Crystal Growth: Physics, Technology and Modeling

Stanisław Krukowski & Michał Leszczyński
Institute of High Pressure Physics PAS
01-142 Warsaw, Sokołowska 29/37
e-mail: stach@unipress.waw.pl, mike@unipress.waw.pl

Zbigniew Żytkiewicz
Institute of Physics PAS
02-668 Warsaw, Al. Lotników 32/46
E-mail: zytkie@ifpan.edu.pl

Lecture 8. Transport processes in liquid and vapor phases

http://w3.unipress.waw.pl/~stach/cg-2022-23/

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**

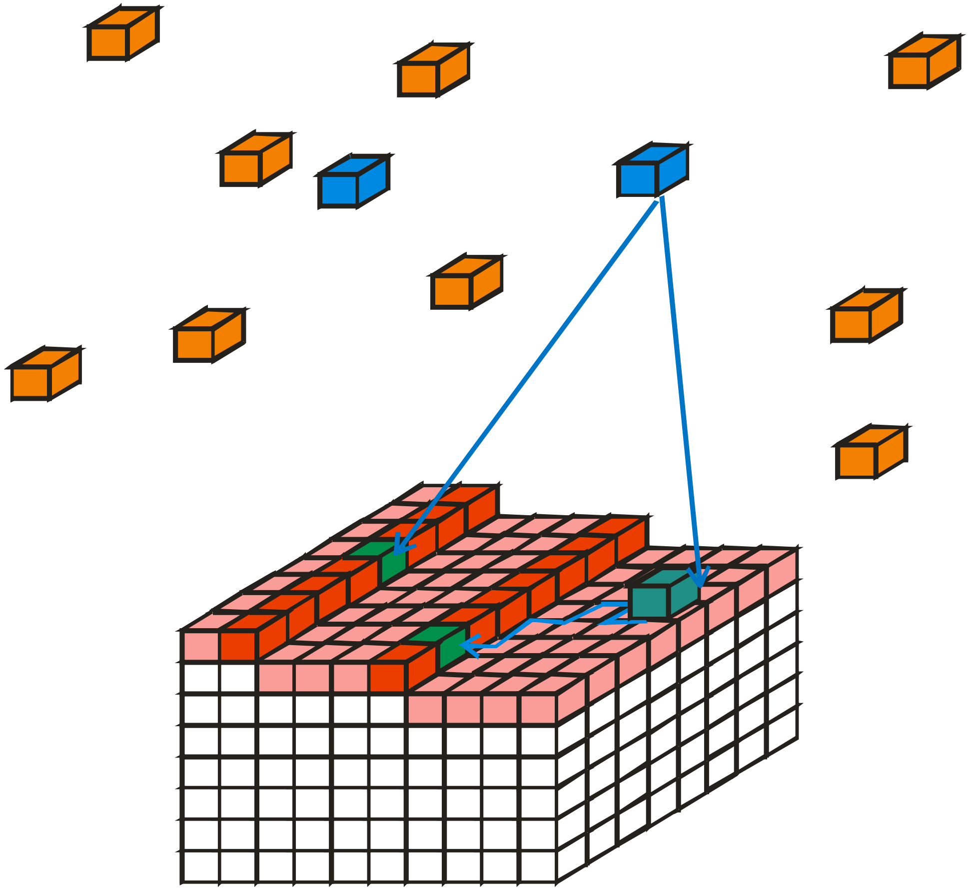
  $$L_V \gg \lambda \sim 1\mu$$

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

- **Surfaces – characteristic lengths L_s**

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

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



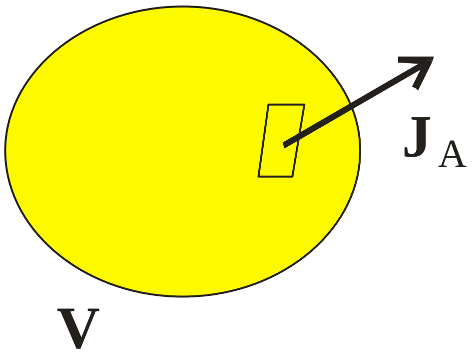
Surface – bulk coupling

- **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:**



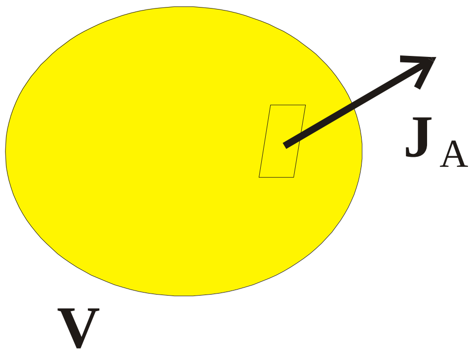
$$\frac{\partial A}{\partial t} = -\oint \left(\overrightarrow{J_A} \cdot \vec{n}\right) d^2S + R_A$$

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

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

Green theorem

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



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

$\vec{n}$- 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:**

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

- **Source efficiency :**

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

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

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

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.

Diffusive 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))**

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

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

Mass conservation law - single component (total mass) system

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

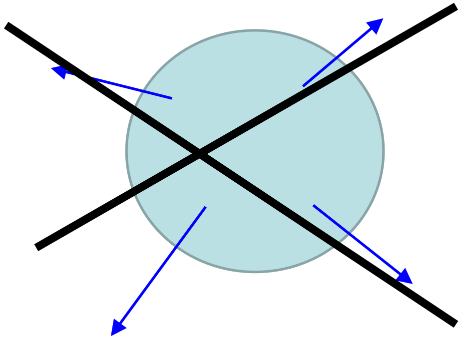
$$\rho(\vec{r},t) = \sum_i \rho_i(\vec{r},t)$$

