ChemE 530

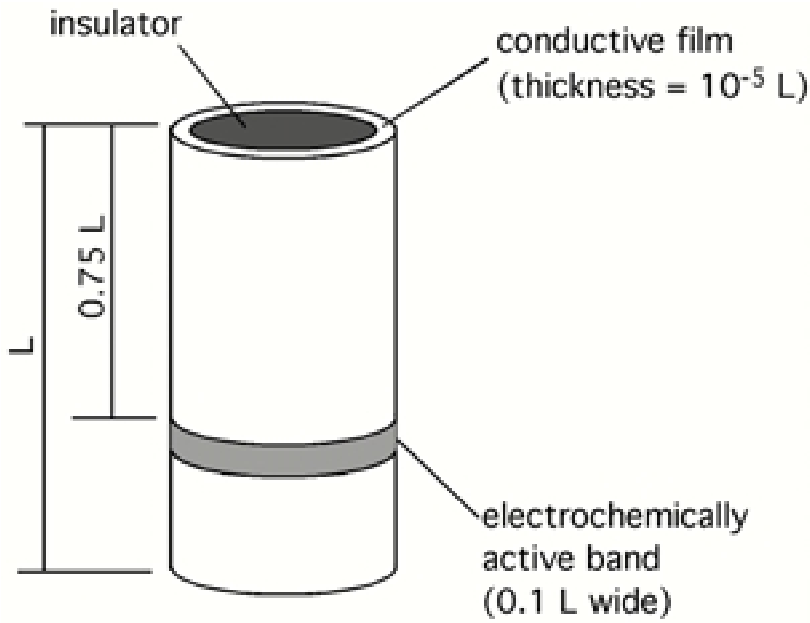
Final Exam

Due Monday 3/17/03, by 4 pm in the 303 BNS Chemical Engineering Office

You are not to discuss this exam nor collaborate with others in any manner. Violation of this rule will be deemed a serious breach of the university code of ethics, with grave consequences.

Problem 1. (50 pts)

A thin conductive film is grown on an insulating cylindrical spindle of length L. The film thickness is $H=10^{-5}*L$. The conducting film is not electrochemically-active. Three quarters of the way down the cylinder is an electrochemically-active band with kinetics given by a linearized Butler-Volmer experession identical to that used in Project 1. The band is 0.1*L wide (it goes from 0.75L to 0.85L). The entire top edge of the film has a contact with potential ϕ^c and the electrochemically-active band is in a solution with potential $\phi^{sol}=0$.



(a) Define appropriate non-dimensional variables. Write the governing equation that describes charge conservation in the conducting thin film. Provide all the necessary boundary conditions.

(b) Describe the traits of the problem that permit a reduction in dimensionality. Write the equations and boundary conditions for the reduced dimensionality problem.

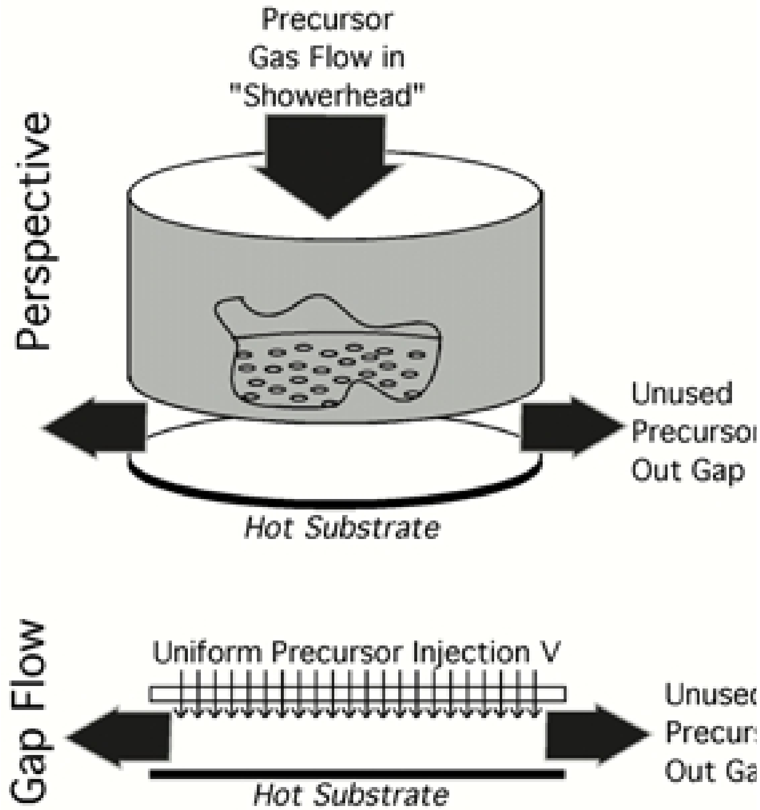
(c) Solve the reduced dimension problem USING FEMLAB for the limit $Wa \rightarrow 0$.

