

Crystal Growth: Physics, Technology and Modeling

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Lecture 8. Transport processes in liquid and vapor phases

<http://www.unipress.waw.pl/~stach/cg-2021-22>

Scope

- **Conservation laws**
- **Constitutive relations**
- **Navier Stokes equations**
- **Convection**
- **Diffusion**
- **Thermal conductivity**
- **Radiation**

Surface and bulk phases – characteristic lengths

- Bulk phases – characteristic lengths L_V - macroscopic

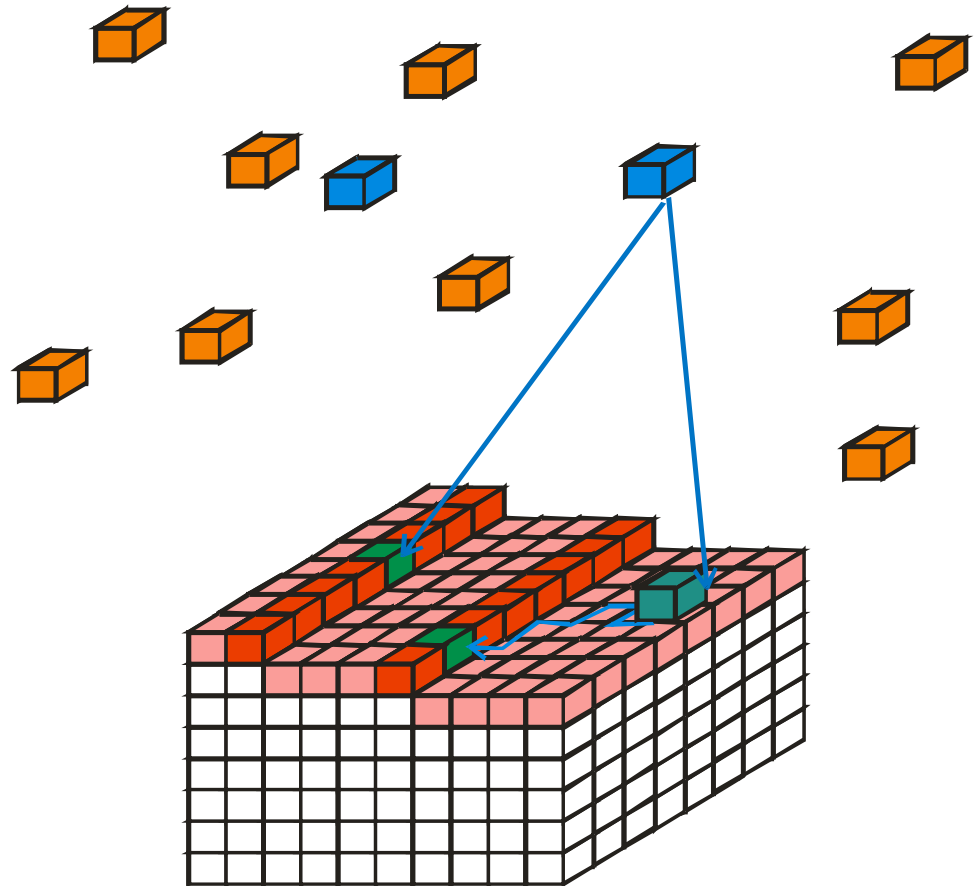
$$L_V \gg \lambda \sim 1\mu$$

$$L_V \sim 100\mu \div 1m$$

- Surfaces – characteristic lengths L_s

$$L_s \gg x_{sun} \sim 5nm$$

$$L_s \sim 10nm \div 100 nm$$



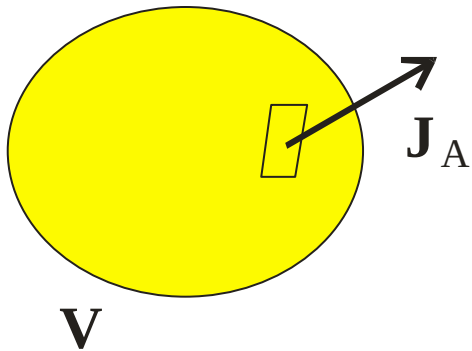
Surface – bulk coupling

- Bulk phase is usually uniform on the surface diffusion length scale
- Step motion in uniform bulk supersaturation - σ_v
- Growth instability – by creation of macrosteps
- Face instability – different parameter values across the face
- Use of parametric growth model – effectively decoupled – weak coupling by parameter value

Conservation laws

- The temporal change of the value of the conserved quantity **A** is composed of two contributions: flux across boundary **J** and production of internal sources **R**:

$$\frac{\partial A}{\partial t} = - \oint (\vec{J}_A \cdot \vec{n}) d^2S + R_A$$



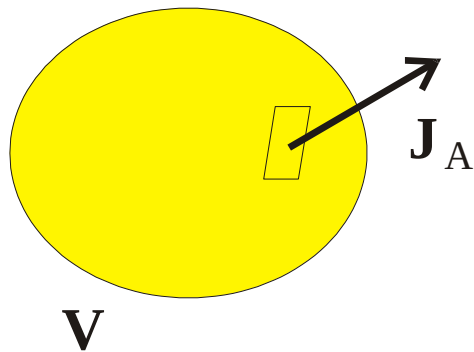
$\vec{n}$ - unit normal vector, pointing to outside – the surface term is negative

$$A(t) = \int_V d^3r \rho_A(\vec{r}, t)$$

$$R_A(t) = \int_V d^3r r_A(\vec{r}, t)$$

Green theorem

- For any closed surface and the vector field $\vec{J}$ (C^1), the following holds:



$$\int_S (\vec{J} \cdot \vec{n}) d^2S = \oint_V \text{div}(\vec{J}) d^3r$$

$\vec{n}$ - unit normal vector, directed outside of V

Differential form of conservation laws

- Denote by a the density of A for mass unit. Then we have:

$$A(t) = \int_V a(\vec{r}, t) \rho(\vec{r}, t) d^3r$$

- Employing Green theorem to any volume V gives general conservation law equation:

$$\frac{\partial [a(\vec{r}, t) \rho(\vec{r}, t)]}{\partial t} = -\text{div}(\vec{J}_A) + r_A$$

- Source efficiency :

$$R_A(t) = \int_V d^3r r_A(\vec{r}, t)$$

- Center of mass position $\vec{r}_{CM}$:

$$\vec{r}_{CM} = \frac{\int_V \vec{r} \rho(\vec{r}, t) d^3r}{\int_V \rho(\vec{r}, t) d^3r}$$

External fluxes

- **Flux of the conserved, additive physical quantity A is sum of convective and diffusive contributions:**

$$\vec{J}_A(\vec{r}, t) = \vec{J}_A^{conv}(\vec{r}, t) + \vec{J}_A^{dif}(\vec{r}, t)$$

- **Convective flux is due to center of mass motion:**

$$\vec{J}_A^{conv}(\vec{r}, t) = a(\vec{r}, t)\rho(\vec{r}, t)\vec{v}_{CM}(\vec{r}, t)$$

- **Center of mass velocity $\vec{v}_{CM}$:**

$$\vec{v}_{CM} = \frac{d\vec{r}_{CM}}{dt}$$

Naturally in the center of mass system convective flux is zero.

Diffusion fluxes

- Diffusion flux are determined in center of mass system:

$$\vec{J}_A^{dif}(\vec{r}, t) = \vec{J}_{A,CM}(\vec{r}, t)$$

- Diffusion flux – Fick law:

$$\vec{J}_A^{dif}(\vec{r}, t) = -D \nabla n_A(\vec{r}, t)$$

D – diffusion coefficient ($m^2 s^{-1}$)

- Domination of single component A (CM approximated by CM(A))

$$\vec{J}_A^{dif}(\vec{r}, t) = 0$$

$$\vec{J}_B^{dif}(\vec{r}, t) = -D_B \nabla n_B(\vec{r}, t) = -D_B n_A \nabla c_B(\vec{r}, t)$$

Single component (**total mass**) system – mass conservation law

- **No diffusion**
- **No sources**
- **Mass density flux is convective only**

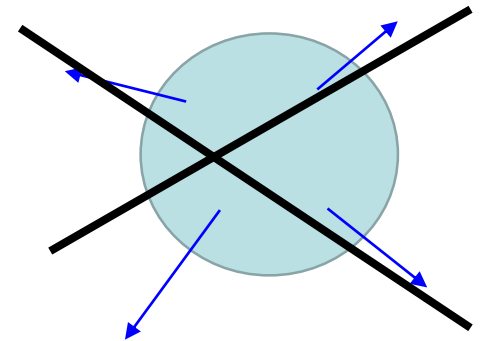
$$\rho(\vec{r}, t) = \sum_i \rho_i(\vec{r}, t)$$

$$\vec{J}(\vec{r}, t) = \vec{J}^{conv}(\vec{r}, t) = \rho(\vec{r}, t) \vec{v}(\vec{r}, t)$$

- **Mass conservation law is given by the equation**

$$\frac{\partial[\rho(\vec{r}, t)]}{\partial t} + \text{div}(\rho(\vec{r}, t) \vec{v}(\vec{r}, t)) = 0$$

$$\frac{\partial}{\partial t} \int_V d^3r \rho_A(\vec{r}, t) = - \oint (\rho(\vec{r}, t) \vec{v}(\vec{r}, t) \cdot \vec{n}) d^2S$$



**Could not happen
in stationary result**

Mass conservation law in single component system – stationary (i.e. time independent) flow

