F4280 Technology of thin film deposition and surface treatment
2. Gas Kinetics

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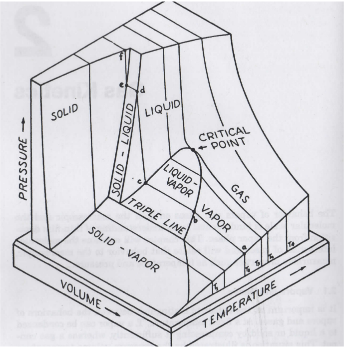
Outline - chapter 2. Gas Kinetics

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 = 6.02×10^{23}).



Lines = cuts through the p-V-T surface **for fixed** T ⇒ relationship between p and V_{m} (molar volume).

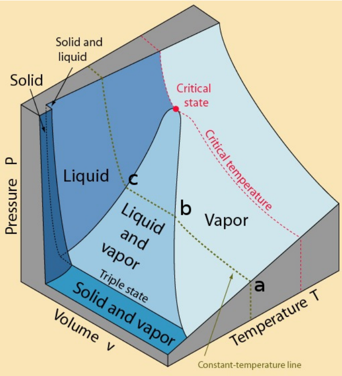
Line $a - b - c$ below the critical point (at T_2):

- 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 $b - c$ ⇒ **non-equilibrium supersaturated vapors**. Supersaturation is an important drivign force in the nucleation and growth of thin films.

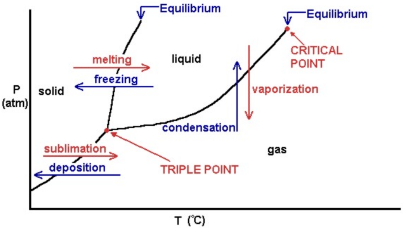
p-V-T diagram

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

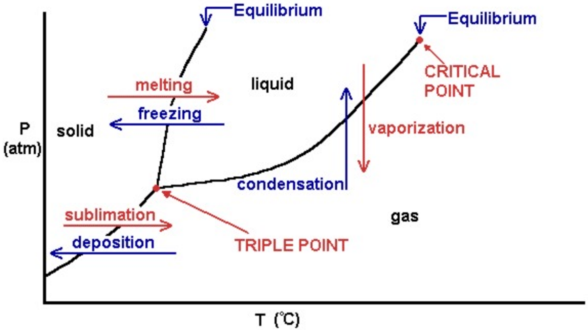


- **vapors**: can be condensed to liquid or solid by compression at fixed $T \Rightarrow$ below **critical point** defined by p_c, V_c and T_c
- **gases**: monotonical decrease of V upon compression $\Rightarrow$ no distinction between the two phases

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

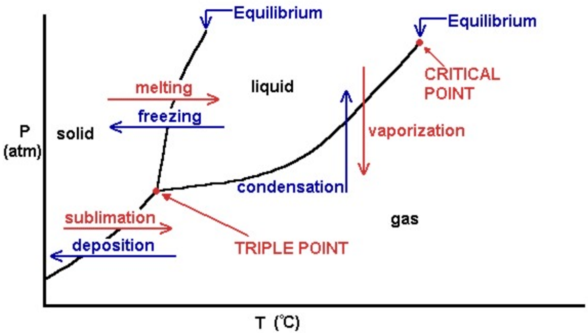


p-T diagram



- **triple point**: from triple line ⊥ to p-T plane
- below T of triple point: liquid-phase region vanishes ⇒ 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 $p_{\rm v}$ increases exponentially with T up to $p_{\rm c}$
- $p_{\rm c}$ is well above 1 atm $\Rightarrow$ **deposition of thin films** is performed at $p \ll p_{\rm c}$, either $p > p_{\rm v}$ (supersaturated vapors) or $p < p_{\rm v}$
- first two steps in the deposition (source supply and transport to substrate) should be carried out at $p < p_{\rm v}$ 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

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

where $k_{\mathrm{B}} = 1.38 \times 10^{-23}$ m^2 kg s^{-2} K^{-1} (or 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. $\vec{v} \equiv \vec{V}$.

