Modeling molecular transport in composite membranes with tubular fillers

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ABSTRACT

Nanotubes have been shown to possess intriguing mass transport properties, and are being incorporated into polymeric membranes for molecular separations. Although models have been developed to predict the effective permeability and selectivity of composite membranes with non-spherical fillers, they only apply to fillers with isotropic transport properties. However, molecular transport in tubular fillers is essentially one-dimensional. Here, an analytical model is developed – including the orientational distribution, aspect ratio, volume fraction, permeability of the fillers, and membrane non-idealities – to describe molecular transport in composite membranes with tubular fillers. Using the model, the effects of various structural and operational parameters of the composite membrane are assessed. It is found that the filler volume fraction, as opposed to the filler orientation, intrinsic permeability, and aspect ratio, has the most significant impact on the membrane permeability. Several case studies of binary mixture separations by ideal and non-ideal composite membranes with tubular fillers are discussed. Finally, an advanced composite membrane configuration that allows exploitation of the unique transport properties of tubular fillers is discussed.

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1. Introduction

Nanotubes are considered emerging nanostructured materials for use in membrane separation applications that aim for high throughput as well as low energy usage and capital costs [1]. They possess intriguing transport properties [2–7] related to their unique one-dimensional geometry and high aspect ratio [8–13]. Previous studies on transport of gas molecules and water in carbon nanotubes have suggested that they possess intrinsically high mass transport rates that are 1–3 orders of magnitude larger than other materials with similar channel sizes, such as zeolites [14–16]. Metal oxide (aluminoisilicate) nanotubes show fast water transport [6,7] and high water/alcohol selectivity [17], and are promising materials for a variety of separations. Recent progress has also been made on modification of nanotube interiors with functional groups [18], and the fabrication of polymer/nanotube composite membranes [19–23] as well as nanotube membranes [3]. Polymer/nanotube composite (“mixed-matrix”) membranes, in analogy to polymer/zeolite composite membranes [24–30], are attractive because of a combination of good processibility of the polymeric matrix and high separation performance of the nanotube fillers. This paper concerns the modeling of transport properties of polymer/nanotube composite membranes, of which there is currently little understanding.

Polymer/zeolite composite membranes for molecular separations have been studied for more than two decades. The well-known Maxwell model [31–33] provides a description of their performance in terms of the permeability and volume fractions of each phase (the polymer and the filler):

\[
P_{\text{eff}} = \frac{P_f + (n-1)P_m - (n-1)(P_m - P_f)\Phi_f}{P_f + (n-1)P_m + (P_m - P_f)\Phi_f}
\]

(1)

where \(P_{\text{eff}}\) is the effective permeability of the composite membrane, \(P_m\) is the permeability of the polymer matrix, \(P_f\) is the permeability of the filler, \(\Phi_f\) is the volume fraction of the filler (varies from 0 to 1), and \(n\) is the shape factor of the filler. When considering near-spherical fillers, such as typical zeolite crystals, the shape factor \(n\) is taken as \(n = 3\). Eq. (1) is then known as the “original Maxwell model”, and has been widely used to predict the permeability of polymer/zeolite composite membranes. On the other hand, \(n = 6\) for cylindrical fillers in a matrix, such as nanorods in a fluid. In this case, Eq. (1) is also known as the Hamilton–Crosser model [34,35]. Although the Maxwell model inclusive of a shape factor can model permeation in composite membranes containing cylindrical fillers, the assumption that the fillers have isotropic permeability renders it inapplicable to nanotubes, wherein molecular transport is confined to the axial direction of the nanotubes. Furthermore, the Maxwell model for non-spherical fillers assumes that the fillers are randomly oriented in the matrix, whereas previous studies have suggested that nanotubes can be well-aligned in a
Fig. 1. (a) An illustration of various molecular permeation paths through a composite membrane containing tubular fillers; and the total resistances-in-parallel attributed to each possible permeation pathway. (b) Molecular permeation through two artificial membrane domains: one without, and one with, tubular fillers; and the transport resistances of the two domains in parallel. (c) The specifications of a tubular filler, and the total resistance contributed by the resistance of the matrix and fillers in series.

liquid-phase dispersion [10,36] or a solid-phase matrix [9,13]. Hence, inclusion of the one-dimensional transport phenomena through nanotubes, and the orientation of the tubular fillers in the matrix, are both critical for a reasonable estimation of effective permeability in nanotube-containing composite membranes. An analytical model incorporating these factors would be useful in the design and evaluation of nanotube-containing membranes for separations applications.

