

# ECH5261 - Advanced Transport Phenomena I

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July 11, 2025



**Project :** This project is related to Spin Coating. All the codes are attached in a zip file and all questions are well addressed.

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## Problem 1 : Spin Coating

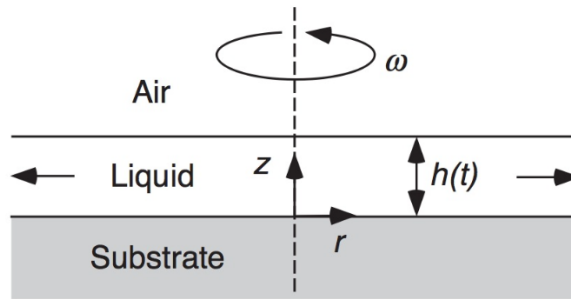


Figure 1: Spin Coating. Rotation of the horizontal substrate causes radial flow of a liquid film, which thins over time

### NOTE 1 : Boundary Conditions

1. At  $z = 0$  (No slip condition at the substrate);

$$V_r(r, z = 0, t) = 0$$

2. At  $z = h(t)$  (Zero shear stress at the liquid-air interface);

$$\mu \frac{\partial V_r}{\partial z} \Big|_{z=h} = 0 \implies \frac{\partial V_r}{\partial z} \Big|_{z=h} = 0$$

(a)

As in the question, it is given that the  $r$  momentum equation be reduced to

$$\frac{\partial^2 V_r}{\partial z^2} = -\frac{\omega^2 r}{\nu}$$

where  $\omega$  is the angular velocity,  $r$  is the radial distance and  $\nu$  is the kinematic viscosity.

$$\begin{aligned} \int \frac{\partial^2 V_r}{\partial z^2} dz &= - \int \frac{\omega^2 r}{\nu} dz \\ \implies \frac{\partial V_r}{\partial z} &= -\frac{\omega^2 r}{\nu} z + A \\ \int \frac{\partial V_r}{\partial z} dz &= - \int \frac{\omega^2 r}{\nu} z dz + \int A dz \\ \implies V_r &= -\frac{\omega^2 r}{\nu} \frac{z^2}{2} + Az + B \end{aligned}$$

$$\text{Boundary Condition 1} \implies V_r \Big|_{z=0} = 0 = B \implies B = 0$$

$$\text{Boundary Condition 2} \implies \frac{\partial V_r}{\partial z} \Big|_{z=h} = 0 = -\frac{\omega^2 h(t)r}{\nu} + A \implies A = \frac{\omega^2 h(t)r}{\nu}$$

$$\therefore V_r = -\frac{\omega^2 r}{\nu} \frac{z^2}{2} + \frac{\omega^2 h r}{\nu} z$$

$$\boxed{\therefore V_r(r, z, t) = \frac{\omega^2 h^2 r}{\nu} \left[ \left( \frac{z}{h} \right) - \frac{1}{2} \left( \frac{z}{h} \right)^2 \right]}$$

The radial flow rate per unit of circumference is given by  $\frac{q}{2\pi r}$  where  $2\pi r = 1$ , since the unit circumference.

$$\begin{aligned} q &= \int_0^{h(t)} V_r(z, r, t) 2\pi r' dr' \\ \frac{q}{2\pi r'} &= \int_0^{h(t)} V_r(z, r, t) dr' \\ \implies q &= \frac{\omega^2 h^2 r}{\nu} \left[ \frac{r'^2}{2h} - \frac{r'^3}{6h^2} \right]_0^h = \frac{\omega^2 h^2 r}{\nu} \frac{2h}{6} \\ \boxed{\therefore q(r, t) &= \frac{\omega^2 h^3 r}{3\nu}} \end{aligned}$$

(b)

$$\text{Input} + \text{Generation} = \text{Output} + \text{Consumption} + \text{Accumulation}$$



Figure 2: Mass balance with chemical reaction

Here we don't have any input, generation and consumption.

$$\text{Output} + \text{Accumulation} = 0$$

$$M = \text{density} \times \text{volume} = \rho \pi r^2 h$$

$$M_{out} = \text{UnitFlowRate}(q) \times \text{density} \times 2\pi r$$

$$\therefore M_{out} + \frac{dM}{dt} = 0$$

$$\frac{d[\rho \pi r^2 h]}{dt} + 2\pi r \frac{w^2 h^3 r}{3\nu} \rho = 0$$

$$\boxed{\therefore \frac{dh}{dt} = -\frac{2w^2 h^3}{3\nu}}$$

Next, the initial condition is given by  $h(0) = h_0$ . By integrating

$$\begin{aligned} \int \frac{1}{h^3} dh &= -\frac{2\omega^2}{3\nu} \int 1 dt \\ \implies -\frac{1}{2h^2} &= -\frac{2\omega^2}{3\nu} t + C \end{aligned}$$

$$\text{Initial condition} \implies h(0) = h_0 \implies C = -\frac{1}{2h_0^2}$$

$$\begin{aligned} \therefore -\frac{1}{2h^2} &= -\frac{2\omega^2}{3\nu} t - \frac{1}{2h_0^2} \\ \implies \frac{1}{h^2} &= \frac{4\omega^2}{3\nu} t + \frac{1}{h_0^2} \\ \implies h^2 &= \frac{3\nu h_0^2}{4\omega h_0^2 t + 3\nu} \end{aligned}$$