(d) Is your solution good? Show that charge is in fact conserved (i.e., current measured at the top edge matches current entering the electroactive band).

(e) Compare the FEMLAB solution with an analytical solution for current at the top contact when Wa=0.

Problem 2 (50 pts)

Semiconductor quantum well structures are often made using organometallic chemical vapor deposition (OMCVD). A quantum well structure is comprised of alternating semiconductor films (ABABAB) with nanometer dimensions. To deposit semiconductor A requires a specific organometallic precursor gas, whereas deposition of B requires a different gas precursor.



The most common commercial reactors for OMCVD are "showerhead" reactors, where precursor gases are pumped through a "showerhead" injector placed close to the (hot) deposition substrate. Precursor is injected with a spatially uniform axial velocity into the gap between the showerhead and the hot substrate where deposition occurs. See schematic to right. We are interested in various aspects of flow in the thin gap between the showerhead injector and the substrate (the gap height, H, is much smaller than the substrate radius, R).

To make quantum structures, the precursor gas must be switched often, involving rapid starting and stopping of the flow. We are interested in this transient flow.

(a) Show that a velocity field of the functional form $\mathbf{v} = r\, f(z,t)\, \mathbf{e_r} + w(z,t)\, \mathbf{e_z}$ is compatible with the Navier-Stokes equations, continuity equation, and boundary conditions for transient flow in the gap. What functional form must the pressure take to remain compatible with this velocity field?

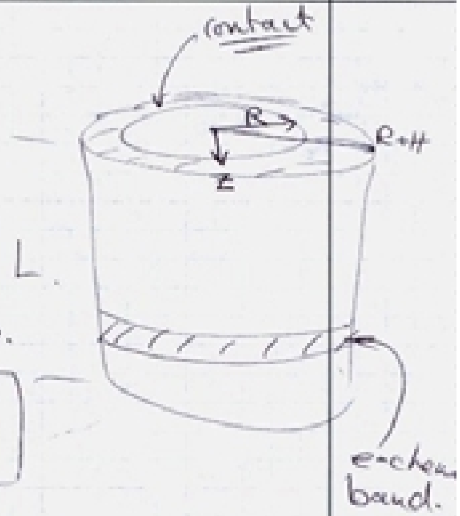
(b) Using the velocity form given in (a), non-dimensionalize the Navier-Stokes and continuity equations, and boundary conditions. Make clear what you use for the characteristic time, length, velocity, and pressure (if needed). Be sure to define the resulting Reynolds number.

(c) If we start with a static fluid in the gap, and at time t=0 we instantaneously begin pumping precursor into the gap with an injection velocity V, what do you think the transient start-up flow will look like as it develops? Sketch a series of transient RADIAL flow profiles as the flow comes to steady state. Consider two separate cases: low and high Reynolds number start-up flows. Try to have the sketches accurately reflect mass conservation.

(d) Formulate a perturbation solution and solve for the STEADY-STATE velocity when the Reynolds number is small to moderate. Plot the nondimensional form of the RADIAL velocity function f(z) when Re=0.5

1 (a) Charge conservation

$$\nabla^2 \phi = 0$$



in cylinderical coordinates, noting a lack of Θ dependance.

G.E. $$\boxed{\frac{\partial^2 \phi}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \phi}{\partial r}\right) = 0}$$

Next, Boundary conditions

$\phi = \phi_c$ @ contact edge.

$-\kappa(\underline{n}\cdot\underline{\nabla}\phi) = \frac{i_0 nF}{RT}\phi$ @ echem band (w/ $\phi^{sol}=0$)

or

$$-\kappa\frac{d\phi}{dr} = \frac{i_0 nF}{RT}\phi \qquad r = R+H,\ 0.75L < z < 0.85L$$

$\underline{n}\cdot\underline{\nabla}\phi = 0$ everywhere else.

