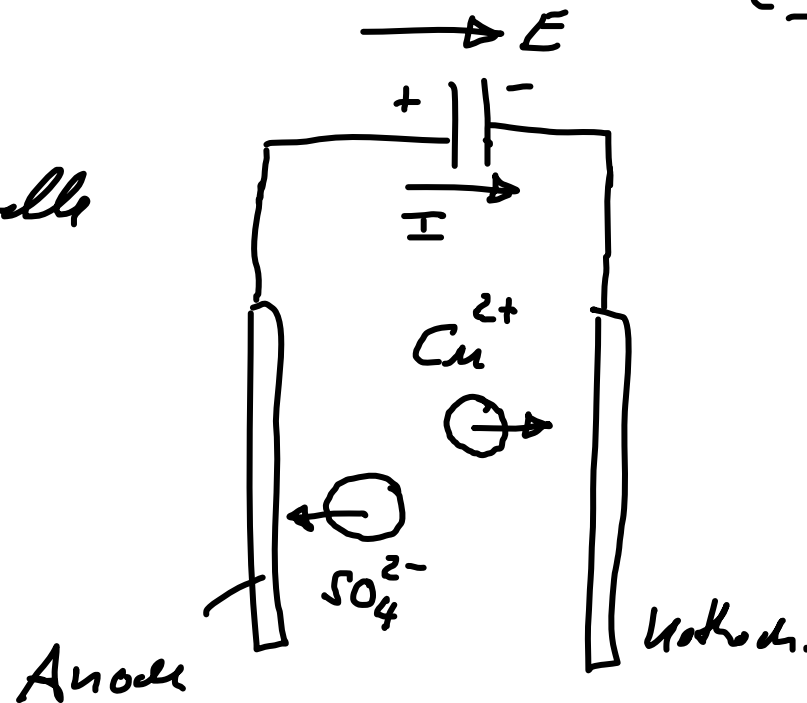


$$\psi(r,x) \rightarrow C_+(r,x), C_-(r,x) \rightarrow \begin{aligned} \vec{c}_+ \cdot \vec{e}_r &= 0 \\ \vec{c}_- \cdot \vec{e}_r &= 0 \end{aligned}$$

Im Gegensatz dazu  
Elektrolytische Zelle



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$$\vec{i} = \int \mu (\vec{E}) \quad \text{Ohmsches Gesetz.}$$



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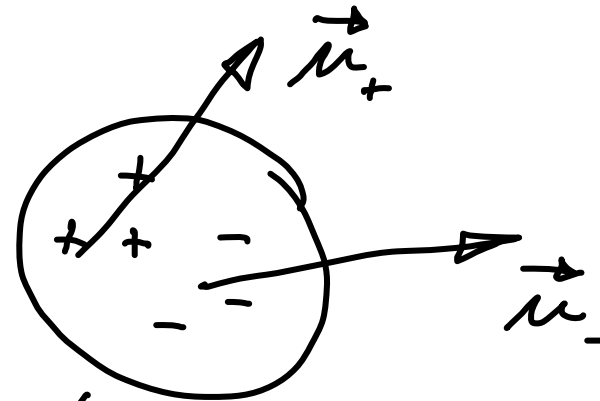
Definition vgl. Fluidtransport

$$\vec{i}_+ := F_2 \vec{j}_+^* = F_2 \left( \vec{u}_+ c_+ + \vec{j}_+^* \right)$$

Diffusion + Coulombsche Aktiv.

Molare Stoffstromdichte der  $k$ -ten Komponente

$$\vec{j}_k^* = \underbrace{\vec{u}_k c_k}_{\text{Konvektion}} + \underbrace{\vec{j}_k}_{\text{relativer Strom.}}$$



