Research Note:

MS Local Flux Model and Numerical Method Write-up

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1.1 Model Equations Derivation

1.1.1 General Problem Statement

Membrane transport models can take many forms. Here we consider a local flux model for complex mixture transport across an asymmetric membrane layer. The goal of the model is to calculate the degree of separation and total amount of material permeating. The assumptions built into this model are that all transport and thermodynamic parameters are known. Also a suitable thermodynamic model for each

phase is also assumed to be known. Another assumption here is that the resistance to transport in the support layer is negligible such that in our case the properties in the support layer are equal to that of the permeate. Note this may not always be the case in a global membrane module model. There may be bulk mixing in the permeate stream that needs to be taken into account for the overall global module model. However, the model and preceding numerical method would still be the same for the properties in the support layer. And lastly, assuming the equilibrium partitioning kinetics are much faster than the diffusional transport, the sorption-diffusion model can be used. The basic idea behind the sorption-diffusion model of membrane transport has three main steps:

I. thermodynamic equilibrium between bulk feed phase (I) and the active layer membrane phase (II)

II. diffusion through the active layer membrane phase (II)

III. thermodynamic equilibrium between active layer membrane phase (II) and support layer membrane phase (III)

Please note that this model is looking at the interface between the active and support layer whereas usually the equilibrium is analyzed with the interface between the membrane and permeate phases. This is chosen cleverly such that a relationship relating the ratio of the fluxes to the outlet composition in the support layer can be used to solve the problem with less inputs to the model.

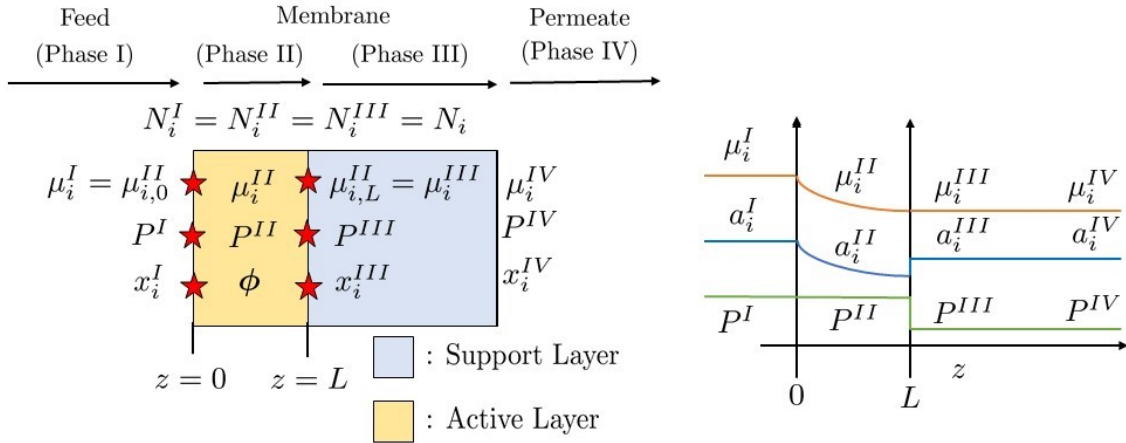See figure below for a visual representation of what has been said thus far:

Figure 1: System set-up for local point on asymmetric membrane layer. Shown here are all required properties to solve the system. Note $i = 1, 2, ..., n$.

With that picture in mind, the variables for the system can be listed as:

$$\text{Known Variables: } \left(\mathbf{x}^I, L, T, P^I, P^{II}, P^{III}, n\right)$$

$$\text{Unknown Variabels: } \left(\mathbf{a}_0^{II}, \mathbf{a}_L^{II}, \phi_0, \phi_L, \mathbf{x}^{III}, \mathbf{N} \right)$$

And with that list of variables set-up; we can now look at the different steps of the soprtion-diffusion model to calculate local fluxes of a complex mixture across a membrane layer.

1.1.2 Thermodynamic Equilibrium

The next point of understanding is the thermodynamics associated with the phase equilibrium between phase I & II, and II & III. As you can see from the figure, the chemical potentials are equated as:

$$\mu_{i,0}^I = \mu_{i,0}^{II}, \ i = 1, 2, ..., n \tag{1}$$

$$\mu_{i,L}^{II} = \mu_{i,L}^{III}, \ i = 1, 2, ..., n \tag{2}$$

Looking at the definition of activity $(RT \ln(a_i^y) = \mu_i^y(T, P^y) - \mu_i^{y+}(T, P)^y)$, where the $+$ indicates that the chemical potential is a reference state, (chosen to be the pure component state) evaluated at T and P^y. After adding and subtracting the the pure component chemical potential at at the same temperature and a different reference pressure P°, a substitution of the fundamental property relation for the pure component Gibbs free energy can be substituted, and then integrated to get the expressions for chemical potential of component i in the respective phases to look like (see Appendix B for explicit derivation):

$$\mu_i^\circ + RT \ln(a_{i,0}^I) + V_i(P^I - P^\circ) = \mu_i^\circ + RT \ln(a_{i,0}^{II}) + V_i(P^{II} - P^\circ), \ i = 1, 2, ..., n \tag{3}$$

$$\mu_i^\circ + RT \ln(a_{i,L}^{II}) + V_i(P^{II} - P^\circ) = \mu_i^\circ + RT \ln(a_{i,L}^{III}) + V_i(P^{III} - P^\circ), \ i = 1, 2, ..., n \tag{4}$$

From the figure $P^I = P^{II} \geq P^{III}$ so the two expressions simplify to:

$$a_{i,0}^I = a_{i,0}^{II}, \ i = 1, 2, ..., n \tag{5}$$

$$a_{i,L}^{II} = a_{i,L}^{III} \exp(-V_i(P^{II} - P^{III})/RT), \ i = 1, 2, ..., n \tag{6}$$

And substituting the definition of activity for phase I and III, the final working expressions become (and letting $\eta = \exp(-V_i(P^{II} - P^{III})/RT)$):

$$a_{i,0}^{II} = \gamma_{i,0}^I x_i^I, \ i = 1, 2, ..., n \tag{7}$$

$$a_{i,L}^{II} = \gamma_{i,L}^{III} x_i^{III} \exp(-V_i(P^{II} - P^{III})/RT) = \gamma_{i,L}^{III} x_i^{III} \eta, \ i = 1, 2, ..., n \tag{8}$$

Note the second assumption above about having a sufficient thermodynamic model for each of the phases implies there exist functions such that:

$$a_i^{II} = g_i^{II}(\phi, \mathbf{s}, T, P^{II}), \ i = 1, 2, ..., n \tag{9}$$

$$\gamma_i^I = g_i^I(\mathbf{x}^I, \mathbf{s}, T, P^I), \ i = 1, 2, ..., n \tag{10}$$

$$\gamma_i^{III} = g_i^{III}(\mathbf{x}^{III}, \mathbf{s}, T, P^{III}), \ i = 1, 2, ..., n \tag{11}$$

Note with equations (7), (9), (10); the feed volume fractions in the membrane phase (II) can be solved

for given feed compositions. And then with equations (8), (9), (11); the phase III outlet conditions can be solved for using the values of $\phi_{i,L}$. This information completes the thermodynamical analysis in steps I & III of the sorption-diffusion model.

1.1.3 Diffusional Transport

Now the next step to focus on step II of the sorption-diffusion model which is the transport of permeants through the membrane phase (II) by applying the Maxwell-Stefan multicomponent mass transport framework.

Please refer to Krishna's review on the Maxwell-Stefan multicomponent transport model for full derivation from a force balance.[5] Here we will assume one is familiar with this starting equation for component i transporting through a polymer membrane layer rewritten in terms of volume fractions [9]:

$$-\frac{\phi_i(z)}{RT}\nabla\mu_i^{II}(T(z),P(z),\boldsymbol{\phi}(z))|_{T,P} = \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\phi_j(z)N_i^V - \phi_i(z)N_j^V}{\text{Đ}_{ij}^V} + \frac{\phi(z)_m N_i^V}{\text{Đ}_{im}^V}, \;\; i = 1,2,...,n \qquad (12)$$

Note the component $n+1$ is equivalent to the membrane phase (II), or subscript m. Another fact of the model is that the membrane phase (II) is stationary (i.e $N_m^V = 0$).

Also as a bit of clarification, is the subtlety that the defined system in equation (12) are only written for the first n components. This is because only n MS equations are independent by the Gibbs-Duhem relation that must always be satisfied. So the activity change in the membrane is a result of the activity change of all the other components; and is not a new piece of information for our system. Another way of thinking about this is that there the membrane phase (II) compositions are related by the summation rule:

$$\sum_{j=1}^{n+1} \phi_j = 1 \qquad (13)$$

For a more detailed analysis, see Appendix A.