Here, we present an analytical model to estimate permeation in composite membranes with tubular fillers. Several limiting cases of the model are assessed. This model is then used to investigate the permeation performance of composite membranes as a function of parameters including the filler volume fraction, orientation, and aspect ratio, as well as the relative permeabilities of the nanotubes and the matrix material. Furthermore, the effects of defects such as voids at the filler/matrix interfaces (due to poor compatibility between the two phases) [24,27,30,37,38] and pinholes that sometimes form under non-ideal membrane fabrication conditions (for example, fast evaporation of the solvent, or the size of the fillers being close to the membrane thickness) [39], are included. The performance of ideal (defect-free) and non-ideal (defective) composite membranes with tubular fillers in binary mixture separation is investigated using the model. Finally, we assess the potential performance enhancement of a state-of-the-art polymeric membrane by tubular and spherical fillers, and an advanced configuration of composite membrane with tubular fillers is discussed.

2. Model derivation

2.1. Transport derivation

Membrane permeation can be considered as being driven by the pressure differential between the feed and the permeate side of a membrane. The molecular flux (number of molecules transported across the membrane per unit time per unit membrane surface area) can be estimated by a simple permeance equation [33,40–42] that depicts the linear dependence between the flux (J) and the partial pressure differential of a certain species (Δp):

\[ J = \frac{P_{\text{eff}}}{t} \Delta p \]

where \( t \) is the thickness of the membrane, and \( P_{\text{eff}} \) is the effective permeability which is the product of diffusivity (kinetic effect) and solubility coefficient (thermodynamic effect) of the molecular species in the membrane material. One can also consider \( t/P_{\text{eff}} \) as the resistance of the membrane.

During mass transport in a composite membrane with tubular fillers, each potential molecular path (involving a different number of tubular fillers) has a different transport resistance (Fig. 1a). The resistance of the path without any tubular filler can be expressed as \( t_0/t_{\text{m}} \), where \( t_0 \) the product of the membrane thickness (t) and the tortuosity, \( \tau \), caused by the detour taken by molecules that strike the impermeable part (i.e. the side wall) of the tubular filler. However, because the outer diameter of the tubular filler (<20 nm) is often much smaller than the membrane thickness (>1 μm), the detour is seen to be quite minor for moderate or low volume fractions of the fillers. In other words, \( \tau \) can be taken as close to unity for these cases, in contrast to the greater tortuosity caused by other filler shapes (e.g. the total resistance of a path containing a certain number of fillers (\( n_f \)) can be modeled as two resistances in series: the matrix (\( t_{m,\text{avg}}/P_{m} \)) and the tubular fillers (\( t_{f,\text{avg}}/P_{m} \), where \( t_{m,\text{avg}} \) and \( t_{f,\text{avg}} \) are the path lengths of the molecule through the matrix and the filler respectively, for the pathway containing \( n_f \) fillers. To estimate the total membrane resistance from all the possible resistances-in-parallel, the volume fraction of each distinct path (i.e. containing different number of tubular fillers and different path lengths) must be known. Unfortunately, it is difficult to measure these individual volume fractions experimentally or estimate them theoretically. Hence, an analytical result cannot easily be derived from this model.