$\therefore$  The thickness of the fluid film as a function of time is given by,

$$\boxed{h(t) = \frac{1}{\sqrt{\frac{4\omega^2}{3\nu} t + \frac{1}{h_0^2}}}}$$

### (c) Usage of the order of magnitude estimates

1. **Regard the flow as Pseudosteady :** The time scale over which the film thickness changes significantly is given by  $T_h = \frac{h}{|dh/dt|}$  where units are  $[T_h] = \frac{m}{m/s} = s$ . Also the time scale for momentum diffusion across the film thickness is given by  $T_m = \frac{h^2}{\nu}$  where units are  $[T_m] = \frac{m^2}{m^2/s} = s$ . For the flow to be considered pseudosteady then the film thickness changes slowly compared to the momentum diffusion time. *i.e.*

$$\frac{T_h}{T_m} = \frac{\nu}{h|dh/dt|} = \frac{3\nu^2}{2\omega^2 h^4} \gg 1$$

$$\therefore \frac{h^2 \omega}{\nu} \ll 1$$

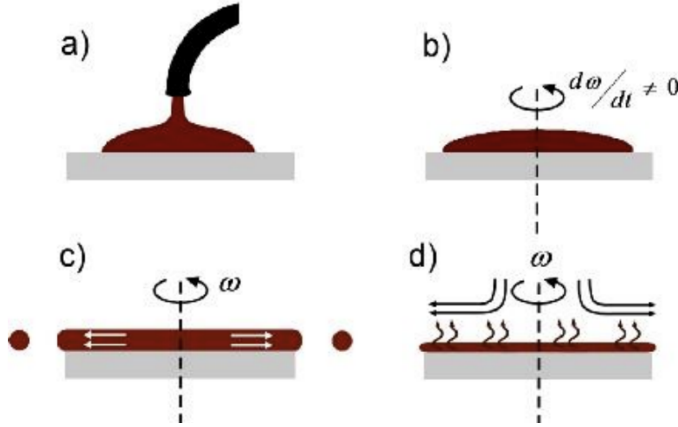


Figure 3: Four distinct stages(dispense, spin up -low speed, spin off -high speed and evaporation) to spin coating (Hellstrom 2007)

2. **Neglect the remaining inertial terms in the r-momentum equation :** To neglect the inertial term(convective acceleration), the Reynold Number( $Re$ )  $\ll 1$ . *i.e.* A small Reynolds number demonstrates that viscous forces dominate over inertial forces.

$$Re := \frac{\rho V_r h}{\mu} = \frac{V_r h}{\nu}$$

According the Spin Coating problem and from the Navier-Stokes equation in cylindrical coordinated  $r$  components we can write

- Inertial term( Convective Acceleration)  $= \rho V_r \frac{\partial V_r}{\partial r} \sim \rho V_r \frac{V_r}{r}$  because  $V_r$  varies with  $r$  weakly and we can estimate  $\frac{\partial V_r}{\partial r} \sim \frac{V_r}{r}$ .
- Viscous term  $= \mu \frac{\partial^2 V_r}{\partial z^2} \sim \mu \frac{V_r}{h^2}$

The inertial term is negligible when,

$$\rho V_r \frac{V_r}{r} \ll \mu \frac{V_r}{h^2}$$

$$\implies \frac{\rho V_r h^2}{\mu r} \ll 1$$

From part (a), when  $z = h$  we can write  $V_r = \frac{\omega^2 h^2 r}{2\nu}$

$$\implies \frac{\rho \omega^2 h^4}{2\nu \mu} = \frac{\omega^2 h^4}{2\nu^2} \ll 1$$

$$\boxed{\therefore Re := \frac{\omega^2 h^4}{2\nu^2} \ll 1}$$

units are given by  $[Re] = \frac{1/s^2 \cdot m^4}{m^4/s^2} = 1$

### 3. Neglect the absent viscous term in the r-momentum equation :

**IMPORTANT :** Here the objective is to neglect radial viscous terms compared to axial viscous terms. I faced difficulties to figure that out. But since we are using Lubrication Approximations and this approximation is based on certain assumptions due to the geometry and flow characteristics of thin films, we have

$$\frac{h}{r} \ll 1$$

$\therefore$  Gradients in the axial direction are much larger than gradients in the radial direction.

$$\frac{\partial}{\partial z} \gg \frac{\partial}{\partial r}$$

From the Navier-Stokes equation in cylindrical coordinated r components we can have

- Dominating axial viscous term  $= \mu \frac{\partial^2 V_r}{\partial z^2} \sim \mu \frac{V_r}{h^2}$
- Negligible radial viscous term  $= \mu \left( \frac{\partial^2 V_r}{\partial r^2} + \frac{1}{r} \frac{\partial V_r}{\partial r} - \frac{V_r}{r^2} \right) \sim \mu \frac{V_r}{r^2}$

$\therefore$  The ratio implies

$$\frac{V_r/r^2}{V_r/h^2} \ll 1$$

$$\boxed{\therefore \frac{h}{r} \ll 1}$$

**NOTE 2 :** Explanation of why does the axial viscous term cannot be negligible. In thin films the velocity changes significantly across the film thickness  $h$ . The axial velocity gradient  $\frac{\partial V_r}{\partial z}$  is large. This results in significant shear stress  $\tau_{rz} = \mu \frac{\partial V_r}{\partial z}$ . Also the r momentum equation simplifies to

$$\rho \omega^2 r = \mu \frac{\partial^2 V_r}{\partial z^2}$$

where  $\rho \omega^2 r = \text{Centrifugal Force}$ .