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

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

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

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



Could not happen in stationary result

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

- **Density is time independent**

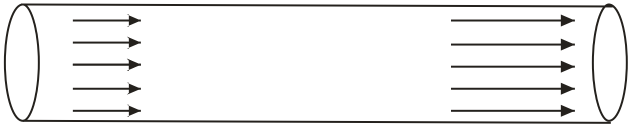
$$\rho(\vec{r},t) = \rho(\vec{r})$$

- **Mass conservation law is reduced to**

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

- **Example: mass flow in MOVPE reactor**

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



$$S_1 = S_2$$

$$p = \frac{\rho R T}{m}$$

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

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

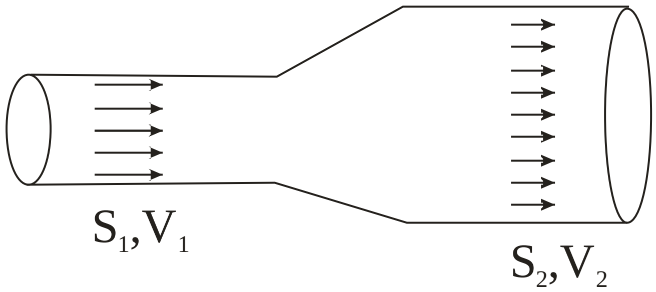
- **Density is constant**

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

- **Mass conservation law is reduced to**

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

- **Example: mass flow in MOVPE reactor**



$$v_1 S_1 = v_2 S_2$$

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

$$vS = V \qquad V_1 = V_2$$

Multi-component system

- **Concentrations of the components**

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

- **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**

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

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

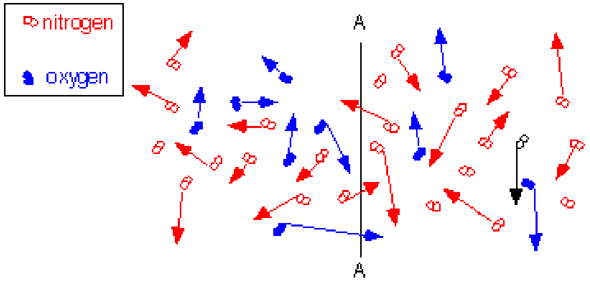
$$\sum_i r(\vec{r},t) = 0$$

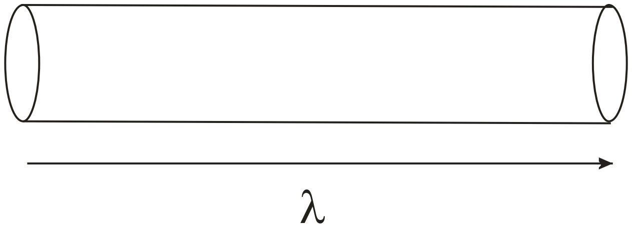
- **Density is constant (no convection) standard diffusion law**

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

Gas phase diffusion

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





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

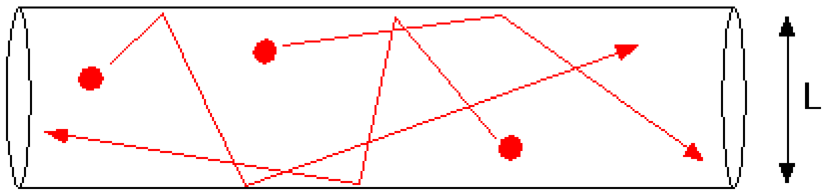
- **Diffusion coefficient – D:**

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

Gas phase – ballistic and diffusive transport

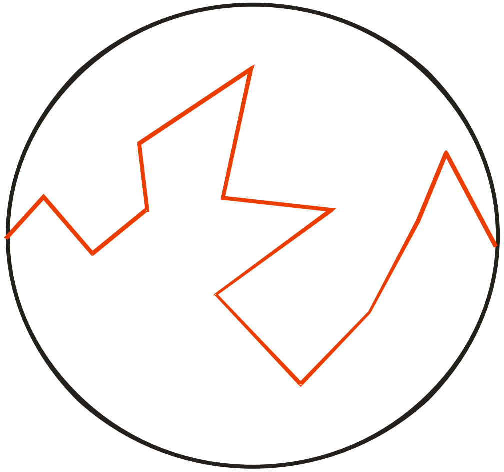
- **Knudsen number - Kn**

$$Kn = \frac{L}{\lambda}$$



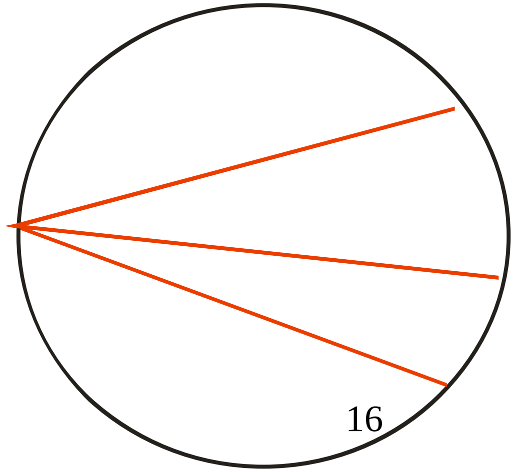
- **Ballistic transport - MBE**

$$Kn \ll 1$$



- **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**

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

- **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**

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

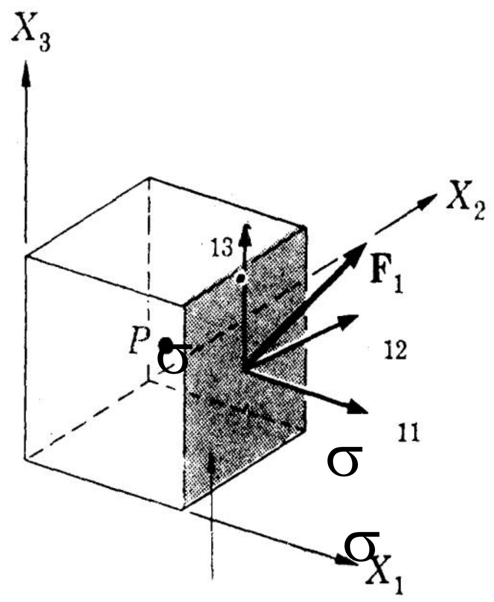
- **Momentum flux is changed by the surface force:**

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

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

$\boldsymbol{n_\beta}$ **- component of unit vector, normal (perpendicular) to the surface**

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

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:** $\hat{\sigma}_{\alpha\beta} = (1 - \delta_{\alpha\beta})\sigma_{\alpha\beta}$