To deduce an analytical estimate of the effective permeability of a composite membrane with tubular fillers, the above model is simplified to that of a membrane composed of two types of resistances in parallel: one without fillers and one with fillers (Fig. 1b). For the resistance of the molecular path containing fillers, one can consider an “average” path with an average number of fillers. Hence the resistance of the domain containing fillers can be expressed by two resistances in series: one from the matrix (\( t_{m,\text{avg}}/P_{m} \)) and one from the tubular fillers (\( t_{f,\text{avg}}/P_{m} \)), where \( t_{m,\text{avg}} \) and \( t_{f,\text{avg}} \) are the path length of a molecule passing through the matrix and the filler respectively, for an average number of fillers. However, it is challenging to determine the filler volume fraction in the domain with the average number of fillers (since it would be larger than the bulk volume fraction of fillers); as well as the volume ratio between the domains with, and without, fillers. Hence, this two-domain model also does not lead to an analytical expression unless further simplified (below). Nevertheless, three cases are examined in which the permeability of the filler (for the desired molecular species) is much larger than, much smaller than, or similar to, the permeability of the matrix. When the filler permeability is much larger than that of the matrix, the resistance of the domain with fillers would be considerably smaller than the resistance of the domain without fillers. The overall resistance would be dominated by the domain with fillers and the permeability can be estimated by the two types of the resistances in that domain. In this case, the model of Fig. 1b can be simplified into that of Fig. 1c. Furthermore, in the
case that the filler permeability is much smaller than that of the matrix, the resistance of the domain with fillers can be expected to be much larger than that of the domain without fillers. Hence, the effective permeability would be either close to the permeability of the matrix (for low volume fraction of the fillers) or significantly lower than the permeability of the matrix (for high volume fraction of the fillers, due to the high tortuosity caused by the large amount of low-permeability fillers). Finally, for the case where the filler permeability is of the same order of magnitude as the matrix permeability, the effective permeability for the composite membrane would be close to the permeability of the matrix. Of these three cases, it is observed that only the first case (i.e., filler permeability much larger than the matrix permeability) can have a positive impact upon the effective permeability. Considering the fact that fillers are presumably incorporated to enhance the permeability of the membrane towards the desirable molecular species, it is appropriate to focus on this case (Fig. 1c).

2.2. Resistance-in-series model for a fixed tubular filler orientation

Permeation through a composite membrane with tubular fillers oriented in a fixed direction is considered first (Fig. 1c), wherein the matrix and the filler are described by the permeabilities $P_m$ and $P_f$, respectively. The tubular filler is described by an outer diameter $d$, length $l$, and an orientation described by an angle $\theta$ (varying from 0 to $\pi/2$ radians) with respect to the axis parallel to the bulk-phase transport direction. The 3-D orientation of the tubular filler is most rigorously described by two independent parameters, but only one degree of freedom ($\theta$) is necessary to describe permeation through a membrane since the fillers can be reasonably projected on a 2-D plane that provides an equivalent permeation pathway for a given membrane permeation process. The total resistance of this composite membrane is derived by considering the path of a single molecule traversing the membrane from the feed side to the permeate side. For the case of a “thick composite membrane” (i.e., the thickness of the membrane is much larger than the largest dimension of the filler), the path of a single molecule traverses both the matrix and the filler phases. Therefore, the total resistance is expressed as a series combination of the resistance from the matrix and the resistance from the filler in series (Fig. 2c). The permeance equation becomes:

$$J = \frac{\Delta p}{t_m / P_m + t_f / P_f}$$

(3)

where $t_m$ and $t_f$ are the total “transport lengths” of the molecule through the matrix and the filler respectively. Furthermore, $t_f$ can be expressed in terms of the filler dimensions and the average number of fillers ($n_f$) in the path from the feed to the permeate side: $t_f = l \cdot n_f$. On the other hand, $t_m$ can be considered as a “reduced” membrane thickness due to the incorporation of fillers, and can be written as:

$$t_m = t - n_f \cdot l \cdot \cos \theta$$

(4)

The projected 1-D length in the membrane transport direction for a single tubular filler, according to Fig. 1c, is $l \cos \theta + d \sin \theta$. The number of fillers in the molecular path, $n_f$, can be related to the total membrane thickness, the projected length of a single tubular filler, and the filler volume fraction, $\Phi_f$:

$$n_f = \frac{t}{l \cdot \cos \theta + d \cdot \sin \theta} \Phi_f$$

(5)

