Mathematical Problems in Industry (MPI) Workshops
W.L. Gore & Associates Presentation
Drying in Porous Media

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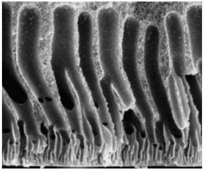
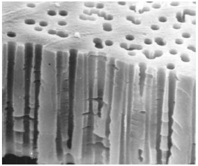
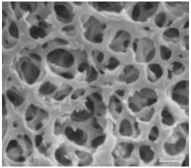
June 18, 2021

Membrane filters

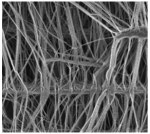


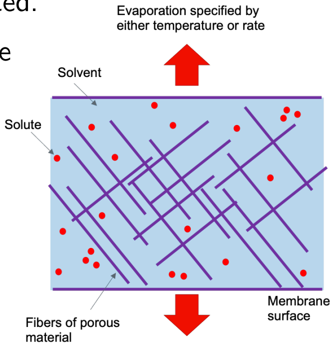
- Membrane filters: Thin layers of porous media, through which “feed solution”, carrying particles, passes. Designed to remove particles of a certain size range from the feed.

Problem presented by W.L. Gore & Associates

- We have a porous material that is filled with a liquid solution containing solute molecules (can be multiple species) with known concentration. As the solvent evaporates solute molecules deposit on the internal pore walls within the material.



- Develop a mathematical model that will predict the mass distribution of solutes inside a porous medium after the solvent has evaporated.
- How does the mass distribution change upon subsequent cycles of wetting?
- How do the porosity and pore size distribution, the initial concentration of solute species and evaporation rate affect the solute distribution?



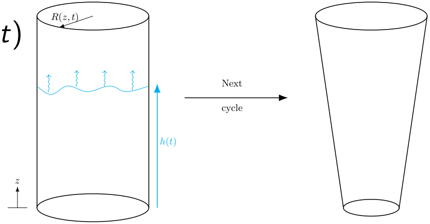
Extension of MPI 2020 model for particle deposition

- Coupled eqns for particle conc $C(z,t)$ and pore radius $R(z,t)$.
- Evolution of pore radius, initial condition $R(z,0) = R^0(z)$,

$$\frac{\partial R}{\partial t} = -\chi Q_w(C), \quad 0 \le z \le h(t).$$

- Flat evaporation interface, $z = h(t)$ (neglect curved meniscus)

$$\frac{dh}{dt} = -E.$$



- Reduced reaction diffusion equation, initial condition $C(z,0) = C^0(z)$,

$$\begin{cases} \dfrac{\partial}{\partial t}(CR^2) = D\dfrac{\partial}{\partial z}\left(R^2\dfrac{\partial C}{\partial z}\right) - 2RQ_w(C), & 0 \le z \le h(t), \\ D\dfrac{\partial C}{\partial z} + \dfrac{dh}{dt}C = 0 \quad \text{at } z = h, & D\dfrac{\partial C}{\partial z} = 0 \quad \text{at } z = 0. \end{cases}$$

Extension of MPI 2020 model

- Change of variables for fixed computational domain

$$\hat{C}(y,t) = C(z,t), \quad \hat{R}(y,t) = R(z,t),$$

where $z = h(t)y$ with $0 \leq y \leq 1$.

- Explicit time-stepping finite-difference numerics in MATLAB.

Fixed-domain BVP on $0 \leq y \leq 1$:

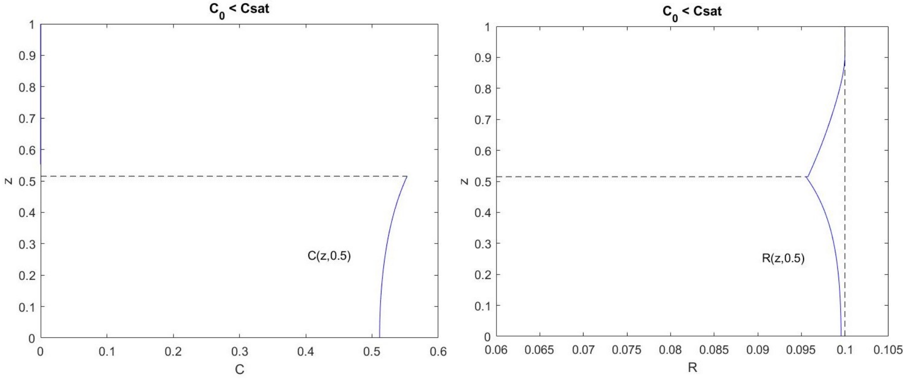
- Change of radius eqn:

$$\frac{\partial \hat{R}}{\partial t} - \frac{h'}{h} y \frac{\partial \hat{R}}{\partial y} = -\chi Q_w(\hat{C}).$$

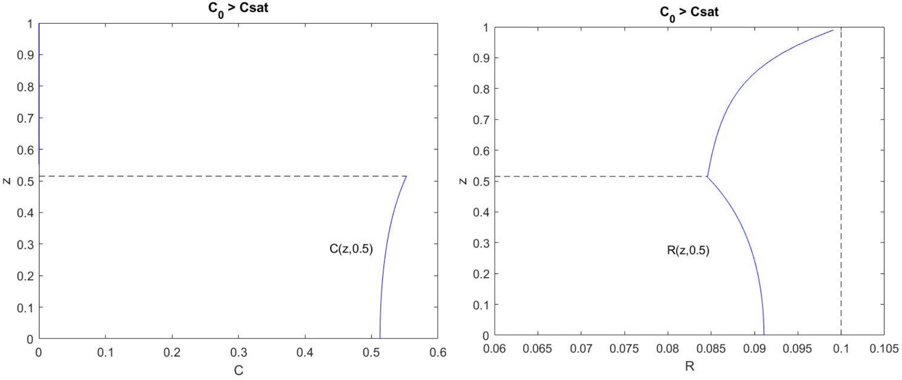
- Reaction diffusion eqn:

$$\begin{cases} \dfrac{\partial(\hat{C}\hat{R}^2)}{\partial t} - \dfrac{h'}{h} y \dfrac{\partial(\hat{C}\hat{R}^2)}{\partial y} = \dfrac{D}{h^2}\dfrac{\partial}{\partial y}\left(\hat{R}^2 \dfrac{\partial \hat{C}}{\partial y}\right) - 2\hat{R}Q_w(\hat{C}), \\ \dfrac{D}{h}\dfrac{\partial \hat{C}}{\partial y} + h'\hat{C} = 0 \quad \text{at } y = 1, \qquad \dfrac{\partial \hat{C}}{\partial y} = 0 \quad \text{at } y = 0. \end{cases}$$