- **Unixial stress:** $\hat{\sigma}_{\alpha\beta} = \sigma_{11}$

- **Bixial 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:**

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

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

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

- **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)**

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

- **Units (CGS)**

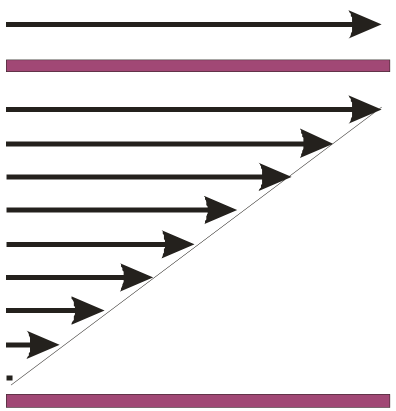
$$[\mu] = \frac{g}{cm\ s} = Poise$$

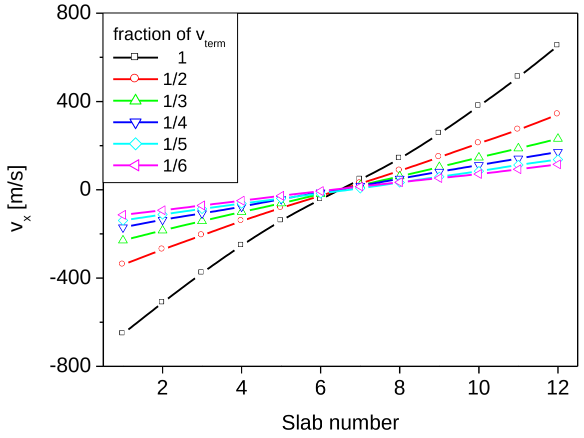
Shear viscosity

- **Incompressible fluid flow:** $$div(\vec{v}(\vec{r},t)) = \sum_{\alpha=1}^{3}\left(\frac{\partial r_\alpha}{\partial r_\alpha}\right) = 0$$
- **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):**

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

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

$$\rho(T) = \rho(T_o)\beta_T(T - T_o) \qquad \rho(c) = \rho(0)\beta_c c$$

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**

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

Energy conservation law

- **Energy conservation law reads:**

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

ε – energy density (for unit of mass)

- **Energy as the temperature change:**

$$d\varepsilon = C_p\, dT$$

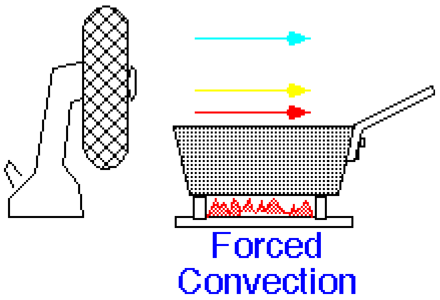
- **Temperature change equation:**

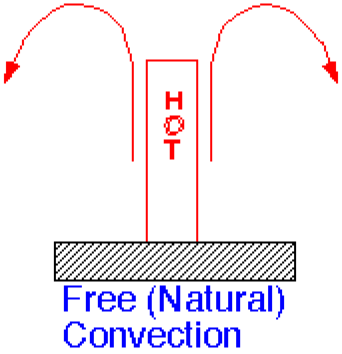
$$\frac{\partial\left[C_p(T)T(\vec{r},t)\rho(\vec{r},t)\right]}{\partial t} + \rho(\vec{r},t)C_p(T)(\vec{v}(\vec{r},t)\cdot\nabla)T(\vec{r},t) = -div(\vec{j}_\varepsilon) + r_\varepsilon$$

Energy fluxes

- **Convection:**

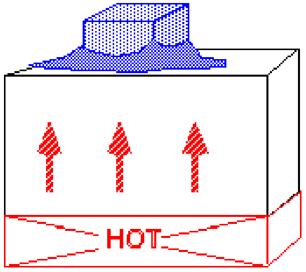
$$\vec{j}_{\varepsilon} = \rho(\vec{r},t)\varepsilon(\vec{r},t)\vec{v}(\vec{r},t)$$





- **Thermal conductivity (Fourier law) :**

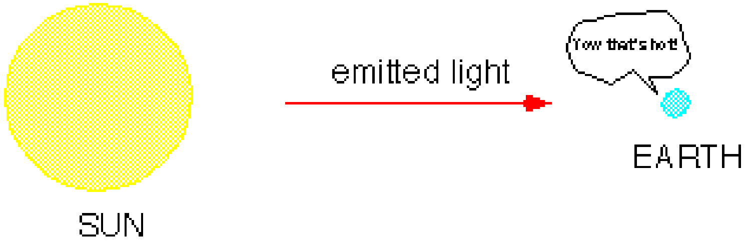
$$\vec{j}_{\varepsilon} = -\kappa\nabla T(\vec{r},t)$$