Combining Eqs. (3)–(5), the flux through a composite membrane with tubular fillers is written as:

$$J = \frac{\Delta p}{t_m (1 - \frac{l \cos \theta}{l \cos \theta + d \sin \theta} \Phi_f) + \frac{t_f}{P_f}}$$

(6)

Comparing Eqs. (2) and (6), the permeability enhancement factor ($P_{eff}/P_m$) is defined, which describes the change in permeability of the nanotube-containing membrane over the pure matrix material:

$$P_{eff}/P_m = \left[ \left( 1 - \frac{\cos \theta}{\cos \theta + \frac{d}{l} \sin \theta} \Phi_f \right) + \frac{P_m}{P_f} \left( \frac{1}{\cos \theta + \frac{d}{l} \sin \theta} \Phi_f \right) \right]^{-1}$$

(7)

where $\alpha = l/d$ is the aspect ratio of the tubular fillers. Eq. (7) summarizes the model (referred to as the “KJI model” in this paper) for permeation in a composite membrane with tubular fillers of a fixed orientation. According to the model, $P_{eff}/P_m$ is a function of the filler volume fraction ($\Phi_f$), orientation ($\theta$), aspect ratio ($\alpha$), and the permeability ratio of the filler and the matrix ($P_f/P_m$). Since the permeability is a product of the diffusivity and the solubility coefficient (Section 2.1), the permeability ratio used in this work includes the relative kinetics of molecules transporting through the interface between the matrix and the filler phase, as well as the solubility equilibrium at the matrix–filler interfaces.

2.3. Transport in composite membranes with a distribution of tubular filler orientations

Although a few experimental studies suggest that tubular fillers can be aligned in a specific direction in composite membranes [9,13], the conventional solvent-evaporation fabrication method yields membranes with tubular fillers that are randomly oriented [1,19–21,43]. Eq. (7) should hence be extended to include the distribution of filler orientations. Consider first a membrane with fillers of two orientations, $\theta_1$ and $\theta_2$ (Fig. 2a). It is first assumed that the fillers with different orientations are uniformly dispersed in the matrix. Based upon the assumption of uniform dispersion, every “artificial slice” (of thickness $t$, cut along the molecular transport direction, and no wider than the dimensions of one filler, as shown in Fig. 2b) has an identical effective permeability. Hence, only the
unit slice shown in Fig. 2b need be taken into account. It is then assumed that within the unit slice, different permutations of fillers along the molecular path will provide an identical permeation performance. Hence, one can group fillers with the orientation of \( \theta_1 \) on the top of the slice, and fillers with the orientation of \( \theta_2 \) on the bottom (Fig. 2c). These two domains occupy a thickness of \( t_{\theta_1} \) and \( t_{\theta_2} \), and are assigned effective permeabilities \( P_{\text{eff},\theta_1} \) and \( P_{\text{eff},\theta_2} \) respectively. The total resistance of the unit slice can be considered as a series combination of resistances (Fig. 2d), and the flux through the unit slice is:

\[
J = \frac{\Delta p}{(t_{\theta_1}/P_{\text{eff},\theta_1}) + (t_{\theta_2}/P_{\text{eff},\theta_2})}
\]

The thickness of each domain is proportional to the fraction of the fillers with a given orientation \( (f(\theta)) \) amongst all the fillers present in the whole membrane:

\[
\frac{t_{\theta_1}}{f(\theta_1)} = \frac{t_{\theta_2}}{f(\theta_2)}
\]

The summation of \( f(\theta_1) \) and \( f(\theta_2) \) must be unity, and the summation of the domain thicknesses must equal the membrane thickness \( t \). Therefore Eq. (9) can be rewritten as:

\[
J = \frac{\Delta p}{t/(f(\theta_1)/P_{\text{eff},\theta_1}) + (f(\theta_2)/P_{\text{eff},\theta_2})}
\]