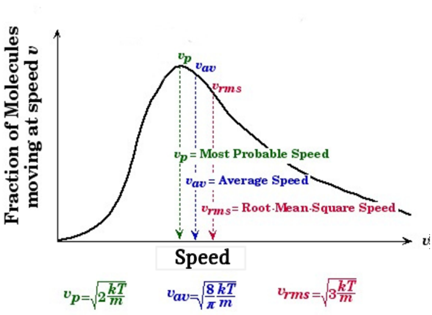
Maxwell-Boltzmann distribution is isotropic $\Rightarrow F(v)$ distribution of speeds $v \equiv |\vec{v}|$ can be defined by integration of $f(v)$ in spherical coordinates

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

resulting in

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

Mean (Average) Speed, Molecular Impingement Flux



Mean speed:

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

or

$$v_{\mathrm{av}} = \sqrt{\frac{8RT}{M}} \tag{5}$$

using **molar mass** $M = mN_{\mathrm{A}}$ in kg/mol and **gas constant**

$$R = k_{\mathrm{B}} N_{\mathrm{A}} = 8.31\,\mathrm{J mol^{-1} K^{-1}}$$

where $N_{\mathrm{A}} = 6.02 \times 10^{23}$ mol^{-1} is Avogadro's number

Root-mean-square (rms) speed:

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

The **most probable speed** v_{p}:

$$\left(\frac{dF(v)}{dv}\right)_{v=v_{\mathrm{p}}} = 0 \Rightarrow v_{\mathrm{p}} = \sqrt{\frac{2 k_{\mathrm{B}} T}{m}} \tag{7}$$

Ideal-Gas Law

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

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

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

$$p = nk_{\mathrm{B}} T \qquad \text{or} \qquad \frac{pV}{T} = Nk_{\mathrm{B}} \tag{9}$$

where N is the number of particles.

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

- molar concentration $n_{\mathrm{m}} = n/N_{\mathrm{A}} \Rightarrow p = n_{\mathrm{m}} RT$
- number of moles $N_{\mathrm{m}} = N/N_{\mathrm{A}} \Rightarrow p = N_{\mathrm{m}} RT/V$
- molar volume $V_{\mathrm{m}} = V/N_{\mathrm{A}} \Rightarrow p = RT/V_{\mathrm{m}}$

The **ideal gas is obeyed if**

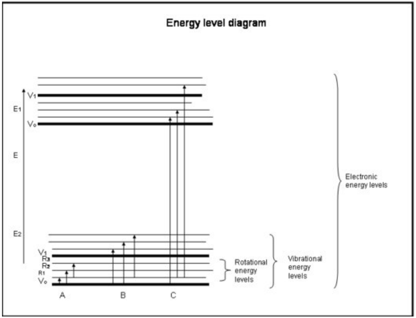
- the volume of molecules in the gas is much smaller than the volume of the gas
- the cohesive forces between the molecules can be neglected.

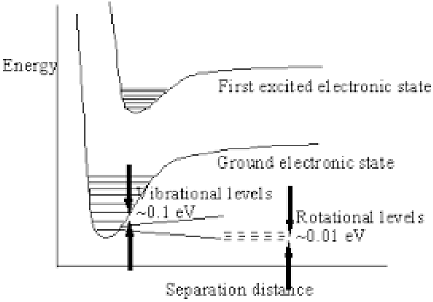
Both assumptions are fulfilled for low $n \Rightarrow$ always fulfilled for thin film deposition from the vapor phase ($T \geq T_{\mathrm{room}}$ and $p \leq p_{\mathrm{atm}}$), i.e. well away from the critical point (most materials $p_{\mathrm{c}} \gg 1$ atm or if not $T_{\mathrm{c}} \ll 25$ °C)

Energy Forms Stored by Molecules

Molecules can store energy in various forms. Their energetic states are quantized (spacing between energy levels ΔE)