κ – thermal conductivity coefficient

- **Radiation (Stefan-Boltzmann law)**

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



Stefan-Boltzmann constant

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

e – emissivity $0 < e \leq 1$

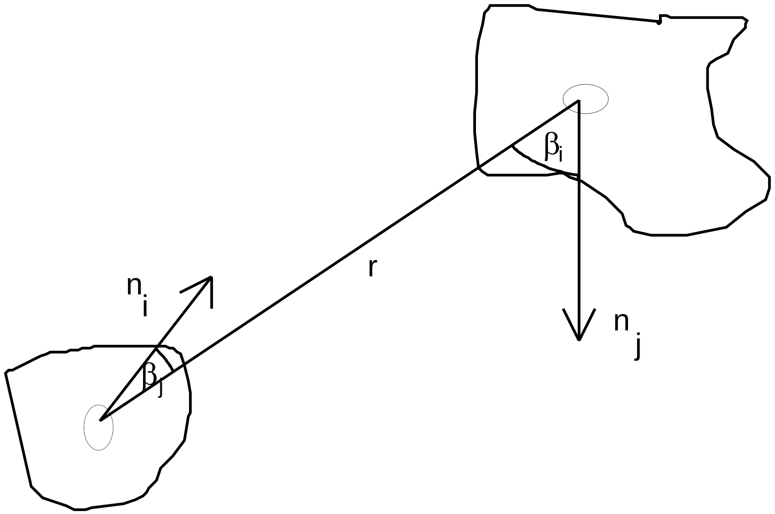
Radiation

- **Radiation heat exchange**

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

- **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:**

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

Summary – conservation laws – compressible fluid

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

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

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

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

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

Summary – conservation laws – incompressible fluid

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

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

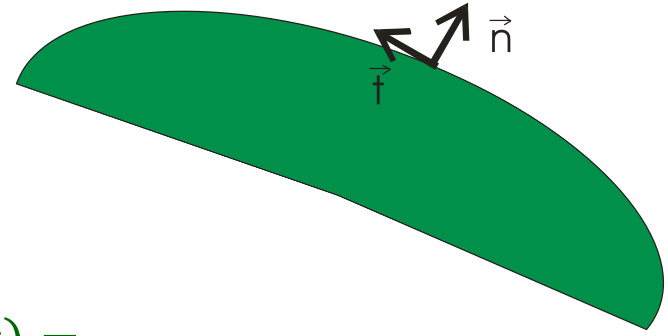
$$\rho_o C_p(T)\left[\frac{\partial[T(\vec{r},t)]}{\partial t} + (\vec{v}(\vec{r},t)\cdot\nabla)T(\vec{r},t)\right] = div\left(\kappa\nabla T(\vec{r},t)\right) + r_\varepsilon$$

- **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**

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

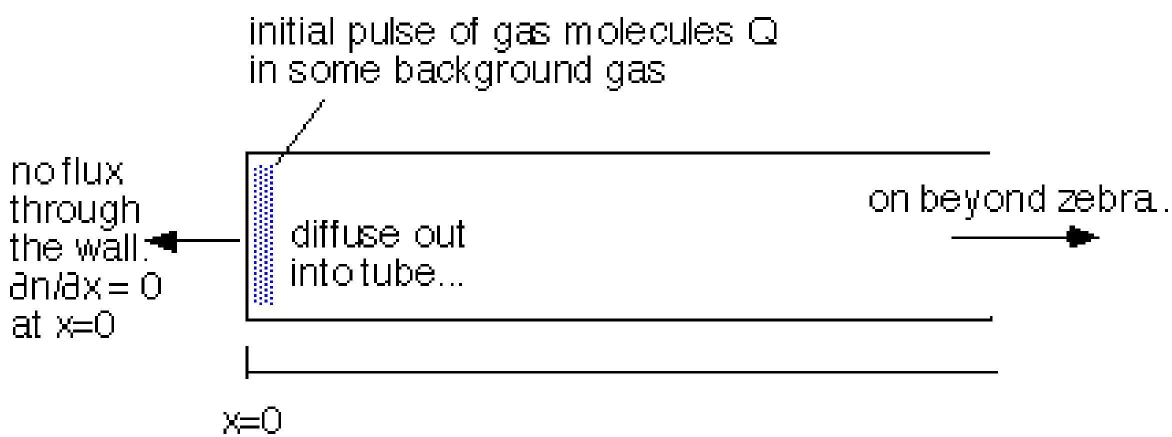
- **Source Q at x = 0:**

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

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

Q – source

A - area



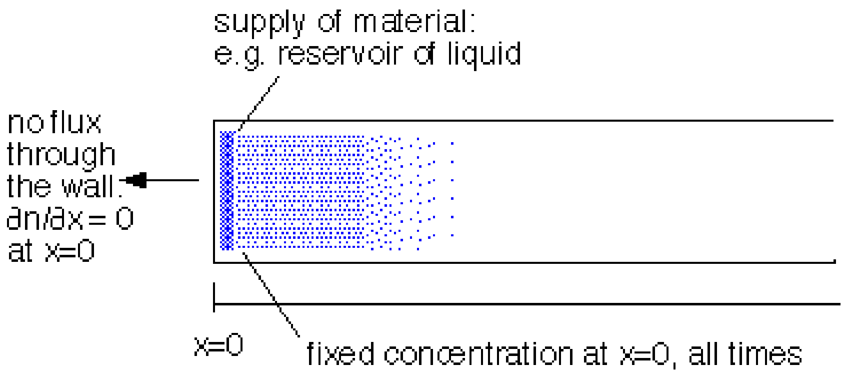
Diffusion - constant source – 1d

- **Diffusion equation**

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

- **c(0) = const for x = 0:**

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



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

Diffusion – stationary flow

- **Diffusion equation – time independent**

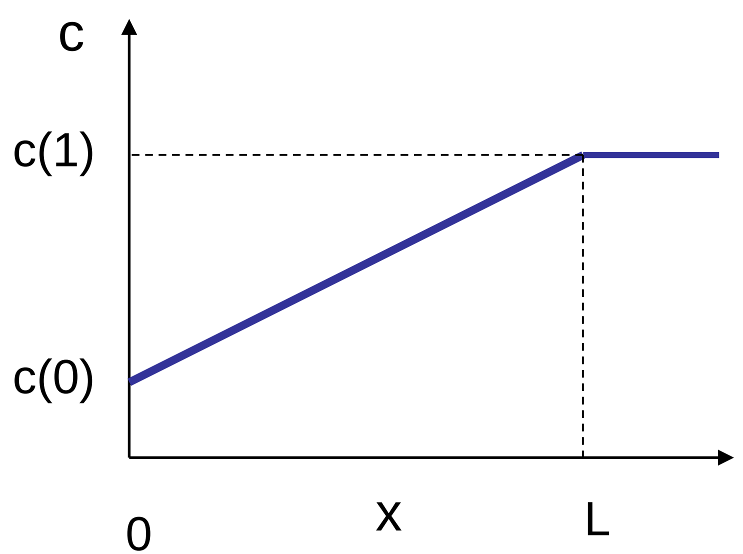
$$D\Delta c = \frac{\partial c}{\partial t} \quad \Rightarrow \quad D\Delta c = 0 \quad \Rightarrow \quad D\frac{\partial^2 c}{\partial x^2} = 0$$