Results: deposition from under-saturated fluid



Results: deposition from over-saturated fluid

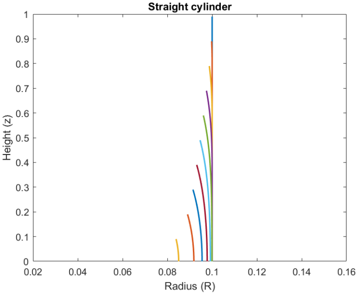


Results: pore radius/deposited particles

Uniform vs conical (slanted) pore

$$E = 1, D = 1, \chi = 0.8, \lambda = 1, C_{sat} = 0.5, C_0 = 0.45,$$

$$R_{uni_0} = 0.1, R_{con_0} = 0.1 + 0.1(y - 0.5).$$

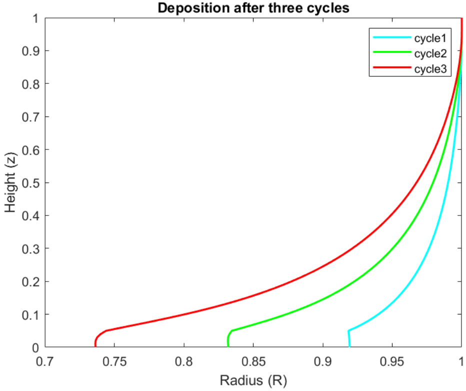


Results

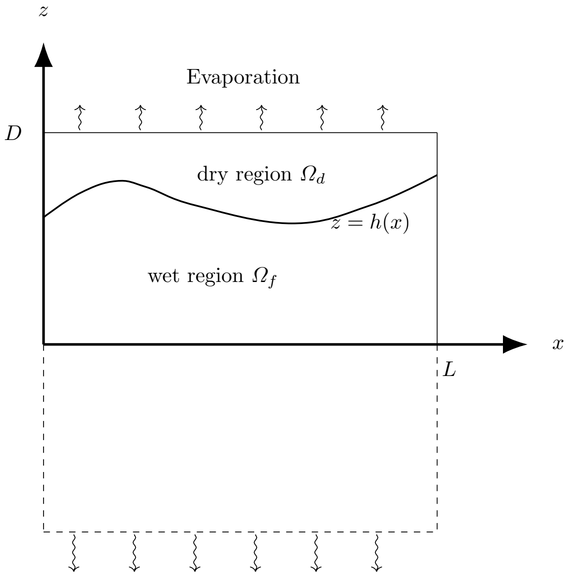
Results: deposition for repeated wetting/drying cycles

Three cycles:

$$E = 1, D = 1, \chi = 0.8, \lambda = 1, C_{sat} = 0.5, C_0 = 0.45, R_0 = 1$$



Macroscopic model

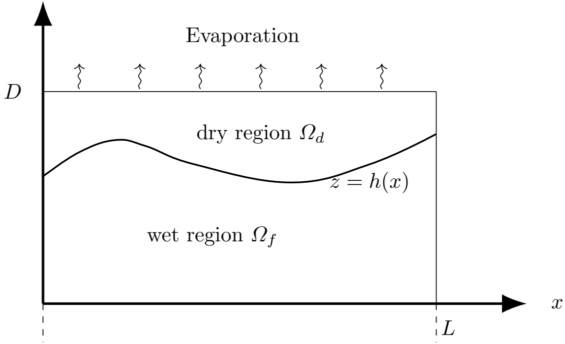


Governing equations

$$\frac{\partial(\phi c)}{\partial t} = \nabla \cdot (\mathcal{D}\nabla(\phi c)) - f(\phi, c), \quad \text{in} \quad \Omega_f,$$

$$\left.\frac{\partial(\phi c)}{\partial x}\right|_{x=0} = \left.\frac{\partial(\phi c)}{\partial x}\right|_{x=L} = \left.\frac{\partial(\phi c)}{\partial z}\right|_{z=0} = 0,$$

$$\mathcal{D}\nabla(\phi c) \cdot \boldsymbol{n}\big|_{z=h(x)} = -\tilde{\lambda} E c\phi\Big|_{z=h(x)}.$$



Governing equations

- Evolution of porosity ϕ due to particle deposition
$$\frac{\partial \phi}{\partial t} = -f(\phi, c),$$
$$f(\phi, c) = \tilde{\alpha}\phi^{1/2}(c - c^*), \quad c^* = \text{saturation concentration.}$$

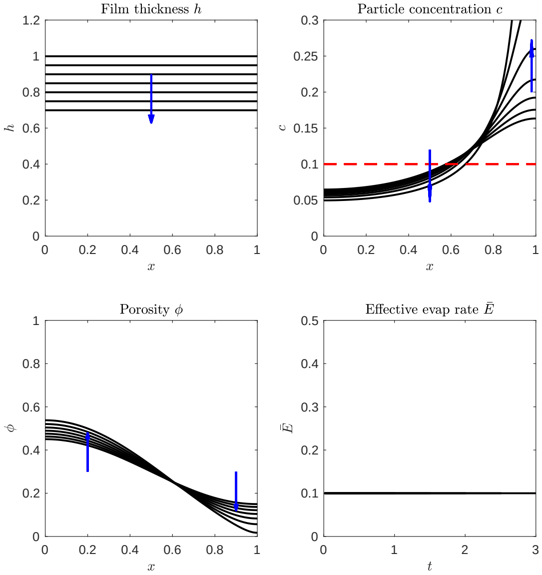
- Evolution of the dry/wet interface $z = h(x, t)$ due to evaporation
$$\frac{\partial h}{\partial t} = -E(\phi, c, h), \quad E(\phi, c, h) = \frac{E_0 \phi h}{\mathcal{K} + c} \quad \text{or} \quad E \equiv E_0.$$