If we neglect the axial viscous term then the equation reduces to  $0 = \rho \omega^2 r$  which is a contradiction. Ergo, the axial term cannot be neglected.

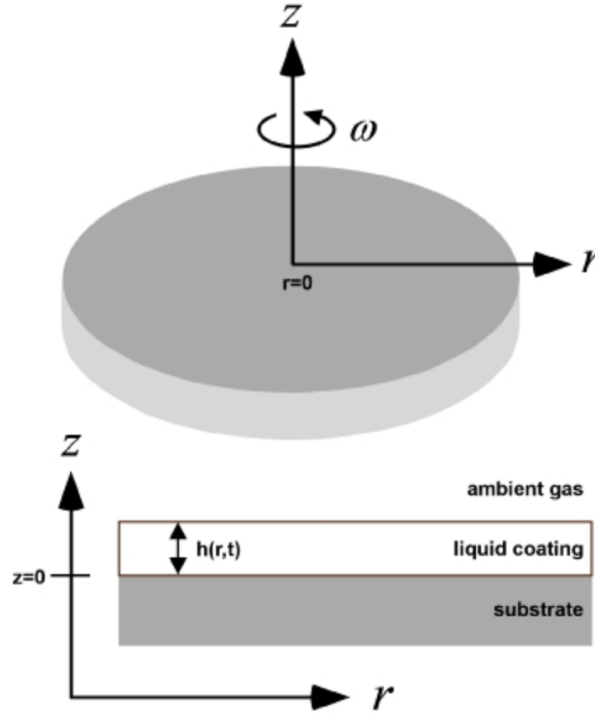


Figure 4: Schematic illustrating the spin coating problem with relevant variables.

**NOTE 3 :** In Figure 4, geometrically we can say that the radial viscous term is negligible because of the lower gradient compares to the axial gradient.

4. **Neglect  $\frac{\partial P}{\partial r}$  :**

The r-momentum equation can be written as

$$\rho \left( \frac{\partial V_r}{\partial t} - V_r \frac{\partial V_r}{\partial r} + V_z \frac{\partial V_z}{\partial z} - \frac{V_\theta^2}{r} \right) = -\frac{\partial P}{\partial r} + \mu \left( \frac{\partial^2 V_r}{\partial r^2} + \frac{1}{r} \frac{\partial V_r}{\partial r} - \frac{V_r}{r^2} + \frac{\partial^2 V_r}{\partial z^2} \right)$$

This r-momentum equation is simplified to this equation

$$0 = -\frac{\partial P}{\partial r} + \rho\omega^2 r + \mu \frac{\partial^2 V_r}{\partial r^2}$$

According to the given criteria, the centrifugal force should dominate. *i.e.*

$$\boxed{\rho\omega^2 r \gg \left| \frac{\partial P}{\partial r} \right|}$$

To be more specific, we have to keep the  $\mu \frac{\partial^2 V_r}{\partial r^2}$  because it represents the axial viscous term. According to the given problem the boxed above argument should be hold to represent the given logic.

**5. Assume that  $V_\theta$  is independent of  $z$  :**

- Viscous diffusion time in  $\theta$  direction;  $T_{diff} = \frac{h^2}{\nu}$ . Units are,  $[T_{diff}] = \frac{m^2}{m^2/s} = s$
- Time scale of rotation;  $T_\omega = \frac{1}{\omega}$ . Units are,  $[T_\omega] = \frac{1}{1/s} = s$

The viscous effect is negligible if the time scale for viscous diffusion must be much larger than the rotational time scale,

$$\frac{T_{diff}}{T_\omega} = \frac{h^2/\nu}{1/\omega} \gg 1$$

$$\therefore \frac{h^2\omega}{\nu} \gg 1$$

**NOTE 4 :** The Reynolds Number( $Re$ ) =  $\frac{h^2\omega}{\nu}$ . Units are  $[Re] = \frac{m^2 \cdot 1/s}{m^2/s} = 1$ . For  $V_\theta$  to be independent of  $z$  we need,

$$\boxed{Re = \frac{h^2\omega}{\nu} \gg 1}$$

## (d) Plugging values and the calculations

Given Parameters :

- Kinematic viscosity ( $\nu$ ) :  $0.001 - 0.01 \frac{m^2}{s}$
- Initial film thickness ( $h_0$ ) =  $1 \times 10^{-3}m$
- Final film thickness ( $h_p$ ) :  $1 - 10\mu m = 1 \times 10^{-6} - 1 \times 10^{-5}m$
- Angular velocity ( $\omega$ ) :  $1000 - 5000rpm$