- **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**

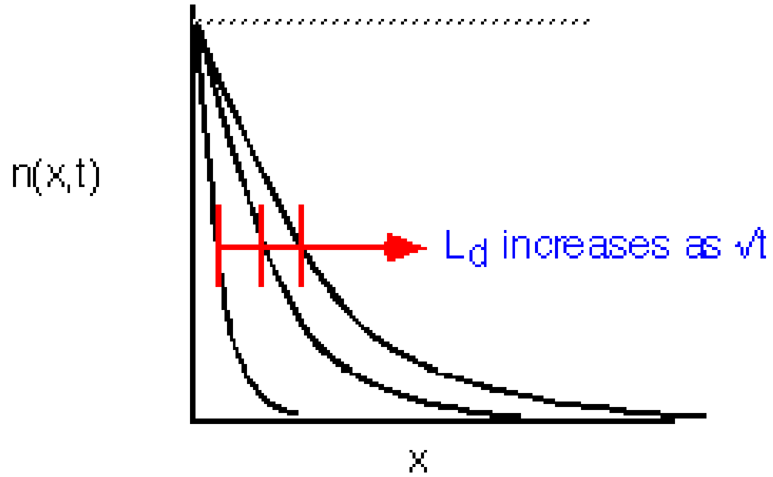
$$\vec{j} = -D\,\nabla c(x,t) = -\frac{D[c(1) - c(0)]}{L}$$



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:**

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

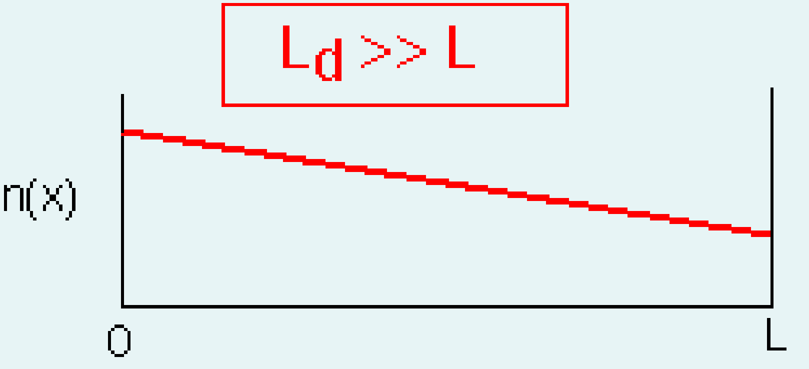
Peclet number – diffusion and convection

- **Peclet number – diffusion or Convection transport control**

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

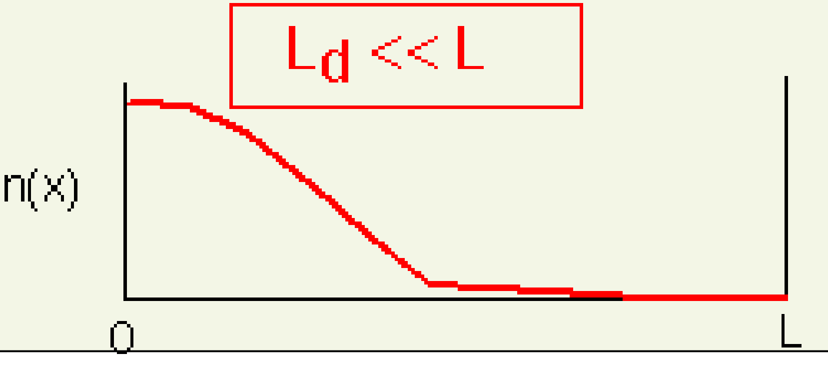
- **Pe << 1 – Diffusion control:**

$L_D >> L$



- **Pe << 1 – Convection control:**

$L_D << L$



Convection – Reynolds number Re

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

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

- **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} :**

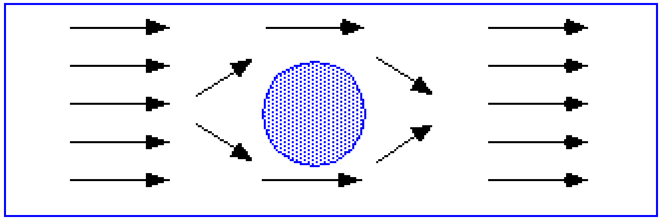
$$Re \equiv 4\left(\frac{L}{L_{dp}}\right) = \frac{4L^2}{4\mu L/\rho U} = \frac{\rho U L}{\mu}$$

Laminar and turbulent flows

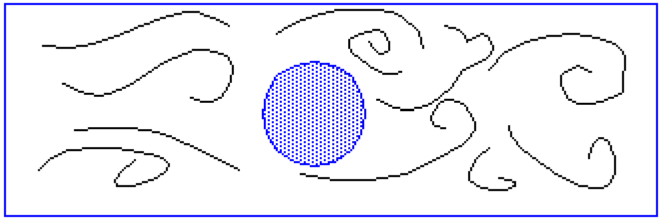
- **Reynolds number Re – control of the flow type**

