numerical examples:

A 0.3 nm diameter molecule's mean free path at 1 Pa (~7 mTorr) and 25°C:

$$l_i = \frac{1}{\sqrt{2}\pi a^2 n} \quad n = \frac{pN_A}{RT} \quad \therefore \ell \approx 1.03 \text{ cm}$$

From the ideal gas law, we know  $p=nkT$ . For a given T, we know that p is proportional to n. Therefore, it makes sense that *l* is inversely proportional to n and thus to p. It is worth remembering that *l*~ 1 cm at room T and under 1 Pa.

Similarly, *l*~10<sup>-5</sup> cm =0.1 μm at room T under 1 atm.

### 2.10.5 Knudsen number:

Knudsen number is a dimensionless quantity that characterizes the gas molecule interaction: whether the dominating interaction is molecule-molecule or molecule-wall.

$$K_n = \frac{\ell}{L}$$

L -- characteristic dimension of the container

$K_n > 1$  is known as **molecular flow regime**

$K_n < 0.01$  is known as **viscous flow regime**

In between is the intermediate flow regime.

## 2.11 Transport Properties: Diffusion, viscosity, and heat conduction

2.11.1 All these transports are described by an equation of the form:

$$\text{Flux of A} = -(\text{proportionality factor}) \times (\text{gradient in A})$$

See Table 2.1 on the next slide for equations in one-dimensional case, while keeping in mind that the general form of the equations should be three-dimensional with the gradient being  $\nabla \cdot A$  instead of  $\frac{\partial A}{\partial x}$

*The subject to be discussed throughout the rest of the chapter:*

*The functional forms of the **proportionality constants** derived from molecular kinetics with emphasis on the **T-dependence**.*

## 2.11 Transport Properties: Diffusion, viscosity, and heat conduction

TABLE 2.1 Gas Transport Properties\*

Transported quantity	Describing equation	Proportionality factor	
		Derivation from elementary kinetic theory	Typical value at 300 K, 1 atm
Mass	Diffusing flux = $J_A \left( \frac{mc}{cm^2 \cdot s} \right) = -D_{AB} \left( \frac{dn_A}{dx} \right)$ (Fick's law)	Diffusivity = $D_{AB} \left( \frac{cm^2}{s} \right) = \frac{1}{4} \bar{c} l \propto \frac{T^{7/4} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}}{p(a_A + a_B)^2}$	Ar-Ar: 0.19 cm <sup>2</sup> /s Ar-He: 0.72
Momentum	Shear stress = $\tau (N/m^2) = \eta \frac{du}{dx}$	Viscosity = $\eta (\text{Poise})^\dagger = \frac{1}{4} n m \bar{c} l \propto \frac{\sqrt{MT}}{a^2}$	Ar: 2.26×10 <sup>-4</sup> Poise <sup>†</sup> He: 2.02×10 <sup>-4</sup>
Energy (heat)	Conductive heat flux = $\Phi \left( \frac{W}{cm^2} \right) = -K_T \frac{dT}{dx}$ (Fourier's law)	Thermal conductivity = $K_T \left( \frac{W}{cm \cdot K} \right) = \frac{1}{2} n \left( \frac{c_v}{N_A} \right) \bar{c} l \propto \sqrt{\frac{T}{M}} \frac{c_v}{a^2}$	Ar: 0.176 mW/cm·K He: 1.52
Charge	Current density = $j \left( \frac{A}{cm^2} \right) = \frac{-1}{\rho} \frac{dV}{dx} = -s \frac{dV}{dx}$ (Ohm's law)		

\*cm-g-s (cgs) units appear here instead of SI units when they are commonly used for these quantities.

†1 Poise = 1 g/cm·s = 0.1 kg/m·s or N·s/m<sup>2</sup> or Pa·s.