- Substrate radius ( $R$ ) :  $10cm = 0.1m$
- Process time ( $t_p$ ) :  $10 - 60s$
- Density ( $\rho$ )  $\approx 1000kg/m^3$
- Converting angular velocity to rad/s :

$$\omega(rad/s) = \omega(rpm) \times \frac{2\pi}{60}$$

$$\omega_1 = 1000rpm \implies \omega_1 = 1000 \times \frac{2\pi}{60} = 104.72rad/s$$

$$\omega_2 = 5000rpm \implies \omega_2 = 5000 \times \frac{2\pi}{60} = 523.60rad/s$$

### 1. Regarding the flow as Pseudosteady :

- **Case 1** :  $h_0$

- when  $\nu_1, \omega_1$  are here,  $\frac{\omega_1 h_0^2}{\nu_1} = \frac{104.72 \times (1 \times 10^{-3})^2}{0.001} = 0.10472$
- when  $\nu_2, \omega_2$  are here,  $\frac{\omega_2 h_0^2}{\nu_2} = \frac{523.60 \times (1 \times 10^{-3})^2}{0.01} = 0.05236$

- **Case 2** :  $h_p$

- when  $\nu_1, \omega_2$  are here,  $\frac{\omega_2 h_0^2}{\nu_2} = \frac{523.60 \times (1 \times 10^{-6})^2}{0.001} = 5.236 \times 10^{-4}$

**CONCLUSION 1:** The case I considered, all are

$$\frac{h^2 \omega}{\nu} \ll 1$$

Ergo, the flow can be considered Pseudosteady.

### 2. Neglect the remaining inertial terms in the r-momentum equation :

The Reynold number is given by

$$Re = \frac{\omega^2 h^4}{2\nu^2}$$

- This part also similar to the above part.
- After plugging values for different cases we get values much less than one.

**CONCLUSION 2:** Inertial terms in the r-momentum equation can be neglected

$$Re \ll 1$$



### 3. Neglect the radial viscous term in the r-momentum equation :

Let's check  $\frac{h}{r} \ll 1$

- $h = h_0 = 1 \times 10^{-3} \implies \frac{h}{r} = \frac{1 \times 10^{-3}}{0.1} = 0.01 \ll 1$
- $h = h_0 = 1 \times 10^{-6} \implies \frac{h}{r} = \frac{1 \times 10^{-6}}{0.1} = 1 \times 10^{-5} \ll 1$

**CONCLUSION 3:** Radial viscous terms can be neglected.

### 4. Neglect $\frac{\partial P}{\partial r}$ :

Here plugging values for the pressure gradient is challenging. So, I come up with this methodology. The Surface Tension due to the pressure gradient

$$\left| \frac{\partial P}{\partial r} \right| \sim \frac{\sigma h}{r^3}$$

where  $\sigma$  is the surface tension. This came from

- In spin coating the curvature is primarily from the radial direction  $P = \frac{\sigma}{R_r}$  where  $R_r$  is the radial direction.
- The curvature  $\kappa_r$  of the film surface in the radial direction is given by  $\kappa_r = \frac{1}{R_r} = -\frac{\partial^2 h}{\partial r^2}$  where the film thickness  $h(r)$ .
- The radial pressure gradient due to surface tension is

$$\frac{\partial P}{\partial r} = \sigma \frac{\partial}{\partial r} \left( \frac{1}{R_r} \right) = -\sigma \frac{\partial^3 h}{\partial r^3}$$

•

$$\frac{\partial h}{\partial r} \sim \frac{h}{r} \implies \frac{\partial^3 h}{\partial r^3} \sim \frac{h}{r^3}$$

•

$$\therefore \left| \frac{\partial P}{\partial r} \right| \sim \frac{\sigma h}{r^3}$$

Using the previous case in section (c - 4) we can write

$$\begin{aligned} \left| \frac{\partial P}{\partial r} \right| &\sim \frac{\sigma h}{r^3} \ll \rho \omega^2 r \\ \implies \frac{\sigma h}{\rho \omega^2 r^4} &\ll 1 \end{aligned}$$

**CONCLUSION 4:** Need to know the values for  $\sigma$  to find this is acceptable or not.

5. **Assume that  $V_\theta$  is Independent of  $z$  :**

The checking criteria is

$$Re = \frac{h^2\omega}{\nu} \gg 1$$

We check this in part 1. Ergo, this is not valid.

**CONCLUSION 5:** Not Met.  $V_\theta$  is dependent on  $z$  and the viscous diffusion affects the azimuthal velocity profile.

## Problem 2 : Paper reading and related problems

### (1.) Define and discuss the significance of the objective/focus of the assigned paper

The paper focuses on spin coating, a widely used technique for applying thin films of polymer solutions onto substrates and aims to improve the predictive understanding of the process. Specifically, the paper investigates the behavior of a PMMA (polymethylmethacrylate)/chlorobenzene solution during spin coating. Its main objective is to develop a simple yet accurate model that predicts the final dry film thickness based on measurable physical properties without relying on empirical parameters or complex numerical simulations. The study improves upon existing models (Meyerhofer's model) by including the effects of solvent evaporation with changes in viscosity during the convective outflow stage. This allows to predict film thicknesses based on the liquid's physical properties, spin speed, and solvent behavior. By integrating concepts like binary diffusivity, viscosity modeling and vapor liquid equilibrium, the paper enhances the theoretical understanding of spin coating. This contributes to a more comprehensive understanding of coupled mass and momentum transfer phenomena during film formation.

