COMSOL CONFERENCE
2015 GRENOBLE

STUDY OF ELECTROCHEMICALLY GENERATED TWO-PHASE FLOWS

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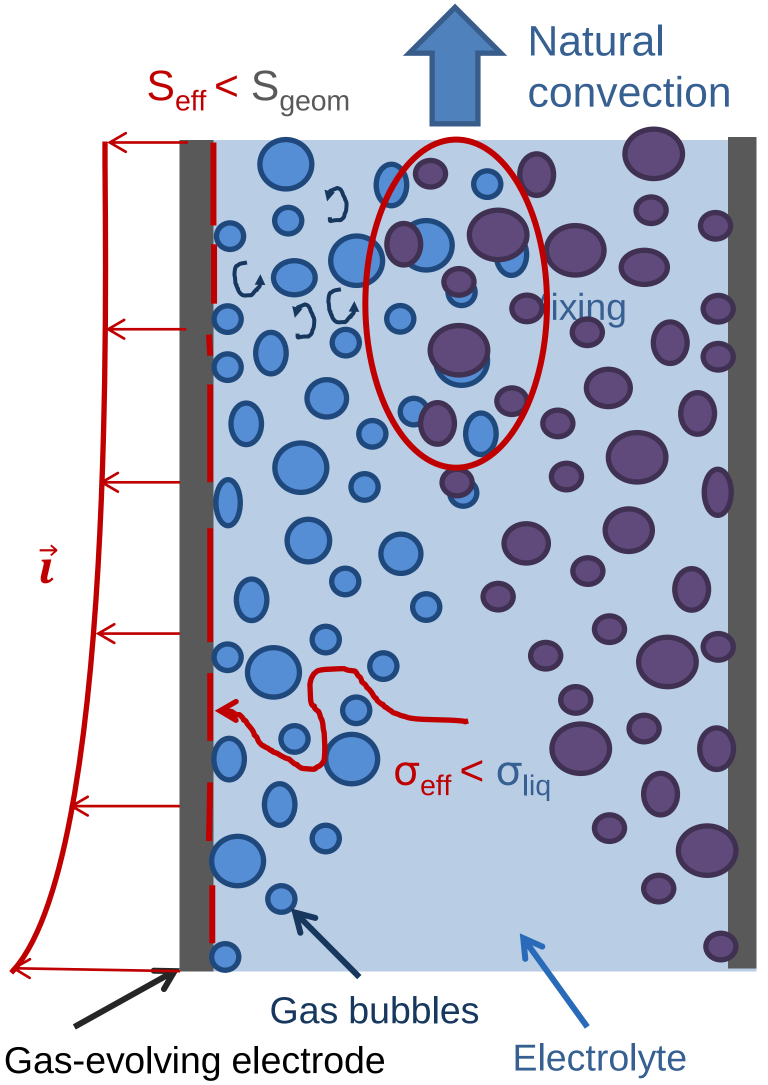
1 - CONTEXT

1.1 – CONTEXT : GAS GENERATION DURING ELECTROCHEMICAL PROCESSES

- **Gas bubbles** are frequently generated in electrochemical processes
  - **As principal product** (e.g. in electrolysis)
    - High **gas recuperation rate** must be reached
  - **As a by-product** (e.g. in electrodeposition)
    - **Negative impact** on the principal reaction should be avoided
- Bubbles behavior in electrolyte **strongly affects process performances**

