

# F4280 Technology of thin film deposition and surface treatment

## 2. Gas Kinetics

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## Outline - chapter 2. Gas Kinetics

- 2.1 Vapors and Gases
- 2.2 Maxwell-Boltzmann Distribution
- 2.3 Ideal-Gas Law
- 2.4 Units of Measurement
- 2.5 Knudsen Equation
- 2.6 Mean Free Path
- 2.7 Knudsen number
- 2.8 Transport Properties

# p-V-T diagram

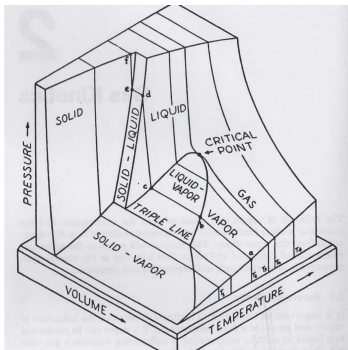
The possible equilibrium states can be represented in **pressure-volume-temperature (p-V-T) space for fixed amount of material** (e.g. 1 mol =  $6.02 \times 10^{23}$ ).

**Lines** = cuts through the p-V-T surface **for fixed  $T$**   $\Rightarrow$  relationship between  $p$  and  $V_m$  (molar volume).

Line  $a - b - c$  below the critical point (at  $T_2$ ):

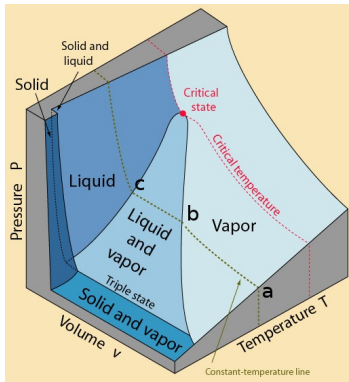
- ▶ point  $a$ : highest  $V$  (lowest  $p$ ) - vapor phase
- ▶ from point  $a$  to  $b$ : reducing  $V \rightarrow$  increasing  $p$
- ▶ point  $b$ : condensation begins
- ▶ from point  $b$  to  $c$ :  $V$  is decreasing at fixed  $p$  ( $b - c$  line is  $\perp$  to the p-T plane,  $p$  is called **saturation vapor pressure  $p_v$**  or just **vapor pressure**)
- ▶ point  $c$ : condensation completed

If  $V$  is abruptly decreased in  $b - c$  transition  $p$  would be pushed above the line  $b - c \Rightarrow$  **non-equilibrium supersaturated vapors**. Supersaturation is an important drivign force in the nucleation and growth of thin films.



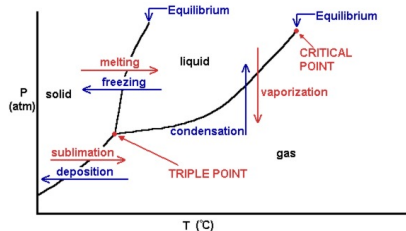
# p-V-T diagram

It is important to distinguish between the behaviors of **vapors** and **gases**:

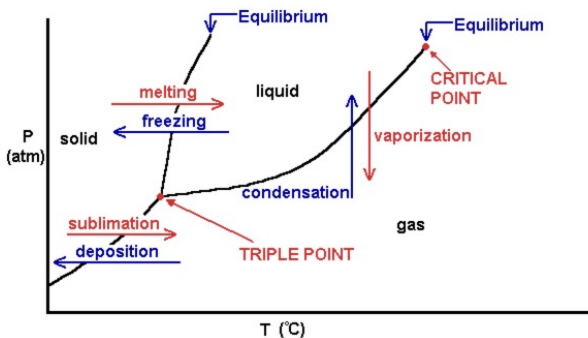


- ▶ **vapors**: can be condensed to liquid or solid by compression at fixed  $T \Rightarrow$  below **critical point** defined by  $p_c$ ,  $V_c$  and  $T_c$
- ▶ **gases**: monotonical decrease of  $V$  upon compression  $\Rightarrow$  no distinction between the two phases

Surfaces “liquid-vapor”, “solid-vapor” and “solid-liquid” are perpendicular to the p-T plane  $\Rightarrow$  their projection on that plane are lines.