---

non-dimensionalize with

$$\Phi = \phi/\phi_c \quad \eta = z/L. \quad \rho = \frac{r-R}{H}$$

Then, gov. eq^n's and BC's become.

②

$$\left(\frac{H}{L}\right)^2 \frac{\partial^2 \Phi}{\partial \eta^2} + \left[\frac{1}{\rho + \left(\frac{R}{H}\right)}\right] \frac{\partial}{\partial \rho}\left(\left[\rho + \frac{R}{H}\right] \frac{\partial \Phi}{\partial \rho}\right) = 0$$

since $\rho \le 1$ and $\frac{R}{H} >> 1$ all terms $\rho + \frac{R}{H} \approx \frac{R}{H}$, yielding

charge conservation gov. eqn

$$\boxed{\left(\frac{H}{L}\right)^2 \frac{\partial^2 \Phi}{\partial \eta^2} + \frac{\partial^2 \Phi}{\partial \rho^2} = 0}$$

looks like a planar film when $\frac{R}{H} >> 1$

$\Phi = 1$ @ $\eta = 0$, ρ

$\frac{\partial \Phi}{\partial \eta} = 0$ @ $\eta = 1$, ρ

$\frac{\partial \Phi}{\partial \rho} = 0$ @ $\rho = 0$, η

$\frac{\partial \Phi}{\partial \rho} = 0$ @ $\begin{cases} \rho = 1 & \eta \le 0.75 \\ & 1 \ge \eta \ge 0.85 \end{cases}$

$\frac{\partial \Phi}{\partial \rho} = -\frac{i_o n F H}{\kappa R T} \Phi$ @ $\{ \rho = 1 \quad 0.75 < \eta < 0.85$

(b) because we have a very thin film, most pot'l variation will be in η-direction, not ρ-direction

$\Rightarrow$ Reduce to 1-D problem by defining average $\langle\Phi\rangle$ in ρ-direction

$$\langle\Phi\rangle = \int_{\rho=0}^{\rho=1} \Phi \, d\rho = \frac{1}{H}\int_{R}^{R+H} (\phi/\phi_{\ell}) \, dr$$

Apply $\langle\Phi\rangle$ integral to GE & BCs.

$$\int_0^1 \left[\left(\frac{H}{L}\right)^2 \frac{\partial^2 \Phi}{\partial \eta^2} + \frac{\partial^2 \Phi}{\partial \rho^2}\right] d\rho = 0$$

$$\left(\frac{H}{L}\right)^2 \frac{d^2\langle\Phi\rangle}{d\eta^2} + \left[\left.\frac{d\Phi}{d\rho}\right|_{\rho=1} - \left.\frac{d\Phi}{d\rho}\right|_{\rho=0}\right] = 0.$$

$$\left\{\begin{array}{l} \left.\begin{array}{l} 0.85 \le \eta \\ 0.75 \ge \eta \end{array}\right\} = 0 \\ 0.75 < \eta < 0.85 = -\frac{i_0 n F H}{\kappa \xi T}\langle\Phi\rangle \end{array}\right.$$

$= 0$

$\therefore$

$$\frac{d^2\langle\Phi\rangle}{d\eta^2} = 0 \quad \{\eta \le 0.75, \ \eta \ge 0.85\}$$

$$\frac{d^2\langle\Phi\rangle}{d\eta^2} - \frac{L^2 i_0 n F}{H \kappa \xi T}\langle\Phi\rangle = 0 \quad \{0.75 < \eta < 0.85\}.$$

or, defining $\dfrac{H \kappa R T}{L^2 i_0 n F} = Wa$.

GE

$$\frac{d^2 \langle \Phi \rangle}{d\eta^2} = 0 \qquad \begin{cases} \eta \le 0.75 \\ \eta \ge 0.85 \end{cases}$$

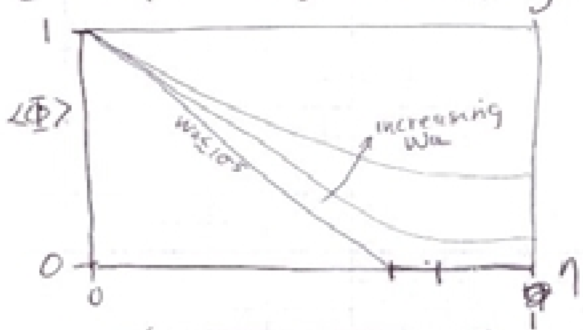
$$\frac{d^2 \langle \Phi \rangle}{d\eta^2} - \frac{1}{Wa} \langle \Phi \rangle = 0 \qquad 0.75 < \eta < 0.85$$