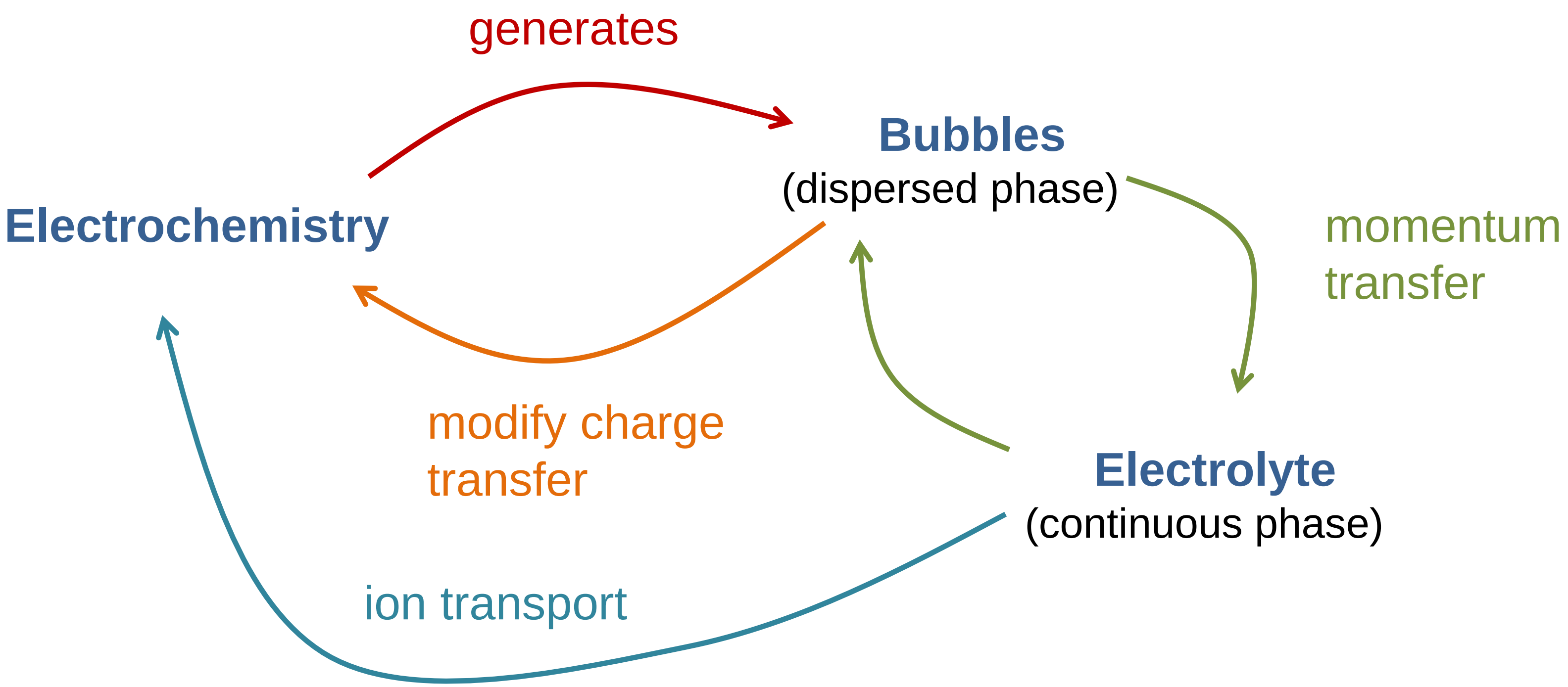
1.1 – CONTEXT : GAS GENERATION DURING ELECTROCHEMICAL PROCESSES



- **Bubble-induced**
  - **Natural convection**
    - **Mixing**
  - **Surface coverage**
    - **Mass transfer limitation**
  - **Bulk conductivity drop**
    - **Current limitation**

- Risk of **plume mixing**
  - **Decreased yield**
  - **Energy production (H_2 + O_2)**

1.2 - PHYSICAL INSIGHT TO ENHANCE CELL'S DESIGN



Strong coupling between physical phenomena

- Difficulty to **control the process**
- Numerous parameters for **empirical analysis**
- Necessity of a **realistic model**

2 – MODEL DESCRIPTION, RESULTS AND DISCUSSION

2.1 - MIXTURE MODEL[1]

- **CFD** equations : Laminar, Newtonian fluid, $\rho_D \ll \rho_C$, **void fraction α**