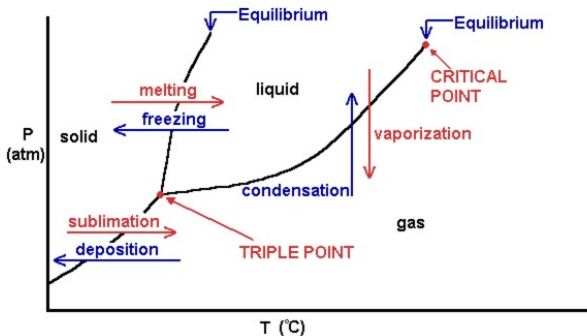


# p-T diagram



- ▶ **triple point:** from triple line  $\perp$  to p-T plane
- ▶ below  $T$  of triple point: liquid-phase region vanishes  $\Rightarrow$  condensation directly to the solid phase, vaporization in this region is **sublimation**
- ▶ pressure along borders of vapor region is **vapor pressure**  $p_v$

# p-T diagram



- ▶ vapor pressure  $p_v$  increases exponentially with  $T$  up to  $p_c$
- ▶  $p_c$  is well above 1 atm  $\Rightarrow$  **deposition of thin films** is performed at  $p \ll p_c$ , either  $p > p_v$  (supersaturated vapors) or  $p < p_v$
- ▶ first two steps in the deposition (source supply and transport to substrate) should be carried out at  $p < p_v$  to avoid condensation
- ▶ condensation should be avoided also during compression in vacuum pumps

# Maxwell-Boltzmann Distribution

Distribution of random velocities  $\vec{V}$  in equilibrium state

$$f(\vec{V}) = n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{mV^2}{2k_B T} \right) \quad (1)$$

where  $k_B = 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$  (or  $\text{J K}^{-1}$ ) is the Boltzmann constant,  $n$ ,  $T$  and  $m$  are particle density, temperature and mass, respectively.

**If the drift velocity is zero** we do not need to distinguish between the velocity and random velocity, i.e.  $\vec{v} \equiv \vec{V}$ .

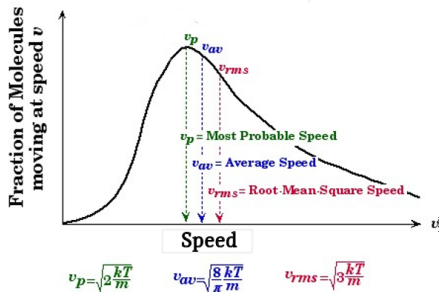
**Maxwell-Boltzmann distribution is isotropic**  $\Rightarrow F(v)$  distribution of speeds  $v \equiv |\vec{v}|$  can be defined by integration of  $f(v)$  in spherical coordinates

$$F(v)dv = \int_0^\pi \int_0^{2\pi} f(v)v^2 \sin \theta d\phi d\theta dv \quad (2)$$

resulting in

$$F(v) = 4\pi v^2 n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{mv^2}{2k_B T} \right) \quad (3)$$

# Mean (Average) Speed, Molecular Impingement Flux



Mean speed:

$$\langle v \rangle = v_{av} = \frac{1}{n} \int_0^{\infty} F(v) v dv = \sqrt{\frac{8k_B T}{\pi m}} \quad (4)$$

or

$$v_{av} = \sqrt{\frac{8RT}{M}} \quad (5)$$

using **molar mass**  $M = mN_A$  in kg/mol and **gas constant**

$$R = k_B N_A = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

where  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$  is Avogadro's number

Root-mean-square (rms) speed:

$$v_{rms} = \sqrt{\frac{1}{n} \int_0^{\infty} F(v) v^2 dv} = \sqrt{\frac{3k_B T}{m}} \quad (6)$$

The **most probable speed**  $v_p$ :

$$\left( \frac{dF(v)}{dv} \right)_{v=v_p} = 0 \Rightarrow v_p = \sqrt{\frac{2k_B T}{m}} \quad (7)$$



# Ideal-Gas Law

From the definition of pressure for ideal gas (not necessary to consider pressure tensor but only scalar pressure)

$$p = \frac{1}{3} mn \langle \vec{V}_x^2 + \vec{V}_y^2 + \vec{V}_z^2 \rangle = \frac{1}{3} mn \langle \vec{V}^2 \rangle = m \int_V V^2 f(V) d^3 V. \quad (8)$$

The ideal-gas law is obtained by integration of (8) using Maxwell-Boltzmann distribution:

$$p = nk_B T \quad \text{or} \quad \frac{pV}{T} = Nk_B \quad (9)$$

where  $N$  is the number of particles.