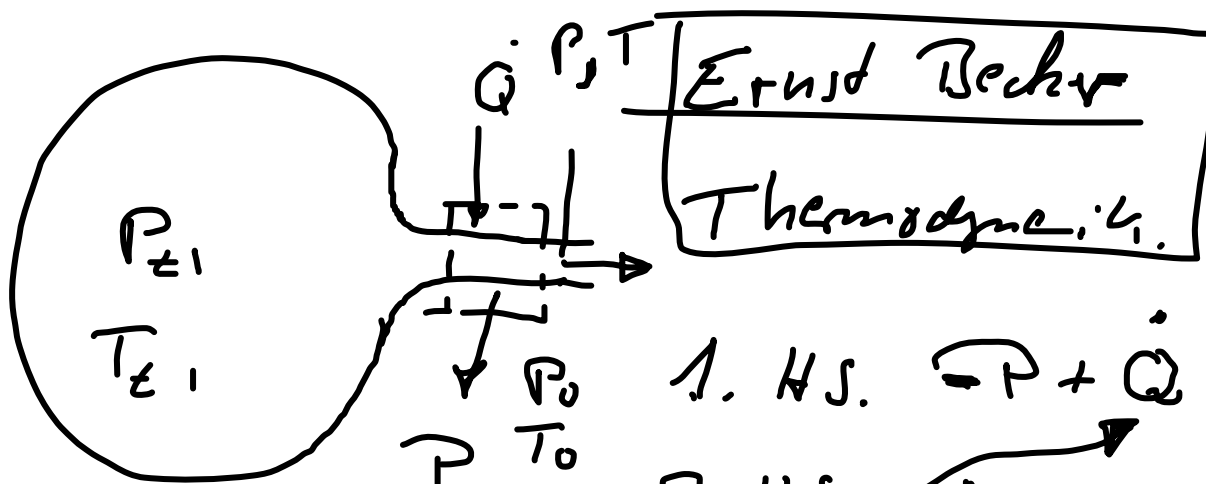
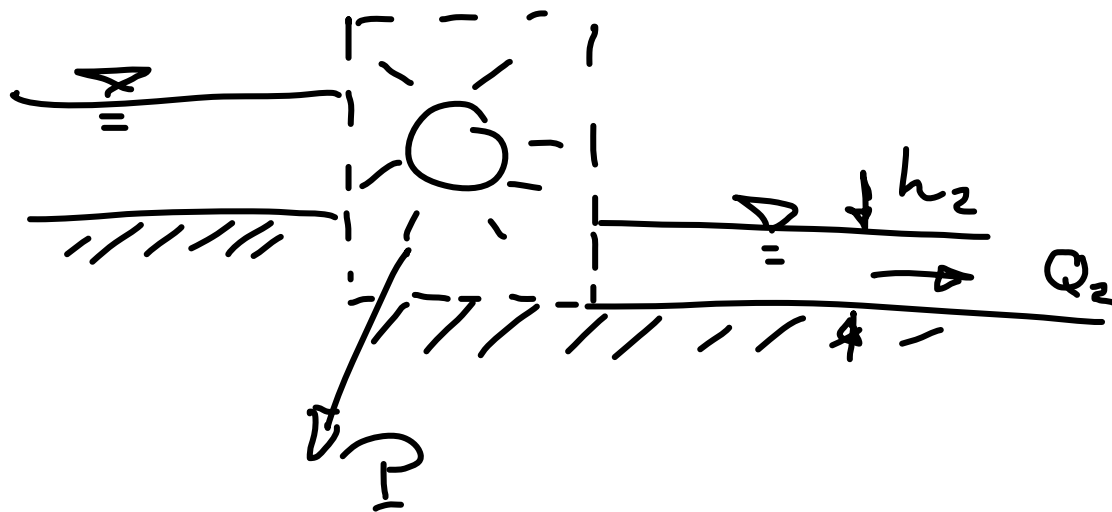
Konzentration der  $k$ -ten Komponente

$c_k$

$$\vec{u}^* = \frac{\sum \vec{u}_k c_k}{\sum c_k} \quad \Bigg| \quad \vec{u} = \frac{\sum \vec{u}_k \rho_k}{\sum \rho_k}$$



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$$1. \text{ H.S. } \dot{P} + \dot{Q} = \dot{m}(h - h_4) \quad (1)$$

$$2. \text{ H.S. } \dot{m}(s - s_1) = \frac{\dot{Q}}{T_0} + \Delta \dot{S}_{\text{irr}} \quad (2)$$