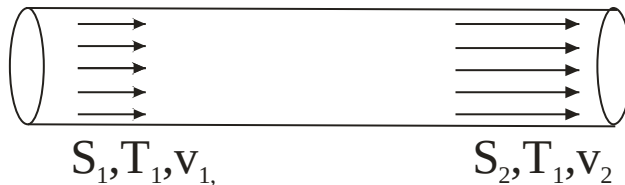
- Density is time independent

$$\rho(\vec{r}, t) = \rho(\vec{r})$$

- Mass conservation law is reduced to

$$\nabla \cdot [\rho(\vec{r}) \vec{v}(\vec{r})] = 0 \qquad \oint (\rho(\vec{r}) \vec{v}(\vec{r}) \cdot \vec{n}) d^2S = 0$$

- Example: mass flow in MOVPE reactor



$$\rho_1 v_1 S_1 = \rho_2 v_2 S_2$$

$$S_1 = S_2$$

$$p = \frac{\rho RT}{m}$$

$$v_2 = v_1 \frac{T_2}{T_1}$$

Mass conservation law in single component system – stationary (i.e. time independent) flow

- Density is constant

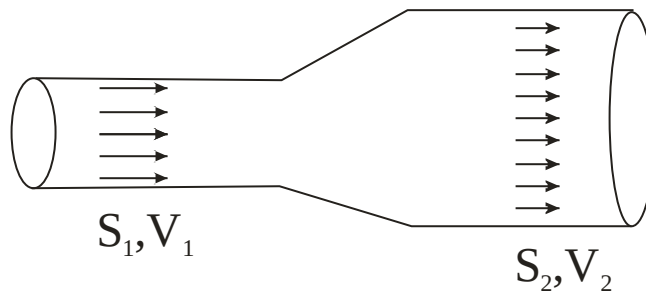
$$\rho(\vec{r}) = \rho_o$$

- Mass conservation law is reduced to

$$\nabla \cdot [\vec{v}(\vec{r})] = 0$$

$$\oint (\rho(\vec{r}) \vec{v}(\vec{r}) \cdot \vec{n}) d^2S = 0$$

- Example: mass flow in MOVPE reactor



$$v_1 S_1 = v_2 S_2$$

$$v_2 = v_1 \frac{S_1}{S_2}$$

$$vS = V$$

$$V_1 = V_2$$

Multi-component system

- **Concentrations of the components**

$$c_i(\vec{r}, t) = \frac{\rho_i(\vec{r}, t)}{\rho(\vec{r}, t)} \quad \rho(\vec{r}, t) = \sum_i \rho_i(\vec{r}, t) \quad \sum_i c_i(\vec{r}, t) = 1$$

- **Convection flux of the component**

$$\vec{j}_i^{conv}(\vec{r}, t) = \rho_i(\vec{r}, t) \vec{v}(\vec{r}, t) = c_i(\vec{r}, t) \rho(\vec{r}, t) \vec{v}(\vec{r}, t)$$

- **Diffusion flux of the component (Fick law)**

$$\vec{j}_i^{dif}(\vec{r}, t) = -D_i(\rho) \nabla \rho_i(\vec{r}, t) = -D_i(\rho) \rho(\vec{r}, t) \nabla c_i(\vec{r}, t)$$

Multi-component system – conservation laws

- **Component (i) conservation law**

$$\frac{\partial[\rho_i(\vec{r}, t)]}{\partial t} + \text{div}(\rho_i(\vec{r}, t)\vec{v}(\vec{r}, t)) = r_i$$

- **r_i – chemical reaction efficiency (for volume unit) - normalization**

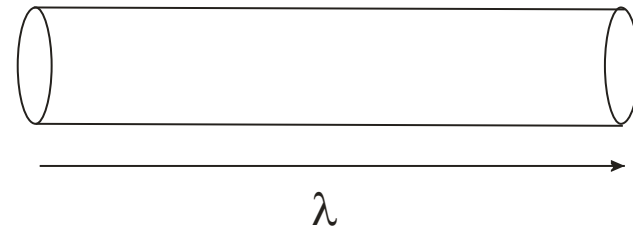
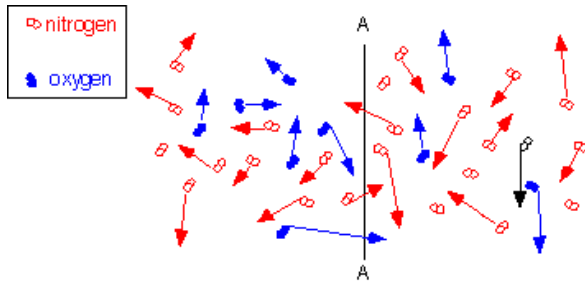
$$\sum_i r_i(\vec{r}, t) = 0$$

- **Density is constant (no convection) standard diffusion law**

$$\frac{\partial[c_i(\vec{r}, t)]}{\partial t} = D_i \Delta[c_i(\vec{r}, t)]$$

Gas phase diffusion

- Random motion of gas molecules - mean free path – λ :



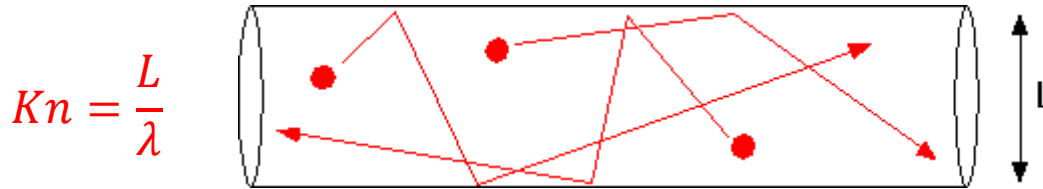
$$\lambda = \frac{1}{\sqrt{2}\pi a^2 \rho} = \frac{5 \text{ cm}}{p \text{ (mTorr)}}$$

- Diffusion coefficient – D :

$$D = \frac{\langle v \rangle \lambda}{3} = \frac{(kT)^{3/2}}{\pi^{3/2} m^{1/2} p a^2}$$

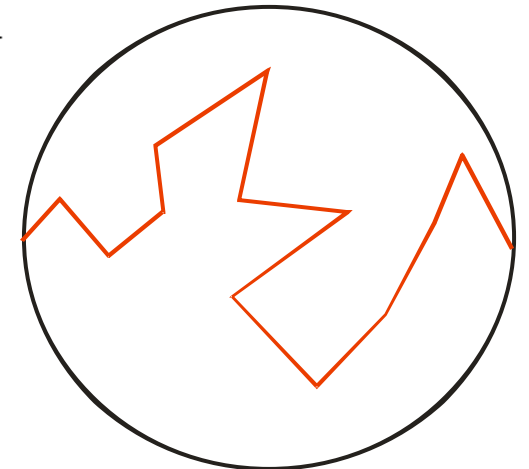
Gas phase – ballistic and diffusive transport

- Knudsen number - Kn



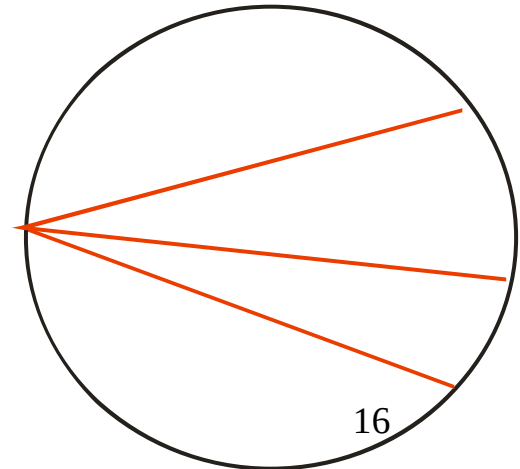
- Ballistic transport - MBE

$$Kn \ll 1$$



- Diffusive transport – VPE, HVPE, MOVPE

$$Kn \gg 1$$



Lattice diffusion

- **No convection**
- **Diffusion – Fick law**

$$\vec{j}_i^{dif}(\vec{r}, t) = -D_i(\rho)\nabla\rho_i(\vec{r}, t) = -D_i(\rho)\rho(\vec{r}, t)\nabla c_i(\vec{r}, t)$$

- **Mass conservation law**

$$\frac{\partial[\rho(\vec{r}, t)]}{\partial t} + \text{div}[D\nabla\rho(\vec{r}, t)] = r_\rho(\vec{r}, t)$$

- **Surface coverage – adsorption and desorption**

$$\frac{\partial[n(\vec{r}, t)]}{\partial t} - D\Delta n(\vec{r}, t) = R_{ads}(\vec{r}, t) - R_{des}(\vec{r}, t)$$

Momentum conservation law

- **Momentum conservation law – velocity density (for each component)**

$$\vec{p} = \int_V \vec{v}(\vec{r}, t) \rho(\vec{r}, t) d^3r$$

- **Any single component of momentum (α) is conserved. Convective flux of momentum could be defined**

$$j_{p_\alpha}^{conv} = \oint (v_\alpha(\vec{r}, t) \rho(\vec{r}, t) \vec{v}(\vec{r}, t) \cdot \vec{n}) d^2S$$

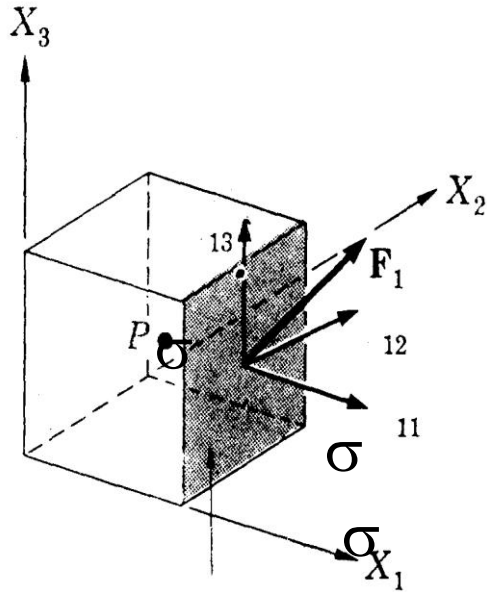
- **Momentum flux is changed by the surface force:**

$$\vec{j}_{p_\alpha}^{stress} = \oint (\hat{\sigma}_\alpha(\vec{r}, t) : \vec{n}) d^2S$$