Taking the LHS of equation (12), expanding the chemical potential of component i through the chain rule w.r.t to each component, realizing only an activity gradient is present (no pressure or temperature changes across membrane layer, and 1D transport), and setting $\Gamma_{ij} = \phi_i \frac{\partial \ln(a_i^{II})}{\partial \phi_j}$:

$$-\frac{\phi_i(z)}{RT}\nabla\mu_i^{II}(T,P,\boldsymbol{\phi}(z))|_{T,P} = -\frac{\phi_i(z)}{RT}\frac{d\mu_i^{II}(\boldsymbol{\phi}(z))}{dz} = -\phi_i(z)\frac{d\ln(a_i^{II}(\boldsymbol{\phi}(z)))}{dz}$$
$$= -\sum_{j=1}^{n}\phi_i(z)\frac{\partial\ln(a_i^{II}(\boldsymbol{\phi}(z)))}{\partial\phi_j(z)}\frac{d\phi_j(z)}{dz} = -\sum_{j=1}^{n}\Gamma_{ij}\frac{d\phi_j(z)}{dz} \qquad (14)$$

Then plugging equation (36) into equation (12):

$$-\sum_{j=1}^{n}\Gamma_{ij}\frac{d\phi_j}{dz} = \sum_{\substack{j=1 \\ j\neq i}}^{n}\frac{\phi_j N_i^V - \phi_i N_j^V}{\text{Đ}_{ij}^V} + \frac{\phi_m N_i^V}{\text{Đ}_{im}^V}, \;\; i = 1,2,...,n \qquad (15)$$

Note for sake of compactness the functional arguments of the chemical potential and the volume fractions

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have been dropped.

And realizing the summation terms in equation (15) can be rewritten as vectors:

$$
\begin{bmatrix} \Gamma_{i1} & \cdots & \Gamma_{in} \end{bmatrix} \begin{bmatrix} \frac{d\phi_1}{dz} \\ \vdots \\ \frac{d\phi_n}{dz} \end{bmatrix} = \begin{bmatrix} -\frac{\phi i}{Ð_{i1}^V} & \cdots & \left(\sum\limits_{\substack{j=1 \\ j \neq i}}^{n} \frac{\phi_j}{Ð_{ij}^V} \right) + \frac{\phi_m}{Ð_{im}^V} & \cdots & -\frac{\phi i}{Ð_{in}^V} \end{bmatrix} \begin{bmatrix} N_1^V \\ \vdots \\ N_i^V \\ \vdots \\ N_n^V \end{bmatrix} , \ i = 1, 2, ..., n \qquad (16)
$$

And realizing this can be written for each component that is permeating through the membrane, an n by n matrix system can be formed (see Appendix C for derivation of various membrane sorption model thermodynamic factor matrix derivation and model description):

$$
\mathbf{\Gamma}(\phi, \mathbf{s}) \frac{d\phi_{1:n}}{dz} = -\mathbf{B}(\phi)\mathbf{n} \qquad (17)
$$

Where:

$$
\Gamma_{ij} = \phi_i \frac{\partial \ln(a_i^{II})}{\partial \phi_j} = \frac{\phi_i}{f_i^{II}} \frac{\partial \hat{f}_i^{II}}{\partial \phi_j}
$$

$$
B_{ii} = \left(\sum\limits_{\substack{j=1 \\ j \neq i}}^{n} \frac{\phi_j}{Ð_{ij}^V} \right) + \frac{\phi_m}{Ð_{im}^V}
$$

$$
B_{ij} = -\frac{\phi_j}{Ð_{ij}^V}
$$

And here we assume all MS diffusivities are known for all i, j pairs, with $i \neq j$. This can be denoted in matrix form as (and letting component $n + 1$ be m for simpler notation):

$$
\mathbf{Ð} = \begin{bmatrix} 1 & Ð_{12}^V & \cdots & Ð_{im}^V \\ Ð_{21}^V & 1 & \ddots & \vdots \\ \vdots & \ddots & 1 & Ð_{nm}^V \\ Ð_{m1}^V & \cdots & Ð_{mn}^V & 1 \end{bmatrix} \qquad (18)
$$

1.1.4 Degrees of Freedom Analysis

Now to proceed and end with a fully specified system to solve for the degree of separation and partial fluxes through the membrane; a relationship that C.Y. Pan applied in modeling gas separation through asymmetric membrane modules is used. [8]. This can first be visualized below by zooming in on the active layer and support layer interface:
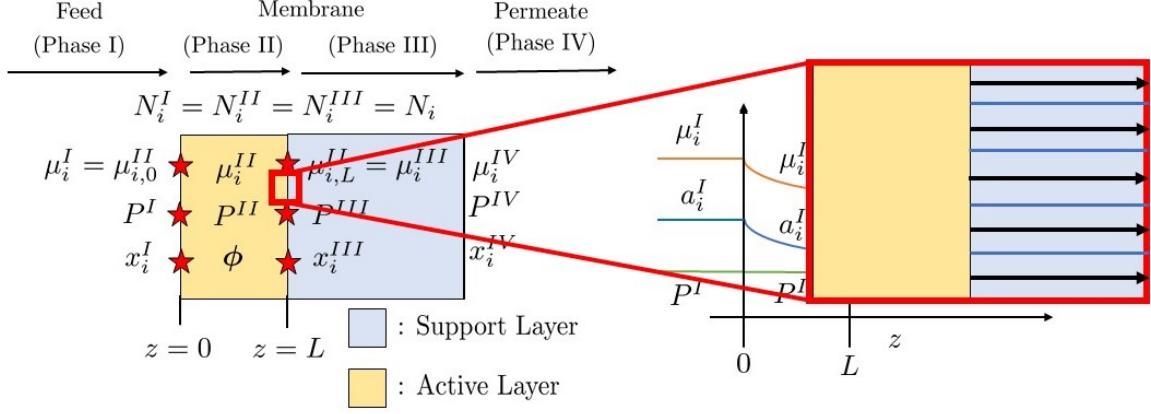
Figure 2: Close up of support and active layer interface

By looking at the support layer channels, the fact that there is no axial mixing allows the phase III mol fraction of component i to be related by the ratio of the molar flux of i to the total molar flux.

Quantitatively the the bulk flow relationship for asymmetric membranes states (letting $N_{tot}^{V*} = \frac{N_{tot}^V \overline{V}_i}{\sum x_j \overline{V}_j}$):

$$N_i = x_i^{III} \sum_{j=1}^{n} N_j = x_i^{III} N_{tot} \implies N_i^V = x_i \overline{V}_i N_{tot}^V / \sum x_j \overline{V}_j = x_i^{III} N_{tot}^{V*}, \ i = 1, 2, ..., n \tag{19}$$

Substituting this into the matrix system defined above:

$$\mathbf{\Gamma}(\boldsymbol{\phi}, \mathbf{s}) \frac{d\boldsymbol{\phi}_{1:n}}{dz} = -\mathbf{B}(\boldsymbol{\phi}) \mathbf{x}^{III} N_{tot}^{V*} \tag{20}$$

Note using the initial conditions of feed volume fractions, and the thickness of the membrane as the span to integrate over, the DAE system of n+1 equations can be used to find the permeate volume fraction of n+1 components:

$$\frac{d\boldsymbol{\phi}_{1:n}}{dz} = -\mathbf{\Gamma}^{-1}(\boldsymbol{\phi}, \mathbf{s}) \mathbf{B}(\boldsymbol{\phi}) \mathbf{x}^{III} N_{tot}^{V*} \tag{21}$$

$$\sum_{j=1}^{n+1} \phi_j = 1, \quad \forall z \in (0, L] \tag{22}$$

or how (22) is differentiated and implemented as an ODE:

$$\frac{d\phi_{n+1}}{dz} = -\sum_{j=1}^{n} \frac{d\phi_j}{dz} \tag{23}$$

One can then realize that ϕ_L and sufficient activity models can be used to find the phase III conditions by using equations (8), (9), (11).