### (2.) The theoretical methods and experimental data that the authors used to approach the problem

**\* Assumptions :**

1. **Uncoupled System** : Both convective outflow and evaporation stages are uncoupled.
2. **Thin film approximation** : The film is assumed to be sufficiently thin that the gravitational effects on the film are negligible and the inertial effects of the liquid flow are ignored.
3. **Constant physical properties** : Density( $\rho$ ), diffusivity( $D_g$ ) in the solvent in air and kinematic viscosity ( $\nu_g$ ) of the gas are constant during the spin coating process.

4. **Radial uniformity** : The film is assumed to be radially uniform. Thickness does not vary with radial position and evaporation occurs uniformly across the surface.
5. **Viscosity** : The viscosity is treated as a function of solvent concentration and shear rate (via a Carreau-like model).
6. **Temperature** : The temperature variations due to evaporation or spinning are considered negligible. The liquid's temperature is assumed to remain nearly constant throughout the process.
7. **Steady state evaporation** : During the evaporation stage, the evaporation rate is assumed to reach a steady state value governed by the concentration gradient and the mass transfer coefficient.
8. **Neglect of airflow effects** : The air above the film is assumed to be quiescent with no turbulence or airflow.
9. **Simplified mass transfer coefficient  $\bar{k}$**  : Assumes laminar airflow and constant diffusivity which may not hold for turbulent or complex environmental conditions.

**\* Theoretical Methods :**

1. **Stages** : There are two stages in the spin-coating process
  - Convective Outflow Stage: Film thinning due to centrifugal forces

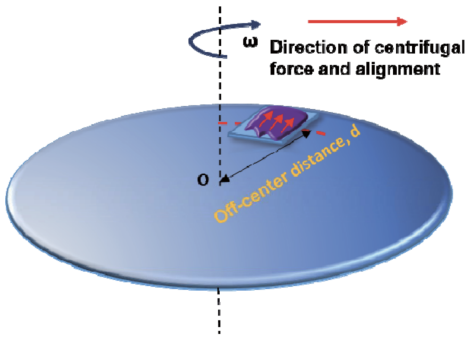


Figure 5: Schematic illustrating of the center centrifugal force

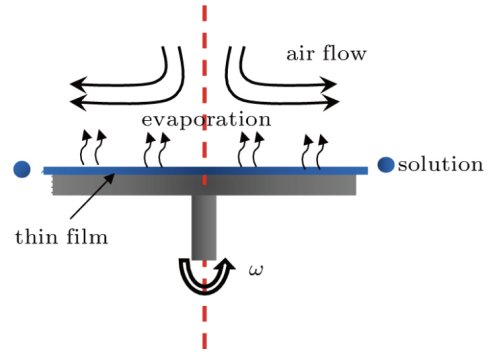


Figure 6: Schematic diagram of process for evaporation, solution spin coating

- Evaporation Stage: Film thinning due to solvent evaporation.

These stages are treated sequentially with mathematical models developed for each.

2. **Convective outflow** : The thinning rate during the convective outflow stage is derived from the balance of centrifugal force and viscous resistance.

$$\frac{\partial h}{\partial t} = -\frac{2\rho\omega^2 h^3}{3\eta_0} \quad (1)$$

where

- $h$  = film thickness
- $\rho$  = density of the liquid
- $\omega$  = angular velocity
- $\eta_0$  = initial viscosity of the solution

This (1) assumes that the solvent concentration is constant during this stage and equation has been derived earlier with  $\nu = \frac{\eta_0}{\rho}$ . This is proved in problem 1 – (b).

3. **Evaporation** : The film thinning is driven by solvent evaporation.

$$\frac{\partial h}{\partial t} = -k(x_A^0 - x_{A\infty}) \quad (2)$$

where

- $k$  = mass transfer coefficient
- $x_A^0$  = initial concentration of solvent in the coating liquid
- $x_{A\infty}$  = mass fraction of solvent in the coating liquid

4. **Viscosity model (Carreau-like model)** :

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)[1 + (\lambda\dot{\gamma})^2]^n \quad (3)$$

where

- $\eta_0$  = zero shear viscosity
- $\eta_\infty$  = infinite shear viscosity
- $\dot{\gamma}$  = shear rate
- $\lambda$  = relaxation time

The model expresses how viscosity changes with solvent concentration and shear rate.

5. **Solvent Concentration Dependence of Viscosity** :

$$\eta_0 = \eta_0^A \exp\left[\eta_0^B(1 - x_s)\right] \quad (4)$$

where

- $x_s$  = solvent mass fraction
- $\eta_b^0$  = constant
- $\eta_A^0$  = viscosity of the pure solvent at low shear
- $\eta_0$  = low shear viscosity

we can replace  $\eta_0$  by  $\eta_\infty$  to get the high shear viscosity with  $\eta_A^0$  by  $\eta_\infty^A$ . The high shear viscosity  $\eta_\infty$  and low shear viscosity  $\eta_0$  are both functions of the solvent mass fraction  $x_s$ .