Chemists are used to work in molar amounts ( $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ ):

- ▶ molar concentration  $n_m = n/N_A \Rightarrow p = n_m RT$
- ▶ number of moles  $N_m = N/N_A \Rightarrow p = N_m RT/V$
- ▶ molar volume  $V_m = V/N_A \Rightarrow p = RT/V_m$

The **ideal gas is obeyed if**

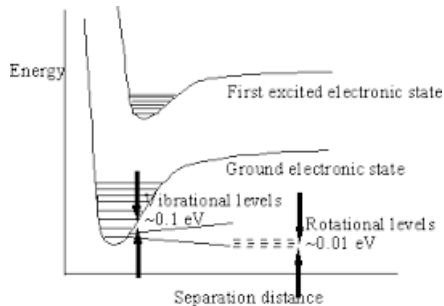
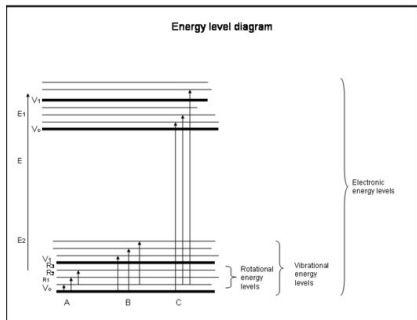
- ▶ the volume of molecules in the gas is much smaller than the volume of the gas
- ▶ the cohesive forces between the molecules can be neglected.

Both assumptions are fulfilled for low  $n \Rightarrow$  always fulfilled for thin film deposition from the vapor phase ( $T \geq T_{\text{room}}$  and  $p \leq p_{\text{atm}}$ ), i.e. well away from the critical point (most materials  $p_c \gg 1 \text{ atm}$  or if not  $T_c \ll 25 \text{ }^\circ\text{C}$ )

# Energy Forms Stored by Molecules

Molecules can store energy in various forms. Their energetic states are quantized (spacing between energy levels  $\Delta E$ )

- ▶ electronic excitations -  $\Delta E_e$  is highest, transitions between different electronic states are possible only for extremely high  $T$  or collision with energetic particle
- ▶ vibrational excitations - energy levels correspond to different vibration modes of the molecule,  $\Delta E_v \approx 0.1$  eV (1 eV = 11 600 K)
- ▶ rotational excitations - different rotational modes of the molecule,  $\Delta E_r \approx 0.01$  eV
- ▶ translational energy - above performed description of molecular random motion  $E_t = 1/2mV^2$ , no details of inner molecule structure are considered,  $\Delta E_t$  negligible at ordinary  $T$ .



## Energy Content of Gas

From definition of absolute temperature - the mean thermal energy  $kT/2$  belongs to each translational degree of freedom and molecular translation energy is

$$E_t = \frac{3}{2} k_B T \quad (10)$$

⇒ **equipartition theorem of classical statistical mechanics**. Classical statistical treatment assumes very close quantized energy levels of molecules, i.e. **approximated as a continuum**. It is a good assumption for **translational** energy when  $T \gg 0$  K.

- ▶ For **atomic** gases,  $E_t$  is total kinetic energy content.
- ▶ For **molecular** gases,  $E_r$  is added at ordinary  $T$  and  $E_v$  at very high  $T$ :

**Molar heat capacity at constant volume**  $c_V$  (for molecular gas) [J/(mol.K)] - increase of total kinetic energy for increasing  $T$ :

$$c_V = \frac{dE_m}{dT} N_A = \frac{d(E_t + E_r + E_v)}{dT} N_A \quad (11)$$

for atomic gases

$$c_V = \frac{3}{2} R = \frac{3}{2} k N_A$$

for small diatomic molecules at room  $T$

$$c_V = \frac{5}{2} R$$

- two rotational degrees of freedom are excited but vibrational ones are not

## Energy Content of Gas

The heat capacity of any gas is larger when measured at constant pressure  $c_p$  - heat input is doing  $p dV$  work on the surroundings in addition to adding kinetic energy to the molecules:

$$c_p = c_v + R \quad (12)$$

We can write from thermodynamics

$$c_v = \left( \frac{\partial U_m}{\partial T} \right)_v \quad (13)$$

where  $U_m$  is internal energy per mol  $U_m = E_m N_A$  and

$$c_p = \left( \frac{\partial H_m}{\partial T} \right)_p \quad (14)$$

where  $H_m$  is enthalpy per mol  $H_m = U_m + pV_m \Rightarrow$

$$\left( \frac{\partial H_m}{\partial T} \right)_p = \left( \frac{\partial U_m}{\partial T} \right)_p + p \left( \frac{\partial V_m}{\partial T} \right)_p \quad (15)$$

giving  $c_p = c_v + R$

## 2.4 Units of Measurement

SI units?!