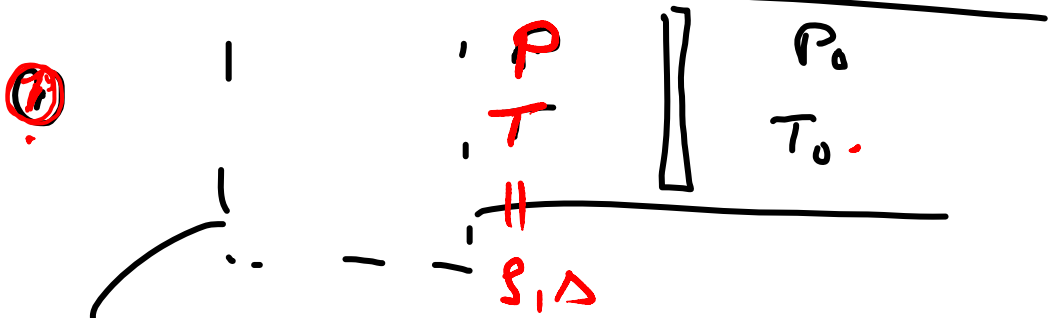
$$\dot{Q} = \dot{m}(T_0 s - T_0 s_1) - \Delta \dot{S}_{\text{irr}} T_0$$

$$\dot{P} = \dot{m} \left[ (h_1 - T_0 s_1) - (h - T_0 s) \right] - \dot{s}_{irr} T_0$$

$$\zeta \equiv 1 \Rightarrow \dot{s}_{irr} \equiv \sigma \quad h - \frac{p}{\rho} = e$$

$$\dot{P}_{max} = \dot{m} \left[ (h_1 - T_0 s_1) - (h - T_0 s) \right] - \underline{\underline{\frac{\dot{m}}{\rho} (p + p_0)}}.$$

$$= \dot{m} \left[ (h_1 - T_0 s_1) - e(s, s) + T_0 s - \frac{p_0}{\rho} \right]$$



$$\left. \begin{aligned} \frac{\partial \dot{P}_{max}}{\partial s} \Big|_v &= 0 \\ \frac{\partial \dot{P}_{max}}{\partial v} \Big|_s &= 0 \end{aligned} \right\} \begin{aligned} p &= p_0 \\ T &= T_0 \end{aligned}$$



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$$P_{max, opt} = \dot{m} \left[ \underset{=}{h_1} - \underset{=}{h_0} - \underset{=}{T_0} \dot{\Omega}_1 + \underset{=}{T_0} \dot{\Omega}_0 \right]$$

$$\frac{P_{max, opt}}{\dot{m}} := Ex_{typic.} \quad A_0 \rho_0 \mu_0 \underbrace{\quad}_{\text{①}_0}$$



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Der gesamte Stoffstromvektor  $\vec{j}_+$  setzt  
sich aus einem konvektiven Anteil  $c_+ \vec{u}_+$   
und einem relativen Anteil zusammen

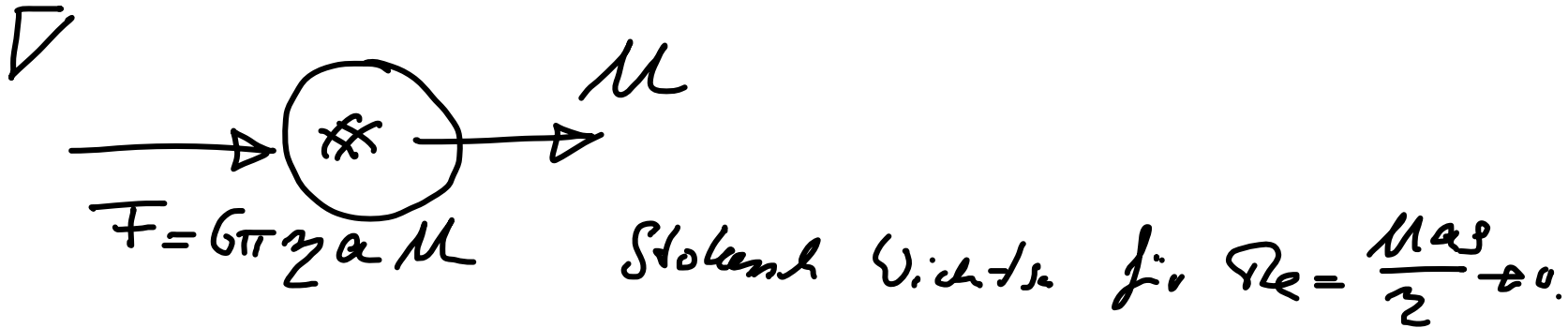
$$\vec{j}_+ = c_+ \vec{u}_+ + \vec{j}_+$$