#### 6. Vapor Liquid Equilibrium (using Flory-Huggins theory) :

$$p_s = p_s^0 \exp[\ln x_s + (1 - x_s) + \chi(1 - x_s)^2] \quad (5)$$

where

- $p_s$  = solvent partial pressure,
- $p_s^0$  = vapor pressure of pure solvent
- $x_s$  = solvent mass fraction
- $\chi$  = Flory-Huggins interaction parameter.

This equation is used to calculate the equilibrium concentration of the solvent.

7. **Binary diffusivity** : Since direct data for PMMA/chlorobenzene is unavailable, the binary diffusivity of the solvent in the polymer solution is estimated empirically based on related systems.

$$D = (7.24 \times 10^{-7} \text{ cm}^2/\text{s}) \exp\left(-\frac{0.240}{0.0277 + x_s^{2.19}}\right) \quad (6)$$

This captures the concentration dependent diffusivity.

#### 8. Wet film thickness :

$$h_{wet} = \left[ \left( \frac{3\eta_0}{2\rho\omega^2} \right) k(x_A^0 - x_{A\infty}) \right]^{\frac{1}{3}} \quad (7)$$

where  $k = \bar{k}\omega^{1/2}$

#### 9. Dry film thickness :

$$h_f = (1 - x_A^0) h_{wet}$$

$$h_f = (1 - x_A^0) \left[ \left( \frac{3\eta_0}{2\rho} \right) \bar{k}(x_A^0 - x_{A\infty}) \right]^{\frac{1}{3}} \frac{1}{\omega^{1/2}} \quad (8)$$

$$\bar{k} = \left( \frac{cD_g}{\nu_g^{1/2}\rho} \right) \left( \frac{p_A^* M_A}{RT} \right) \quad (9)$$

where

- $c$  = constant which depends on the Schmidt number
- $D_g$  = binary diffusivity of the solvent in the overlying gas
- $\nu_g$  = kinematic viscosity of the overlying gas
- $p_A^*$  = vapor pressure of pure solvent A at temperature T
- $R$  = ideal gas constant
- $M_A$  = molecular weight of solvent A

**\* Comparison between models :** Here with I'm gonna compare the Meyerhofer's model with the new modified model by Bornside in the paper I.

Aspect	Meyerhofer's Model	Modified Model by Bornside
Evaporation in Convective Stage	Unknown Parameter	Computed
Viscosity Assumptions	Assumed constant during convective stage	Assumed constant during convective stage
Coupling Between Stages	None: Stages are independent	None
Accuracy	Underpredicts film thickness, especially at high solids	Better but still underpredicts at high solids due to simplified treatment of evaporation

**\* Derivation of equations 2, 7 and 8 :** The rate of evaporation depends on how quickly the evaporated molecules can leave the vicinity of the liquid surface. Diffusion governs how efficiently the solvent vapor can move away from the liquid surface. Fick's first law of diffusion gives a constitutive equation to describe the rate at which molecules diffuse. The equation is given below:

$$J = D \frac{C_s - C_\infty}{\delta}$$

where

- $J$  = Molar diffusive flux
- $D$  = Diffusivity
- $C_s$  = Solvent concentration at the surface

- $C_\infty$  = Solvent concentration far away
- $\delta$  = Diffusive length

Expressing the flux in terms of mass fraction, using the ideal gas law we have

$$c = \frac{p_A}{RT}$$

where

- $p_A$  = partial pressure of solvent vapor
- $R$  = Gas constant
- $T$  = Temperature

Then substituting above two equation as well as multiplying through by molecular weight ( $M_A$ ) to convert to mass flux ( $\dot{m}$ ) gives

$$\dot{m} = \frac{DM_A}{RT} \frac{p_A - p_{A\infty}}{\delta}$$

This is further expressed using mass fraction by using Raoult's law which gives this relationship

$$p_A = x_A p_{A,sat}$$

where

- $p_{A,sat}$  is saturation pressure of the solvent

$$\dot{m} = \frac{DM_A}{RT} \frac{p_{A,sat}(x_A^0 - x_\infty^0)}{\delta}$$

We can absorb the constants and express it with a single variable,  $k$

$$k = \frac{DM_A}{RT\delta} p_{A,sat}$$

So we have,

$$\boxed{\therefore \dot{m} = k(x_A^0 - x_\infty^0)}$$

which is same as equation (2).

The equation for  $h_{wet}$  is derived by analyzing the balance between the convective outflow thinning rate and the evaporation rate when the transition occurs. The key idea is to determine the point at which the radial flow of the liquid due to centrifugal forces slows to the point where evaporation becomes the primary mechanism for thinning. The equation

(1) governs the rate of thinning due to radial outflow and depends on the film's thickness  $h$  and the liquid's viscosity. The equation (2) describes how the film thickness decreases due to the evaporation of solvent. At the transition point between the two stages

$$\text{Convective Outflow Rate} = \text{Evaporation Rate}$$

$$\frac{2\rho\omega^2 h^3}{3\eta_0} = k(x_A^0 - x_{A\infty})$$

$$\Rightarrow h_{wet} = \left[ \left( \frac{3\eta_0}{2\rho\omega^2} \right) k(x_A^0 - x_{A\infty}) \right]^{\frac{1}{3}}$$

which is same as the equation (7).