- electronic excitations - $\Delta E_{\rm e}$ 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, $\Delta E_{\rm v} \approx 0.1$ eV (1 eV = 11 600 K)
- rotational excitations - different rotational modes of the molecule, $\Delta E_{\rm r} \approx 0.01$ eV
- translational energy - above performed description of molecular random motion $E_{\rm t} = 1/2mV^2$, no details of inner molecule structure are considered, $\Delta E_{\rm t}$ 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

$$E_\mathrm{t} = \frac{3}{2} k_\mathrm{B} T \tag{10}$$

$\Rightarrow$ **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:

$$c_\mathrm{V} = \frac{\mathrm{d}E_\mathrm{m}}{\mathrm{d}T} N_\mathrm{A} = \frac{\mathrm{d}(E_\mathrm{t} + E_\mathrm{r} + E_\mathrm{v})}{\mathrm{d}T} N_\mathrm{A} \tag{11}$$

for atomic gases

$$c_\mathrm{V} = \frac{3}{2} R = \frac{3}{2} k N_\mathrm{A}$$

for small diatomic molecules at room T

$$c_\mathrm{V} = \frac{5}{2} R$$

- 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 $p\mathrm{d}V$ work on the surroundings in addition to adding kinetic energy to the molecules:

$$c_{\mathrm{p}} = c_{\mathrm{V}} + R \tag{12}$$

We can write from thermodynamics

$$c_{\mathrm{V}} = \left(\frac{\partial U_{\mathrm{m}}}{\partial T}\right)_V \tag{13}$$

where U_{m} is internal energy per mol $U_{\mathrm{m}} = E_{\mathrm{m}} N_{\mathrm{A}}$ and

$$c_{\mathrm{p}} = \left(\frac{\partial H_{\mathrm{m}}}{\partial T}\right)_p \tag{14}$$

where H_{m} is enthalpy per mol $H_{\mathrm{m}} = U_{\mathrm{m}} + pV_{\mathrm{m}} \Rightarrow$

$$\left(\frac{\partial H_{\mathrm{m}}}{\partial T}\right)_p = \left(\frac{\partial U_{\mathrm{m}}}{\partial T}\right)_p + p\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_p \tag{15}$$

giving $c_{\mathrm{p}} = c_{\mathrm{V}} + R$

2.4 Units of Measurement

SI units?!
1 Torr = 133 Pa = 1 mm Hg
1 bar = 750 Torr = 1.0×10^5 Pa = 0.99 atm (standard atmosphere)
The “standard” conditions of T and p (stp) are 0°C and 1 atm (760 Torr). From ideal gas law at stp $V_{\mathrm{m}} = 22400\,\mathrm{cm}^3$.
These conditions are different from standard conditions to which thermodynamic data are referenced: 25°C and 1 bar.

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

2.5 Knudsen Equation

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

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

Substituting Maxwell-Boltzmann distribution

$$\Gamma = n\left(\frac{k_\mathrm{B} T}{2\pi m}\right)^{1/2} = \frac{1}{4} n\, v_\mathrm{av} \qquad (17)$$

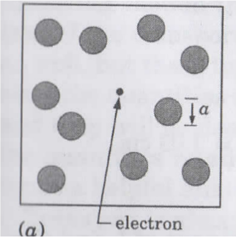
and using ideal gas law

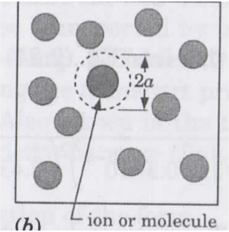
$$\Gamma = p\left(\frac{1}{2\pi k T m}\right)^{1/2} = pN_A\left(\frac{1}{2\pi RTM}\right)^{1/2} \qquad (18)$$

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

Calculate molecular impinging flux for CO_2 molecules (44 a. u., 330 pm), 25 °C, 10^{-3} 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

$$\lambda = \frac{1}{\sigma_\mathrm{m} n} \tag{19}$$

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

$$\lambda_\mathrm{e} = \frac{1}{\pi/4a^2 n} \tag{20}$$

It's approximation, σ_m is function of el. energy

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

$$\lambda_\mathrm{i} = \frac{1}{\pi a^2 n} \tag{21}$$

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

$$\lambda_\mathrm{m} = \frac{1}{\sqrt{2}\pi a^2 n} \tag{22}$$

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**:

$$Kn = \lambda / L \tag{23}$$

where L is a characteristic dimension in the process, e. g. distance between the source and the substrate, λ 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

... quantify the rate of transport 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 2.1 (p. 26) summarizes the quantities and eqs. It include also el. current (~~flow of el.~~ transp. of charge) because it's helpful analogy.