$\hat{\sigma}_{\alpha\beta}(\vec{r}, t)$ - stress tensor

Surface forces – stress tensor - momentum flux

- Surface force – equivalent of diffusion flux:



$$F_{\alpha}(\vec{r}, t) = \sum_{\beta} \hat{\sigma}_{\alpha\beta} n_{\beta}$$

F_{α} - force acting on the surface

n_{β} - component of unit vector,
normal (perpendicular) to the surface

$\hat{\sigma}_{\alpha\beta}(\vec{r}, t)$ - stress tensor

Units of stress (pressure)

- **SI unit – Pascal (Pa)** $1Pa = 1 \frac{N}{m^2}$

- **Imperial (US customary) unit – psi (pound per square inch)**

$$1psi = 6894.757 Pa = 6.894757 kPa$$

- **Non SI unit – bar**

$$1 bar = 100\,000 Pa = 100 kPa$$

- **Non SI unit – atmosphere (atm)**

$$1 atm = 101\,325 Pa = 101.325 kPa$$

- **Non SI unit – Torr (mm Hg)**

$$1 Torr = 133.322\,368\,412 Pa$$

[https://en.wikipedia.org/wiki/Standard_atmosphere_\(unit\)](https://en.wikipedia.org/wiki/Standard_atmosphere_(unit))

Stress tensor – different cases

- Isotropic or hydrostatic stress (pressure) : $\hat{\sigma}_{\alpha\beta} = -p\delta_{\alpha\beta}$

Kronecker symbol or Kronecker delta

$$\delta_{\alpha\beta} = \begin{cases} 0 & \alpha \neq \beta \\ 1 & \alpha = \beta \end{cases}$$

- Normal stress: $\hat{\sigma}_{\alpha\beta} = \delta_{\alpha\beta}\sigma_{\alpha}$
- Shear stress: $\hat{\sigma}_{\alpha\beta} = (1 - \delta_{\alpha\beta})\sigma_{\alpha\beta}$
- Uniaxial stress: $\hat{\sigma}_{\alpha\beta} = \sigma_{11}$
- Biaxial stress: $\sigma_{1\alpha} = 0$
- Triaxial stress: $\hat{\sigma}_{\alpha\beta}$

Force action – bulk component

- Bulk forces – bulk source of momentum

$$r_\alpha(\vec{r}, t) = f_\alpha(\vec{r}, t)\rho(\vec{r}, t)$$

$f_\alpha(\vec{r}, t)$ - force acting for mass unit

- Gravitational field – field intensity γ_α

$$f_\alpha(\vec{r}, t) = \gamma_\alpha(\vec{r}, t)$$

- At the Earth surface – gravitational acceleration g_α :

$$f_\alpha(\vec{r}, t) = g_\alpha(\vec{r}, t)$$

Momentum conservation – dynamic equation of motion

- **Green theorem for velocity density gives:**

$$\frac{\partial [\rho(\vec{r}, t) \vec{v}(\vec{r}, t)]}{\partial t} + \text{div} [\rho(\vec{r}, t) \vec{v}(\vec{r}, t) \vec{v}(\vec{r}, t)] = \text{div}(\hat{\sigma}) + \rho(\vec{r}, t) \vec{f}(\vec{r}, t)$$

- **Mass conservation law could be used to obtain:**

$$\rho(\vec{r}, t) \left[\frac{\partial \vec{v}(\vec{r}, t)}{\partial t} + (\vec{v}(\vec{r}, t) \cdot \nabla) \vec{v}(\vec{r}, t) \right] = \text{div}(\hat{\sigma}) + \rho(\vec{r}, t) \vec{f}(\vec{r}, t)$$

- **Equation is nonlinear in velocity**
- **Stress tensor has to be determined**

Stress tensor in liquid – hydrostatic and viscous

- **Pressure:** $\hat{\sigma}_{\alpha\beta} = -p\delta_{\alpha\beta}$ $p = -\frac{1}{3}Tr(\hat{\sigma}_{\alpha\beta})$

- **Viscosity**

$$\hat{\sigma}_{\alpha\beta} = -p\delta_{\alpha\beta} + \left[\left(\frac{\partial v_\alpha}{\partial r_\beta} \right) + \left(\frac{\partial v_\beta}{\partial r_\alpha} \right) \right] + \left(\mu_b - \frac{2}{3}\mu \right) \sum_{\gamma=1}^3 \left(\frac{\partial v_\gamma}{\partial r_\gamma} \right) \delta_{\alpha\beta}$$

μ – shear viscosity coefficient

μ_b – bulk viscosity coefficient

- **Units (SI)**

$$[\mu] = Pa \cdot s = \frac{kg}{m \cdot s} = 10 \text{ Poise}$$

- **Units (CGS)**

$$[\mu] = \frac{g}{cm \cdot s} = \text{Poise}$$

Shear viscosity

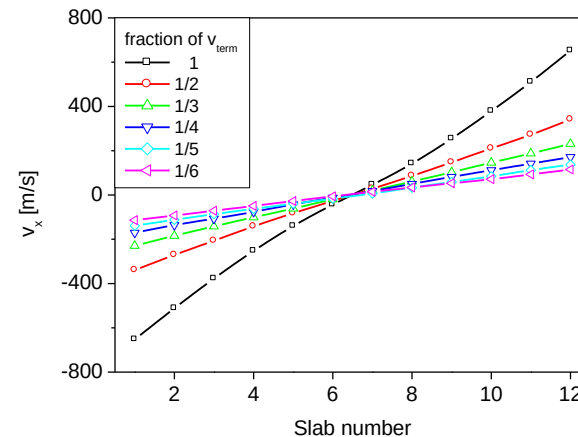
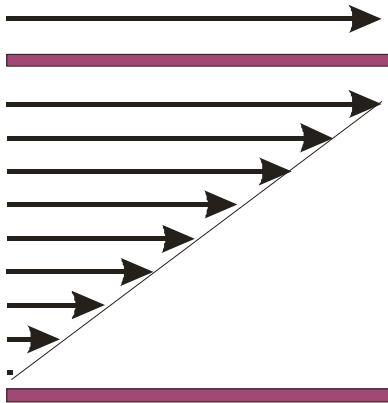
- **Incompressible fluid flow:**

$$\text{div}(\vec{v}(\vec{r}, t)) = \sum_{\alpha=1}^3 \left(\frac{\partial r_{\alpha}}{\partial r_{\alpha}} \right) = 0$$

- **Viscous force (only shear):**

$$f_{\beta} = \sum_{\alpha=1}^3 \left(\frac{\partial \hat{\sigma}_{\alpha\beta}}{\partial r_{\alpha}} \right) = \mu \sum_{\alpha=1}^3 \frac{\partial}{\partial r_{\alpha}} \left[\left(\frac{\partial v_{\alpha}}{\partial r_{\beta}} \right) + \left(\frac{\partial v_{\beta}}{\partial r_{\alpha}} \right) \right] = \mu \sum_{\alpha=1}^3 \left(\frac{\partial^2 v_{\beta}}{\partial r_{\alpha} \partial r_{\alpha}} \right) = \mu \Delta v_{\beta}$$

- **Example – Couette flow**



P. Strak & S. Krukowski J. Phys. Chem. B 115 (2011) 4359

Navier-Stokes equation

- **Dynamic equation for incompressible liquid (Navier-Stokes equation):**

$$\rho(\vec{r}, t) \left[\frac{\partial \vec{v}(\vec{r}, t)}{\partial t} + (\vec{v}(\vec{r}, t) \cdot \nabla) \vec{v}(\vec{r}, t) \right] = -\nabla p(\vec{r}, t) + \mu \Delta \vec{v}(\vec{r}, t) + \rho(\vec{r}, t) \vec{f}(\vec{r}, t)$$

- **Density changes due to temperature or concentration of components**

$$\rho(T) = \rho(T_o) \beta_T (T - T_o)$$

$$\rho(c) = \rho(0) \beta_c c$$

Thermal expansion coefficient

$$\beta_T = -\frac{1}{\rho} \left(\frac{\partial \rho(T)}{\partial T} \right)_{T=T_o} \sim 10^{-4} T^{-1}$$

**Thermal expansion coefficient
(ideal gas – the largest possible)**

$$\beta_T = -\left(\frac{\partial \rho(T)}{\partial T} \right)_{T=T_o} = -\frac{1}{T}$$

Concentration density change

$$\beta_c = -\frac{1}{\rho} \left(\frac{\partial \rho(c)}{\partial c} \right)_{c=0}$$

Boussinesq approximation

- **Pressure – due to hydrostatic force**

$$p(z) = -\rho(T)g(z - z_o)$$

- **Pressure gradient – due to hydrostatic force only**

$$-\nabla p(z) = -\rho(T)\vec{f}$$

- **Equation of motion**

$$\rho_o \left[\frac{\partial \vec{v}(\vec{r}, t)}{\partial t} + (\vec{v}(\vec{r}, t) \cdot \nabla) \vec{v}(\vec{r}, t) \right] = \mu \Delta \vec{v}(\vec{r}, t) + \rho_o [\beta_T(T - T_o) + \beta_c c] \vec{f}(\vec{r}, t)$$