1 Torr = 133 Pa = 1 mm Hg

1 bar = 750 Torr =  $1.0 \times 10^5$  Pa = 0.99 atm (standard atmosphere)

The “standard” conditions of  $T$  and  $p$  (stp) are  $0^\circ\text{C}$  and 1 atm (760 Torr). From ideal gas law at stp  $V_m = 22400 \text{ cm}^3$ .

These conditions are different from standard conditions to which thermodynamic data are referenced:  $25^\circ\text{C}$  and 1 bar.

In gas supply monitoring - the term “mass” flow rate measured in standard  $\text{cm}^3$  per minute (second or liters per minute): sccm, sccs, slm. Standard means  $0^\circ\text{C}$  and 1 atm.

## 2.5 Knudsen Equation

The **molecular impingement flux** at a surface is a fundamental determinant of film deposition rate:

$$\Gamma = n \langle v \cos \theta \rangle = \int_0^\infty \int_0^{\pi/2} \int_0^{2\pi} f(v) v^3 \cos \theta \sin \theta d\phi d\theta dv \quad (16)$$

Substituting Maxwell-Boltzmann distribution

$$\Gamma = n \left( \frac{k_B T}{2\pi m} \right)^{1/2} = \frac{1}{4} n v_{av} \quad (17)$$

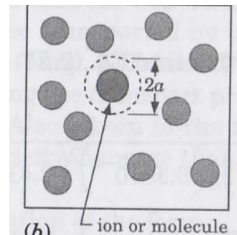
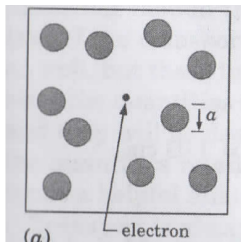
and using ideal gas law

$$\Gamma = p \left( \frac{1}{2\pi k T m} \right)^{1/2} = p N_A \left( \frac{1}{2\pi R T M} \right)^{1/2} \quad (18)$$

where  $M = mN_A$  and  $R = kN_A$  ( $M$  is molar mass)

Calculate molecular impinging flux for CO<sub>2</sub> molecules (44 a. u., 330 pm), 25 °C, 10<sup>-3</sup> Pa. Considering the molecule diameter of 330 pm calculate monolayer deposition rate considering all impinging molecules stick to the surface.

## 2.6 Mean Free Path



Unless  $T$  is extremely high,  
 $p$  is the main determinant of  $l$ ,  
 $l \approx 1/p$ .

### Mean free path

$$\lambda = \frac{1}{\sigma_m n} \quad (19)$$

- ▶ **electrons travelling through gas:** electrons are much smaller than molecules  $\Rightarrow$  collision cross section  $\sigma_m$  is just projected area of the gas molecule

$$\lambda_e = \frac{1}{\pi/4 a^2 n} \quad (20)$$

It's approximation,  $\sigma_m$  is function of el. energy

- ▶ **ions travelling through gas:** similar diameter

$$\lambda_i = \frac{1}{\pi a^2 n} \quad (21)$$

- ▶ **molecule-molecule collisions:** "target" particles are not steady (comparable velocities)  $\Rightarrow$  mean speed of mutual approach is  $\sqrt{2}v_{av}$  rather than  $v_{av}$  (on average they approach each other at  $90^\circ$ )  $\Rightarrow$  it shortens  $l$  by  $\sqrt{2}$

$$\lambda_m = \frac{1}{\sqrt{2}\pi a^2 n} \quad (22)$$

## 2.7 Knudsen number

It is worth remembering that the mean free path at 1 Pa and room  $T$  is about 1 cm for small molecules.

The order of magnitude of  $l$  is very important in film deposition, because it determines whether the process is operating in the high-vacuum or the fluid-flow regime. The regime is determined by the **Knudsen number**:

$$Kn = \lambda/L \quad (23)$$

where  $L$  is a characteristic dimension in the process, e. g. distance between the source and the substrate,  $\lambda$  is the mean free path.