- After scaling, the leading-order equation for particles for $\epsilon = D/L \ll 1$
$$-h_x(\phi c)_x + \left[-\mathcal{D}(\phi c)_{xx} + f(\phi, c)\right] h + \tilde{\lambda} E \phi c = 0.$$

- Effective evaporation rate: $\bar{E} = \frac{1}{L}\int_0^L E(\phi, c, h)\, dx$.

For simulations, we set $\tilde{\alpha} = \tilde{\lambda} = \mathcal{K} = 1, c^* = 0.1.$

Results

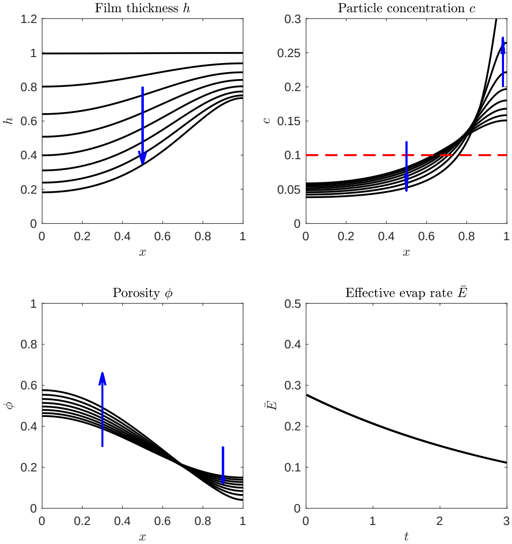


Const. evaporation rate $\quad E \equiv E_0, \quad E_0 = 0.1, \quad \mathcal{D} = 1.$

ICs: $\quad h_0 \equiv 1, \quad \phi_0 = 0.3(1 + 0.5\cos(\pi x/L)),$ $\qquad$ BCs: $c_x = 0$ at $x = 0, L.$

Results

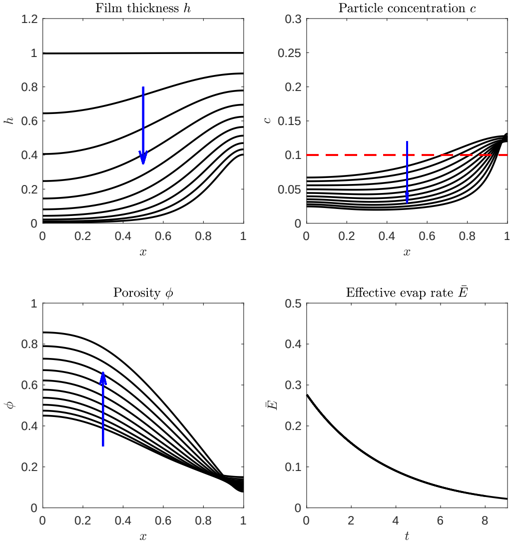
Results



$$E(\phi, c, h) = \frac{E_0 \phi h}{\mathcal{K} + c}, \quad E_0 = 1, \quad \mathcal{D} = 1.$$

Results

Results



$$E(\phi, c, h) = \frac{E_0 \phi h}{\mathcal{K} + c}, \quad E_0 = 1, \quad \mathcal{D} = 0.2.$$