Energy conservation law

- Energy conservation law reads:

$$\frac{\partial [\varepsilon(\vec{r}, t) \rho(\vec{r}, t)]}{\partial t} = -\text{div}(\vec{j}_\varepsilon) + r_\varepsilon$$

ε – energy density (for unit of mass)

- Energy as the temperature change:

$$d\varepsilon = C_p dT$$

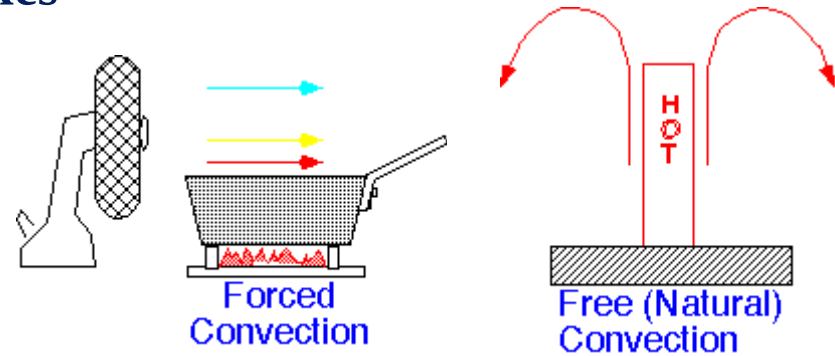
- Temperature change equation:

$$\frac{\partial [C_p(T) T(\vec{r}, t) \rho(\vec{r}, t)]}{\partial t} + \rho(\vec{r}, t) C_p(T) (\vec{v}(\vec{r}, t) \cdot \nabla) T(\vec{r}, t) = -\text{div}(\vec{j}_\varepsilon) + r_\varepsilon$$

Energy fluxes

- Convection:**

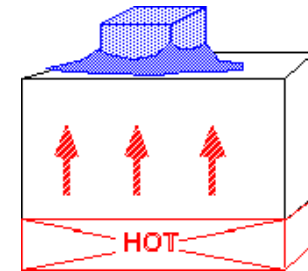
$$\vec{j}_\varepsilon = \rho(\vec{r}, t) \varepsilon(\vec{r}, t) \vec{v}(\vec{r}, t)$$



- Thermal conductivity (Fourier law) :**

$$\vec{j}_\varepsilon = -\kappa \nabla T(\vec{r}, t)$$

κ – *thermal conductivity coefficient*

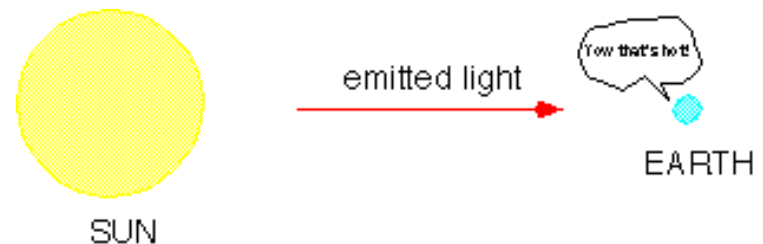


- Radiation (Stefan-Boltzmann law)**

$$\vec{j}_\varepsilon = e \sigma T^4(\vec{r}, t)$$

Stefan-Boltzmann constant

$$\sigma = 5.670374 \frac{W}{m^2 K^4}(\vec{r}, t)$$



e – *emissivity*

$$0 < e \leq 1$$

Radiation

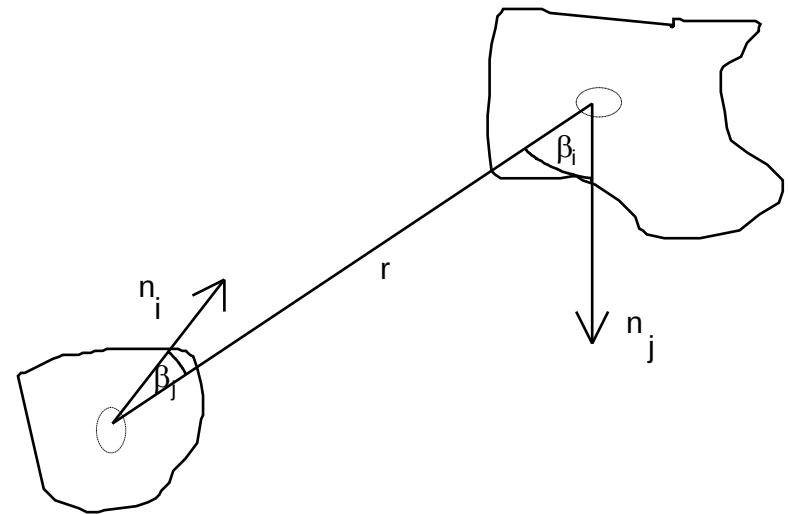
- Radiation heat exchange

$$\sum_{j=1}^N \left(\frac{\delta_{ij}}{e_j} - F_{ij} \frac{1-e_j}{e_j} \right) J_{\varepsilon,r}^j = \sum_{j=1}^N (\delta_{ij} - F_{ij}) \sigma T^4$$

- F_{ij} - viewfactors for i and j surfaces

$$F_{ij} = \frac{1}{A_i} \int_{A_i} \int_{A_j} \frac{\cos \beta_i \cos \beta_j dA_i dA_j}{\pi r^2}$$

$$0 < F_{ij} \leq 1$$



Energy sources

- **Viscosity:**

$$r_\varepsilon = \frac{\mu}{2} \sum_{\alpha, \beta=1}^3 \left(\frac{\partial v_\alpha}{\partial r_\beta} + \frac{\partial v_\beta}{\partial r_\alpha} \right)^2$$

- **Chemical reaction energy:**

$$r_\varepsilon = Q \left(\frac{\partial n}{\partial t} \right)$$

Q – heat of reaction

- **Volume change - pressure:**

$$r_\varepsilon = -p \sum_{\alpha, \beta=1}^3 \frac{\partial v_\alpha}{\partial r_\alpha} = -p \operatorname{div}(\vec{v})$$

Summary – conservation laws – compressible fluid

$$\frac{\partial[\rho(\vec{r}, t)]}{\partial t} + \operatorname{div}(\rho(\vec{r}, t) \vec{v}(\vec{r}, t)) = 0$$

$$\rho(\vec{r}, t) \left[\frac{\partial \vec{v}(\vec{r}, t)}{\partial t} + (\vec{v}(\vec{r}, t) \cdot \nabla) \vec{v}(\vec{r}, t) \right] = -\nabla p(\vec{r}, t) + \mu \Delta \vec{v}(\vec{r}, t) + \rho(\vec{r}, t) \vec{f}(\vec{r}, t)$$

$$\frac{\partial [C_p(T) T(\vec{r}, t) \rho(\vec{r}, t)]}{\partial t} + \rho(\vec{r}, t) C_p(T) (\vec{v}(\vec{r}, t) \cdot \nabla) T(\vec{r}, t) = \operatorname{div}(\kappa \nabla T(\vec{r}, t)) + r_\varepsilon$$

- **6 variables: velocity components, density, pressure, temperature**
- **5 equations + equation of state**

$$p = p(\rho, T)$$

Summary – conservation laws – incompressible fluid

$$\operatorname{div}(\vec{v}(\vec{r}, t)) = 0$$

$$\rho_o \left[\frac{\partial \vec{v}(\vec{r}, t)}{\partial t} + (\vec{v}(\vec{r}, t) \cdot \nabla) \vec{v}(\vec{r}, t) \right] = \mu \Delta \vec{v}(\vec{r}, t) + \rho_o [\beta_T (T - T_o) + \beta_c c] \vec{f}(\vec{r}, t)$$

$$\rho_o C_p(T) \left[\frac{\partial [T(\vec{r}, t)]}{\partial t} + (\vec{v}(\vec{r}, t) \cdot \nabla) T(\vec{r}, t) \right] = \operatorname{div}(\kappa \nabla T(\vec{r}, t)) + r_\varepsilon$$

- **5 variables: velocity components, pressure, temperature**
- **5 equations + equation of state**

Boundary conditions - velocity

- **Solid surfaces – no-slip condition:**

$$\vec{v}(\vec{r}, t) = 0$$

- **Solid surface – crystal growth (surface is nonmaterial, no-slip):**

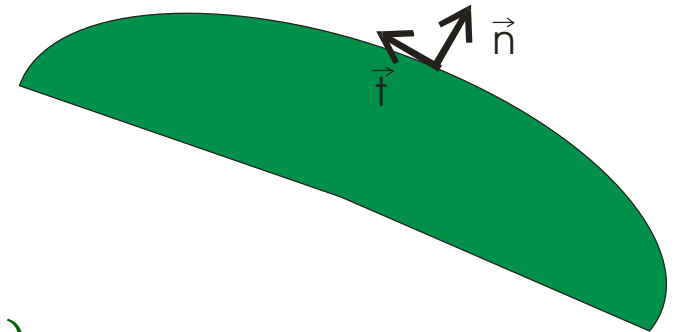
$$\vec{v}(\vec{r}, t) \cdot \vec{t}(\vec{r}, t) = 0$$

$$\rho_l(\vec{r}, t)[\vec{v}(\vec{r}, t)c_l(\vec{r}, t) - D_l \nabla c_l(\vec{r}, t)] \cdot \vec{n}(\vec{r}, t) = \rho_s(\vec{r}, t)[\vec{u}(\vec{r}, t)c_s(\vec{r}, t) - D_s \nabla c_s(\vec{r}, t)] \cdot \vec{n}(\vec{r}, t)$$