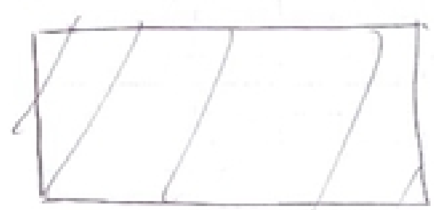
BCs

$$\Phi = 1 \quad @ \; \eta = 0$$

$$\frac{d\Phi}{d\eta} = 0 \quad @ \; \eta = 1$$

(c) Solve w/ 1-D Helmholz. with 3-subdomain eqns, as given above, and BCs above





(d)

$$i_{cont.} = -\kappa \frac{d\Phi}{dz}$$

$$= -\left(\frac{\kappa \Phi_c}{L}\right) \frac{d\langle\Phi\rangle}{d\eta}\bigg|_{\eta=0}$$

at contact

current density

$$I_{cont} = \int_0^{2\pi}\int_R^{R+H} i_{cont}\, r\, dr\, d\theta$$

since $i_{cont} = \text{const.}$

$$= -\left(\frac{\kappa \Phi_c}{L}\right) \frac{d\langle\Phi\rangle}{d\eta}\bigg|_{\eta=0} A_{contact}$$

$$= -\left(\frac{\kappa \Phi_c}{L}\right) \frac{d\langle\Phi\rangle}{d\eta}\bigg|_{\eta=0} 2\pi R H \quad \text{for } R >> H$$

$$I_{band.} = \int_0^{2\pi}\int_{0.75L}^{0.85L} \frac{i_o n F}{RT} \phi\, r\, d\theta\, dz$$

$$= \int_0^{2\pi}\int_{0.75L}^{0.85L} L\left(\frac{i_o n F \Phi_c}{RT}\right) \langle\Phi\rangle (R+H)\, d\theta\, d\eta$$

$$= \frac{i_o n F \Phi_c}{RT} 2\pi R L \int_{0.75}^{0.85} \langle\Phi\rangle\, d\eta \quad \text{for } R >> H$$

For $I_{cont} = I_{Band}$

$$\boxed{-\frac{d\langle\Phi\rangle}{d\eta} = \frac{1}{Wa}\int_{0.75}^{0.85} \langle\Phi\rangle\, d\eta}$$

(e) What is analytical current when $Wa = 0$?

$\Rightarrow$ For Band region, we can set $Wa = 0$ in G.E. and get estimate for pot'l in that region

$$Wa \frac{d^2\langle\Phi\rangle}{d\eta^2} - \langle\Phi\rangle = 0$$

or $\langle\Phi\rangle = 0$ @ $Wa = 0$

This is an "outer" sol$^{\underline{n}}$ that is not accurate in very thin region near $\eta = 0.75$, but we can ignore this, since we want current @ contact (far from $\eta = 0.75$).

So, for film between band and contact.

$$\frac{d^2\langle\Phi\rangle}{d\eta^2} = 0 \overset{\text{integrate}}{\Rightarrow} \langle\Phi\rangle = a\eta + b. \quad \eta \le 0.75$$

use $\langle\Phi\rangle = 1$ @ $\eta = 0$ and sol$^{\underline{n}}$ for band ($\langle\Phi\rangle = 0$ @ $\eta \ge 0.75$). to get

$$\boxed{\langle\Phi\rangle = 1 - 1.333\eta} \quad \eta \le 0.75$$

$\therefore$ ~~$\Phi_{cont} = -d\Phi$~~

non-dimensional current @ contact is:

$$\boxed{-\left.\frac{d\langle\Phi\rangle}{d\eta}\right|_{\eta=0} = 1.33\bar{3}}$$

which matches properly done FEMLab!

---

problem

2 (a) Test compatibility of $\underline{v} = rf(z,t)\underline{e}_r + w(z,t)\underline{e}_z$ w/ N-S and find pressure f^{n}c.