Results

Single pore toy model

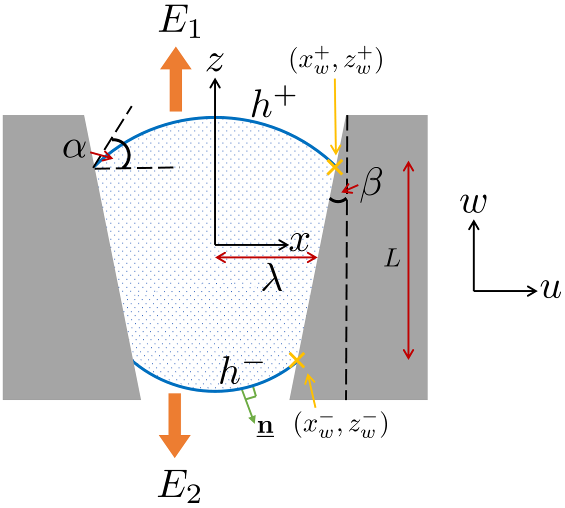


Figure: Problem sketch.

Meniscus equations

Equation for the wall is given by:

$$f\left(z, t=0\right) = \tan(\beta) z + \lambda \ .$$

Shape of the meniscus at the top and bottom is given by:

$$h^{+} = z_w^{+} - \left(\lambda + \tan\left(\beta\right) z_w^{+}\right) \cot\left(\alpha + \beta\right) + \sqrt{{r^{+}}^{2} - x^{2}} \ ,$$
$$h^{-} = -z_w^{-} + \left(\lambda + \tan\left(\beta\right) z_w^{-}\right) \cot\left(\alpha - \beta\right) - \sqrt{{r^{-}}^{2} - x^{2}} \ ,$$

respectively, where the radii of curvature for the menisci $h^{\pm}$ are

$$r^{\pm} = x_w^{\pm} \csc(\alpha \pm \beta) = \left(\lambda + \tan(\beta) z_w^{\pm}\right) \csc(\alpha \pm \beta),$$

and the menisci touch the wall at points $(\pm x_w^{+}(t), z_w^{+}(t))$ and $(\pm x_w^{-}(t), -z_w^{-}(t))$, respectively.

Fluid non-dimensionalisation

We non-dimensionalised assuming that the pore is long and thin, and that the velocity scale is given by the capillary terms. Our governing equations are given by:

$$
\begin{aligned}
0 &= \frac{\partial U}{\partial X} + \frac{\partial W}{\partial Z}, \\
0 &= -\frac{1}{\delta^2}\frac{\partial P}{\partial X} + \frac{\partial^2 U}{\partial X^2} + \delta^2 \frac{\partial^2 U}{\partial Z^2}, \\
0 &= -\frac{\partial P}{\partial Z} + \frac{\partial^2 W}{\partial X^2} + \delta^2 \frac{\partial^2 W}{\partial Z^2},
\end{aligned}
$$

with boundary conditions on the wall, $X = \pm F(Z)$:

$$(\delta U, W) \cdot \hat{\mathrm{n}} = 0 \quad \text{and} \quad (\delta U, W) \cdot \hat{\mathrm{t}} = 0.$$

Fluid non-dimensionalisation

At the upper meniscus, $Z = H^+$:

$$P = \frac{\Gamma}{R^+(Z_w^+)},$$

and at the lower meniscus, $Z = H^-$:

$$P = \frac{\Gamma}{R^-(Z_w^-)},$$

We impose evaporation at the interfaces by writing

$$\frac{\partial Z_W^\pm}{\partial T} = \overline{W}(Z_W^\pm) \mp \eta,$$

where we define the dimensionless parameters $\eta = \mu E/\delta\gamma_0$ and $\overline{W}(Z)$ is the cross-sectionally averaged velocity.