The effective permeability of the membrane is hence given by:

\[
\frac{1}{P_{\text{eff}}} = \frac{f(\theta_1)}{P_{\text{eff},\theta_1}} + \frac{f(\theta_2)}{P_{\text{eff},\theta_2}}
\]

The effective permeability of each domain with a fixed filler orientation, i.e., \( P_{\text{eff},\theta_1} \) and \( P_{\text{eff},\theta_2} \), can be calculated by Eq. (7), where the filler volume fraction in each domain is the same as the filler volume fraction in the bulk phase (i.e. \( \Phi_{\theta_1} = \Phi_{\theta_2} = \Phi_{\theta} \)) regardless of the orientation and the thickness for each domain described in Eq. (10). An arbitrary distribution of filler orientations can now be generalized and Eq. (12) can be extended into the following form:

\[
\frac{1}{P_{\text{eff}}} = \int_{\theta=0}^{\theta=\pi/2} \frac{g(\theta)}{P_{\text{eff},\theta}} d\theta
\]

where \( g(\theta) \) is the normalized orientation distribution function of the filler with a tilt angle \( \theta \) in relation to direction of membrane transport. The continuous function \( g(\theta) \) has dimensions of \( 1/\theta \). Therefore, the permeability enhancement factor \( (P_{\text{eff}}/P_m) \) predicted by the BLN model is:

\[
\frac{P_{\text{eff}}}{P_m} = \left[ \int_{\theta=0}^{\theta=\pi/2} \frac{P_m}{P_{\text{eff},\theta}} g(\theta) d\theta \right]^{-1}
\]

where \( P_m/P_{\text{eff},\theta} \) is again given by Eq. (7). The integral of \( g(\theta) \) from 0 to \( \pi/2 \) with respect to \( \theta \) should equal to unity. Hence, the distribution function, \( g(\theta) \), of a membrane with a completely random distribution of orientations of tubular fillers can be considered a constant equal to \( 2/\pi \). Hence the permeability enhancement factor becomes:

\[
\frac{P_{\text{eff}}}{P_m} = \frac{\pi}{2} \left[ \int_{0}^{\pi/2} \frac{P_m}{P_{\text{eff},\theta}} d\theta \right]^{-1}
\]

2.4. Defects in composite membranes

The model developed in Sections 2.1–2.3 describes perfect membranes with no defects, whereas different types of defects are often formed during composite membrane fabrication. Specifically, as summarized in Fig. 3a, the incompatibility between the filler and

\[
\text{the matrix can create a void space surrounding the fillers. Additionally, the membrane may contain pinholes extending from the feed to the permeate side of the membrane. Such defects can significantly affect the membrane performance. Hence, it is critical to include them in permeation models and quantitatively assess their impact. When interfacial voids and pinholes are present, two more permeation paths are introduced. Firstly, a molecule at the filler/matrix interface can either diffuse through the tubular channel, or diffuse through the surrounding void space without entering the filler (since the side-wall of the tubular channel is insulated from the adjacent void space). Secondly, a pinhole can be modeled as an isolated channel with a relatively high permeability that allows molecules to bypass the membrane. A membrane with these two types of defects can be modeled as containing three pieces of side-by-side layers (Fig. 3b). These include: (i) a defect-free membrane with tubular fillers, (ii) a membrane composed of matrix and voids, and (iii) a pinhole. Applying the resistances-in-parallel concept (Fig. 3c), the effective permeability of a defective composite membrane \( (P_{\text{eff}}) \) is a linear combination of the permeability of each piece, weighted by its volume fraction [29,44]:

\[
P_{\text{eff}} = \frac{\Phi_j}{P_{j} + \Phi_j} P_{\text{eff},j} + \frac{\Phi_v}{P_{v} + \Phi_v} P_{\text{eff},v} + \frac{\Phi_p}{P_{p} + \Phi_p} P_{\text{eff},p}
\]

where \( P_{\text{eff},j} \) and \( P_{\text{eff},v} \) are the effective permeabilities of the regions of the membrane composed of filler/matrix and void/matrix respectively; \( P_p \) is the permeability of the pinhole; and \( \Phi_j, \Phi_v, \) and \( \Phi_p \) are the volume fractions of the imaginary pieces composed of
filler/matrix, void/matrix, and pinhole respectively. The volume fraction is constrained by conservation of volume:

\[ \Phi_f + \Phi_v + \Phi_p + \Phi_m = 1 \]  