- ▶ For  $Kn > 1$ , the process is in **high-vacuum regime (molecular flow regime)**.
- ▶ For  $Kn \ll 0.01$ , the process is in **fluid flow regime**.

Intermediate values of  $Kn$  constitute a transition regime where the equations applicable to either of limiting regimes are not strictly valid.

Plasma processes often operate in the transition regime. High-vacuum processes require  $p < 10^{-2}$  Pa for typical chamber sizes to ensure  $Kn > 1$ .



## 2.8 Transport Properties

Transport properties quantify the transport rate of

- ▶ mass (diffusion)
- ▶ momentum (viscous shear)
- ▶ energy (heat conduction)

through a fluid (we mean gaseous fluid).

Transport to be discussed here occurs by **random molecular motion** through a gas which has no bulk flow in the direction of the transport. Mass and heat can be also transported by bulk (drift) flow but it is not discussed here.

Table on the next slide summarizes the quantities and eqs. It include also el. current (transport of charge) because it's helpful analogy.

Transport is always described by eq. in the form:

$$\text{flux of } A = -\text{proportionality factor} \times \text{grad } A$$

General form is in 3D but we will discuss for simplicity 1D problem. Example for el. density current (familiar Ohm's law):

$$j_x [\text{A}/\text{m}^2] = S \frac{dV}{dx}$$

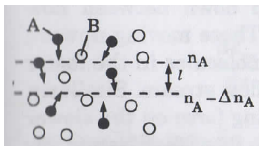
where  $S$  is conductivity per unit length (resistivity is  $\rho = 1/S$ ),  $dV/dx$  is gradient of el. potential (voltage) [V/m]

## 2.8 Transport Properties - Overview

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

Table 2.1 Gas transport properties from the book by Donald L. Smith, Thin-Film Deposition: Principles & Practice, McGraw-Hill 1995.

## 2.8.1 Diffusion



Molecular diffusion is demonstrated using mixture of molecules A (black) and B (white). Consider, the concentration of black molecules A is decreasing from  $n_A$  to  $n_A - \Delta n_A$  in the  $x$ -direction over a distance of *one mean free path*  $\lambda \Rightarrow$   
**Diffusion of A occurs in the direction of decreasing  $n_A$ .**

A rough estimate of diffusion flux can be made by calculating the net flux through an imaginary slab of thickness  $\lambda$  ( $l$  in D. Smith book), using

$$\Gamma = \frac{1}{4} n \langle v \rangle \quad \text{where } \langle v \rangle = \sqrt{\frac{8kT_B}{\pi m}}$$

for the fluxes in opposite directions  $\downarrow$  and  $\uparrow \Rightarrow \Gamma_A = \Gamma(x) - \Gamma(x + \lambda) = 1/4 \Delta n_A \langle v \rangle$

Since  $\Delta n_A = \lambda \frac{-dn_A}{dx}$ , we have  $\Gamma_A = -\frac{1}{4} \langle v \rangle \lambda \frac{dn_A}{dx} \Rightarrow$

$$\Gamma_A = -D_{AB} \frac{dn_A}{dx}$$

**Fik's law**,  $D_{AB}$  **diffusion coefficient** of A through B

Inserting expression for  $\langle v \rangle$  and molecule-molecule mean free path  $\lambda = \frac{1}{\sqrt{2} \pi a^2 n}$  we find

$$D_{AB} \sim \frac{T^{3/2}}{\sqrt{m} a^2 p}$$

Empirically, it should be  $T^{7/4}$ , and  $m$  and  $a$  are averaged to account for A-B mixture, see next slide.

## 2.8.1 Diffusion

$$D_{AB} = \frac{T^{3/4} \left( \frac{1}{m_A} + \frac{1}{m_B} \right)^{1/2}}{\rho (a_A + a_B)^2}$$

but  $D_{AB}$  has to be anyway determined empirically for given binary mixtures

Typical value at 300K, 1atm

Ar-Ar :	0,19 cm <sup>2</sup> /s
Ar-He :	0,72 cm <sup>2</sup> /s

and dependence of  $D_{AB}$  on  $p, T$  can be extrapolated using empirically determined values and our expression  $D(p, T)$  with accuracy of  $\sim$  factor two.