So the final system of equations, knowns, and unknowns becomes:

Sorption-Diffusion Step I

$$\gamma_i^I = g_i^I(\mathbf{x}^I, \mathbf{s}, T, P^I), \ i = 1, 2, ..., n$$

$$a_{i,0}^{II} = \gamma_{i,0}^I x_i^I, \ i = 1, 2, ..., n$$

$$a_{i,0}^{II} = g_i^{II}(\boldsymbol{\phi}_0, \mathbf{s}, T, P^{II}), \ i = 1, 2, ..., n$$

$$\sum_{j=1}^{n+1} \phi_{j,0} = 1$$

Sorption-Diffusion Step III

$$\gamma_i^{III} = g_i^{III}(\mathbf{x}^{III}, \mathbf{s}, T, P^{III}), \ i = 1, 2, ..., n$$

$$a_{i,L}^{II} = \gamma_{i,L}^{III} x_i^{III} \eta, \ i = 1, 2, ..., n$$

$$a_{i,L}^{II} = g_i^{II}(\boldsymbol{\phi}_L, \mathbf{s}, T, P^{II}), \ i = 1, 2, ..., n$$

$$\sum_{j=1}^{n} x_j^{III} = 1$$

Known variables:

$$(\mathbf{x}^I, L, T, P^I, P^{II}, P^{III}, \mathbf{s}, \mathbf{Đ}, n)$$

Sorption-Diffusion Step II

$$\frac{d\boldsymbol{\phi}_{1:n}}{dz} = -\boldsymbol{\Gamma}^{-1}(\boldsymbol{\phi}, \mathbf{s})\mathbf{B}(\boldsymbol{\phi})\mathbf{x}^{III} N_{tot}^{V*}$$

$$\frac{d\phi_{n+1}}{dz} = -\sum_{j=1}^{n} \frac{d\phi_j}{dz}$$

Unknown variables:

$$(\boldsymbol{\gamma}^I, \boldsymbol{\gamma}^{III}, \mathbf{a}_0^{II}, \mathbf{a}_L^{II}, \boldsymbol{\phi}_0, \boldsymbol{\phi}_L, \mathbf{x}^{III}, N_{tot}^{V*})$$

DoF: $4n + 3(n+1)$ equations
$-4n + 3(n+1)$ unknowns
= 0 DoF

The fact that the degrees of freedom is equal to zero means the system is fully specified and can be solved for using a proper numerical method.

Note that this approach assumes there is an explicit membrane activity function (like in the case of the Flory-Huggins membrane sorption model) in terms of strictly membrane phase (II) volume fractions.

In the case of an implicit membrane sorption model that is in terms of membrane phase (II) volume fraction and fugacities, there are extra algebraic equations that must be accounted for since the thermodynamic facotr matrix will now include fugacities and volume fractions. See equation system below:

Sorption-Diffusion Step I

$$\gamma_i^I = g_i^I(\mathbf{x}^I, \mathbf{s}, T, P^I), \ i = 1, 2, ..., n$$

$$\hat{f}_{i,0}^{II} = \gamma_{i,0}^I x_i^I f_i^\circ, \ i = 1, 2, ..., n$$

$$\hat{f}_{i,0}^{II} = g_i^{II}(\boldsymbol{\phi}_0, \mathbf{s}, T, P^{II}), \ i = 1, 2, ..., n$$

$$\sum_{j=1}^{n+1} \phi_{j,0} = 1$$

Sorption-Diffusion Step II

$$\frac{d\boldsymbol{\phi}_{1:n}}{dz} = -\boldsymbol{\Gamma}^{-1}(\boldsymbol{\phi}, \mathbf{f}^{II}, \mathbf{s})\mathbf{B}(\boldsymbol{\phi})\mathbf{x}^{III} N_{tot}^{V*}$$

$$\frac{d\phi_{n+1}}{dz} = -\sum_{j=1}^{n} \frac{d\phi_j}{dz}$$

$$\mathbf{w}(\boldsymbol{\phi}, \mathbf{f^{II}}) = 0$$

Sorption-Diffusion Step III

$$\gamma_i^{III} = g_i^{III}(\mathbf{x}^{III}, \mathbf{s}, T, P^{III}), \ i = 1, 2, ..., n$$

$$\hat{f}_{i,L}^{II} = \gamma_{i,L}^{III} x_i^{III} f_i^\circ \eta, \ i = 1, 2, ..., n$$

$$\hat{f}_{i,L}^{II} = g_i^{II}(\boldsymbol{\phi}_L, \mathbf{s}, T, P^{II}), \ i = 1, 2, ..., n$$

$$\sum_{j=1}^{n} x_j^{III} = 1$$

Known variables:

$$(\mathbf{x}^I, L, T, P^I, P^{II}, P^{III}, \mathbf{s}, \mathbf{Đ})$$

Unknown variables:

$$(\boldsymbol{\gamma}^I, \boldsymbol{\gamma}^{III}, \mathbf{f}_0^{II}, \mathbf{f}_L^{II}, \boldsymbol{\phi}_0, \boldsymbol{\phi}_L, \mathbf{x}^{III}, N_{tot}^{V*})$$

DoF: $4n + 3(n + 1)$ equations
$-4n + 3(n + 1)$ unknowns
$= \mathbf{0\ DoF}$

1.2 Numerical Method: General Approach

Analyzing the problem in terms of degrees of freedom ensures the problem is solvable. Now the nonlinear equations used to iterate towards a solution can be built. Cleverly, the information in section 2.1 (mainly the ODE system) presents a way to guess and iterate until the final integrator values related to the phase III conditions matches the guess of the phase III conditions from the solver.

In a quantitative sense, we can define x_{iter}^{III} as the iteration variable from the overall solver and $x_i^{III}(\boldsymbol{\phi}_L)$ as the value that is found from solving the sorption-diffustion step III using $\boldsymbol{\phi}_L$. Now expressions can be written that the non-linear solver must satisfy to some tolerance to have found a solution:

$$\mathrm{h}_i = x_{i,iter}^{III} - x_i^{III}(\boldsymbol{\phi}_L) = 0, \ i = 1, 2, ..., n \tag{24}$$

$$h_{n+1} = 1 - \sum x_i^{III} = 0 \tag{25}$$

With these equations, the system is square with $n + 1$ equations and $n + 1$ unknowns; and can be solved using any nonlinear equation solver.

In some cases the membrane unit operation may be operated in pervaporation mode such that the permeate interface is considered "dry" as the permeants are instantaneously evaporated after transporting through the membrane. In a mathematical sense this means the final values from the integrator should be zero. So instead of using the matrix system in equation 19 and then the other equations defined in 5-8,

one would instead use this expression shown in equation 6:

$$\mathbf{\Gamma}(\boldsymbol{\phi}, \mathbf{s})\frac{d\boldsymbol{\phi}_{1:n}}{dz} = -\mathbf{B}(\boldsymbol{\phi})\mathbf{n} \tag{26}$$

And the equations to iterate over would be:

$$\mathbf{h}_{1:n} = \boldsymbol{\phi}_{1:n}\Big|_{z=L} = \mathbf{0} \tag{27}$$

Then iterate until values of the partial fluxes were found that satisfy the above equations. Note here there are only n equations and n unknowns. Also, using this form of the equations for modes other than pervaporation will lead to over prediction of driving forces, and therefore over prediction of the transmembrane fluxes through the membrane. Note functionality to be added at later date, see citation for more information [9].

With that general method in mind, the next part is to present our contribution formulation compared to the main method that solves this rigorous formulation and does not make any simplifications as seen here [4] [3].

1.3 Classic Method: Full Discritization (FUD)

1.3.1 For an ODE System

This method [2] uses the same asymmetric membrane relationship outlined in (1.1.4). Here we are using a modified version to match our nonlinear solver system of equations. This will allow a fair comparison based solely on the methods.