Leading order problem

In the limit of small δ, *i.e.* a long thin pore, the leading order behaviour of the system is:

$$0 = \frac{\partial U}{\partial X} + \frac{\partial W}{\partial Z},$$
$$0 = -\frac{\partial P}{\partial X},$$
$$0 = -\frac{\partial P}{\partial Z} + \frac{\partial^2 W}{\partial X^2},$$

with boundary conditions on the wall (assuming the wall is stationary in time) reducing to

$$U = 0 \quad \text{and} \quad W = 0 \text{ at } X = \pm F(Z)\ ,$$
$$P = \frac{\Gamma}{R^+(Z_w^+)} \text{ at } Z = H^+\ ,$$
$$P = \frac{\Gamma}{R^-(Z_w^-)} \text{ at } Z = H^-\ .$$

Leading order problem

We can solve for the pressure,

$$P = \frac{\Gamma}{R^+} + \frac{\left(\frac{\Gamma}{R^+} - \frac{\Gamma}{R^-}\right)\left(\left(\frac{\tan(\beta)}{\delta}Z_w^+ + 1\right)^{-2} - \left(\frac{\tan(\beta)}{\delta}Z + 1\right)^{-2}\right)}{\left(\frac{\tan(\beta)}{\delta}Z_w^- + 1\right)^{-2} - \left(\frac{\tan(\beta)}{\delta}Z_w^+ + 1\right)^{-2}},$$

and we also find that the cross-sectionally averaged velocity, $\overline{W}$, is related to the pressure via

$$\overline{W}(Z) = -\frac{1}{3}P_Z F^2.$$

This gives

$$\overline{W} = \frac{2\tan(\beta)\left(\frac{\Gamma}{R^+} - \frac{\Gamma}{R^-}\right)}{3\delta\left(\frac{\tan(\beta)}{\delta}Z + 1\right)\left(\left(\frac{\tan(\beta)}{\delta}Z_w^- + 1\right)^{-2} - \left(\frac{\tan(\beta)}{\delta}Z_w^+ + 1\right)^{-2}\right)}.$$

Leading order solution

We use our equation for evaporation at the interfaces to obtain an ODE for the movement height of the menisci at the wall over time, given by

$$\frac{\partial Z_w^{\pm}}{\partial T} = \overline{W}(Z_w^{\pm}) \mp \eta$$

with appropriate initial conditions for the menisci height starting points.

Leading order solution

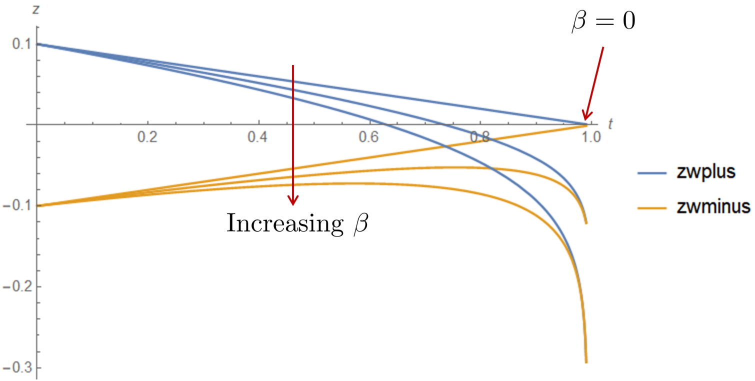
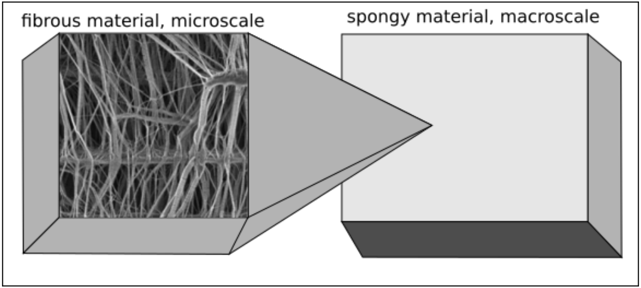


Figure: Movement of the menisci at the wall over time, for varying β .

Homogenization model, main idea



- Build equations on the microscale first.
- Homogenize equations to build macroscopic laws
- Large scale behavior should depend on integrated version of microstructure as expressed by porosity- (and hence spatially-) dependent parameters in macroscale equations parameters

References: Luckins *et al.* 2019: clean up of contaminant with interface motion; Dalwadi *et al.* 2016: filtering with Darcy flow through microstructure with growing obstacles.

