F4280 Technologie depozice tenkých vrstev a povrchových úprav
2. Gas Kinetics

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Outline - chapter 2. Gas Kinetics

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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}):

A cut through the p-V-T surface below critical point for fixed $T \Rightarrow$ relationship between $p$ and $V_m$ (molar volume):

- 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 $p$ and $T$ ($b – c$ line is ⊥ 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**
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.
- **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** \( p_v \)
- \( p_v \) increases exponentially with \( T \) up to \( p_c \) that is well above 1 atm
  \( \Rightarrow \) deposition of thin films is performed at \( p \ll p_c \), either \( p > p_v \) (supersaturated vapors) or \( p < p_v \)
Maxwell-Boltzmann Distribution

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

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

where $k_B = 1.38 \times 10^{-23}$ 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

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

resulting in

$$F(v) = 4\pi v^2 n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{k_B T}\right)$$
Mean (Average) Speed, Molecular Impingement Flux

Mean speed:

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

or

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

using molar mass \(M = mN_A\) in kg/mol and gas constant

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

where \(N_A = 6.02 \times 10^{23} \text{ mol}^{-1}\) is Avogadro’s number

Root-mean-square (rms) speed:

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

The most probable speed \(v_p\):

$$\left( \frac{dF(v)}{dv} \right)_{v=v_p} = 0 \Rightarrow v_p = \sqrt{\frac{2k_B T}{m}}$$ (7)
### Ideal-Gas Law

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

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

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

\[
p = nk_B T \quad \text{or} \quad \frac{pV}{T} = Nk_B \tag{9}\n\]

where \( N \) is the number of particles.

Chemists are used to work in molar amounts:

- 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 (\( T > T_{\text{room}} \) 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 \( T_c \ll 25 \, ^\circ\text{C} \).
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 level diagram](image)
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

\[
E_t = \frac{3}{2} k_B T
\]  

⇒ 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) [\( \text{J}/(\text{mol.K}) \)] - increase of total kinetic energy for increasing \( T \):

\[
\frac{c_V}{N_A} = \frac{dE_m}{dT} = \frac{d(E_t + E_r + E_v)}{dT}
\]

for atomic gases

\[
c_V = \frac{3}{2} R = \frac{3}{2} kN_A
\]

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 $p \, d \, V$ work on the surroundings in addition to adding kinetic energy to the molecules:

$$c_p = c_V + R$$  \hspace{1cm} (12)

We can write from thermodynamics

$$c_V = \left( \frac{\partial U_m}{\partial T} \right)_V$$  \hspace{1cm} (13)

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

$$c_p = \left( \frac{\partial H_m}{\partial T} \right)_p$$  \hspace{1cm} (14)

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

$$\left( \frac{\partial H_m}{\partial T} \right)_p \, = \, \left( \frac{\partial U_m}{\partial T} \right)_p + p \left( \frac{\partial V_m}{\partial T} \right)_p$$  \hspace{1cm} (15)

giving $c_p = c_V + R$
Molecular Impingement Flux - Knudsen Equation

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

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

Substituting Maxwell-Boltzmann distribution

\[
\Gamma = n \left( \frac{k_B T}{2\pi m} \right)^{1/2} = \frac{1}{4} n v_{av}
\]  
(17)
2.5 Units of Measurement

see Smith’s book
2.6 Knudsen Equation

see Smith’s book
2.7 Mean Free Path

see Smith’s book
2.8 Transport Properties

see Smith’s book