$$Re = \frac{\rho U L}{\mu}$$

- **Reynolds number Re << 2000 laminar flow**

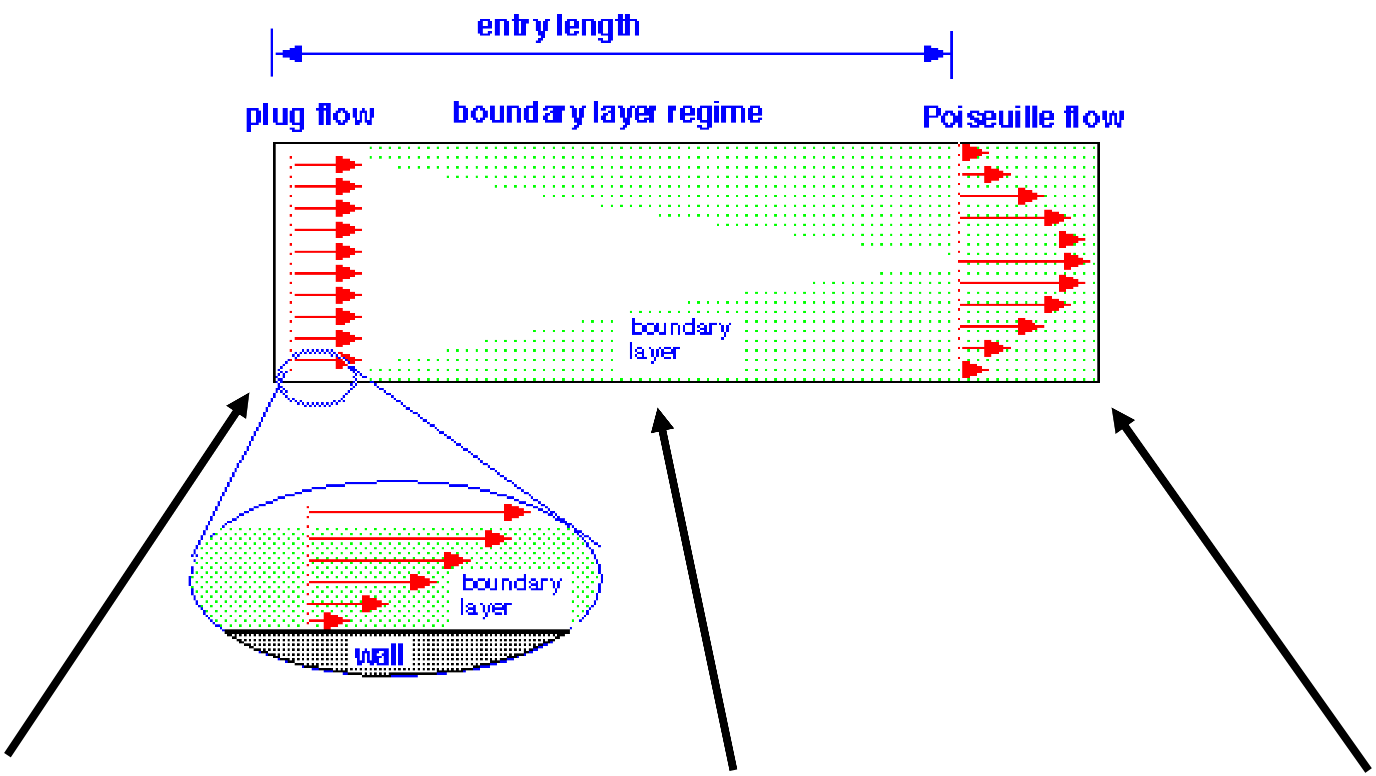


- **Reynolds number Re ~ 2000 – turbulent flow**



In our description we will assume the laminar flow.

Flow into the pipe



First stage (plug flow)

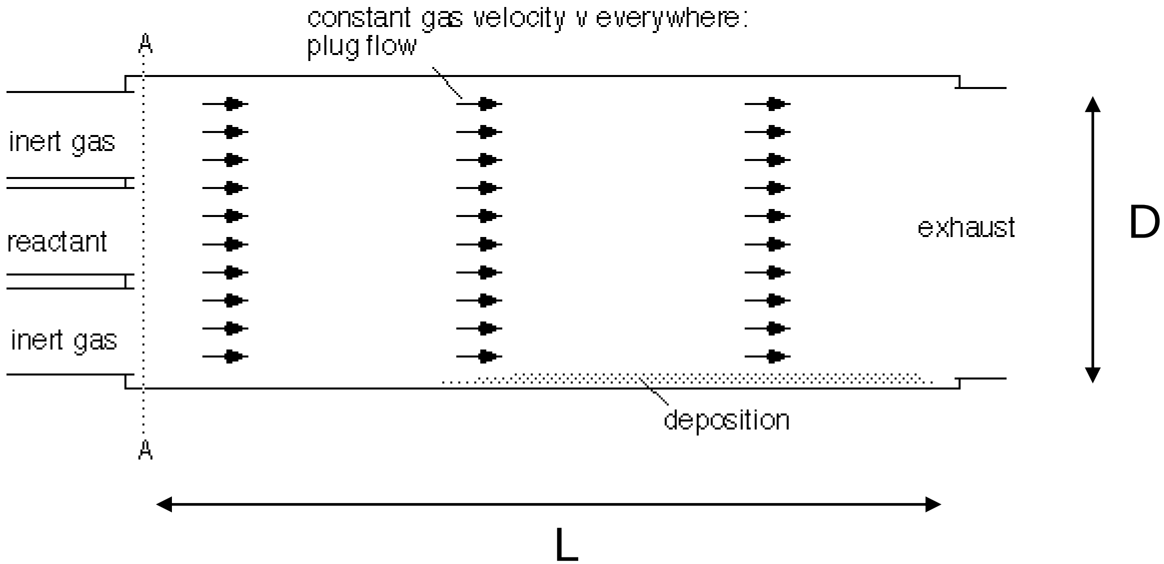
Boundary layer

Full flow

First stage - plug flow

- **Bulk flow into the reactor**

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



F – Bulk flow - flux
A – Area

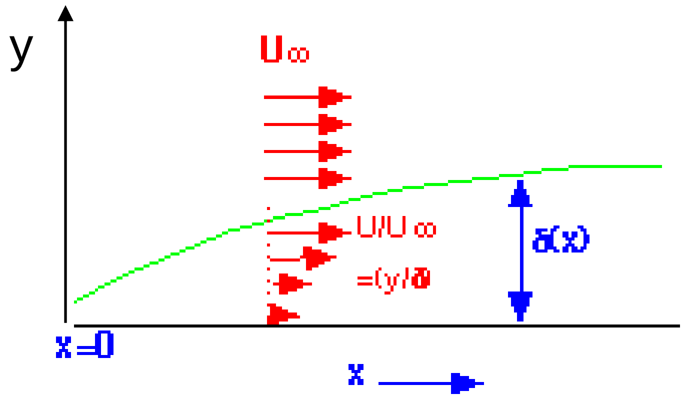
Boundary layer

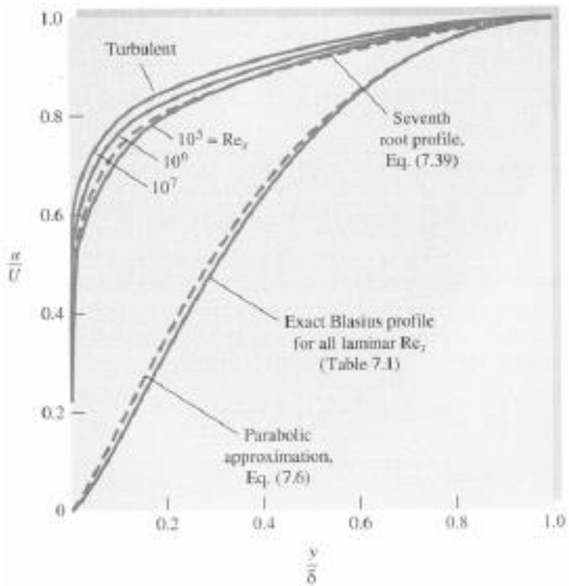
$$\delta(x) = \sqrt{4D_{dp}t} = \sqrt{\frac{4\mu x\mu U_\infty}{\rho}}$$