Transport is always described by an eq. of the form

$$(\text{flux of } A) = -(\text{proportional factor}) \times (\text{grad in } A)$$

general form is 3D but we will give it in 1D for simplicity.

Example for electrical current density j_x : $j_x\,(A/m^2) = \sigma \cdot \frac{dV}{dx}$ — grad. of el. potential (voltage) V/m

σ … el. conductivity $\frac{A}{V.m} = \frac{1}{\Omega.m}$

familiar Ohm's law

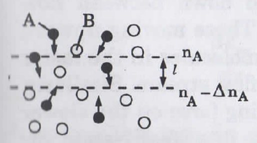
$\frac{1}{\sigma} = \rho$ … el. resistivity

2.8 Transport Properties - Overview

Transported quantity	Describing equation	Proportionality factor: Derivation from elementary kinetic theory	Proportionality factor: 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^2/s Ar-He: 0.72
Momentum	Shear stress = $\tau(N/m^2) = \eta\frac{du}{dx}$	Viscosity = $\eta(\text{Poise})^{\dagger} = \frac{1}{4}nm\bar{c}l \propto \frac{\sqrt{MT}}{a^2}$	Ar: 2.26×10^{-4} Poise† He: 2.02×10^{-4}
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)		

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 $n_{\rm A}$ to $n_{\rm A} - \Delta n_{\rm A}$ in the x-direction over a distance of *one mean free path* $\lambda \Rightarrow$ **Diffusion of A occurs in the direction of decreasing $n_{\rm A}$.**

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

$$\Gamma = \frac{1}{4} n \langle v \rangle \ \text{where} \ \langle v \rangle = \sqrt{\frac{8kT_{\rm B}}{\pi m}}$$

for the fluxes in opposite directions $\downarrow$ and $\uparrow \Rightarrow \Gamma_{\rm A} = \Gamma(x) - \Gamma(x + \lambda) = 1/4 \Delta n_{\rm A} \langle v \rangle$

Since $\Delta n_{\rm A} = \lambda \frac{-{\rm d}n_{\rm A}}{\rm dx}$, we have $\Gamma_{\rm A} = -\frac{1}{4} \langle v \rangle \lambda \frac{{\rm d}n_{\rm A}}{\rm dx} \Rightarrow$

$$\Gamma_{\rm A} = -D_{\rm AB} \frac{{\rm d}n_{\rm A}}{\rm dx}$$

Fik's law, $D_{\rm AB}$ **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

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

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

$$D_{AB} = \frac{T^{7/4}\left(\frac{1}{m_A}+\frac{1}{m_B}\right)^{1/2}}{p\,(a_A+a_B)^2} \quad \left\{\frac{m^2}{s}\right\}$$

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

Typical value at 300K, 1 atm: Ar–Ar: 0,19 cm^2/s; Ar–He: 0,72 cm^2/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 ~ factor two.

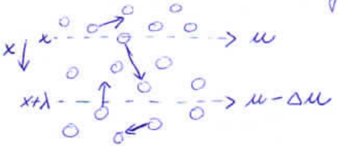
Dependence of D_{AB} on p is particularly important, since it can be lower than 1 atm by many orders of magnitude in depos. processes $\Rightarrow \uparrow D_{AB}$.