$\Rightarrow$ continuity in cyl. coordinates

$$\frac{\partial v_r}{\partial r} + \frac{v_r}{r} + \frac{\partial v_z}{\partial z} = 0$$

$$\frac{\partial (rf)}{\partial r} + \frac{rf}{r} + \frac{\partial w}{\partial z} = 0$$

$$\underbrace{2f + \frac{\partial w}{\partial z} = 0}_{\text{function of } z, t \text{ only}}$$

✓

r-momentum:

$$\frac{\partial v_r}{\partial t} + v_r\frac{\partial v_r}{\partial r} + v_z\frac{\partial v_r}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial r} + \nu\left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(r v_r)\right) + \frac{\partial^2 v_r}{\partial z^2}\right]$$

$$\frac{\partial(rf)}{\partial t} + rf\frac{\partial(rf)}{\partial r} + w\frac{\partial(rf)}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial r} + \nu\left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(r^2 f)\right) + \frac{\partial^2(rf)}{\partial z^2}\right]$$

$$\underbrace{\frac{\partial f}{\partial t}}_{z\,\&\,t} + \underbrace{f^2}_{z\,\&\,t} + \underbrace{w\frac{\partial f}{\partial z}}_{z\,\&\,t} = \underbrace{-\frac{1}{\rho}\left(\frac{1}{r}\right)\frac{\partial p}{\partial r}}_{?} + \nu\underbrace{\left[\frac{\partial^2 f}{\partial z^2}\right]}_{z\,\&\,t}$$

⇐ note: I divided all by r

functions of

to be compatible $-\frac{1}{\rho}\left(\frac{1}{r}\right)\frac{\partial p}{\partial r}$ __must not__ be a function of r ∴ in most general terms:

$$-\frac{1}{\rho}\left(\frac{1}{r}\right)\frac{\partial p}{\partial r} = a(z,t)$$

our 1st guess @ p ⇒ or. $\boxed{p = -\frac{1}{2}r^2 a(z,t) + b(z,t)}$

z-comp. of momentum

$$\frac{\partial v_z}{\partial t} + v_r\frac{\partial v_z}{\partial r} + v_z\frac{\partial v_z}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left[\frac{1}{r}\left(\frac{\partial}{\partial r}\left(r\frac{\partial v_z}{\partial r}\right)\right) + \frac{\partial^2 v_z}{\partial z^2}\right]$$

$$\underbrace{\frac{\partial w}{\partial t} + rf\cancelto{0}{\frac{\partial w}{\partial r}} + w\frac{\partial w}{\partial z}}_{\text{functions of } z\,\&\,t \text{ only}} = \underbrace{-\frac{1}{\rho}\frac{\partial}{\partial z}\left(\frac{1}{2}r^2 a + b\right)}_{\text{BAD: if } a = a(z,t) \text{ then this is function of } r,\,z\,\&\,t} + \nu\underbrace{\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\cancelto{0}{\frac{\partial w}{\partial r}}\right) + \frac{\partial^2 w}{\partial z^2}\right]}_{\text{function of } z\,\&\,t}$$

clearly can't have $a = a(z,t)$.
so, if $a = a(t)$ then all is fine and we get

$$\boxed{p = -\tfrac{1}{2} r^2 a(t) + b(z,t)}$$

form p must take to be compatible w/ N-S.

and the we get the following gov. eq$^{\underline{n}}$s:

cont: $2f + \dfrac{\partial w}{\partial z} = 0$

r-mom: $\dfrac{\partial f}{\partial t} + f^2 + w\dfrac{\partial f}{\partial z} = + \dfrac{a(t)}{\rho} + \nu \dfrac{\partial^2 f}{\partial z^2}$

z-mom: $\dfrac{\partial w}{\partial t} + w\dfrac{\partial w}{\partial z} = -\dfrac{1}{\rho}\dfrac{\partial b}{\partial z} + \nu \dfrac{\partial^2 w}{\partial z^2}$

We only need to find f & w, and won't worry about z-momentum eq$^{\underline{n}}$.

Boundary condition

$$\left.\begin{array}{l} v_r = 0 \ @ \ z = 0, H \\ v_z = 0 \ @ \ z = 0 \\ v_z = -V \ @ \ z = H \end{array}\right\} \Rightarrow \boxed{\begin{array}{l} f(0) = f(H) = 0 \\ w(0) = 0 \\ w(H) = -V \end{array}}$$

radial dependence has dropped out!

(b) Non-dimensionalize

$\Rightarrow$ Do what makes logical sense, and that is clearly.

$$W = \frac{w}{V}$$

why? because we know the axial velocity has a magnitude V, and thus, non-dimensional variable W is $O(1)$ ... that's a good thing!