$\vec{t}(\vec{r}, t)$ - vector tangential to the surface

$\vec{n}(\vec{r}, t)$ - vector normal to the surface

$\vec{u}(\vec{r}, t)$ - crystallization velocity



Boundary conditions - temperature

- Solid –vapor/liquid interface – perfect thermal contact:

$$T_l(\vec{r}, t) = T_s(\vec{r}, t)$$

- Solid surface – crystal growth (surface is nonmaterial, no-slip):

$$[C_l \rho_l(\vec{r}, t) \vec{v}_l(\vec{r}, t) - C_s \rho_s(\vec{r}, t) \vec{v}_s(\vec{r}, t)] \cdot \vec{n}(\vec{r}, t) = \\ [\kappa_l \nabla T_l(\vec{r}, t) - \kappa_s \nabla T_s(\vec{r}, t) + \rho_s(\vec{r}, t) \vec{u}(\vec{r}, t) H] \cdot \vec{n}(\vec{r}, t) + Q$$

H – latent heat

Q – radiation flux

Diffusion - finite source – 1d

- Diffusion equation

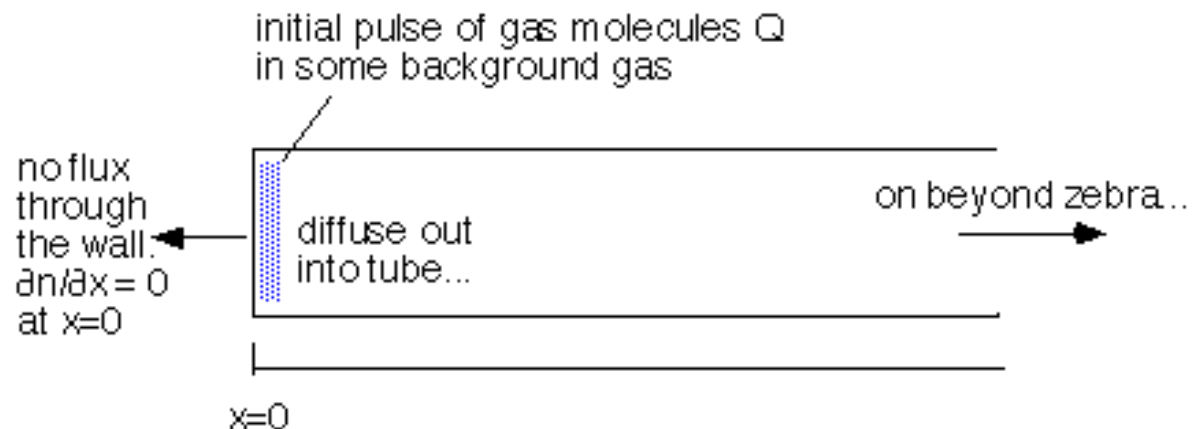
$$D\Delta c = \frac{\partial c}{\partial t} \quad \longrightarrow \quad D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$$

- Source Q at $x = 0$:

$$c(x, t) = \frac{2Q}{A\sqrt{4Dt}} \exp\left(-\frac{x^2}{4Dt}\right) = \frac{2q}{\sqrt{4Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

$$q = \frac{Q}{A}$$

Q – source
 A – area



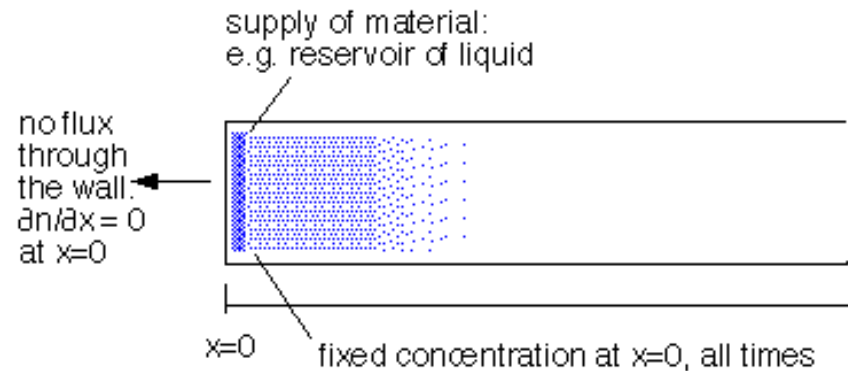
Diffusion - constant source – 1d

- Diffusion equation

$$D\Delta c = \frac{\partial c}{\partial t} \quad \longrightarrow \quad D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$$

- $c(0) = \text{const}$ for $x = 0$:

$$c(x, t) = c(0) \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right)$$



$$\operatorname{erfc}(z) = 1 - \operatorname{erf}(z) = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\infty} dy \exp(-y^2)$$

Diffusion – stationary flow

- Diffusion equation – time independent

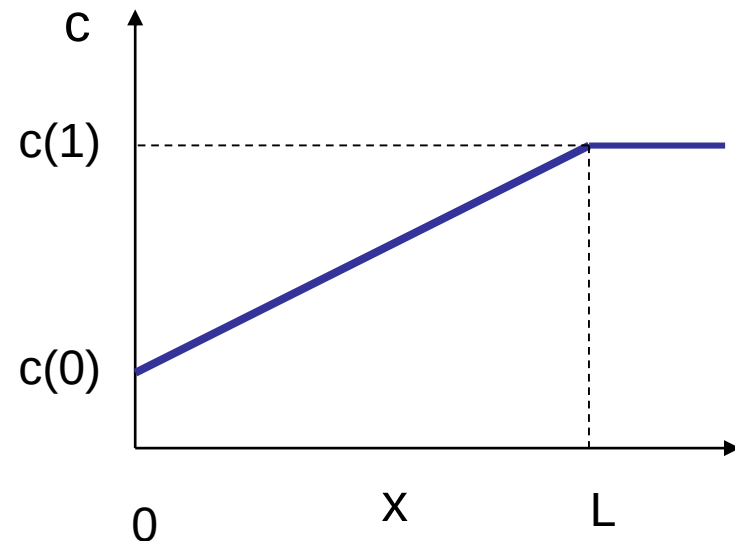
$$D\Delta c = \frac{\partial c}{\partial t} \quad \longrightarrow \quad D\Delta c = 0 \quad \longrightarrow \quad D \frac{\partial^2 c}{\partial x^2} = 0$$

- Concentration set $c(0)$ at $x = 0$ and $c(1)$ for $x = L$:

$$c(x, t) = \frac{[c(1) - c(0)]x}{L}$$

- Diffusion flux

$$\vec{j} = -D \nabla c(x, t) = -\frac{D[c(1) - c(0)]}{L}$$



Diffusion – diffusion length and Peclet Pe number

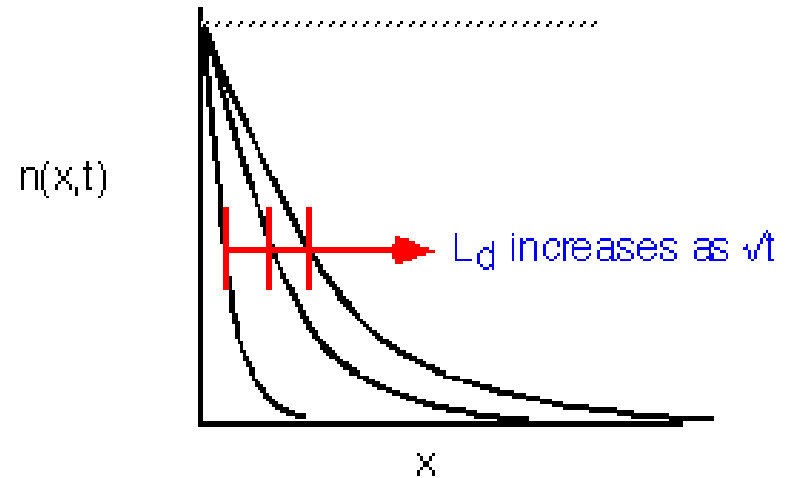
- The diffusion length L_D is:

$$L_D = \sqrt{4Dt} = \sqrt{\frac{4DL}{U}}$$

- Time of residence is:

$$t = \frac{L}{U}$$

U - velocity



- Peclet number Pe –square of the system size L to diffusion length ratio L_d :

$$Pe = 4 \left(\frac{L}{L_D} \right)^2 = \frac{4L^2}{4D \left(\frac{K}{U} \right)} = \frac{LD}{U}$$

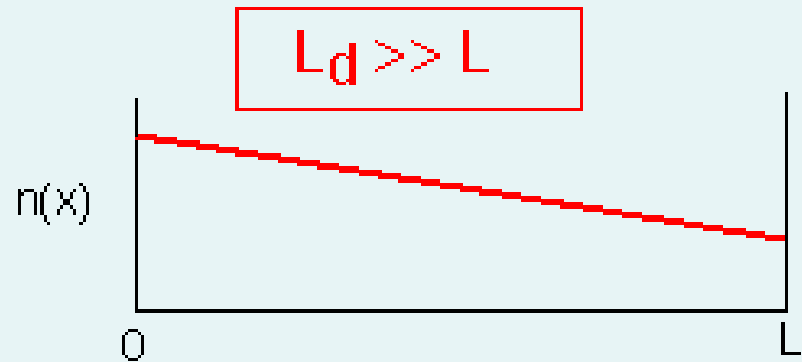
Peclet number – diffusion and convection