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

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

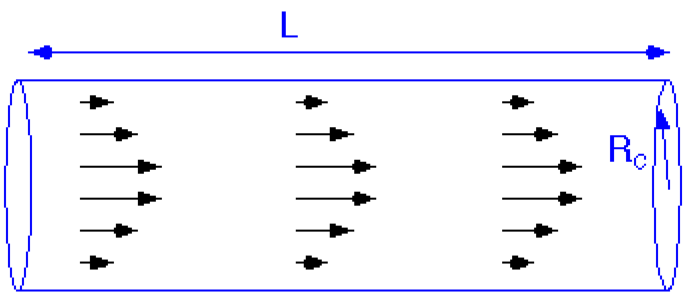
Approximate flow pattern (parabolic - von Karman)





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**

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

analogous to two component transport equation

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

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**

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

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

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

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

Heat transfer – Prandtl number

- **Fourier component**

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

- **Relaxation times:**

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

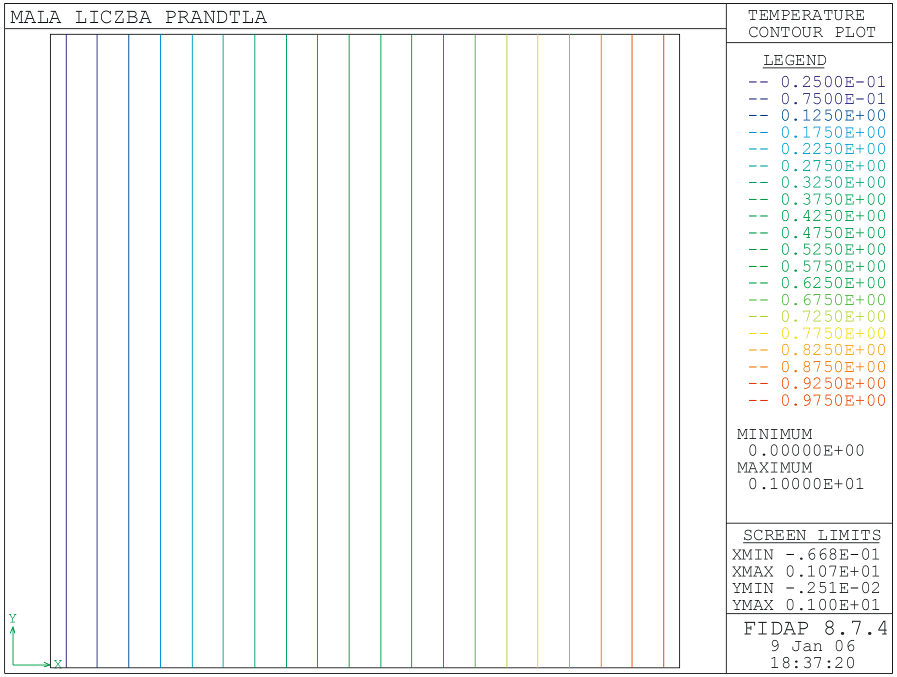
- **Prandtl number Pr – relaxation time ratio:**

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

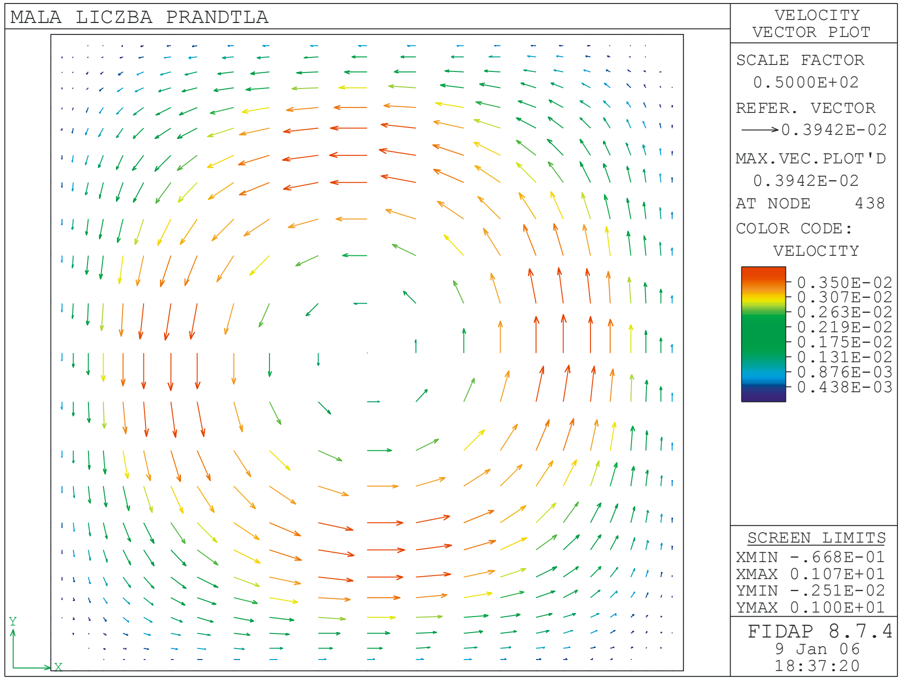
- **Pr << 1, relaxation of the temperature field is independent of the velocity**
- **Pr ~ 1, velocity and temperature fields are coupled**