Microscale field equations

- Incompressible Stokes flow

$$-\tilde{\nabla}\tilde{p} + \mu\tilde{\nabla}^2\tilde{\boldsymbol{u}} = 0, \quad 0 = \tilde{\nabla}\cdot\tilde{\boldsymbol{u}}.$$

- Solute within fluid can diffuse and is carried around by flow

$$\frac{\partial\tilde{c}}{\partial\tilde{t}} + \tilde{\nabla}\cdot(\tilde{c}\tilde{\boldsymbol{u}}) = \tilde{\nabla}\cdot(D\tilde{\nabla}\tilde{c}).$$

- Boundaries:
  1. Solute particles can deposit on fibers in a solid layer (conservation of mass + chemical potential/other formulations depending on underlying physics. Assume circular cross-sections).
  2. Evaporation front (conservation of mass for solute and fluid; stress boundary condition).

Microscale boundary conditions

1. Solid deposition: front with radius $\tilde{R}$ moves at speed $\dot{\tilde{R}}$ with unit normal $\boldsymbol{n}$.
   - Various mechanisms encapsulated by general equations

$$\tilde{\boldsymbol{u}} = -\nu_1 \dot{\tilde{R}} \boldsymbol{n}, \quad \tilde{c} - \tilde{c}_{\mathrm{sat}} = -\nu_2 D \frac{\partial \tilde{c}}{\partial \tilde{n}}, \quad \dot{\tilde{R}} = -\nu_3 D \frac{\partial \tilde{c}}{\partial \tilde{n}},$$

     where ν_1, ν_2, ν_3 are constants, relating flow to expansion of boundary and concentration flux.
   - c_{sat} is the saturation concentration (nonlinear generalizations of these conditions are possible as in the MPI2020 report).
2. Evaporation front $\tilde{S}$ moving at speed $\dot{\tilde{S}}$ with unit normal $\boldsymbol{n}$ evaporation rate, E, assumed constant.
   - Conservation of mass for solute and solvent

$$-D \frac{\partial \tilde{c}}{\partial \tilde{n}} + \tilde{c} E = 0, \quad \tilde{\boldsymbol{u}} \cdot \boldsymbol{n} - \dot{\tilde{S}} = E.$$

   - Balance stresses to obtain a dynamic boundary condition.

Nondimensionalization

- Devil in the details. Delay choices for now (probably E for velocity). Goal is to have $O(1)$ balance between $\dot{R}$ and c.
- Critical parameter is $\epsilon = R_0/L$, ratio of micro- to macro-scales.
- Field equations:

$$0 = \nabla \cdot \boldsymbol{u}, \quad 0 = -\nabla P + \epsilon^2 \nabla^2 \boldsymbol{u},$$
$$\alpha \frac{\partial c}{\partial t} + \nabla \cdot (c\boldsymbol{u}) = \mathrm{Pe}^{-1} \nabla \cdot (D \nabla c).$$

- Evaporation boundary:

$$\boldsymbol{u} \cdot \boldsymbol{n}_e - \dot{S} = e, \quad -\frac{\partial c}{\partial n} + \lambda \epsilon c = 0, \quad \text{dynamic b.c.}$$

- Deposition boundary:

$$\boldsymbol{u} = \beta \epsilon \frac{\partial c}{\partial n} \boldsymbol{n}, \quad c + \epsilon \frac{\partial c}{\partial n} = c_{\mathrm{sat}}, \quad \dot{R} = c.$$

Homogenization and expected equations

- Darcy-type equation relating $\boldsymbol{u}$ and P within fluid

$$\boldsymbol{U} = -\mathcal{K}(\phi)\nabla P.$$

- $\mathcal{K}$ and $\mathcal{D}$ below come from solving a single "cell" problem (tensors if the microstucture is not sufficiently symmetric).
- ϕ is macroscopic porosity, related to obstacle growth by $\phi\partial R/\partial t = C$.
- Compressible flow driven by deposition of material on fibers