## 2.11.2 Diffusion: mass transport

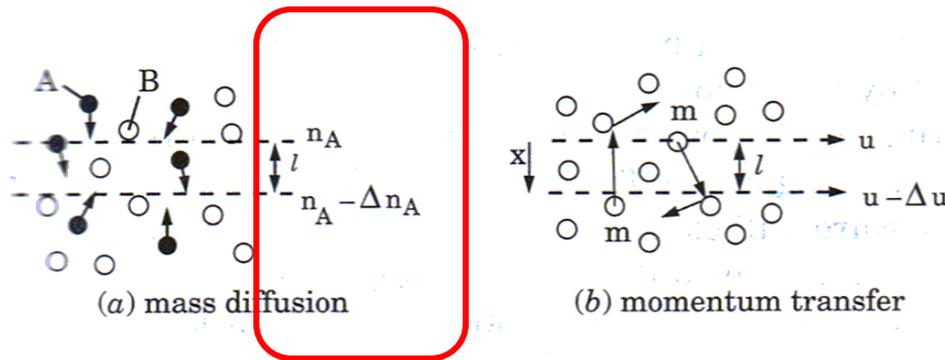
“Deriving” the 1-D diffusion equation (see Fig. 2.7a). Consider a slab of thickness (mean-free path), and the vapor is composed of molecules of type A and type B. We focus on the diffusion of type A molecule along its own concentration gradient while there is no pressure gradient in the enclosure.

Recall from our discussion on molecular impingement rate:  $J_i = \frac{1}{4} n \bar{c}$

Now we have for the upward and the downward flux:

$$J_{A_u} = \frac{1}{4} (n_A - \Delta n_A) \bar{c} \quad \& \quad J_{A_D} = \frac{1}{4} n_A \bar{c}$$

The net downward flux is:  $J_A = J_{AD} - J_{AU} = \frac{1}{4} \Delta n_A \bar{c}$



**Figure 2.7** Illustration of transport properties on a molecular scale. Flux is downward in the  $x$  direction.

## 2.11.2 Diffusion: mass transport

Now make the approximation:  $\frac{\Delta n_A}{l} = - \frac{\partial n_A}{\partial x}$

*The “-” sign comes from the definition of  $J_A$  being the net “downward” flux, i.e. along the direction of negative  $x$ .*

then  $J_A = -\left(\frac{1}{4} \ell \bar{c}\right) \bullet \frac{\partial n_A}{\partial x} \equiv -D_A \frac{\partial n_A}{\partial x}$  (Fick's law)    where  $D_A = \frac{1}{4} \ell \bar{c}$

i.e.,  $D_A$  is related to how mobile the molecules are and their mean free path, which means the pressure,  $M$ , and  $T$ !

### 2.11.2 Diffusion: mass transport (continued)

Note: the equation is in the same form regardless of how the x-direction is defined or the magnitude of  $l$ .

$$\begin{aligned} \therefore \quad l &\propto \frac{1}{n}; & n &= \frac{pN_A}{RT}; & \bar{c} &= \sqrt{\frac{8RT}{\pi M}}; & \text{and} & \quad D_A \propto \bar{c}l \\ \therefore \quad D_A &\equiv D_{AB} \propto \frac{T^{3/2}}{\sqrt{M} a^2 p} \end{aligned}$$

The empirical value is  $T^{7/4}$ , a fairly good agreement with  $T^{3/2}$ .

Under constant  $p$ ,  $D$  depends super-linearly on  $T$ .

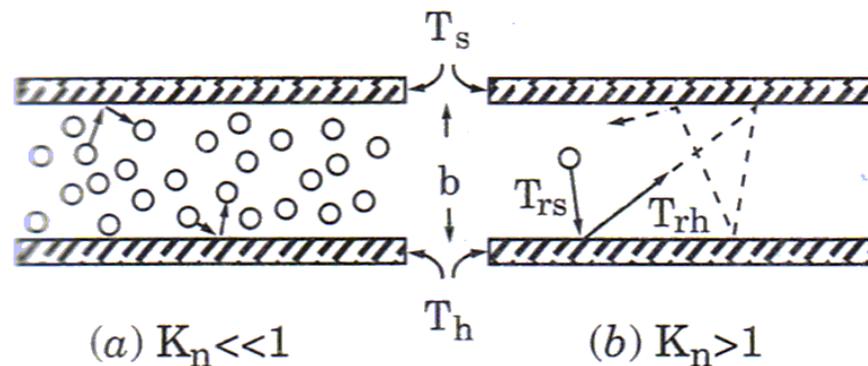
### 2.11.4.3 Generalized expression of gaseous heat conduction for both gas flow regimes:

Consider the heat conduction between two parallel plates as shown in fig.2.8, the heat flux can be rewritten into the following form:

$$\Phi = h_c (T_h - T_s)$$

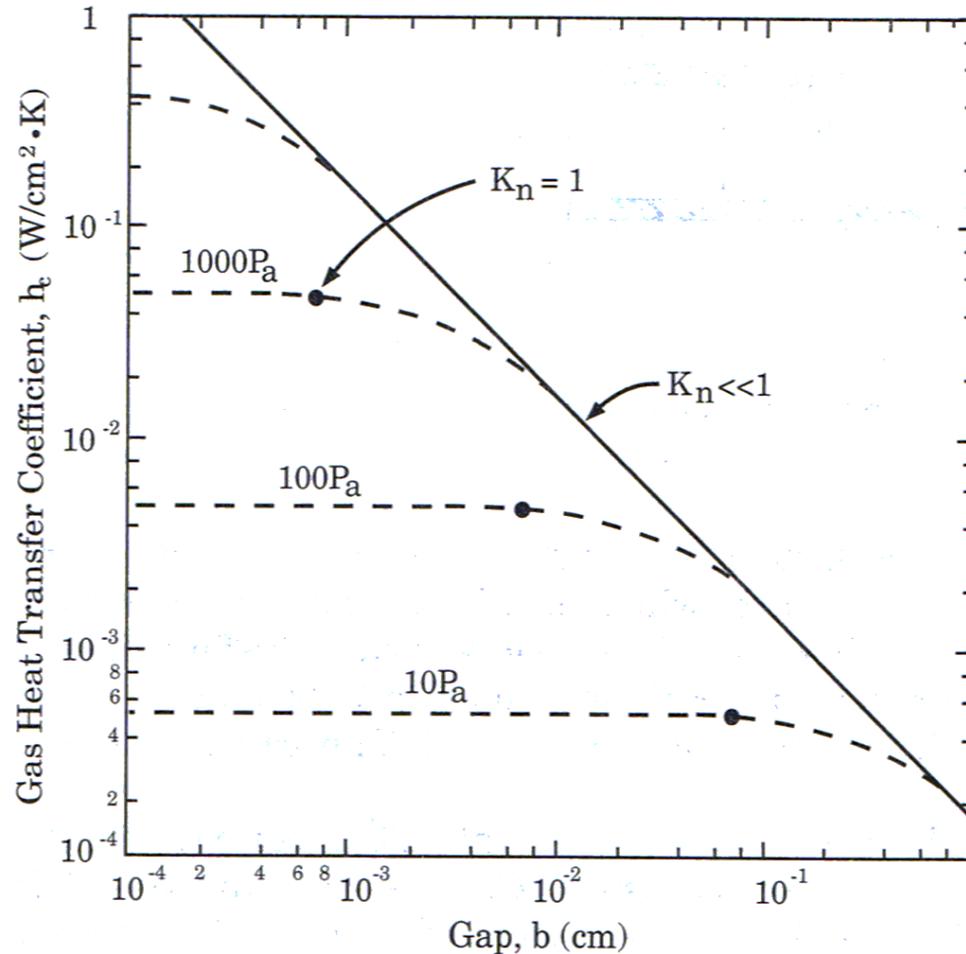
where the subscripts h and s stand for heater and substrate, respectively.

$h_c$  is the heat transfer coefficient in  $\text{W}/\text{cm}^2\text{-K}$ ;



**Figure 2.8** Gas-conductive heat transfer between parallel plates at (a) low and (b) high Knudsen numbers,  $Kn$ .

### 2.11.4.3 Generalized expression of gaseous heat conduction for both gas flow regimes:



$$K_n = \frac{\ell}{L}$$

Figure 2.9 Gas-film heat-transfer coefficient,  $h_c$ , vs. plate gap,  $b$ , for various pressures of Ar. For  $\text{Kn} \ll 1$ ,  $h_c = K_T/b$ , where  $K_T$  = bulk thermal conductivity of the gas.