(16)

where \( \Phi_m \) is the overall volume fraction of the matrix material in the composite membrane. To apply Eq. (15), Eq. (13) can be utilized to estimate the effective permeability of the layer of an ideal composite membrane with tubular fillers (\( P_{\text{eff}} \)). The effective permeability (\( P_{\text{eff}} \)) of the piece containing the matrix and void spaces can be predicted by the Hamilton–Crosster model [34,35], assuming that the void space is cylindrical in shape and the diffusion in the void space is isotropic:

\[ \frac{P_{\text{eff},v}}{P_m} = \frac{P_v + 5P_m - 5(P_m - P_v)\Phi_v}{P_v + 5P_m + (P_m - P_v)\Phi_v} \]  

(17)

Here \( P_v \) is the permeability in the void space. A previous study [33] has suggested that the permeation mechanism in the void can be considered as Knudsen diffusion; and that the solubility coefficient \( S \) can be estimated by the ideal gas law (\( S_C = 1/RT \)). It is reasonable to assume that the pinholes follow the same permeation mechanism as the void spaces. As a result, the permeabilities of the void space (\( P_v \)) and of the pinhole (\( P_p \)) can be written as:

\[ P_v = P_p = S_C \cdot D_{Kn} = \frac{1}{RT} \sqrt{\frac{32\pi^2 RT}{9}\frac{M}{v}} \]  

(18)

where \( D_{Kn} \) is the Knudsen diffusivity, \( r \) is the average diameter of the pinhole or void space, and \( M \) is the molecular weight of the transported molecule.

3. Limiting cases of the model

3.1. Membranes without fillers or matrix

For the membrane comprised of only the matrix material or the fillers, \( \Phi_f = 0 \) or 1. Therefore Eq. (6) reduces to that expected for single-phase membranes. For the membrane composed only of fillers (\( \Phi_f = 1 \)) with an undesired orientation (\( \theta = \pi/2 \)), Eq. (6) becomes:

\[ J = \frac{\Delta p}{(1/P_m) \cdot \ell + (1/P_f) \cdot \alpha \cdot t} \]  

(19)

The permeability of the matrix (\( P_m \)) is still present in the permeance equation because the gas molecules have to “hop” between the tubular fillers along the membrane transport direction in order to be able to pass through the membrane. However, since there is no matrix material really present in this system, one can assume that the inter-tubular “hops” from the tip of one nanotube to the other occur very fast relative to permeation through the fillers, i.e., the permeability of the hypothetical connecting “matrix” \( P_m \to \infty \). Hence, one obtains:

\[ J = \frac{P_m}{\alpha \cdot t} \Delta p \]  

(20)

where the effective permeability now becomes the permeability of the filler (\( P_f \)), and the characteristic length becomes the membrane thickness (\( t \)) multiplied by the aspect ratio of the tubular filler (\( \alpha \)). When the tubular filler is entirely oriented in the undesired transverse direction, \( \alpha \) is the “tortuosity” factor that increases the path length from the feed to the permeate side, thereby reducing the flux.

![Fig. 4. Effect of relative permeability (\( P_f/P_m \)) on the membrane permeability enhancement factor at different filler volume fractions, when (a) \( P_f/P_m > 1 \) and (b) \( P_f/P_m < 1 \).](image)

3.2. Composite membrane with fillers aligned in the desired orientation

For a membrane with fillers aligned in the desired orientation (\( \theta = 0 \)), Eq. (6) becomes:

\[ J = \frac{\Delta p}{[(1/P_m) - \Phi_f] \cdot \ell + (1/P_f) \cdot \Phi_f \cdot \alpha \cdot t} \]  

(21)

In this case, the flux is independent of the aspect ratio of the filler (\( \alpha \)). Fillers with the same permeability and volume fraction would hence provide the same flux regardless of filler geometry. This result may be modified if the surface resistances at the pore entrance/exit are significant in relation to the resistance for transport through the nanotube.