Materialpunkt für die relative Stoffstr.

$$\vec{j}_+ = -D_+ \nabla c_+ + v_+ F z c_+ \vec{E}$$

Fick'sche Gesetze.  
Coulomb'sches Gesetz.

$$v_+ := \text{Mobilität} = \frac{\text{Geschwindigkeit}}{U_{\text{Ges}}}$$



Mobilität  $u = \frac{M}{F} = \frac{1}{6\pi\zeta a}$

vgl. David Urey: Theory of Brownian Movement.

$$v_+ = \frac{D_+}{RT} \quad \left( \begin{array}{l} \text{Nernst-Einstein-} \\ \text{Relation.} \end{array} \right)$$



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$$\begin{aligned}
 \vec{i}_+ &= Fz C_+ \vec{u}^* + \text{Konvektion} & \vec{i}_- &= -Fz C_- \vec{u}^* + \\
 & - Fz D_+ \nabla C_+ + \text{Diffusion} & & + Fz D_- \nabla C_- + \\
 & + (Fz)^2 v_+ \vec{E} & \text{Migration} & - (Fz)^2 v_- \vec{E} \\
 v_+ &:= \frac{D_+}{RT} & & v_- = \frac{D_-}{RT}
 \end{aligned}$$



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Gesamte Stromvektor

$$\vec{i} = \vec{i}_+ + \vec{i}_-$$

$$= F_2 \vec{u}^+ (c_+ - c_-) + \text{Konv.}$$

$$- F_2 (D_+ \nabla c_+ - D_- \nabla c_-) + \text{Diff.}$$

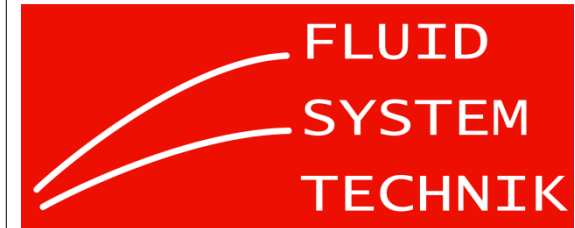
$$+ \sigma \vec{E}, \quad \text{Migration}$$

mit der Abzahl (Wert)

$$\sigma := \left( F_2 \right)^2 \frac{c_+ D_+ - c_- D_-}{RT}$$



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# Spezialfall Eberswolffsch

$$\vec{c}_+ \cdot \vec{e}_r = \sigma$$

$$\vec{u} \cdot \vec{e}_r = \sigma$$

$$\vec{c}_- \cdot \vec{e}_r = \sigma$$

$$\sigma = - \cancel{\frac{1}{r}} \frac{\partial c_+}{\partial r} - \cancel{\frac{1}{RT}} F_2 c_+ \frac{\partial \psi}{\partial r} \quad (1)$$

3  
5+

$$\sigma = - \frac{\partial c_-}{\partial r} + \frac{F_2}{RT} \frac{\partial \psi}{\partial r} c_- \quad (2)$$

→ System von partiellen DGL für  $c_+$  &  $c_-$

→ Lösung ist eine Boltzmannverteilung

$$s = kT$$



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$$c_{\pm} = c_0 \exp\left(\pm \frac{zF}{RT} \psi\right)$$

Zurück zum Anfang.