- Peclet number – diffusion or Convection transport control

$$Pe = \frac{LD}{U}$$

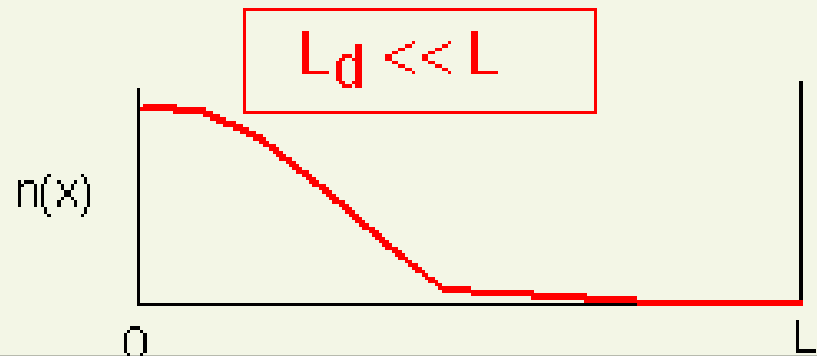
- $Pe \ll 1$ – Diffusion control:

$$L_D \gg L$$



- $Pe \ll 1$ – Convection control:

$$L_D \ll L$$



Convection – Reynolds number Re

- **Viscosity force (velocity shear) estimate**

$$f_{vis} = \text{div}(\hat{\sigma}) = \mu(\Delta v) \approx \frac{\mu U}{L^2}$$

- **Inertia force estimate**

$$f_{in} = \rho (v \cdot \nabla) v = \frac{\rho U^2}{L}$$

- **Reynolds number Re – inertia to viscosity force ratio**

$$Re \equiv \frac{f_{in}}{f_{vis}} = \frac{\rho U^2 / L}{\mu U / L^2} = \frac{\rho U L}{\mu}$$

Reynolds number Re – second interpretation

- **Momentum diffusion**

$$\rho_o \left(\frac{\partial v(\vec{r}, t)}{\partial t} \right) = \mu \Delta v(\vec{r}, t)$$

- **Momentum diffusion length L_{dp} :**

$$L_{dp} = \sqrt{\frac{4\mu t}{\rho}} \approx \sqrt{\frac{4\mu L}{\rho U}}$$

- **Reynolds number Re – square of the system size L to momentum diffusion length ratio L_{dp} :**

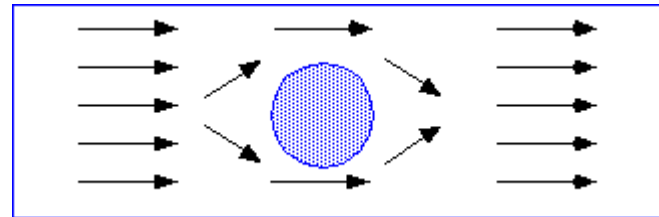
$$Re \equiv 4 \left(\frac{L}{L_{dp}} \right) = \frac{4L^2}{4\mu L / \rho U} = \frac{\rho U L}{\mu}$$

Laminar and turbulent flows

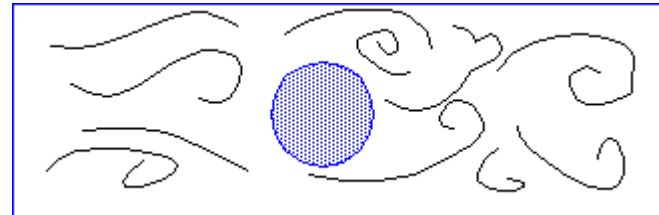
- Reynolds number Re – control of the flow type

$$Re = \frac{\rho UL}{\mu}$$

- Reynolds number $Re \ll 2000$
laminar flow

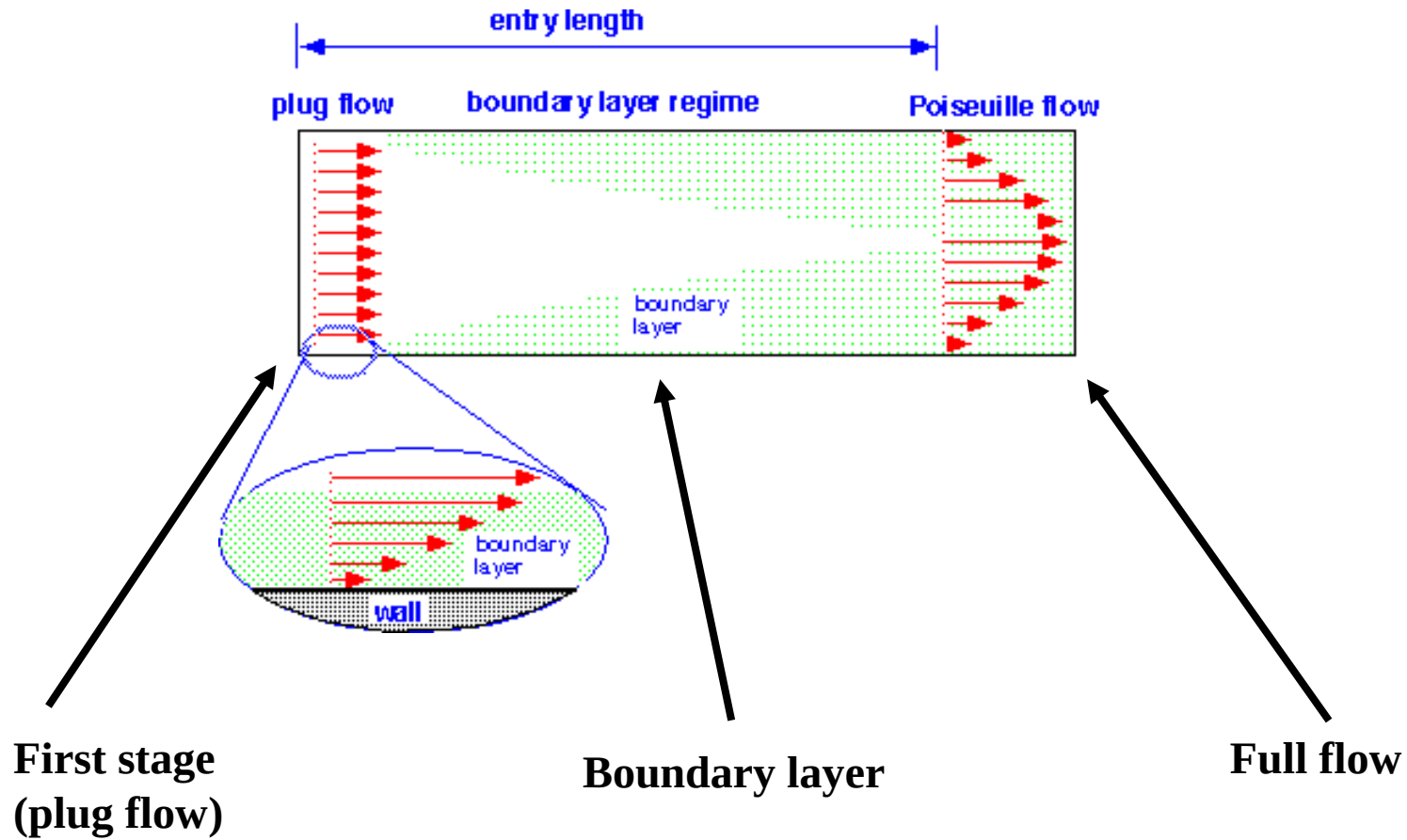


- Reynolds number $Re \sim 2000$ –
turbulent flow



In our description we will assume the laminar flow.