4. Predictions of separation properties

4.1. Relative permeability effects

The relative permeability (\( P_f/P_m \)) effect on the permeability enhancement factor of composite membranes (\( P_{\text{eff}}/P_m \)) is shown for \( P_f/P_m > 1 \) and \( P_f/P_m < 1 \) (Fig. 4a and b). The tubular fillers are assumed to have \( \alpha = 50 \) and a random orientation. Eq. (14) was numerically integrated to obtain the permeability. For \( P_f/P_m > 1 \),
a monotonic increase of \( P_{\text{eff}}/P_m \) with filler volume fraction \( \Phi_f \) is observed. However, the increase of \( P_{\text{eff}}/P_m \) becomes insignificant as \( P_f/P_m > 100 \). In other words, a tubular filler with a permeability much higher than the matrix does not provide a further permeability enhancement since the overall transport rate is now strongly limited by the resistance of the matrix. On the other hand, for \( P_f/P_m < 1 \), a monotonic decrease of \( P_{\text{eff}}/P_m \) is observed when increasing the filler volume fraction \( \Phi_f \). A decrease of \( P_{\text{eff}}/P_m \) is also observed for the case when \( P_f/P_m = 1 \). This is due to the random orientation of the tubular fillers, which creates tortuosity in the permeation path. One must be cautioned that when the permeability of the filler is much smaller than that of the matrix, the present resistance-in-series model may no longer be valid since the majority of the molecules may take the faster route through the matrix, which forms the continuous phase in the membrane. Such a concern can be taken into account with the inclusion of a parallel resistance for the continuous phase of the matrix, as addressed in Section 2.1. For applications of the composite membranes, a filler of higher permeability than the matrix will typically be used to improve the permeability of the membrane.

4.2. Filler orientation effects

The effect of the filler orientation \( (\theta) \) is summarized in Fig. 5a and b, for \( P_f/P_m \) values of 1000 and 10 respectively, and \( \alpha = 50 \). For \( P_f/P_m = 1000, P_{\text{eff}}/P_m \) is insensitive to the filler orientation over most orientations, and only creates a significant drop in when the completely undesired orientation \( (\theta = \pi/2) \) is approached. On the other hand, when the filler permeability is closer to that of the matrix \( (P_f/P_m = 10) \), the enhancement factor becomes more sensitive to the filler orientation. Based upon the KJN model predictions, it is suggested that the alignment of the tubular fillers in the most desired orientation \( (\theta = 0) \) provides no significant improvement in performance than the randomly oriented configuration. However, the undesired orientation \( (\theta = \pi/2) \) should be avoided during composite membrane fabrication. It is also seen that the sensitivity of the permeability enhancement factor \( (P_{\text{eff}}/P_m) \) to the filler orientation becomes higher when the permeability of the filler is somewhat similar to that of the matrix.

4.3. Aspect ratio effects

The effect of the filler aspect ratio \( (\alpha) \) when \( P_f/P_m = 1000 \) is summarized in Fig. 6a-c for fillers that at \( \theta = 0^- \), randomly oriented, and at \( \theta = \pi/2 \), respectively. For the case of fillers aligned in the direction of membrane transport \( (\theta = 0^-) \), the permeability enhancement is independent of the aspect ratio. As shown in Section 3.2, the only filler volume fraction \( \Phi_f \) and the relative permeability \( (P_f/P_m) \) affect the effective permeability in this case. On the other hand, randomly oriented fillers with higher aspect ratios (i.e. the longer tubers) enhance the permeability more substantially, since the molecules remain in the more permeable phase for a longer time. However, when the filler is undesirably oriented at \( \theta = \pi/2 \), fillers with a higher aspect ratio create a longer detour and result in a lower effective permeability. The KJN model may not apply to the case when the fillers are oriented at \( \theta = \pi/2 \) because a gas molecule would be unlikely to enter the tubular fillers when they are undesirably oriented. For such a case, the transport through the matrix may dominate the effective permeability, and thus the relative permeability \( (P_f/P_m) \) would be close to unity.