Die Götze sind Quelle für das elektr. Feld

$$\Delta\psi = -\frac{\rho_e}{\epsilon}$$

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) = -\frac{Fz}{\epsilon} (c_+ - c_-)$$

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) = \frac{c_0 Fz}{\epsilon} \sinh\left(\frac{zF}{RT} \psi\right)$$

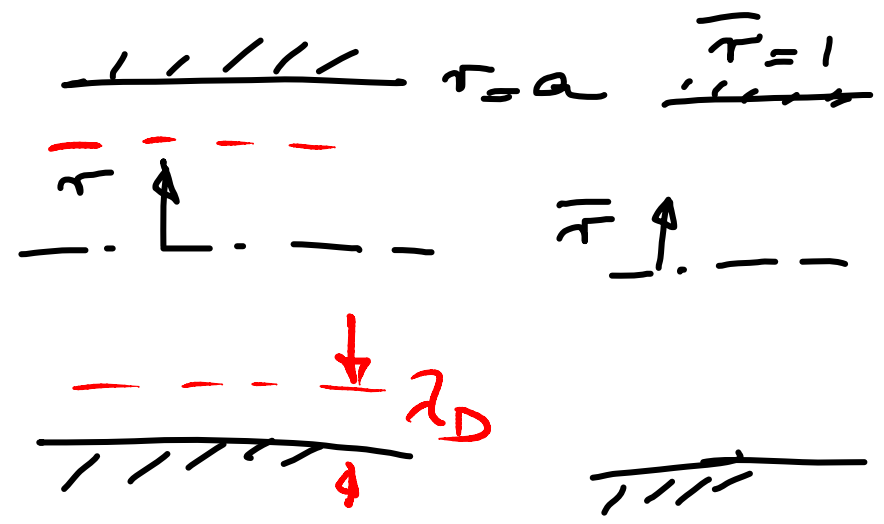
19.01.2011 PDCL für  $\psi$



# Dimensionslose Darcy (inspektionsche Darcy)

$$\tau = \bar{\tau} a$$

$$\psi = \bar{\psi} \frac{RT}{zF}$$



$$\frac{1}{\tau} \frac{\partial \tau}{\partial y} = \left( \frac{\partial \bar{\psi}}{\partial \bar{y}} \right) = \left( \frac{a}{\lambda_D} \right)^2 \sinh \bar{\psi}$$