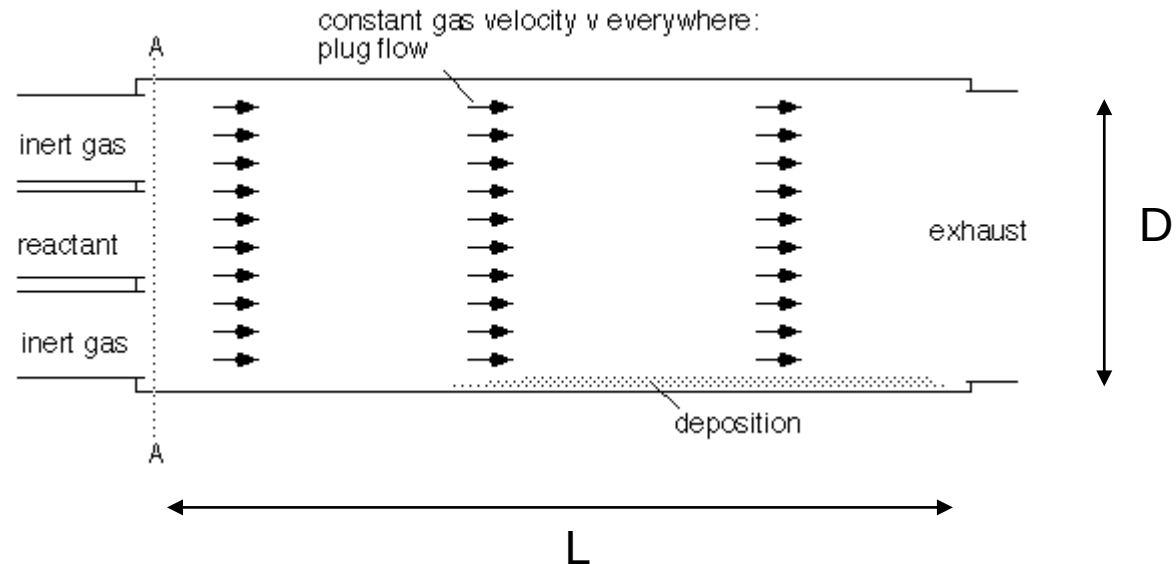
Flow into the pipe



First stage - plug flow

- Bulk flow into the reactor

$$u = \frac{F}{A}$$



F – Bulk flow - flux

A – Area

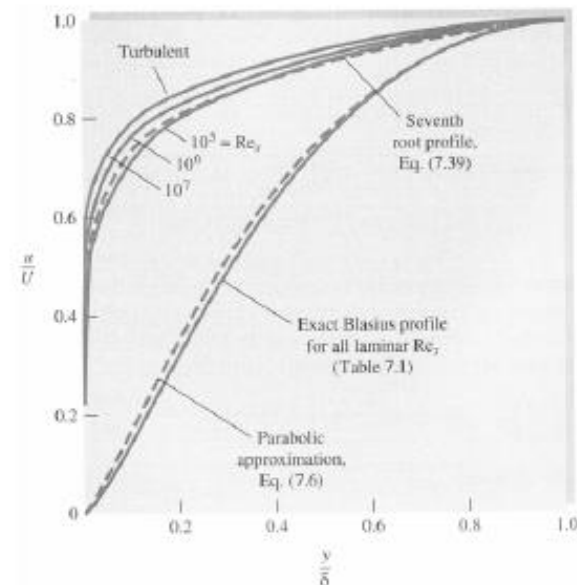
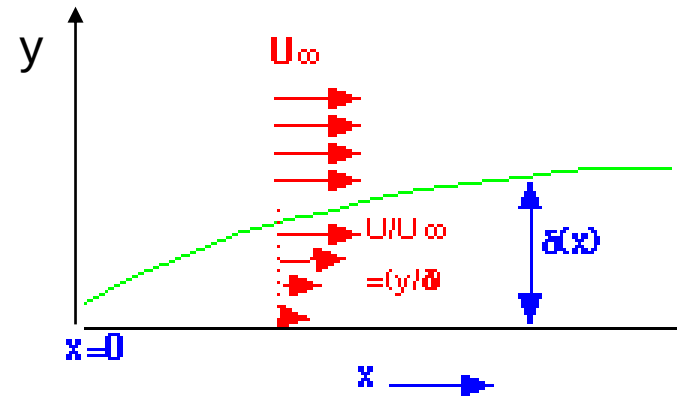
Boundary layer

$$\delta(x) = \sqrt{4D_{dp}t} = \sqrt{\frac{4\mu x \mu U_{\infty}}{\rho}}$$

$$D_{dp} = \nu = \frac{\mu}{\rho}$$

$$U_x(y) = U_{\infty} \left(\frac{2y}{\delta} - \frac{y^2}{\delta^2} \right)$$

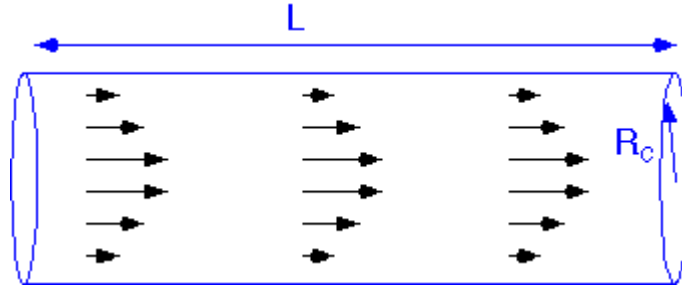
*Approximate flow pattern
(parabolic - von Karman)*



Poiseuille flow

$$U_x(r) = 2u_{av} \left(1 - \frac{r^2}{R_c^2} \right)$$

$$u_{av} = -\frac{R_c^2}{8\mu} \left(\frac{dp}{dx} \right)$$



- **Total flow into the reactor**

$$F = \rho \int_0^{R_c} 2\pi r u \, dr = \pi \rho u_{av} R_c^2 = \frac{\pi \rho R_c^4}{8\mu} \left(\frac{dp}{dx} \right)$$

Energy conservation law

- Energy conservation law – temperature equation

$$C(\rho_o, T)\rho_o \left[\frac{\partial T(\vec{r}, t)}{\partial t} + (\vec{v}(\vec{r}, t) \cdot \nabla) T(\vec{r}, t) \right] = \text{div}(\kappa \nabla T(\vec{r}, t)) + r_\varepsilon$$

analogous to two component transport equation

$$\left[\frac{\partial \rho_i(\vec{r}, t)}{\partial t} + (\vec{v}(\vec{r}, t) \cdot \nabla) \rho_i(\vec{r}, t) \right] = \text{div}(D \nabla \rho_i(\vec{r}, t)) + r_i$$

for small concentration:

$$\rho_i = \rho_o c_i(\vec{r}, t)$$

correspondence

$$c_i(\vec{r}, t) \leftrightarrow T(\vec{r}, t) \qquad D_{th} = \frac{\kappa}{\rho C} \leftrightarrow D$$

Heat transfer – linear form

- Equations

$$\rho_o \left[\frac{\partial \vec{v}(\vec{r}, t)}{\partial t} + (\vec{v}(\vec{r}, t) \cdot \nabla) \vec{v}(\vec{r}, t) \right] = \mu \Delta \vec{v}(\vec{r}, t) + \rho_o [\beta_T (T - T_o) + \beta_c c] \vec{f}(\vec{r}, t)$$

$$\rho_o C_p(T) \left[\frac{\partial [T(\vec{r}, t)]}{\partial t} + (\vec{v}(\vec{r}, t) \cdot \nabla) T(\vec{r}, t) \right] = \text{div}(\kappa \nabla T(\vec{r}, t)) + r_\varepsilon$$

- Linear form in: $\vec{v}(\vec{r}, t)$ & $\delta T(\vec{r}, t)$

$$\rho_o \left[\frac{\partial \vec{v}(\vec{r}, t)}{\partial t} \right] = \mu \Delta \vec{v}(\vec{r}, t) \qquad \rho_o C_p(T) \left[\frac{\partial [T(\vec{r}, t)]}{\partial t} \right] = \text{div}(\kappa \nabla T(\vec{r}, t))$$

Heat transfer – Prandtl number

- **Fourier component**

$$\vec{v}(\vec{r}, t) = v_o \exp \left[i \left(\vec{q} \cdot \vec{r} - \frac{t}{\tau_v} \right) \right] \quad \delta T(\vec{r}, t) = \delta T_o \exp \left[i \left(\vec{q} \cdot \vec{r} - \frac{t}{\tau_T} \right) \right]$$

- **Relaxation times:**

$$\tau_v = \frac{\rho_o}{\mu q} \quad \tau_T = \frac{C \rho_o}{\kappa q^2}$$

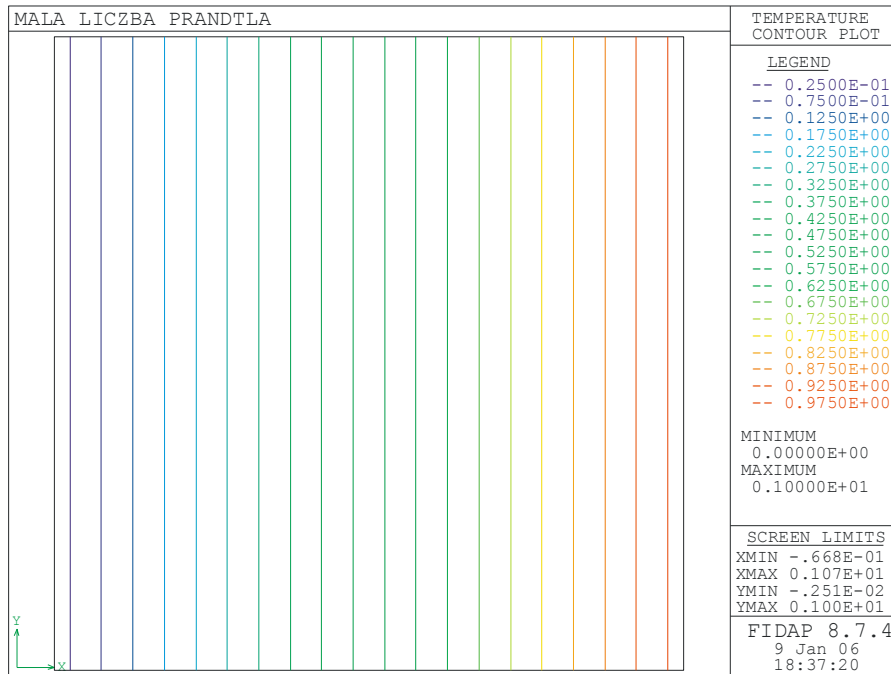
- **Prandtl number Pr – relaxation time ratio:**

$$Pr \equiv \frac{\tau_T}{\tau_v} = \frac{\mu C}{\kappa}$$

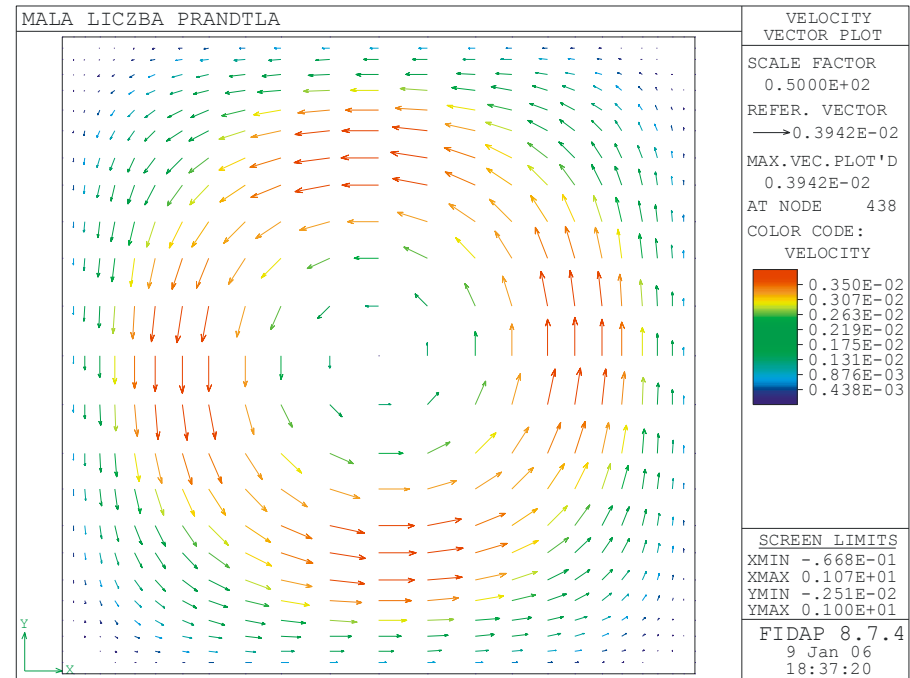
- **Pr << 1, relaxation of the temperature field is independent of the velocity**
- **Pr ~ 1, velocity and temperature fields are coupled**