The basic idea to solve this 2-point boundary value problem is to discritize the active layer into equal parts and assign nodal state variables to solve for as a large system of non-linear equations. See figure below (as an example, 6 nodes are chosen):
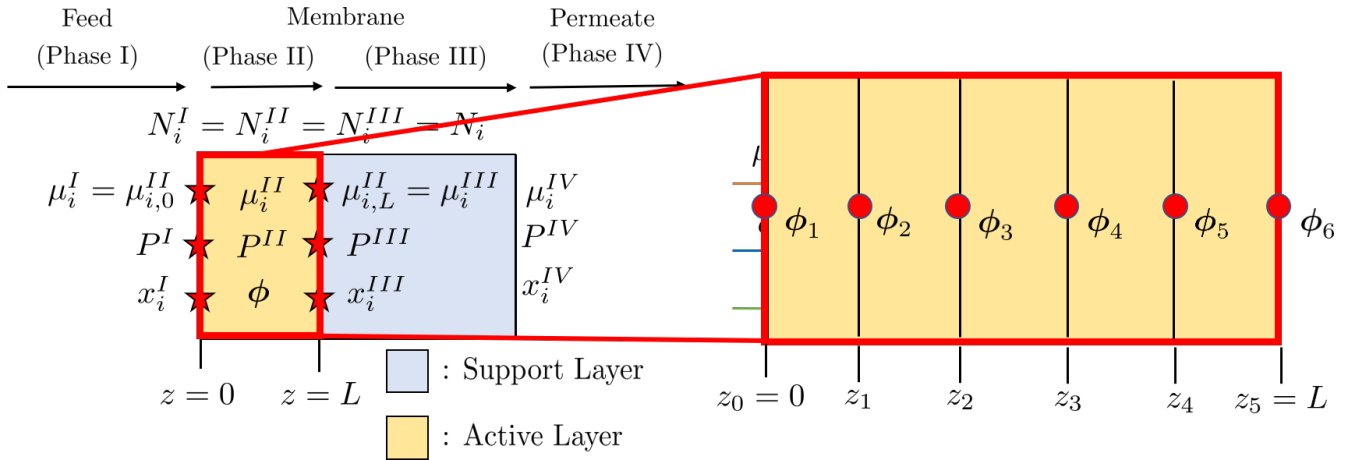

Figure 3: BVP discritized active layer

In order to build this system of non-linear equations from the ODE matrix system given in (21) and the

derivative of (23) and solved for $\frac{d\phi_{n+1}}{dz}$, one must assign each node an ODE (except for the left boundary condition, and apply finite differences approximation for the derivative terms to transform the system of equations into implicit algebraic expressions that can be solved using a nonlinear equation solver. Note for the first node, the nonlinear equation is just the solver guess minus the boundary condition that was solved for using SD step 1 equations. For the middle nodes, central difference approximations are used. And for the last node, backwards difference approximations are used. Note also $\phi_6 = \phi(L)$. In a mathematical sense:

First node:

$$\mathbf{h}_1(\boldsymbol{\phi}) = \mathbf{0} = \boldsymbol{\phi}_1 - \boldsymbol{\phi}(0) \tag{28}$$

Middle nodes (N=3 as example):

$$\frac{d\boldsymbol{\phi}_3}{dz} = -\boldsymbol{\Gamma}^{-1}(\boldsymbol{\phi}_3)\mathbf{B}(\boldsymbol{\phi}_3)\mathbf{x}^{III}N_{tot}^{V*} \Rightarrow \mathbf{h}_3(\boldsymbol{\phi}) = \mathbf{0} = \frac{(\boldsymbol{\phi}_4 - \boldsymbol{\phi}_2)}{z_4 - z_2} + \boldsymbol{\Gamma}^{-1}(\boldsymbol{\phi}_3)\mathbf{B}(\boldsymbol{\phi}_3)\mathbf{x}^{III}N_{tot}^{V*} \tag{29}$$

Terminal node:

$$\frac{d\boldsymbol{\phi}_6}{dz} = -\boldsymbol{\Gamma}^{-1}(\boldsymbol{\phi}_6)\mathbf{B}(\boldsymbol{\phi}_6)\mathbf{x}^{III}N_{tot}^{V*} \Rightarrow \mathbf{h}_6(\boldsymbol{\phi}) = \mathbf{0} = \frac{(\boldsymbol{\phi}_6 - \boldsymbol{\phi}_5)}{z_6 - z_5} + \boldsymbol{\Gamma}^{-1}(\boldsymbol{\phi}_6)\mathbf{B}(\boldsymbol{\phi}_6)\mathbf{x}^{III}N_{tot}^{V*} \tag{30}$$

So with all these equations written out, and in addition to the equations listed in SD I and III–all the nodal values can be found given some guess for the phase III conditions. And in order to find the phase III conditions and total flux through the membrane, one can follow the same procedure outlined in section 2.2 by adding those equations to the list of non-linear equations to solve for, giving a square system.

This method is simple to implement, but the robustness and efficiency of this method when thinking about implementing this into a process simulator for instantaneous transport calculations for any number of components or complex thermodynamics is lacking. That leads us into the presentation of our shooting algorithm after explaining how to treat a DAE system.

1.3.2 For a DAE system

For a DAE system with algebraic equations such as sorption model functions that define the relationship between membrane phase (II) fugacity and volume fraction (as seen in dual mode sorption [DMS] and our novel combined Flory-Huggins-Langmuir [FH-LM]), the idea is the same, but there are now nodal values for the algebraic variables. See figure below:
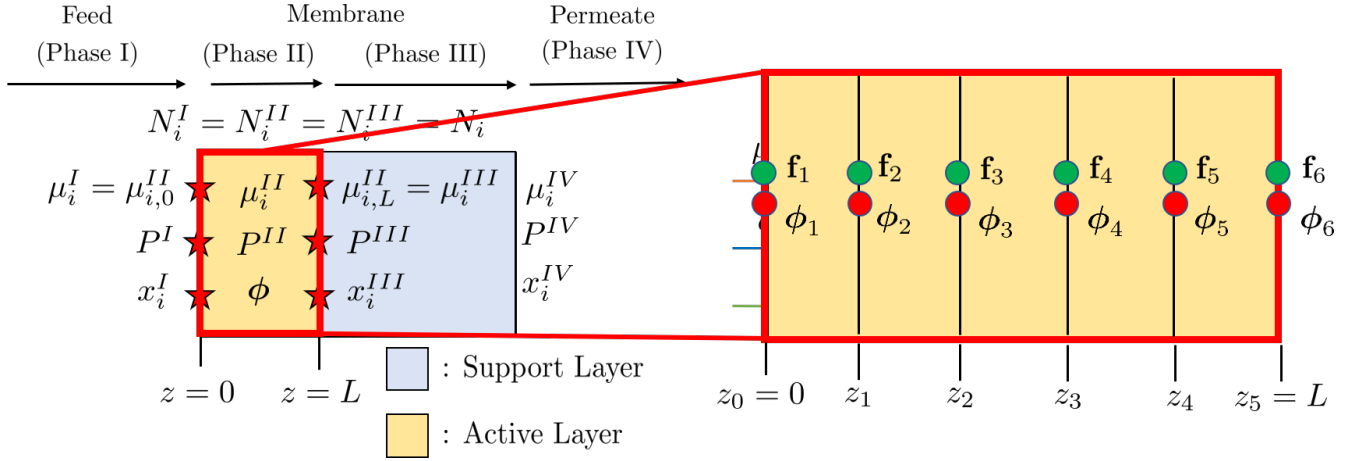
Figure 4: BVP discritized active layer

So in this case there are n component membrane fugacities corresponding to n membrane phase (II) permeant volume fractions. Along with that, there will now be a nonlinear function copy per permeant per node. For the far left boundary condition, again the nodal nonlinear equation is just the solver fugactiy iterate guess minus the fugacity boundary condition that was found assuming ideal solution theory. The middle and terminal nodes then evaluate the membrane sorption model algebraic equation at the nodal membrane phase (II) volume fraction and fugacity. See Appendix C for specific membrane sorption model equations.

1.4 Our First Method: Shooting Algorithm (SA)

In presenting the advantages of our method, first the apparent shortcomings of the full discritization method is that initial guesses of all nodal states must be provided, and in cases with stiff systems; an equal distribution of discritization may not be sufficient without a high number of nodal values. This means with a stiff system of ODEs, an adaptive nodal mesh is needed to capture this stiffness in certain areas; something that a robust integration routine would take care of and allow for sequential calculations rather than solving a large system of equations at once.

That is why our method proposes using the full matrix model and asymmetric membrane relationship outlined in section 2.1, however this method splits the integration and non-linear equation solver into an inner and outer loop shooting algorithm. See figure below as a top-level overview:
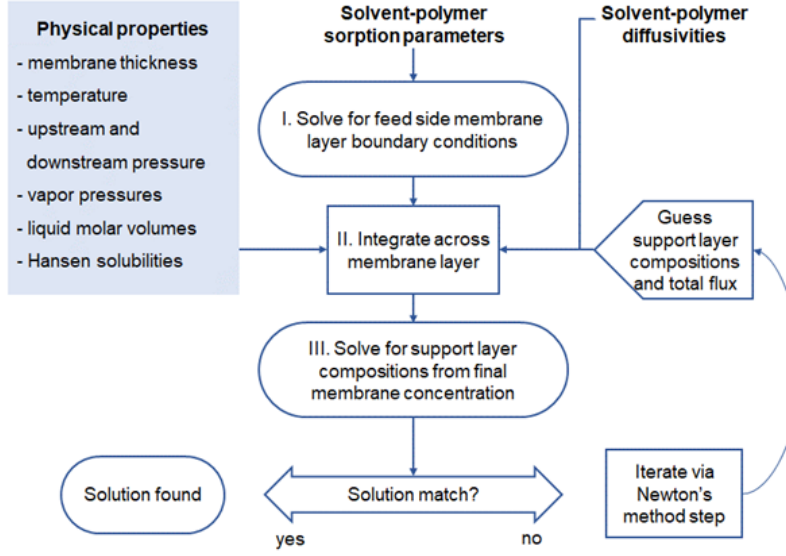
Figure 5: Shooting method algorithm

Again the contribution here is that we are providing a means to efficiently calculate transmembrane fluxes for any number of components, while at the same time taking into account any complex thermodynamic model that the system is postulated to obey. The ultimate goal is to implement this methodology into a full membrane process unit that can be reliably converged in a process simulator flow sheet for efficient plant design and material/condition screening. The other point to highlight is that this method allows for process metrics calculations based solely on feed conditions and membrane properties that can either be found from single or binary permeation experiments.