- from continuity

$$F = f/f^* \quad , \quad \eta = \frac{z}{H}$$

$$2f^* F + \frac{V}{H}\frac{\partial W}{\partial \eta} = 0 \quad \Rightarrow \text{ if } f^* = V/H \text{ then}$$

$$2F + \frac{\partial W}{\partial \eta} = 0 \quad \Rightarrow \quad \text{Both terms are of same magnitude.}$$

So. $$F = \frac{fH}{V}$$

- Now radial momentum becomes

$$\tau = t/t^*$$

$$\frac{V}{Ht^*}\frac{\partial F}{\partial \tau} + \frac{V^2}{H^2}F^2 + \frac{V^2}{H^2}W\frac{\partial F}{\partial \eta} = \frac{a}{\rho} + \frac{\nu V}{H^3}\frac{\partial^2 F}{\partial \eta^2}$$

-or-

$$\frac{H^2}{\nu t^*}\frac{\partial F}{\partial \tau} + \frac{HV}{\nu}\left[F^2 + W\frac{\partial F}{\partial \eta}\right] = \left(\frac{H^3 a}{\rho \nu V}\right) + \frac{\partial^2 F}{\partial \eta^2}$$

IF I set $t^* = H^2/\nu$ and $R = \frac{VH}{\nu}$ as well as $A = \frac{H^3 a}{\rho \nu V}$, I get

r-mom

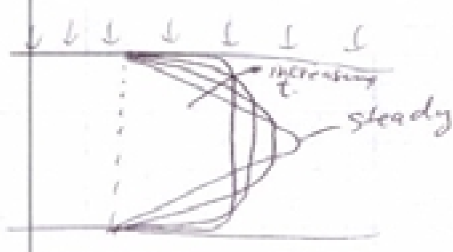
$$\boxed{\frac{\partial F}{\partial t} + Re\left[F^2 + W\frac{\partial F}{\partial \eta}\right] = A + \frac{\partial^2 F}{\partial \eta^2}}$$

why $t^* = \frac{H^2}{\nu}$? because that keeps the first term outside the Re*[ ] terms. Since we are interested in transient behavior, we must choose a time scale that preserves transient response, even when $Re \to 0$.

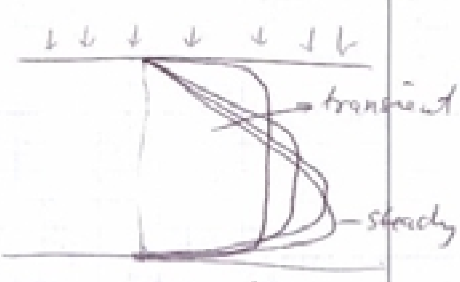
→ Don't worry about z-mom.

(c)

$Re << 1$



$Re >> 1$



in all cases, the integral area under the F curve must be constant to conserve mass.

(d) Need to formulate a perturbation series ... for steady state

$$F = F_0(\eta) + Re\,F_1(\eta) + O(Re^2).$$

$$W = W_0(\eta) + Re\,W_1(\eta) + O(Re^2).$$

$$A = A_0 + Re\,A_1 + O(Re^2).$$

Substitute into steady continuity, r-mom and BCs

cont

$$2F_0 + 2Re\,F_1 + \frac{\partial W_0}{\partial \eta} + Re\frac{\partial W_1}{\partial \eta} = 0$$

r-mom

$$Re\left[(F_0 + Re F_1)^2 + (W_0 + Re W_1)\frac{d(F_0 + Re F_1)}{d\eta}\right] = A_0 + Re A_1 + \frac{\partial^2}{\partial \eta^2}[F_0 + Re F_1].$$

BCs

$F_0 + Re\,F_1 = 0$ @ $\eta = 0,\ \eta = 1$

$W_0 + Re\,W_1 = 0$ @ $\eta = 0$

$W_0 + Re\,W_1 = -1$ @ $\eta = 1$

Sep by $O(Re^n)$

$O(1)$:

$$2F_0 + \frac{dW_0}{d\eta} = 0 \qquad F_0(0) = F_0(1) = 0$$

$$A_0 + \frac{d^2 F_0}{d\eta^2} = 0 \qquad W_0(0) = 0$$

$$W_0(1) = -1$$

Solve $O(1)$.