- **Wet film thickness**  $h_{wet}$  : thickness of the film when convection ceases and evaporation starts.
- **Dry film thickness**  $h_f$  : represents only the solid content that remains after the solvent has completely evaporated.
- **Mass fraction**  $x_A^0$  : mass fraction of the solvent in the wet film.
- **Mass fraction**  $(1 - x_A^0)$  : mass fraction of the solid (polymer).

The volume of the film per unit area (thickness) can be expressed in terms of the mass fraction and the density of the components

$$h_{wet} = \frac{m_{solid} + m_{solvent}}{\rho_{solid}}$$

where

- $m_{solid}$  : mass of the solid (polymer)
- $\rho_{solid}$  : density of the solid
- $m_{solvent}$  : mass of the solvent

After evaporation, the solvent mass  $m_{solvent}$  is removed

$$\therefore h_f = \frac{m_{solid}}{\rho_{solid}} = \left( \frac{m_{solid} + m_{solvent}}{\rho_{solid}} \right) \left( \frac{m_{solid}}{m_{solid} + m_{solvent}} \right)$$

The mass fraction of the solvent in the wet film is given by

$$x_A^0 = \frac{m_{solvent}}{m_{solvent} + m_{solid}}$$



$$\therefore 1 - x_A^0 = \frac{m_{solid}}{m_{solvent} + m_{solid}}$$

Ergo, we can write

$$h_f = h_{wet}(1 - x_A^0)$$

Next,  $k$  and  $\bar{k}$  is also defined like  $k = \bar{k}\omega^{1/2}$  and  $\bar{k}$  is given by the equation (9). After substituting  $k$  values to equation (7) we get

$$h_{wet} = \left[ \left( \frac{3\eta_0}{2\rho\omega^{3/2}} \right) \bar{k}(x_A^0 - x_{A\infty}) \right]^{\frac{1}{3}}$$

$$\Rightarrow h_f = (1 - x_A^0) \left[ \left( \frac{3\eta_0}{2\rho} \right) \bar{k}(x_A^0 - x_{A\infty}) \right]^{\frac{1}{3}} \frac{1}{\omega^{1/2}}$$

which is same as the equation (8).

**\* Potential limitations or errors of the model and experimental data :**

- **Neglect of evaporation during convective outflow :** The model assumes evaporation and convective thinning occur sequentially with evaporation becoming dominant only after the convective outflow ceases. Neglecting evaporation during the convective stage causes the model to underpredict  $h_f$  particularly for solutions with high solid concentrations as solvent evaporation increases viscosity and slowing thinning.
- **Steady state assumption for evaporation :** Evaporation is treated as a steady state process which depends on the concentration gradient. In reality, evaporation rates may fluctuate due to transient temperature or concentration changes.
- **Constant Physical Properties :** This assumes density, diffusivity and other physical properties remain constant during each stage. Spin coating timescales are short and such assumptions simplify the equations. But as a consequence the viscosity changes significantly with solvent evaporation which is only partially addressed using an empirical concentration dependent formula which describes in equation (1), (3), (4).
- **Radial Uniformity :** Assumes the film thickness is radially uniform and ignores edge effects. The high spin speed tends to minimize radial variations in ideal conditions. In real world applications like edge effects, turbulent airflow may cause deviations from uniformity.
- **Measurement Uncertainty :** Viscosity, diffusivity and vapor pressure values are either taken from literature or measured under separate conditions. As a consequence any errors or mismatches between the experimental and modeled conditions propagate into the results affecting accuracy, which will describe next from the recreation of the figure 3 in the original paper.

- **Environmental Factors :** The model assumes quiescent air conditions with negligible solvent vapor in the bulk gas. In the real world factors such as airflow, turbulence buildup in the surrounding air can alter evaporation rates and concentration gradients.
- **Validation of the dataset :** Experiments focus on a narrow range of spin speeds, polymer concentrations and solvent systems. The model's applicability to other polymers, solvents or extreme conditions remains untested.

\* **Challenges to foundational concepts :**

- **Derivation of  $h_{wet}$  :** The derivation of wet film thickness assumes constant viscosity during convective outflow which is ignoring solvent evaporation. This leads to overestimated thinning rates and underpredicted dry film thicknesses.
- **Sequential stages assumption :** The assumption that evaporation and convective thinning are independent and sequential stages simplifies the model but neglects their coupling in reality. Physically the evaporation occurs throughout the convective stage which dynamically affecting viscosity and flow. Coupling these effects would improve accuracy but increase complexity.
- **Mass transfer coefficient  $\bar{k}$  :** The derivation of  $\bar{k}$  uses the combination of the Raoult's law for vapor liquid equilibrium and laminar flow assumptions. This works well for ideal conditions but may fail for turbulent systems or solvents with highly non linear evaporation characteristics.

\* **Recreating the figure 3 in the original paper :**

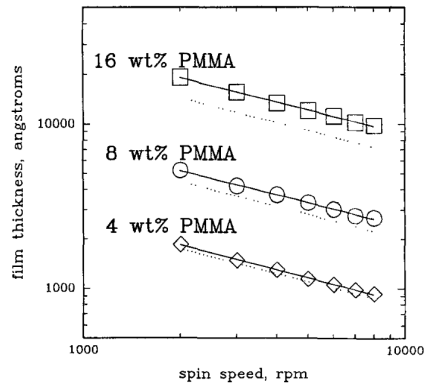


Figure 7: Original Figure 3 in the paper, Bornside et al.