Convection – Pr = 0.01

Temperature



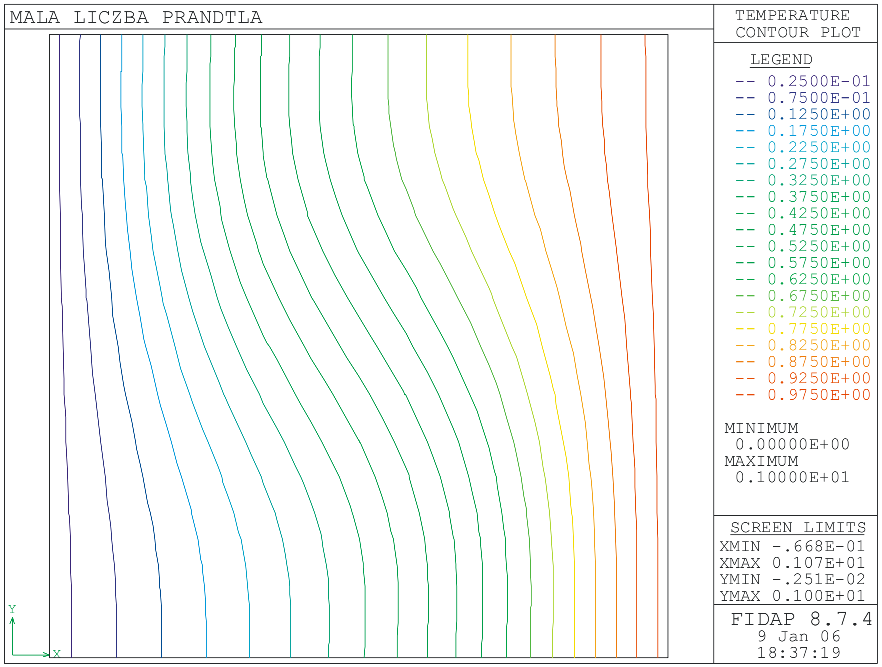
Velocity



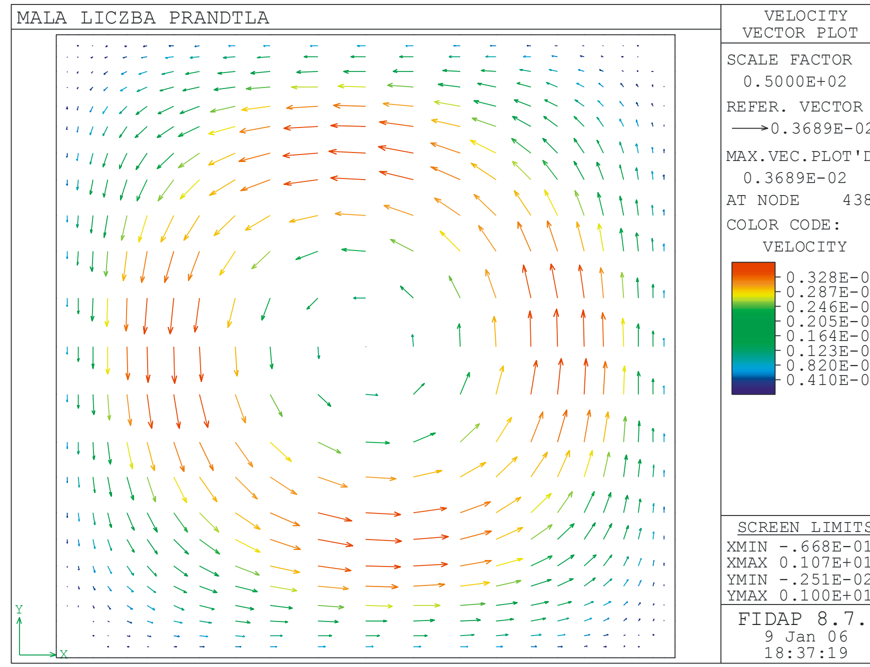
CFD calculations – Fidap: Paweł Kempisty IHPP PAS

Convection – Pr = 1000

Temperature



Velocity



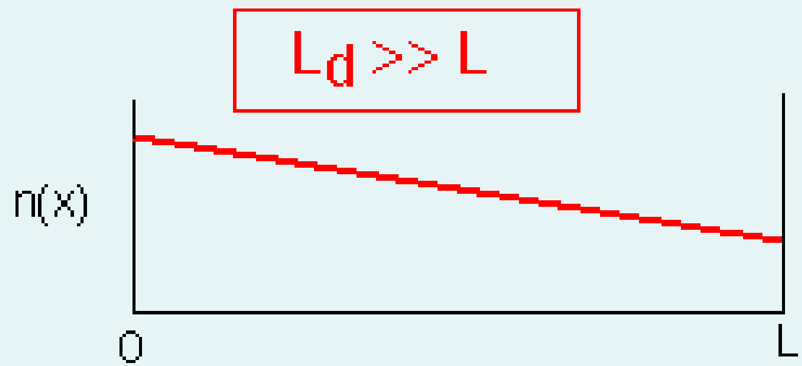
CFD calculations – Fidap: Paweł Kempisty IHPP PAS

Thermal conductivity – thermal Peclet Pe_T number

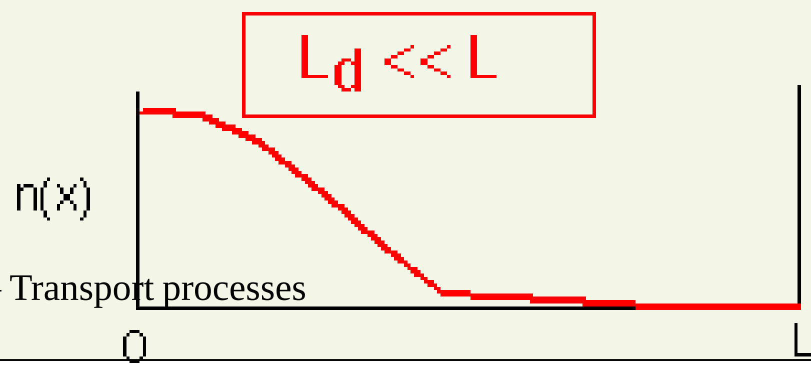
- **Thermal Peclet Pe_T number – square of the system size L to thermal diffusion length L_D ratio:**

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

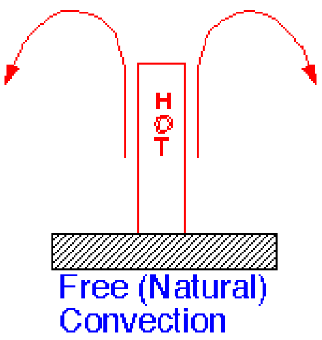
- **Pe_T << 1 – Thermal conductivity control:**



- **Pe_T << 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**

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

- **Momentum diffusivity length**

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

Natural Convection - Rayleigh number Ra

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

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

- **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