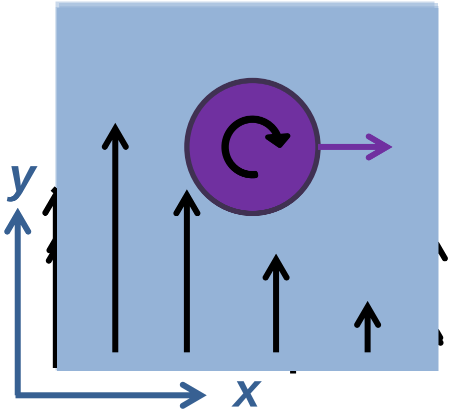
$\vec{\nabla}\cdot\vec{U} = 0$ (**Mixture** volume conservation)

$\vec{\nabla}\cdot\overrightarrow{U_D} = 0$ (**Dispersed phase** volume conservation)

$\rho_C(1-\alpha)\vec{q}\cdot\nabla\vec{q} = -\vec{\nabla}P + \rho_C g\alpha\vec{z} + \left(\vec{\nabla}\cdot[\mu(\alpha)(\nabla\vec{q}+\nabla\vec{q}^T)] - \vec{\nabla}[\frac{2}{3}\mu(\alpha)\vec{\nabla}\cdot\vec{q}]\right)$ (**Momentum** conservation)

- **Closure model for relative** flux : small rigid spheres approximation

$$\overrightarrow{U_R} = \overrightarrow{U_D} - \alpha\vec{U} = \overrightarrow{\boldsymbol{U_{Stokes}}} + \overrightarrow{\boldsymbol{U_{Hdiff}}} + \overrightarrow{\boldsymbol{U_{Sdiff}}} + \overrightarrow{\boldsymbol{U_{Smig}}} + \overrightarrow{\boldsymbol{U_{Saff}}}$$ [2]



[illegible]

concentrated plume

due to a non-uniform shear

Lift force (Saffman force) of a rotating bubble in a sheared plume

$\frac{1}{3}\alpha^2(1+0.5e^{8.8\alpha})$ *hindering function*

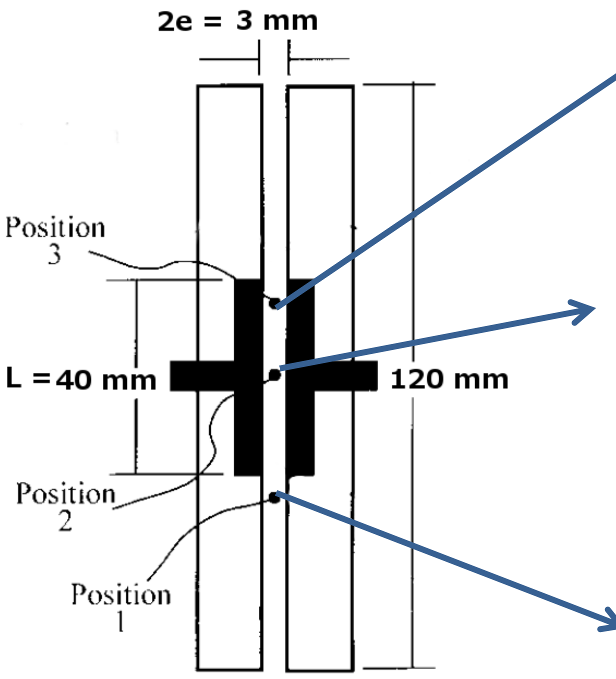
[1] M. Ishii, T. Hibiki, Thermo-Fluid Dynamics of Two-Phase Flow, Springer, New York, NY, 2011.
[2] R. Wedin, A.A. Dahlkild, Ind. Eng. Chem. Res. 40 (2001) 5228–5233