Numerical methods for shooting algorithms are by no means new, but a concise presentation of how to solve this rigorous system of equations as efficiently as possible in the context of asymmetric transmembrane transport is new and has not been seen in the literature. Again many papers have solved such systems of equations with known permeate outlet conditions for purposes of model verification and a form of shooting algorithm is used, but a clear presentation of how to solve such equations is not presented. Also from our work over the past year–it has not been a simple task to fully understand.

That is why we present below a more technical version of figure 3:

Starting again with the list of input variables and guesses for the permeate bulk composition and total flux across the membrane:

$$(\mathbf{x}^I, L, T, P^I, P^{II}, P^{III}, \mathbf{s}, \mathbf{\bar{D}})$$

$$\mathbf{x}^{III}_{guess} = \mathbf{x}^I, \ N^{V*}_{tot,guess} = 0.0001 \frac{L}{m^2 hr}$$

Once input variables and initial guesses are supplied to the nonlinear equation solver, the bulk feed compositions can then be transformed into initial conditions for the integrator using the sorption-diffusion step II equations.

Now inputting the initial conditions and span for the integrator as $[0, L]$, a stiff integration routine such as MATLAB's ODE15s can be used to solve to system in a matter of seconds for an 11 pseudo-component system. This can be improved even more in future work by providing the Jacobian to the integrator

and reduce the number of function evaluations that are usually done to estimate the Jacobian by finite differencing. Improvement from this is TBD. Another angle is to have MATLAB call an integrator that is written in C++ that would increase the speed even more, or try to manually write an explicit integrator and see performance boost. However note when writing manual explicit state-stepping integration scheme, error in solution will be introduced and the trade-off effect is also TBD.

Moving on, once the integration has proceeded with the given initial guesses, conditions, and span; final permeate volume fractions will be outputted and the again the activity model can be used to calculate a permeate bulk composition for each permeant. This calue will be compared to the current iterate guess and nonlinear equations that the outer loop will be attempting to satisfy are as again as follows:

$$h_i = x_{i,iter}^{III} - x_i^{III}(\phi_L) = 0, \ i = 1, 2, ..., n \tag{31}$$

$$h_{n+1} = 1 - \sum x_i^{III} = 0 \tag{32}$$

With the final unknowns listed explicitly as:

$$(\mathbf{x}^{III}, N_{tot}^{V*})$$

Once this square system yields solutions that give function tolerances below a certain value, a solution is found. This is comparable to the FUD method excpet that the time to solve such and the feasible set of solutions is much larger (excat set TBD).

Highlighting that our method does not require knowledge of permeate conditions a priori and is a more physically accurate model for assymetric membranes; as many other papers have hinged this on knowing in order to solve such systems. [9] [11] [10] [7] [6] [1]

1.5 Our Second Method: Multiple Shooting Algorithm

In using our first shooting algorithm for strong cross-diffusional coupling ($Đ_{ij} \Rightarrow 0$) since the MS diffusivity is the reciprocal of the friction coefficient. So higher friction means stronger coupling and consequently MS diffusivity should go to zero for infinite friction. There may be other cases that this solution method is required for larger number of components, but the mathematical idea is that stiffness in the ODE/DAE system casuses unstabililty in the intergrator routines such that the integration thickness needs to be split up into subsections. See figure below for idea of this hybrid method between classical full discritization and our novel approach using a shooting algorithm.
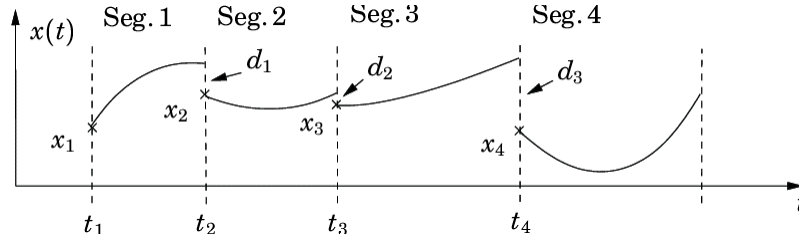

Figure 6: Multiple shooting method algorithm [Åkesson, Johan. (2020). Languages and Tools for Optimization of Large-Scale Systems (Doctoral Dissertation)].

Depending on the number of shooting points ($N = 1$ being the first shooting algorithm), $(N-1)(n+1)$

extra nonlinear functions are required for ODE system and $(N-1)(2n+1)$ for the DAE system taking into account the fugacities. These functions are simply subtracting the iterate guess and the final state variable output from the integrator instance. Quantitatively for 2 shooting points with domain split into $z_o = 0$, $z_1 = 0.5L$, and $z_2 = L$:

ODE:

$$\mathbf{h}_{z_1} = \boldsymbol{\phi}_{z_1}^{iter} - \boldsymbol{\phi}_{z_1}^{intg} \tag{33}$$

DAE:

$$\mathbf{h}_{z_1,1} = \boldsymbol{\phi}_{z_1}^{iter} - \boldsymbol{\phi}_{z_1}^{intg} \tag{34}$$

and

$$\mathbf{h}_{z_1,2} = \mathbf{f}_{z_1}^{iter} - \mathbf{h}_{z_1}^{intg} \tag{35}$$

Using this rigorous numerical method, one gets much better convergence for strong coupling at the expense of solution time and sensitivity to the initial guess. Full comparison TBD in numerical method publication.

1.6 Comparison of Methods

In order to compare methods, it is imperative to understand the metrics associated with a good numerical method. The criteria being quick convergence, mathematically accurate, and generalizability of initial guess.

The simulated systems to provide a good comparison are a three, five, and nine component permeation; the thermodynamic model was assumed to be the multicomponent Flory-Huggin polymer sorption model. The number of nodes was 20. Below are the results compared to our method in terms of solution, percent difference from our method, and solution time. **TBD**

2 Appendix A: Maxwell-Stefan Equation Analysis

Continuing on with argument presented in section 2.1.3 is that only n MS equations are needed, first lets write down the original Maxwell-Stefan equations. Specifically when the change from chemical potential gradients to membrane volume fraction gradients multiplied by a thermodynamic factor in equation (36):

$$
-\frac{\phi_i(z)}{RT}\nabla\mu_i^{II}(T,P,\boldsymbol{\phi}(z))|_{T,P} = -\frac{\phi_i(z)}{RT}\frac{d\mu_i^{II}(\boldsymbol{\phi}(z))}{dz} = -\phi_i(z)\frac{d\ln(a_i^{II}(\boldsymbol{\phi}(z)))}{dz}
$$
$$
= -\sum_{j=1}^{n}\phi_i(z)\frac{\partial\ln(a_i^{II}(\boldsymbol{\phi}(z)))}{\partial\phi_j(z)}\frac{d\phi_j(z)}{dz} = -\sum_{j=1}^{n}\Gamma_{ij}\frac{d\phi_j(z)}{dz} \tag{36}
$$

Note if we wrote the Maxwell-Stefan equations up until the $n+1$ component and took the chain rule (like going from end of line 1 in the above equation to the start of line 2) to get the thermodynamic matrix for $\boldsymbol{\phi}_{1:n+1}$, the matrix system would be rank deficient because of the dependant variable $\phi_{n+1} = \phi_m = 1 - \sum_{j=1}^{n}\phi_j$ and so the system has n independent variables ($\boldsymbol{\phi}_{1:n}$ and n independent Maxwell-Stefan equations. The $n+1$st equation is redundant and also related thermodynamically redundant by the Gibbs-Duhem relationship. It also doesn't make sense to take the chain-rule with dependant variables, as they would cancel each other out.