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

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 λ. 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 — viscous shear stress τ (N/m²) = rate of momentum transfer per unit area ⊥ to $\vec{x}$ ⇒ (viskózní tečné napětí)

τ = molecular flux × momentum gain/loss per molecule ⇒

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

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

Subst. $\eta = \frac{1}{4} n \sqrt{\frac{8kT}{\pi m}} \cdot m \cdot \frac{1}{\sqrt{2}\pi a^2 n} \sim \frac{\sqrt{T \cdot m}}{a^2}$

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

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

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** Φ is analogous to that for momentum transfer, with $m\Delta u$ replaced by $2\Delta E_{\mathrm{m}}$

$$\Phi = \frac{1}{4} n \langle v \rangle 2\lambda \frac{\mathrm{d}E_{\mathrm{m}}}{\mathrm{d}x} \tag{24}$$

with the units J/(s.m^2) or W/m^2.
We can substitute T for E_{m} using Eq. (11) for molar heat capacity at constant volume

$$\frac{\mathrm{d}E_{\mathrm{m}}}{\mathrm{d}x} = \frac{\mathrm{d}E_{\mathrm{m}}}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{c_{\mathrm{V}}}{N_{\mathrm{A}}}\frac{\mathrm{d}T}{\mathrm{d}x} \tag{25}$$

Thus, we obtain Fourier's law

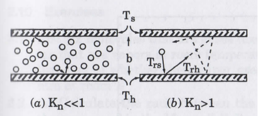
$$\Phi = -K_{\mathrm{T}} \frac{\mathrm{d}T}{\mathrm{d}x} \tag{26}$$

where **thermal conducitivty** $K_{\mathrm{T}} \sim \sqrt{T/m}\, c_{\mathrm{V}}/a^2$. 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 η, 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 $K_{\mathrm{T}} \sim \sqrt{T/m}\, c_{\mathrm{V}}/a^2$)

$$\Phi = -K_{\mathrm{T}}\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{K_{\mathrm{T}}}{b}(T_{\mathrm{h}} - T_{\mathrm{s}}) \tag{27}$$

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 (Γ) times the heat carried per molecule (using Eq. (25)):

$$\Phi = \Gamma\gamma'\frac{c_{\mathrm{V}}}{N_{\mathrm{A}}}(T_{\mathrm{h}} - T_{\mathrm{s}}) \equiv h_{\mathrm{c}}(T_{\mathrm{h}} - T_{\mathrm{s}}) \tag{28}$$

where γ' is the thermal accommodation factor ($\approx$ unity except for He) and h_{c} **is the heat transfer coefficient** (W K/m^2) given as $h_{\mathrm{c}} = \sqrt{N_{\mathrm{A}}/(2\pi R)}\, p/\sqrt{mT}\, \gamma'\, c_{\mathrm{V}}$

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.

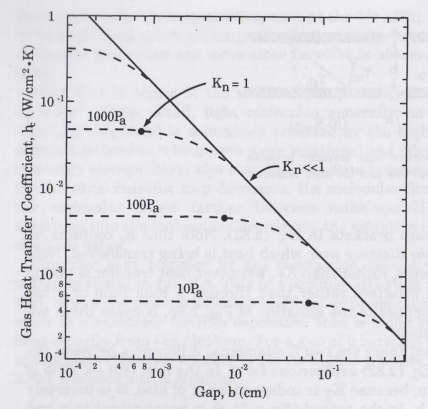
2.8.3 Heat transfer - heat transfer to substrate

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

- Φ is inversely proportional to b for fluid whereas independent of b for molecular regime
- Φ 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 $Kn > 1$.

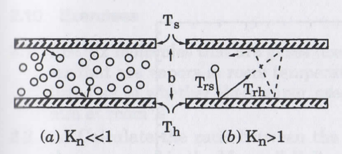
Helium is often chosen to improve the heat transfer because of its high K_{T}, but in fact it is not the best choice when $Kn > 1$ because of the thermal accommodation factor in Eq. (28) - for discussion of γ' see the next slide.



From Eq. (28), the best choice for a heat-transfer gas is one having low molecular mass to give high Γ, 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** γ is defined as

$$\gamma = \frac{T_{\mathrm{rs}} - T_{\mathrm{rh}}}{T_{\mathrm{rs}} - T_{\mathrm{h}}}. \tag{29}$$

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, γ is close to unity, but for He it is 0.1–0.4, depending on the surface.

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

$$\gamma' = \frac{\gamma}{2 - \gamma} \tag{30}$$