2.1 - MIXTURE MODEL : ASSUMPTIONS

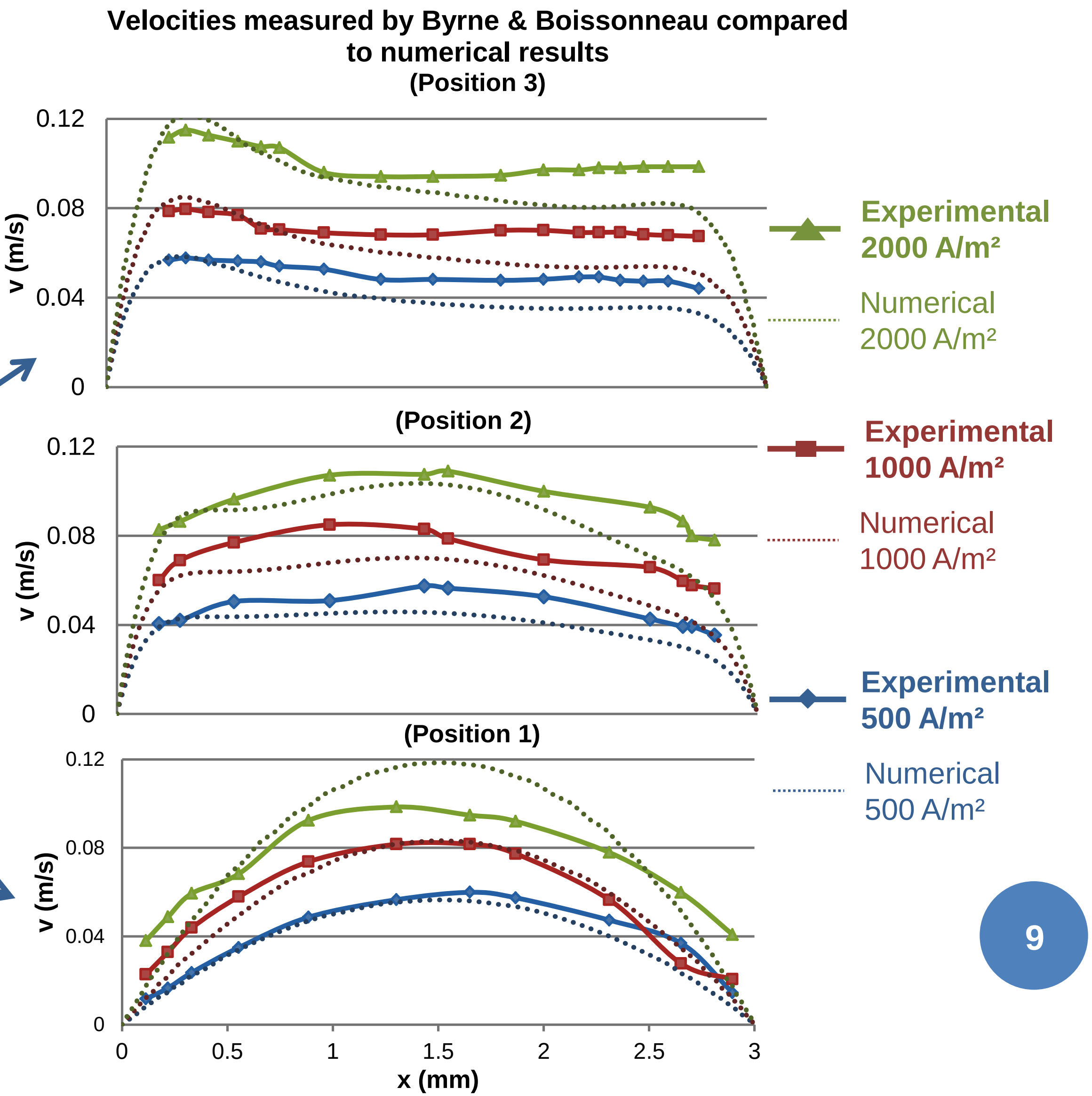
- **Electrokinetics** not computed
  - **Uniform current** approximation
    - **Small influence** on two-phase flow results
- $\boldsymbol{\nabla C \sim 0}$ due to strong **mixing**
- **Heat generation** neglected
  - **Thermal-induced** convection << **bubble-induced** convection