3 Appendix B: Derivation of chemical potential expression

This section is meant to derive a common equation written in membrane literature (see equations (3) and (4).) [12], however understanding its origin is good when seeing the chemical potential written in different ways for a long time without a source of origin. Below starts from the textbook definition of activity at some T,P:

$$RT \ln(a_i) = \mu_i - \mu_i^{\circ}(T, P) = \mu_i - G_i(T, P) + G_i(T, P^{\circ}) - G_i(T, P^{\circ}) \tag{37}$$

Then one can use the integrates fundamental property relation for Gibb's free energy $dG_i = V_i dP - S_i dT$ and fact that pure component $\mu_i^{\circ} = G_i(T, P^{\circ})$:

$$G_i(T, P^{\circ}) - G_i^{(}T, P) = \int_{T,P}^{T,P^{\circ}} V_i dP \tag{38}$$

So we end up with (for incompressible liquid:

$$\mu_i = \mu_i^{\circ} + RT \ln(a_i) + V_i(P - P^{\circ}) \tag{39}$$

or in differential form (constant T):

$$d\mu_i = RTd \ln(a_i) + V_i dP \tag{40}$$

4 Appendix C: Membrane Sorption Model Description

Given the general expression for the thermodynamic factors in equation (36), the next part is to present a specific derivation of such thermodynamic facotrs for complex models such as the multicomponent Flory-Huggins (FH) sorption model, classical dual sorption model (DSM), and the novel dual-mode sorption model of FH combined with the extended Langmuir (FH-LM).

4.0.1 Flory-Huggins Sorption Model

Starting with the multicomponent FH expression:

$$\ln(a_i^{II}) = \ln\left(\frac{\hat{f}_i^{II}}{f_i^{\circ}}\right) = ln(\phi_i) + (1 - \phi_i) - \sum_{\substack{j=1 \\ j \neq i}}^{n+1} \frac{\overline{V}_i}{\overline{V}_j}\phi_j$$

$$+ \left(\sum_{j=1}^{i-1} \chi_{ji}\phi_j\frac{\overline{V}_i}{\overline{V}_j} + \sum_{j=i+1}^{n+1} \chi_{ij}\phi_j\right)\left(\sum_{\substack{j=1 \\ j \neq i}}^{n+1} \phi_j\right) - \sum_{\substack{j=1 \\ j \neq i}}^{n+1}\sum_{k=j+1}^{n+1} \chi_{jk}\frac{\overline{V}_i}{\overline{V}_j}\phi_j\phi_k \tag{41}$$

Since that expression is in the form to differentiate the RHS w.r.t. each component volume fraction, the thermodynamic factors $\Gamma_{ij} = \phi_i \frac{\partial \ln(a_i^{II})}{\partial \phi_j} = \frac{\phi_i}{\hat{f}_i^{II}}\frac{\partial \hat{f}_i^{II}}{\partial \phi_j}$ can be evaluated as:

For $i = j$

$$(\Gamma)_{ij} = \phi_i \left(\frac{1}{\phi_i} - 1 - \overline{V}_i \sum_{k=1}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} + \overline{V}_i \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{\phi_k \chi_{mk}}{\overline{V}_j} + \frac{\overline{V}_i}{\overline{V}_m} - \sum_{k=i+1}^{n} \chi_{ik} \phi_k \right.$$
$$\left. - \overline{V}_i \sum_{k=1}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} - \chi_{im} \sum_{\substack{k=1 \\ k \neq i}}^{n} \phi_k - 2\phi_m \chi_{im} \right) \quad (42)$$

For $i < j$

$$(\Gamma)_{ij} = \phi_i \left(-\frac{\overline{V}_i}{\overline{V}_j} + \overline{V}_i \sum_{k=1}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} + \sum_{\substack{k=i+1 \\ k \neq j}}^{n} \phi_k \chi_{ik} + \chi_{ij} \sum_{\substack{k=1 \\ k \neq i,j}}^{n} \phi_k + 2\phi_j \chi_{ij} - \overline{V}_i \sum_{\substack{k=1 \\ k \neq i}}^{j-1} \frac{\phi_k \chi_{kj}}{\overline{V}_k} \right.$$
$$- \frac{\overline{V}_i}{\overline{V}_j} \sum_{k=j+1}^{n} \phi_k \chi_{jk} + \frac{\overline{V}_i}{\overline{V}_m} - \sum_{\substack{k=i+1 \\ k \neq j}}^{n} \chi_{ik} \phi_k - \overline{V}_i \sum_{k=1}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} - \chi_{im} \sum_{\substack{k=1 \\ k \neq i,j}}^{n} \phi_k + \overline{V}_i \sum_{\substack{k=1 \\ k \neq i,j}}^{n} \frac{\phi_k \chi_{mk}}{\overline{V}_j}$$
$$\left. + (\phi_m - \phi_j)(\chi_{im} + \chi_{ij} - \frac{\overline{V}_i}{\overline{V}_j} \chi_{jm}) - 2\phi_m \chi_{im} \right) \quad (43)$$

For $i > j$

$$(\Gamma)_{ij} = \phi_i \left(-\frac{\overline{V}_i}{\overline{V}_j} + \overline{V}_i \sum_{\substack{k=1 \\ k \neq j}}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} + \sum_{k=i+1}^{n} \phi_k \chi_{ik} + \chi_{ji} \frac{\overline{V}_i}{\overline{V}_j} \sum_{\substack{k=1 \\ k \neq i,j}}^{n} \phi_k + 2\phi_j \chi_{ij} \frac{\overline{V}_i}{\overline{V}_j} - \overline{V}_i \sum_{k=1}^{j-1} \frac{\phi_k \chi_{kj}}{\overline{V}_k} \right.$$
$$- \frac{\overline{V}_i}{\overline{V}_j} \sum_{k=j+1}^{n} \phi_k \chi_{jk} + \frac{\overline{V}_i}{\overline{V}_m} - \sum_{k=i+1}^{n} \chi_{ik} \phi_k - \overline{V}_i \sum_{\substack{k=1 \\ k \neq j}}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} - \chi_{im} \sum_{\substack{k=1 \\ k \neq i,j}}^{n} \phi_k + \overline{V}_i \sum_{\substack{k=1 \\ k \neq i,j}}^{n} \frac{\phi_k \chi_{mk}}{\overline{V}_j}$$
$$\left. + (\phi_m - \phi_j)(\chi_{mi} + \chi_{ij} \frac{\overline{V}_i}{\overline{V}_j} - \frac{\overline{V}_i}{\overline{V}_j} \chi_{jm}) - 2\phi_m \chi_{im} \right) \quad (44)$$

And note the subtlety in the fact that the membrane phase (II) volume fraction $\phi_m = \phi_{n+1}$ is a dependant variable so it must be substituted for equation (13) and then be accounted for in the derivatives as well.

4.0.2 Classical Dual Mode Sorption Model

For the classical dual mode sorption model (DMS), the volume basis is on volume of polymer. The volume fraction based Maxwell-Stefan was derived based on total system volume (defined as skeletal polymer and sorbed molecule(s) volume). Noting these differences, the classsical DMS model can first be written as:

$$c_i^{II,p} = c_{i,Henry}^{II,p} + c_{i,Langmuir}^{II,p} \quad (45)$$

where the superscript p denotes that the concentration is based on polymer volume.

Now assuming the molar volume is constant throughout each phase, we can substitute the relationship between volume fraction and concentration to simplify to volume fractions:

$$\frac{\phi_i^p}{\overline{V}_i} = \frac{\phi_{i,Henry}^p}{\overline{V}_i} + \frac{\phi_{i,Langmuir}^p}{\overline{V}_i} \tag{46}$$

simplifying,

$$\phi_i^p = \phi_{i,Henry}^p + \phi_{i,Langmuir}^p \tag{47}$$

And then substituting for the respective permeant volume based DMS relationships:

$$\phi_i^p = k_i \hat{f}_i^{II} + \frac{C_i^H b_i \hat{f}_i^{II}}{1 + \sum_{k=1}^n b_k \hat{f}_k^{II}} \tag{48}$$

Then finally to put this model on the basis of total system volume to be compatible with the MS framework presented in section 2.1.3, the skeletal polymer volume fraction in the sorped system can be applied as ($\phi_m = 1 - \sum_{j=1}^n \phi_j$):

$$\phi_i = \phi_m \phi_i^p = \phi_m \left(k_i \hat{f}_i^{II} + \frac{C_i^H b_i \hat{f}_i^{II}}{1 + \sum_{k=1}^n b_k \hat{f}_k^{II}} \right) \tag{49}$$

or with units to help understand:

$$\phi_i \left[\frac{cm^3 solv}{cm^3 total} \right] = \phi_m \left[\frac{cm^3 poly}{cm^3 total} \right] \phi_i^p \left[\frac{cm^3 solv}{cm^3 poly} \right] \tag{50}$$

And since there is no way to separate this equation explicitly write fugacity as a function of membrane phase (II) volume fractions, an implicit solution procedure is required to get the thermodynamic factor matrix needed in terms of fugacity:

$$\Gamma = \mathbf{diag}(\phi \circ \mathbf{f}^{-1}) \frac{\partial \mathbf{f}}{\partial \phi} \tag{51}$$

Note that open circle is the element wise multiplication of two vectors (in this case), a vector inverted is also element wise inversion, and then expanded into a diagonal matrix using "$\mathbf{diag}()$" notation.