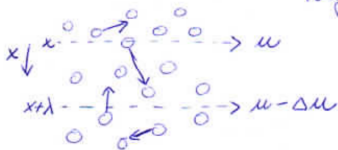
Dependence of  $D_{AB}$  on  $p$  is particularly important, since it can be lower than 1atm by many orders of magnitude in depos. processes  $\Rightarrow \uparrow D_{AB}$ .

When  $p$  is reduced so far that  $Kn > 1$  ( $Kn = \frac{\lambda}{L}$ )  
(molecular flow regime)

diffusion no longer occurs. Instead, molecules travel from wall to wall in molecular flow, without encountering each other in the gas phase.

## 2.8.2 Viscosity

Gas viscosity is the result of molecular momentum transport along a gradient in bulk flow velocity  $u$ . /  $\vec{u} = \langle \vec{v} \rangle$   
(drift velocity)



The  $u$  gradient is along the  $x$  axis, perpendicular to  $\vec{u}$ . This situation is encountered in fluid flow whenever the flow stream approaches a boundary ( $u$  must go to zero). Superimposed is the random molec. motion at velocity  $\langle v \rangle$ .

The random motion causes molecules to continually cross up and down between streams separated by  $\lambda$ . Those moving upward will gain momentum  $m \Delta u$  upon colliding with molecules in the faster flow stream

$\Rightarrow$  drag force on the flow stream at  $x$   
(zpomalující síla!)

## 2.8.2 Viscosity

Similarly, those moving downward will exert an accelerating force on the slower flow stream at  $x+\lambda$

These forces are equal and opposite in a steady state - viskosní tečné napětí  
 stress  $\tau$  ( $\text{N/m}^2$ ) = rate of momentum transfer per unit area  $\perp$  to  $\vec{x} \Rightarrow$

$$\tau = \text{molecular flux} \times \text{momentum gain/loss per molecule} \Rightarrow$$

$$\tau = \frac{1}{4} n \langle v \rangle \cdot m \frac{du}{dx} = \eta \frac{du}{dx}$$

$$\text{viscosity } \left\{ \frac{\text{kg} \cdot \text{s}^{-1}}{\text{m}} = \frac{\text{N} \cdot \text{s}}{\text{m}^2} = \text{Pa} \cdot \text{s} \right\}$$

$$\text{Subst. } \eta = \frac{1}{4} n \sqrt{\frac{3kT}{4m}} \cdot m \cdot \frac{1}{\sqrt{2} \pi a^2 n} \sim \frac{\sqrt{T} \cdot m}{a^2}$$

- Two surprises:
1.  $\eta \uparrow$  with  $T$  (opposite to liquid behaviour)
  2.  $\eta \neq \text{funct.}(p)$

As in the case of diffusion, viscosity has no meaning for  $\text{Kn} > 1$

## 2.8.3 Heat transfer

Gaseous heat conduction occurs by transfer of energy in molecular collisions downward along a gradient in molecular kinetic energy  $E_m$ . Equation for the **heat flux**  $\Phi$  is analogous to that for momentum transfer, with  $m\Delta u$  replaced by  $2\Delta E_m$

$$\Phi = \frac{1}{4}n\langle v \rangle 2\lambda \frac{dE_m}{dx} \quad (24)$$

with the units J/(s.m<sup>2</sup>) or W/m<sup>2</sup>.

We can substitute  $T$  for  $E_m$  using Eq. (11) for molar heat capacity at constant volume

$$\frac{dE_m}{dx} = \frac{dE_m}{dT} \frac{dT}{dx} = \frac{c_V}{N_A} \frac{dT}{dx} \quad (25)$$

Thus, we obtain Fourier's law

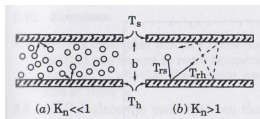
$$\Phi = -K_T \frac{dT}{dx} \quad (26)$$

where **thermal conductivity**  $K_T \sim \sqrt{T/m} c_V / a^2$ . Small, light molecules generally have higher  $K_T$  although this trend is sometimes reversed by the higher  $c_V$  of more complex molecules, which have more rot. and vibr. modes of energy storage.

Like  $\eta$ ,  $K_T$  is independent of  $p$  for the same reason: as  $p \downarrow$ , molecular flux  $\Gamma \downarrow$  but  $\lambda \uparrow$ . However, the **situation changes for so low  $p$  that the gas is in molecular regime** (see next slides).