2.2 - MODEL VALIDATION : SIMULATING EXPERIMENTAL RESULTS

Water alkaline electrolysis, bubble-induced convection



[3] P. Boisonneau, P. Byrne,
J. Appl. Electrochem. 30 (2000) 767–775


Velocities measured by Byrne & Boissonneau compared to numerical results

2.2 - MODEL VALIDATION : SIMULATING EXPERIMENTAL RESULTS

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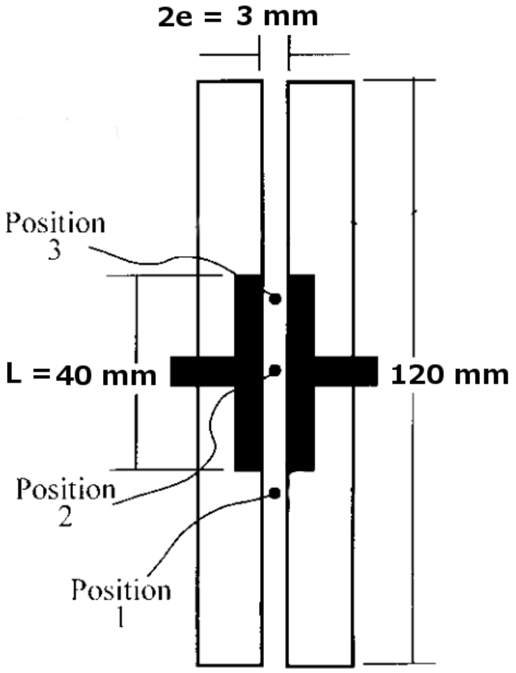

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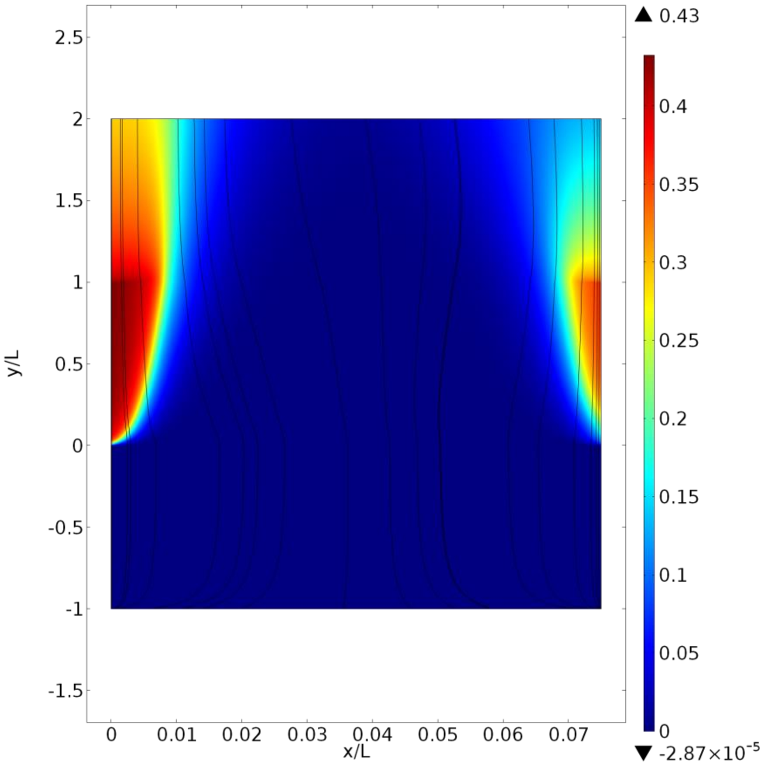
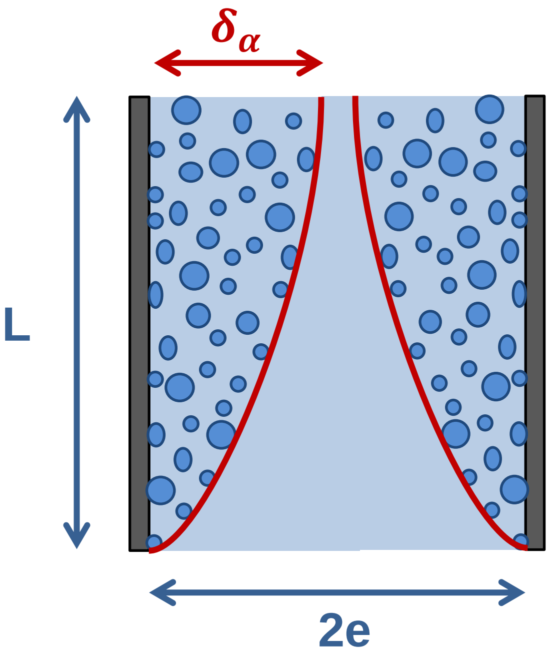
Void fraction evolution and streamlines (2000 A/m²)