r-mom $F_0 = -\frac{A_0}{2}\eta^2 + C_1\eta + C_2$

$F_0(0) = F_0(1) = 0 \Rightarrow C_2 = 0,\ C_1 = \frac{A_0}{2}.$

$\therefore \boxed{F_0 = \frac{A_0}{2}(\eta - \eta^2)}$

continuity

$A_0(\eta-\eta^2) + \frac{dW_0}{d\eta} = 0$

$W_0 = -A_0\left(\frac{1}{2}\eta^2 - \frac{1}{3}\eta^3\right) + C_3$

$W_0 = 0 \ @\ \eta = 0 \Rightarrow C_3 = 0$

$W_0 = 1 \ @\ \eta = 1 \Rightarrow A_0 = 6$

$\therefore \boxed{W_0 = 2\eta^3 - 3\eta^2}$

using A_0, we get

$\boxed{F_0 = 3(\eta - \eta^2).}$

Same exactly as hockey puck problem

Collect term $O(Re)$.

$2F_1 + \frac{dW_1}{d\eta} = 0$

$F_0^2 + W_0\frac{dF_0}{d\eta} = A_1 + \frac{d^2F_1}{d\eta^2}$

BCS

$W_1(0) = W_1(1) = 0$

$F_1(0) = F_1(1) = 0$

$$9(\eta^2 - 2\eta^3 + \eta^4) + (2\eta^3 - 3\eta^2)(3 - 6\eta) = A_1 + \frac{d^2F_1}{d\eta^2}.$$

$$\cancel{9\eta^2} - \cancel{18\eta^3} + 9\eta^4 + 6\eta^3 - \cancel{9\eta^2} - 12\eta^4 + \cancel{18\eta^3} - A_1 = \frac{d^2F_1}{d\eta^2}.$$

$$6\eta^3 - 3\eta^4 - A_1 = \frac{d^2F_1}{d\eta^2}$$

integrate

$$\frac{3}{2}\eta^4 - \frac{3}{5}\eta^5 - A_1\eta + C_1 = \frac{dF_1}{d\eta}$$

integrate

$$\frac{3}{10}\eta^5 - \frac{3}{30}\eta^6 - \frac{A_1}{2}\eta^2 + C_1\eta + C_2 = F_1$$

$$F_1(0) = 0 \Rightarrow C_2 = 0.$$

$$F_1(1) = 0 = \frac{9}{30} - \frac{3}{30} - \frac{15A_1}{30} + C_1$$

$$\therefore C_1 = \frac{A_1}{2} - \frac{1}{5}$$

$$\therefore \boxed{F_1 = \frac{3}{10}\eta^5 - \frac{1}{10}\eta^6 - \frac{A_1}{2}\eta^2 + \left(\frac{A_1}{2} - \frac{1}{5}\right)\eta}$$

continuity

$$- \frac{3}{5}\eta^5 + \frac{1}{5}\eta^6 + A_1\eta^2 - \left(A_1 - \frac{2}{5}\right)\eta = \frac{dW_1}{d\eta}$$

$$W_1 = -\frac{1}{10}\eta^6 + \frac{1}{35}\eta^7 + \frac{A_1}{3}\eta^3 + \left(\frac{1}{5} - \frac{A_1}{2}\right)\eta^2 + C_3$$

$W_1(0) = 0 \Rightarrow C_3 = 0.$

$W_1(1) = 0 = -\frac{1}{10} + \frac{1}{35} + \frac{A_1}{3} + \frac{1}{5} - \frac{A_1}{2}$

$= -\frac{7}{70} + \frac{2}{70} - \frac{A_1}{6} + \frac{14}{70} = 0.$

$\Rightarrow A_1 = 6\left(\frac{9}{70}\right) = \frac{27}{35}$

$$\therefore \quad \boxed{W_1 = -\frac{1}{10}\eta^6 + \frac{1}{35}\eta^7 + \frac{27}{105}\eta^3 - \frac{13}{70}\eta^2}$$

and

$$\boxed{F_1 = \frac{3}{10}\eta^5 - \frac{1}{10}\eta^6 - \frac{27}{70}\eta^2 + \frac{13}{70}\eta}$$

So $F = 3(\eta - \eta^2) + Re\left[\frac{3}{10}\eta^5 - \frac{1}{10}\eta^6 - \frac{27}{70}\eta^2 + \frac{13}{70}\eta\right]$