$$\lambda_D = \sqrt{\frac{\epsilon RT}{2 (zF)^2 c_0}}$$

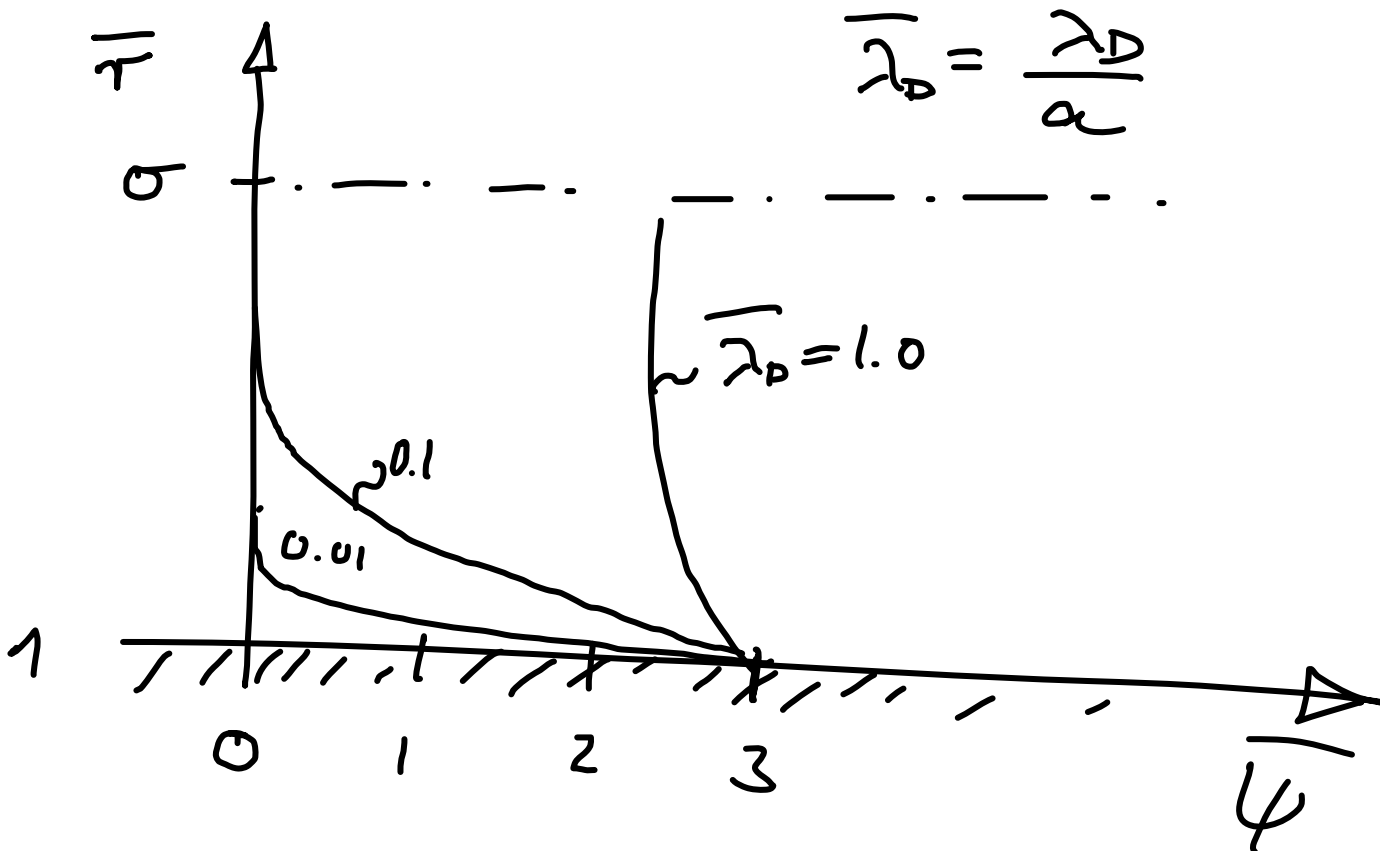
Debye'sche  
Abschirmung



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$$\bar{r}_D^2 \frac{1}{r/a} \frac{\partial}{\partial r/a} \left( r/a \frac{\partial \bar{\psi}}{\partial r/a} \right) = \sin \bar{\psi} \approx \bar{\psi}$$

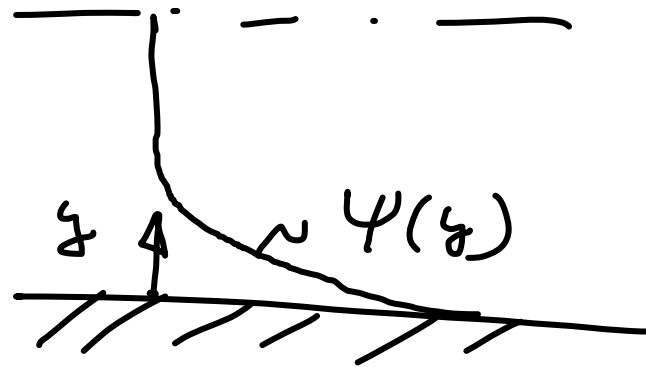
für kleinen  $\bar{\psi}$

$$\bar{\psi} \ll 1, \text{ d.h. } \psi \ll \frac{r_D^2}{2a^2} \leadsto \sin \bar{\psi} \approx \bar{\psi}$$

Debye-Hückel Approximation.

→

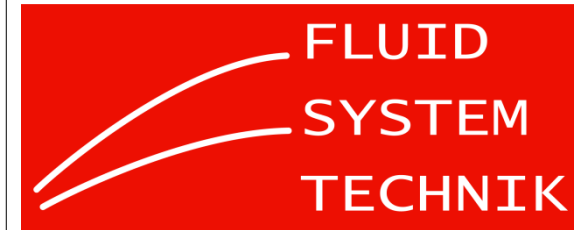
$$\psi = J \exp\left(-\frac{\psi}{\lambda_D}\right)$$



$$u(r) = -\frac{a^2}{4\epsilon} \frac{dp}{dx} \left(1 - \left(\frac{r}{a}\right)^2\right) - \frac{\epsilon J}{2} \left(1 - \exp\left(-\frac{a-r}{\lambda_D}\right)\right)$$



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