2.3 – CREATING NEW MODEL : THE THERMAL ANALOGY[4]

- Bubble **plume** ~ **thermal boundary layer**
  - **Buoyancy forces** and **void fraction** concentrated in the **vicinity of electrodes**



- Dispersed phase **conservation** ~ **convection-conduction equation**
  - $U_x \frac{\partial \alpha}{\partial x} + U_y \frac{\partial \alpha}{\partial y} = \frac{\partial}{\partial x}\left(K_\alpha \frac{\partial \alpha}{\partial x}\right)$
  - $K_\alpha \sim a U_S$

$$\boxed{Pr_\alpha = \frac{\nu}{K_\alpha}}$$

- Boundary layer thickness **scale analysis**
  - **Rayleigh-like number**

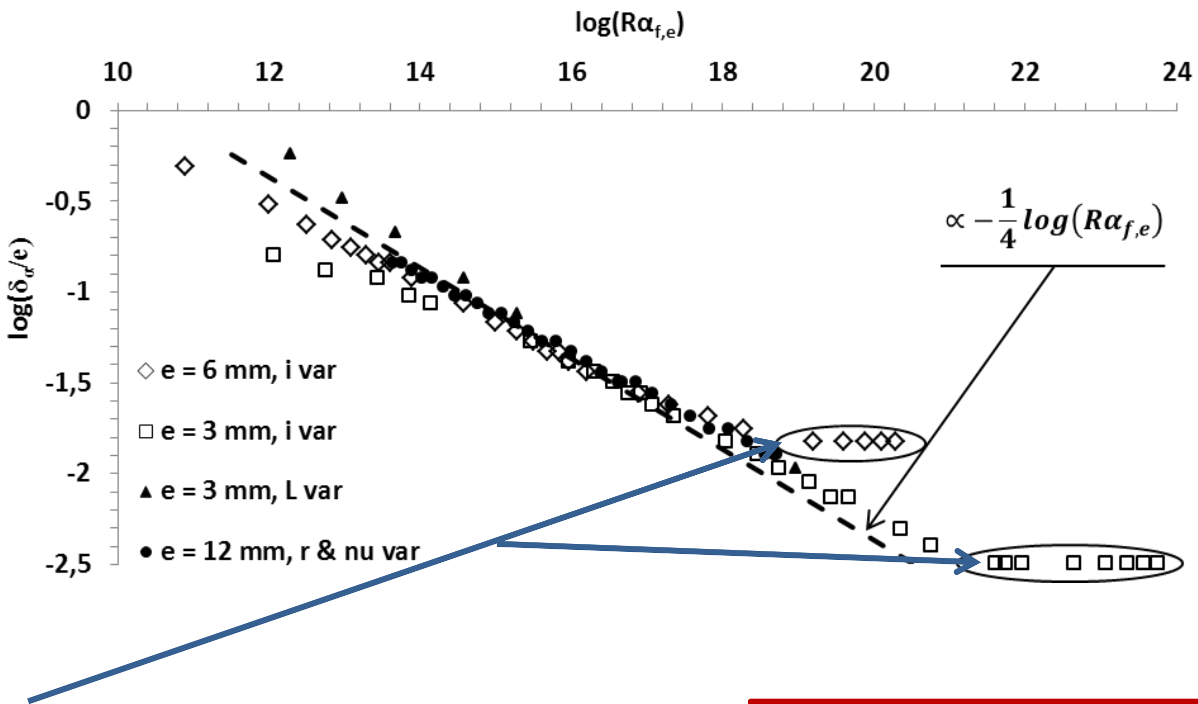
$$\boxed{Ra_{e,f} = \frac{\nu U_g e^5}{a^6 g L}}$$