Convection – $Pr = 0.01$

Temperature



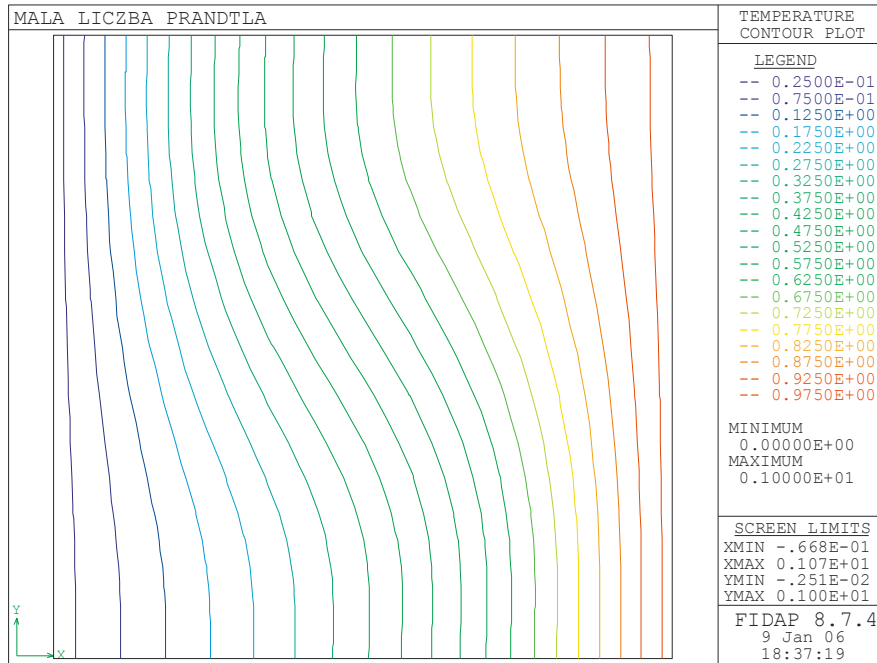
Velocity



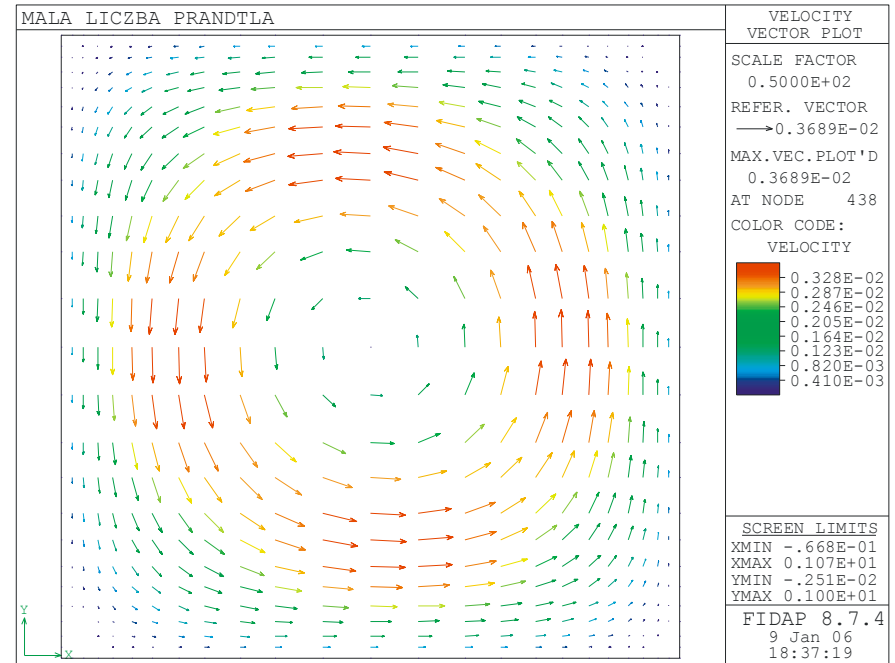
CFD calculations – Fidap: Paweł Kempisty IHPP PAS

Convection – $Pr = 1000$

Temperature



Velocity



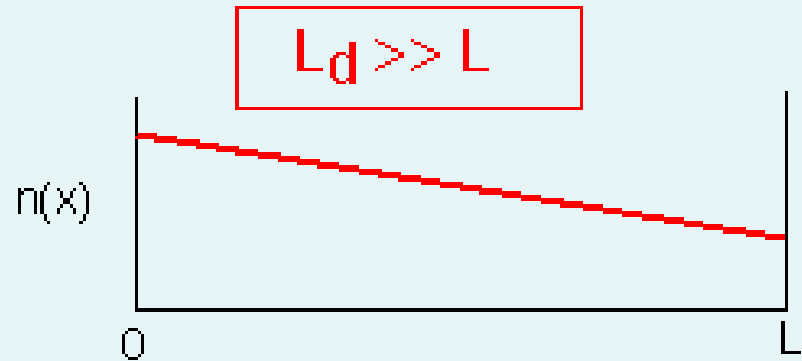
CFD calculations – Fidap: Paweł Kempisty IHPP PAS

Thermal conductivity – thermal Peclet Pe_T number

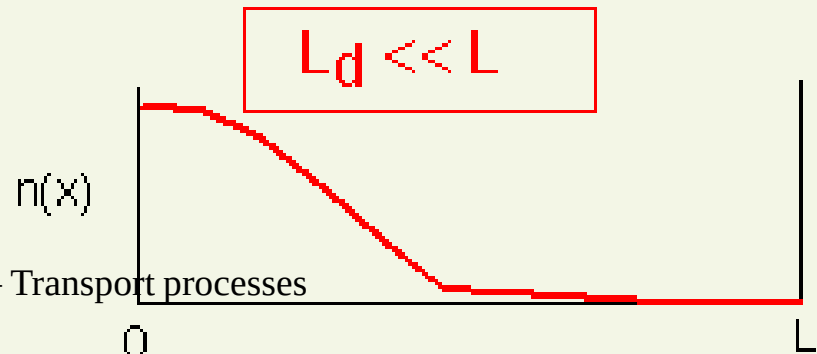
- Thermal Peclet Pe_T number – square of the system size L to thermal diffusion length L_D ratio:

$$Pe \equiv 4 \left(\frac{L}{L_D} \right)^2 = \frac{4L^2}{4D_{th} \left(\frac{L}{\bar{U}} \right)} = \frac{LU}{D_{th}} = \frac{LUC\rho}{\kappa} = \frac{LU\rho\mu C}{\mu\kappa} = Re Pr$$

- $Pe_T \ll 1$ – Thermal conductivity control:



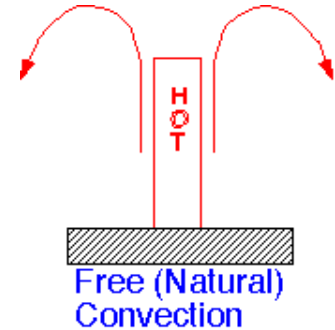
- $Pe_T \ll 1$ – Convection control:



Natural convection – incompressible fluid – temperature difference caused thermal expansion

- Thermal expansion coefficient

$$\beta_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p$$



- Velocity assessment

$$\frac{\rho_o U^2}{2} = (\rho - \rho_o) g L$$

$$U = \sqrt{\frac{(\rho - \rho_o) g L}{\rho_o}} = \sqrt{\beta_T \Delta T g L}$$

- Thermal diffusivity length

$$L_{th} = \sqrt{4D_{th}t} = \sqrt{\frac{4\kappa L}{\rho C U}}$$

- Momentum diffusivity length

$$L_{vis} = \sqrt{4D_{vis}t} = \sqrt{\frac{4\mu L}{\rho U}}$$

Natural Convection - Rayleigh number Ra

- Rayleigh number Ra – square of the system size L to diffusive lengths ratio

$$Ra = \frac{1}{4} \left(\frac{L}{L_{th}} \right)^2 \left(\frac{L}{L_{vis}} \right)^2 = \frac{L^2 U^2}{D_{th} D_{vis}} = \frac{gL^3 \beta_T \rho_o^2}{\kappa \mu}$$

- Rayleigh number Ra – determines the ratio of convective to diffusive transport velocity

High Rayleigh number Ra - Convection domination - Diffusion control

Low Rayleigh number Ra - Diffusion domination – Convection control