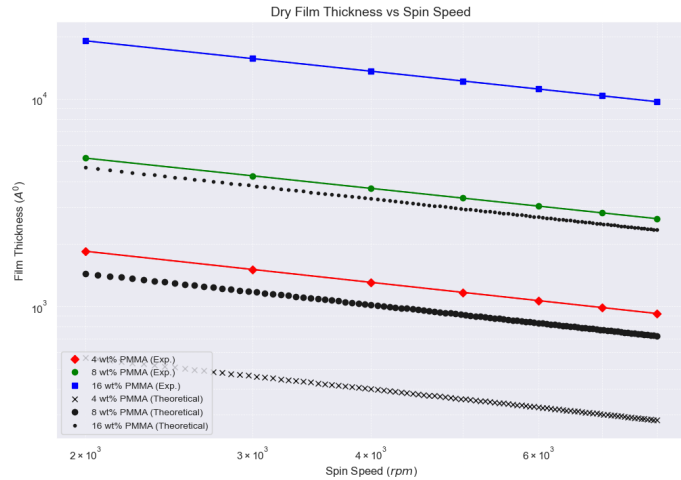


Figure 8: Dry Film Thickness vs Spin Speed. Recreated Figure using  $h_f$  theoretical and experiment values exacted from the original figure.

**IMPORTANT :** The code is in Jupyter Notebook and I attached the code with this.

**NOTE 5 :** As mentioned in the paper, the theoretical values are always less than the experimental values in Figure 8. This is because the model neglects solvent evaporation and the corresponding increase in the viscosity of the coating liquid during the spin off stage.

```
====Regression Results (Experimental Data)====  
4 wt% PMMA:  
Slope: -0.4989, Intercept: 4.9130  
8 wt% PMMA:  
Slope: -0.4850, Intercept: 5.3160  
16 wt% PMMA:  
Slope: -0.4873, Intercept: 5.8890
```

Above, the slope I found for the each w/o percentage using Liner Regression method.

**(3.) The technical soundness of the approach used and identify the possible gaps in either the modeling or experiments. Propose or identify existing research efforts that attempt to rectify these deficiencies.**

- **Model strength :** The model successfully combines Meyerhofer's convective outflow model with additional considerations for evaporation, producing an accessible semi-empirical framework for predicting dry film thickness. By introducing solvent mass fraction and a concentration dependent viscosity model this approach partially addresses the dynamic interplay between evaporation and flow. This model is validated with experimental data for PMMA/chlorobenzene films which is providing confidence in its applicability to similar polymer solvent systems.
- **Model weaknesses :** Treating convective outflow and evaporation as independent the sequential processes neglects their real time coupling which leads to potential inaccuracies in high solid concentration systems. Key parameters such as the mass-transfer coefficient  $\bar{k}$  rely on empirical correlations rather than direct measurements so limiting generalizability.
- **Experimental strength :** The use of controlled spin speeds ensures reliable data collection for validating the model. The approach aligns well with experimental methodologies used in prior spin coating studies such as those by Meyerhofer.
- **Experimental weaknesses :** The experiments focus on a specific polymer solvent system (PMMA/chlorobenzene) and a narrow range of spin speeds and solid concentrations which limit the general applicability. Assumptions of negligible solvent vapor buildup may not hold in practical spin coating environments where airflow and turbulence could significantly impact evaporation rates.

- **Gap in modeling :** The model does not couple evaporation and convective flow dynamics which is neglecting how solvent loss during the convective stage impacts viscosity and flow. This leads to underprediction of the dry film thickness particularly at high solid concentrations.
- **Gap in experiments :** The validation experiments are restricted to PMMA/chlorobenzene and may not generalize to other polymers or solvents with different viscosities or evaporation rates.

**\* Proposals :**

1. Coupled evaporation flow models.
2. Include time dependent changes in physical properties (e.g. viscosity, diffusivity) and transient evaporation rates to capture non equilibrium dynamics.
3. Test the model across a wider range of polymers, solvents and spin speeds to enhance its generality.
4. Use real-time measurement techniques to monitor viscosity and solvent concentration during spin coating.
5. Introduce controlled airflow or turbulence in the experimental setup to mimic real world conditions and study their effects on evaporation and film uniformity.

While the model and experimental approach in the paper provide valuable insights into spin coating dynamics they simplify several critical processes particularly the coupling between evaporation and convective flow. These simplifications limit the accuracy of the predictions especially for high solid concentrations or non ideal polymer solvent systems. Future research should focus on coupled models, transient effects and broader experimental validation. Additionally, adopting advanced vapor liquid equilibrium models and dynamic measurement techniques could significantly improve both the theoretical and experimental understanding of spin coating.

## References

- [1] D. E. Bornside et al , *Spin Coating of a PMMA/Chlorobenzene Solution*. J. Electrochem. Soc. 138 317, Journal of The Electrochemical Society, 1991.
- [2] D. Meyerhofer , J. Appl. Phys., 49, 3993, Journal of The Electrochemical Society, 1978.