In order to apply the implicit solution procedure, one must first define an implicit function from (50) as:

$$Q_i(\phi, \mathbf{f}) = \phi_i - \phi_m \left(k_i \hat{f}_i^{II} + \frac{C_i^H b_i \hat{f}_i^{II}}{1 + \sum_{k=1}^n b_k \hat{f}_k^{II}} \right) \tag{52}$$

Note that since the isotherm provides a continuous mapping of membrane phase (II) volume fractions to a unique membrane phase mixture fugacity, the implicit function can be rewritten as a function of solely membrane phase (II) volume fractions:

$$\lambda_i(\phi) = Q_i(\phi, \mathbf{f}(\phi)) = \phi_i - \phi_m \left(k_i \hat{f}_i^{II} + \frac{C_i^H b_i \hat{f}_i^{II}}{1 + \sum_{k=1}^n b_k \hat{f}_k^{II}} \right) \tag{53}$$

And now the total derivative can be expressed as (in matrix form for simplicity):

$$\frac{d\boldsymbol{\lambda}}{d\boldsymbol{\phi}} = \frac{\partial \mathbf{Q}}{\partial \mathbf{f}}\frac{\partial \mathbf{f}}{\partial \boldsymbol{\phi}} + \frac{\partial \mathbf{Q}}{\partial \boldsymbol{\phi}} = 0 \tag{54}$$

And then part of the thermodynamic factor matrix can be solved for as:

$$\frac{\partial \mathbf{f}}{\partial \boldsymbol{\phi}} = -\left(\frac{\partial \mathbf{Q}}{\partial \mathbf{f}}\right)^{-1}\frac{\partial \mathbf{Q}}{\partial \boldsymbol{\phi}} \tag{55}$$

Note these derivatives of Q above should be taken as if fugacity and volume fraction are independent variables and again $\phi_m = 1 - \sum_{k=1}^{n} \phi_k$:

Now the derivative matrices that are needed for equation (54) can be solved as:

For $i = j$

$$\left(\frac{\partial \mathbf{Q}}{\partial \mathbf{f}}\right)_{ij} = -\phi_m\left(k_i + \frac{(1 + \sum_{k=1}^{n} b_k \hat{f}_k^{II})C_i^H b_i - C_i^H b_i \hat{f}_i^{II} b_j}{(1 + \sum_{k=1}^{n} b_k \hat{f}_k^{II})^2}\right) \tag{56}$$

$$\left(\frac{\partial \mathbf{Q}}{\partial \boldsymbol{\phi}}\right)_{ij} = 1 + k_i \hat{f}_i^{II} + \frac{C_i^H b_i \hat{f}_i^{II}}{1 + \sum_{k=1}^{n} b_k \hat{f}_k^{II}} \tag{57}$$

For $i \neq j$

$$\left(\frac{\partial \mathbf{Q}}{\partial \mathbf{f}}\right)_{ij} = \phi_m\left(\frac{C_i^H b_i f_i b_j}{(1 + \sum_{k=1}^{n} b_k \hat{f}_k^{II})^2}\right) \tag{58}$$

$$\left(\frac{\partial \mathbf{Q}}{\partial \boldsymbol{\phi}}\right)_{ij} = k_i \hat{f}_i^{II} + \frac{C_i^H b_i \hat{f}_i^{II}}{1 + \sum_{k=1}^{n} b_k \hat{f}_k^{II}} \tag{59}$$

Then plugging in derivatives into equation (55) and finally into equation (51), then DMS thermodynamic factor matrix can be built.

4.0.3 Combined Flory-Huggins-Langmuir Model

For the novel combined Flory-Huggins-Langmuir (FHLM), the model can be written similar to DMS but replacing the Henry's Law sorption term with the Flory-Huggins type sorption term as:

$$c_i^{II} = c_{i,Flory-Huggins}^{II} + c_{i,Langmuir}^{II} \tag{60}$$

where the concentrations are normalized by the total system volume (defined as skeletal polymer, micropore volume and sorbed molecule(s) volume).

Making the same assumption with DMS that the partial molar volumes are equal in each phase and equal to the pure component molar volume, the model can be rewritten in terms of volume fractions like:

$$\phi_i = \phi_{i,Flory-Huggins} + \phi_{i,Langmuir} \tag{61}$$

In the classical Langmuir model, the free volume micropore capacity C_i^H is a material property and is normalized by the polymer mass or volume, so a volume correction term is required. Thus, including the volume correction terms for both contributions result in:

$$\phi_i = \phi_{i,Flory-Huggins}^{tmv} + \phi_m \phi_{i,Langmuir}^{p} \tag{62}$$

or with units to help understanding

$$\phi_i \left[\frac{cm^3 solv}{cm^3 total} \right] = \phi_{i,Flory-Huggins}^{tmv} \left[\frac{cm^3 solv}{cm^3 total} \right] + \phi_m \left[\frac{cm^3 poly}{cm^3 total} \right] \phi_{i,Langmuir}^{p} \left[\frac{cm^3 solv}{cm^3 poly} \right] \tag{63}$$

where the superscript p means the volume basis of skeletal polymer volume.

And then substituting for the respective LM relationship and keeping FH volume fraction as is since it is another implicit system of equations to solve for:

$$\phi_i = \phi_{i,FH} + \phi_m \frac{C_i^H b_i \hat{f}_i^{II}}{1 + \sum_{k=1}^{n} b_k \hat{f}_k^{II}} \tag{64}$$

In order to get the required thermodynamic matrix from equation (51), an implicit function must be build for the total membrane phase (II) volume fraction and for FH membrane phase (II) volume fraction using equation (41). Those equations look like:

$$Y(\boldsymbol{\phi}, \boldsymbol{\phi}_{FH}, \mathbf{f}) = \phi_i - \phi_{i,FH} - \phi_m \frac{C_i^H b_i \hat{f}_i^{II}}{1 + \sum_{k=1}^{n} b_k \hat{f}_k^{II}} \tag{65}$$

$$W(\boldsymbol{\phi}, \boldsymbol{\phi}_{FH}, \mathbf{f}) = \ln\left(\frac{\hat{f}_i^{II}}{f_i^\circ} \right) - ln(\phi_i) - (1 - \phi_i) + \sum_{\substack{j=1 \\ j \neq i}}^{n+1} \frac{\overline{V}_i}{\overline{V}_j} \phi_j$$

$$- \left(\sum_{j=1}^{i-1} \chi_{ji} \phi_j \frac{\overline{V}_i}{\overline{V}_j} + \sum_{j=i+1}^{n+1} \chi_{ij} \phi_j \right) \left(\sum_{\substack{j=1 \\ j \neq i}}^{n+1} \phi_j \right) + \sum_{j=1}^{n+1} \sum_{\substack{k=j+1 \\ j \neq i}}^{n+1} \chi_{jk} \frac{\overline{V}_i}{\overline{V}_j} \phi_j \phi_k \tag{66}$$

Now this time an implicit solution procedure must be applied twice since a overall volume fraction uniquely specifies the membrane phase (II) fugacity and FH volume fraction. (i.e. $\boldsymbol{\phi}_{FH}(\mathbf{f}(\boldsymbol{\phi}))$ since $\mathbf{f}(\boldsymbol{\phi})$ for the independent variable $\boldsymbol{\phi}$) See two equations below:

$$\frac{d\boldsymbol{\Lambda}}{d\boldsymbol{\phi}} = \frac{\partial \mathbf{Y}}{\partial \mathbf{f}} \frac{\partial \mathbf{f}}{\partial \boldsymbol{\phi}} + \frac{\partial \mathbf{Y}}{\partial \boldsymbol{\phi}_{FH}} \frac{\partial \boldsymbol{\phi}_{FH}}{\partial \boldsymbol{\phi}} + \frac{\partial \mathbf{Y}}{\partial \boldsymbol{\phi}} = 0 \tag{67}$$

$$\frac{d\mathbf{A}}{d\boldsymbol{\phi}} = \frac{\partial \mathbf{W}}{\partial \mathbf{f}} \frac{\partial \mathbf{f}}{\partial \boldsymbol{\phi}} + \frac{\partial \mathbf{W}}{\partial \boldsymbol{\phi}_{FH}} \frac{\partial \boldsymbol{\phi}_{FH}}{\partial \boldsymbol{\phi}} + \frac{\partial \mathbf{W}}{\partial \boldsymbol{\phi}} = 0 = \frac{\partial \mathbf{W}}{\partial \mathbf{f}} \frac{\partial \mathbf{f}}{\partial \boldsymbol{\phi}} + \frac{\partial \mathbf{W}}{\partial \boldsymbol{\phi}_{FH}} \frac{\partial \boldsymbol{\phi}_{FH}}{\partial \boldsymbol{\phi}} \tag{68}$$