$$\boxed{\frac{\delta_\alpha}{e} \sim {Ra_{e,f}}^{-1/4}}$$

[4] Schillings et al., Int. J. Heat Mass Transfer 85 (2015) 292–299

2.3 - $PR_\alpha >> 1$

Relative plume thickness vs. Rayleigh-like number (log-scale)



At high currents → **Strong shear**

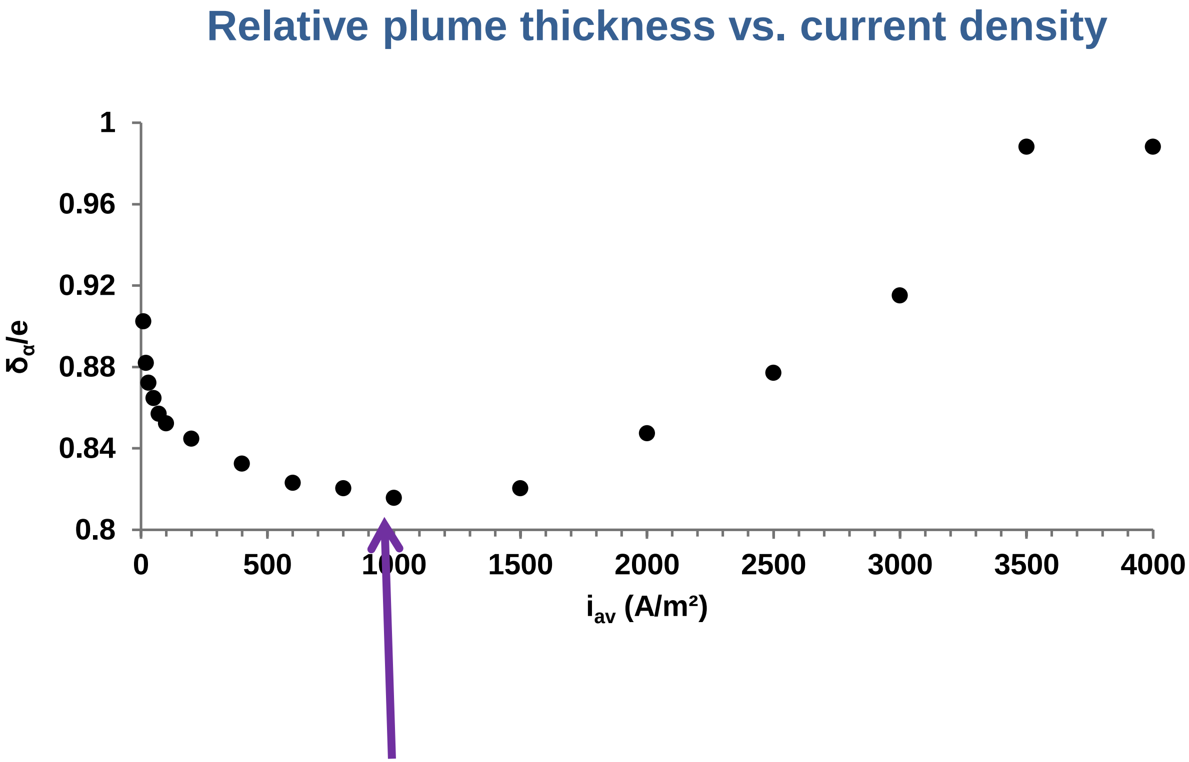
→ $U_{Sdiff,x} \ll U_{Hdiff,x}$ → $K_\alpha \sim {r_b}^2 \dot{\gamma}$