## 2.8.3 Heat transfer - molecular regime

Heat transfer by gas conduction between two parallel plates:



... common situation in the film deposition, where one plate is a heated platform at temperature  $T_h$ , and the other is a substrate being raised to  $T_s$  by the heat transfer from the platform.

For the gap distance  $b$ , the **Knudsen number is**  $Kn = \lambda/b$ .

At the higher  $p$  where  $Kn \ll 1$  (**fluid flow**), the heat flux is (using  $K_T \sim \sqrt{T/m} c_V/a^2$ )

$$\Phi = -K_T \frac{dT}{dx} = \frac{K_T}{b} (T_h - T_s) \quad (27)$$

For  $Kn > 1$  (**molecular flow**), gas molecules are bouncing back and forth from plate to plate without encountering any collisions  $\Rightarrow$  use of  $K_T$  (bulk fluid property) is no longer appropriate. Instead, the heat flux between the plates is proportional to the flux of molecules across the gap ( $\Gamma$ ) times the heat carried per molecule (using Eq. (25)):

$$\Phi = \Gamma \gamma' \frac{c_V}{N_A} (T_h - T_s) \equiv h_c (T_h - T_s) \quad (28)$$

where  $\gamma'$  is the thermal accommodation factor ( $\approx$  unity except for He) and  $h_c$  is the **heat transfer coefficient** ( $\text{W K/m}^2$ ) given as  $h_c = \sqrt{N_A/(2\pi R)} p / \sqrt{mT} \gamma' c_V$

Note that  $h_c$  appears, rather than  $K_T$ , whenever heat transfer is taking place across an interface rather than through a bulk fluid or other material.



## 2.8.3 Heat transfer - heat transfer to substrate

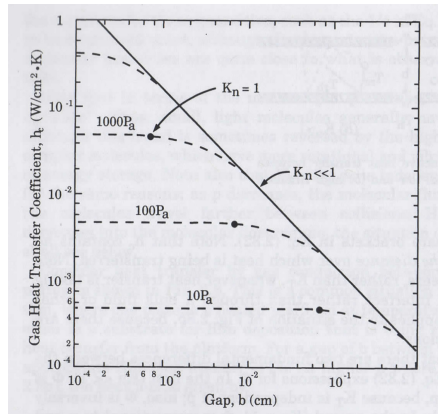
There are two fundamental difference between the heat flux in the case of fluid  $Kn \ll 1$  and molecular  $Kn > 1$  regimes:

- ▶  $\Phi$  is inversely proportional to  $b$  for fluid whereas independent of  $b$  for molecular regime
- ▶  $\Phi$  is independent of  $p$  for fluid whereas proportional to  $p$  for molecular regime

One important conclusion which can be drawn for low  $p$  is that the heat transfer to a substrate from a platform can be increased by increasing  $p$ , but only if the gap is kept small enough that  $Kn > 1$ .

Helium is often chosen to improve the heat transfer because of its high  $K_T$ , but in fact it is not the best choice when  $Kn > 1$  because of the thermal accommodation factor in Eq. (28)

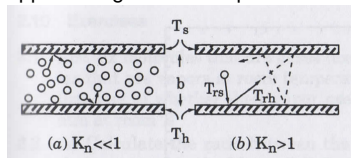
- for discussion of  $\gamma'$  see the next slide.



From Eq. (28), the best choice for a heat-transfer gas is one having low molecular mass to give high  $\Gamma$ , while also having many rotational modes to give high  $c_V$ . Choices will usually be limited by process chemistry.

## 2.8.3 Heat transfer - thermal accommodation coefficient

In molecular flow regime  $Kn > 1$  (right figure), consider the molecule approaching the heated platform.



It has the temperature  $T_{rs}$  acquired when reflected from the substrate. Upon being reflected from the platform, it will have temperature  $T_{rh}$ .

The **thermal accommodation coefficient**  $\gamma$  is defined as

$$\gamma = \frac{T_{rs} - T_{rh}}{T_{rs} - T_h}. \quad (29)$$

It represents the degree to which the molecule accommodates itself to the temperature  $T_h$  of the surface from which it is reflected.

For most molecule-surface combinations,  $\gamma$  is close to unity, but for He it is 0.1–0.4, depending on the surface.

If  $\gamma$  is less than unity and is the same at both surfaces, the **overall reduction in the heat flux represented by  $\gamma'$**  is

$$\gamma' = \frac{\gamma}{2 - \gamma} \quad (30)$$