So first $\frac{\partial \phi_{FH}}{\partial \phi}$ needs to be solved for using equation (68) as:

$$\frac{\partial \boldsymbol{\phi}_{FH}}{\partial \boldsymbol{\phi}} = -\left(\frac{\partial \mathbf{W}}{\partial \boldsymbol{\phi}_{FH}} \right)^{-1} \frac{\partial \mathbf{W}}{\partial \mathbf{f}} \frac{\partial \mathbf{f}}{\partial \boldsymbol{\phi}} \tag{69}$$

This can then be substituted into equation (67) and $\frac{\partial \mathbf{f}}{\partial \phi}$ can be solved for as:

$$\frac{\partial \mathbf{f}}{\partial \phi} = -\left(\frac{\partial \mathbf{Y}}{\partial \mathbf{f}} - \frac{\partial \mathbf{Y}}{\partial \phi_{FH}}\left(\frac{\partial \mathbf{W}}{\partial \phi_{FH}}\right)^{-1}\frac{\partial \mathbf{W}}{\partial \mathbf{f}}\right)^{-1}\frac{\partial \mathbf{Y}}{\partial \phi} \tag{70}$$

Then the thermodynamic factor matrix can be written as (using implicit solution manipulation):

$$\mathbf{\Gamma} = -\mathbf{diag}(\phi \circ \mathbf{f}^{-1})\left(\frac{\partial \mathbf{Y}}{\partial \mathbf{f}} - \frac{\partial \mathbf{Y}}{\partial \phi_{FH}}\left(\frac{\partial \mathbf{W}}{\partial \phi_{FH}}\right)^{-1}\frac{\partial \mathbf{W}}{\partial \mathbf{f}}\right)^{-1}\frac{\partial \mathbf{Y}}{\partial \phi} \tag{71}$$

And below are all the derivatives:
For $i = j$

$$\left(\frac{\partial \mathbf{W}}{\partial \mathbf{f}}\right)_{ij} = \frac{1}{\hat{f}_i^{II}} \tag{72}$$

$$\left(\frac{\partial \mathbf{Y}}{\partial \phi_{FH}}\right)_{ij} = -1 \tag{73}$$

$$\left(\frac{\partial \mathbf{Y}}{\partial \phi}\right)_{ij} = 1 + \frac{C_i^H b_i \hat{f}_i^{II}}{1 + \sum_{k=1}^n b_k \hat{f}_k^{II}} \tag{74}$$

$$\left(\frac{\partial \mathbf{Y}}{\partial \mathbf{f}}\right)_{ij} = -\phi_m\left(\frac{(1 + \sum_{k=1}^n b_k \hat{f}_k^{II})C_i^H b_i - C_i^H b_i \hat{f}_i^{II} b_j}{(1 + \sum_{k=1}^n b_k \hat{f}_k^{II})^2}\right) \tag{75}$$

$$\left(\frac{\partial \mathbf{W}}{\partial \phi_{FH}}\right)_{ij} = -\left(\frac{1}{\phi_i} - 1 - \overline{V}_i \sum_{k=1}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} + \overline{V}_i \sum_{\substack{k=1\\k \neq i}}^n \frac{\phi_k \chi_{mk}}{\overline{V}_j} + \frac{\overline{V}_i}{\overline{V}_m} - \sum_{k=i+1}^n \chi_{ik}\phi_k\right.$$
$$\left. - \overline{V}_i \sum_{k=1}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} - \chi_{im}\sum_{\substack{k=1\\k\neq i}}^n \phi_k - 2\phi_m \chi_{im}\right) \tag{76}$$

For $i < j$

$$\left(\frac{\partial \mathbf{W}}{\partial \phi_{FH}}\right)_{ij} = -\left(-\frac{\overline{V}_i}{\overline{V}_j} + \overline{V}_i \sum_{k=1}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} + \sum_{\substack{k=i+1\\k\neq j}}^n \phi_k \chi_{ik} + \chi_{ij}\sum_{\substack{k=1\\k\neq i,j}}^n \phi_k + 2\phi_j \chi_{ij} - \overline{V}_i \sum_{\substack{k=1\\k\neq i}}^{j-1} \frac{\phi_k \chi_{kj}}{\overline{V}_k}\right.$$
$$\left. - \frac{\overline{V}_i}{\overline{V}_j}\sum_{k=j+1}^n \phi_k \chi_{jk} + \frac{\overline{V}_i}{\overline{V}_m} - \sum_{\substack{k=i+1\\k\neq j}}^n \chi_{ik}\phi_k - \overline{V}_i \sum_{k=1}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} - \chi_{im}\sum_{\substack{k=1\\k\neq i,j}}^n \phi_k + \overline{V}_i \sum_{\substack{k=1\\k\neq i,j}}^n \frac{\phi_k \chi_{mk}}{\overline{V}_j}\right.$$
$$\left. + (\phi_m - \phi_j)(\chi_{im} + \chi_{ij} - \frac{\overline{V}_i}{\overline{V}_j}\chi_{jm}) - 2\phi_m \chi_{im}\right) \tag{77}$$

For $i > j$

$$\left(\frac{\partial \mathbf{W}}{\partial \phi_{FH}}\right)_{ij} = -\left(-\frac{\overline{V}_i}{\overline{V}_j} + \overline{V}_i \sum_{\substack{k=1 \\ k \neq j}}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} + \sum_{k=i+1}^{n} \phi_k \chi_{ik} + \chi_{ji}\frac{\overline{V}_i}{\overline{V}_j} \sum_{\substack{k=1 \\ k \neq i,j}}^{n} \phi_k + 2\phi_j \chi_{ij}\frac{\overline{V}_i}{\overline{V}_j} - \overline{V}_i \sum_{k=1}^{j-1} \frac{\phi_k \chi_{kj}}{\overline{V}_k}\right.$$

$$- \frac{\overline{V}_i}{\overline{V}_j} \sum_{k=j+1}^{n} \phi_k \chi_{jk} + \frac{\overline{V}_i}{\overline{V}_m} - \sum_{k=i+1}^{n} \chi_{ik}\phi_k - \overline{V}_i \sum_{\substack{k=1 \\ k \neq j}}^{i-1} \frac{\phi_k \chi_{ki}}{\overline{V}_k} - \chi_{im} \sum_{\substack{k=1 \\ k \neq i,j}}^{n} \phi_k + \overline{V}_i \sum_{\substack{k=1 \\ k \neq i,j}}^{n} \frac{\phi_k \chi_{mk}}{\overline{V}_j}$$

$$\left. + (\phi_m - \phi_j)(\chi_{mi} + \chi_{ij}\frac{\overline{V}_i}{\overline{V}_j} - \frac{\overline{V}_i}{\overline{V}_j}\chi_{jm}) - 2\phi_m \chi_{im}\right) \quad (78)$$

For $i \neq j$

$$\left(\frac{\partial \mathbf{W}}{\partial \mathbf{f}}\right)_{ij} = 0 \quad (79)$$

$$\left(\frac{\partial \mathbf{Y}}{\partial \phi_{FH}}\right)_{ij} = 0 \quad (80)$$

$$\left(\frac{\partial \mathbf{Y}}{\partial \phi}\right)_{ij} = \frac{C_i^H b_i \hat{f}_i^{II}}{1 + \sum_{k=1}^{n} b_k \hat{f}_k^{II}} \quad (81)$$

$$\left(\frac{\partial \mathbf{Y}}{\partial \mathbf{f}}\right)_{ij} = \phi_m \left(\frac{C_i^H b_i f_i b_j}{(1 + \sum_{k=1}^{n} b_k \hat{f}_k^{II})^2}\right) \quad (82)$$

And with that, the complete thermodynamic matrix for FH-LM can be built.

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