→ $\frac{\delta_\alpha}{e} \sim \frac{({r_b}^2 L)}{e}$

Important result :

$$\frac{\delta_\alpha}{e} \sim \left(\frac{{r_b}^6 g L}{\nu U_g e^5}\right)^{0,25}$$

2.3 - $\mathrm{Pr}_\alpha \ll 1$: LIMITING CASE

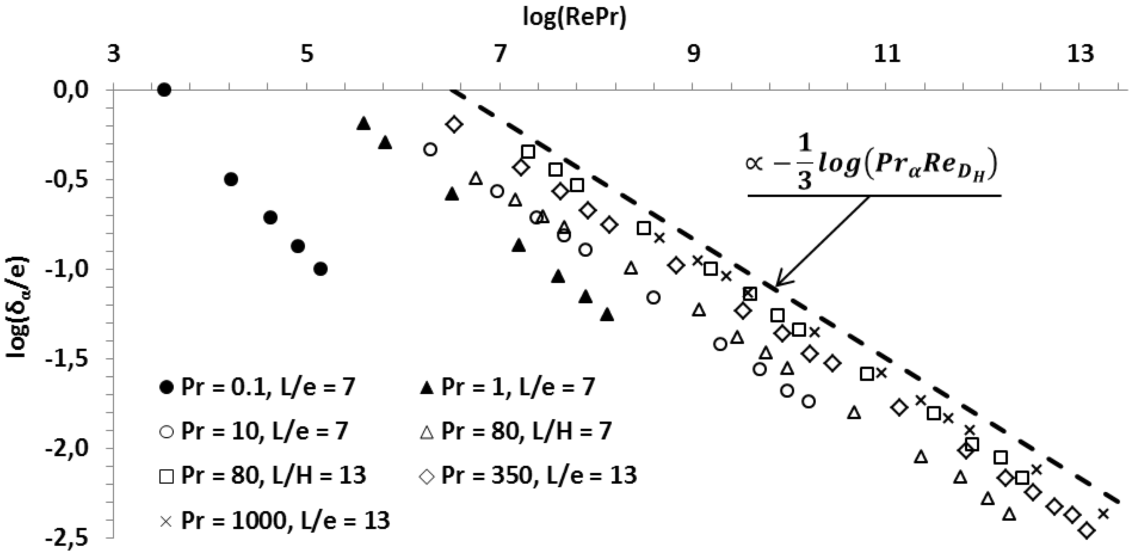


$\overrightarrow{U_{Saff}} \nearrow\nearrow$

2.4 - SENSIBILITY TO FORCED CONVECTION

- **Plume development in a Poiseuille flow :**
  - $\frac{\delta_\alpha}{e} \sim \left(\frac{L}{e}\right)^{1/3} Pr_\alpha{}^{-1/3} Re_{D_H}{}^{-1/3}$

Relative plume thickness vs. Reynolds-Prandtl (log scale)



Forced convection decreases δ_α

3 – RECENT WORKS & PROSPECTS

Experiments

- → High speed camera recorder
- → Flow caracterization (bubble-induced & forced convection)
- → Electrochemical Impedance Spectroscopy

DNS

- → Implementation of Lagrangian tracking
- → Two-way coupling between the dispersed and continuous phase
- → Simulation of collisions between bubbles

ANY QUESTION ?

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