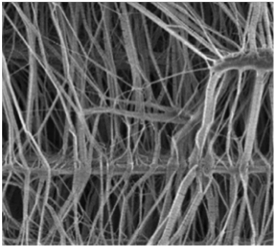
$$\nabla \cdot \boldsymbol{U} = \alpha\gamma\frac{\partial R}{\partial t}.$$

- Advection-diffusion-reaction equation for concentration

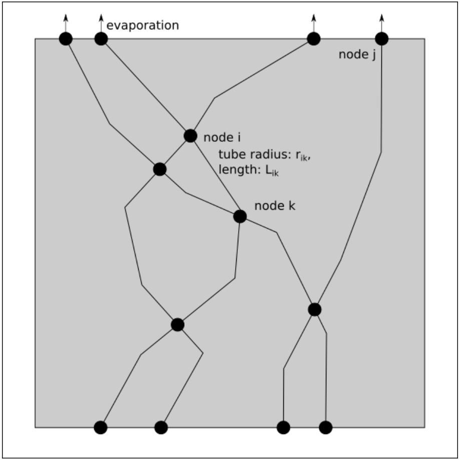
$$\alpha\frac{\partial C}{\partial t} = \nabla \cdot \left(\mathcal{D}(\phi)\nabla C - \frac{C}{\phi}(\boldsymbol{U} + \mathcal{D}(\phi)\nabla\phi)\right) - f(\phi)C,$$

  resemblance to continuum subgroup equations.
- Equation of motion for interface looks like microscale version with coefficients related to homogenization procedure.

Network model main idea



(a) Top down view of fibers of material, view dark regions as pores, which can be connected laterally to others.



(b) Side profile of pore network model structure. Nodes are at entrances/exits and intersections of pores.

Borrowing from a membrane filtration model

- Gu, Kondic, and Cummings recently submitted "A Graphical Representation of Membrane Filtration" which details how pressure drives solution flow through a random network.
- Nodes are connected by capillaries with $\frac{\text{radius}}{\text{length}} \ll 1$, allowing Darcy's Law and Poiseuille's equation to be used to determine the flow rate.
- Solving a matrix equation gives instantaneous flow rates within the network, and can track concentration of the impurity and subsequent pore shrinkage.
- Modifications: Evaporation empties capillaries, capillary forces provide pressure to move solution around. Residue deposition again determined by continuum model.

Governing equations

- Darcy's law, capillary pressure:

$$q_{ij} = k_{ij} p_{ij}, \quad k_{ij} = \frac{\pi r_{ij}^4}{8\mu L_{ij}}, \quad \forall i : \sum_j q_{ij} = 0.$$

- q_{ij} is flow from node i into node j, p_{ij} pressure difference across nodes, k_{ij} pore conductance, r_{ij} and L_{ij} pore radius & length.
- Darcy's law, capillary pressure:

$$p_{ij} = \frac{\gamma \cos\theta}{r_{ij}}.$$

- γ is surface tension, θ contact angle.
- Evaporation brings node exposed to the air down

$$\frac{dL_{ij}}{dt} = \begin{cases} -E_j & \text{Node } j \text{ exposed to air,} \\ 0 & \text{otherwise.} \end{cases}$$

Summary and conclusions

- We considered multiple scales:
  - Microscale (single pore)
    1. Evaporation and deposition without capillary effects.
    2. Evaporation and flow without deposition and considering capillary effects.
  - Macroscale:
    1. Solve a general model without flow, for evaporation and deposition
    2. Consider homogenization taking into account microscale and allowing for fluid flow.
    3. Network model which is not a continuum, but takes into account global capillary effects.
- Models are able to partially answer questions posed by W.L. Gore & Associates.
- Future improvements include linking micro and macro scale models; and considering the three effects of evaporation, deposition, and flow and their interplay.

Acknowledgments

- NSF-DMS 1916281, 2016095, 2016099.
- W.L. Gore & Associates.
- University of Vermont.
- University of Delaware.

Thank you!

Thank You!

Questions??