4.4. Comparisons with current models

The permeability enhancement factor \( (P_{\text{eff}}/P_m) \) of the KJN model – which is based upon a one-dimensional resistance-in-series transport model of molecules in composite membranes with tubular fillers – is compared with current models for isotropic spherical fillers (Maxwell) and for isotropic tubular fillers (Hamilton–Crosser). The comparisons are made at different values of \( P_f/P_m \) for all models; for the KJN model, an aspect ratio of 50 and a random orientation of fillers are considered. The comparison between the KJN model and the isotropic Maxwell model is summarized in Fig. 7a. At any given relative permeability and filler volume fraction, the enhancement factor estimated by the Maxwell model is consistently higher than that predicted by KJN model. For example, with \( P_f/P_m = 1000 \) and \( \Phi_f = 0.7 \) the difference of \( P_{\text{eff}}/P_m \) between the Maxwell and KJN models is as much as a factor of 2.7. The difference of the enhancement factor between KJN and Hamilton–Crosser models is even larger, and is up to a factor of 5 for \( P_f/P_m = 1000 \) and \( \Phi_f = 0.7 \) (Fig. 7b). These differences are due to the fundamental dissimilarity of permeation paths in tubular fillers and isotropic fillers. Typical isotropic fillers such as zeolites or metal organic frameworks (MOFs) with three-dimensional interconnected channels allow molecular transport between the filler and the matrix at any point of the interface of the two materials, whereas for tubular fillers the transport between the filler and the matrix can only take place at the tips of the filler. The “accessible surface area” of the fillers, which strongly correlates to their capability of enhancing the permeability for the matrix, can be quantitatively assessed. For the same volume fraction of

![Fig. 5. Effect of filler orientation effect on permeability enhancement factor at different filler volume fractions, when (a) \( P_f/P_m = 1000 \) and (b) \( P_f/P_m = 10 \).](image-url)
spherical and tubular fillers, it can easily be shown that the ratio of their total accessible surface areas ($R_{s/t}$) is:

$$R_{s/t} = 3 \left( \frac{l}{D} \right)$$  \hspace{1cm} (22)

where $D$ is the diameter of a spherical filler. In general, considering the same size of a spherical and a tubular filler ($l=D$) the isotropic spherical filler has higher accessible surface area in comparison to tubular fillers by a factor of 3 based upon Eq. (22). The previously discussed fact that a tubular filler has an intrinsically smaller surface area than a spherical filler also supports the observations in Fig. 8a, wherein the isotropic spherical filler outperforms the tubular filler in the sense of enhancing the permeability of the matrix. However, the predictions in Fig. 8a are based on KJN and Maxwell models for tubular and isotropic spherical fillers respectively, and neither of them includes the absolute value of particle size (which can potentially play a role in the effective permeability according to aforementioned discussion). Hence a detailed numerical model, which is beyond the scope of the present paper, will be needed in order to capture the effect of filler particle size.

At this stage, a question naturally arises whether the Maxwell-type models can be re-derived to describe permeation in composite membranes containing tubular fillers. In Appendix A, a Maxwell-type model for tubular fillers in a matrix is derived, and subjected it to the same four self-consistency assessments as performed on the present KJN model. It is seen that while the KJN model passes all of these tests, the Maxwell-type model fails when considering filler orientations that are far from the ideal ($\theta = 0$) orientation. Furthermore, it is more difficult to include the filler orientation in the Maxwell-type model. It can be concluded that the KJN model provides more accurate physical insights and broader applicability, and is a more appropriate model for permeation in membranes with tubular fillers.
4.5. Separation of binary mixtures

After studying how the incorporation of tubular fillers in composite membranes impacts the effective permeability, the performance of composite membranes with tubular fillers is now explored in binary mixture separations. In addition to the permeability, the selectivity of the membrane (Sij) defined as the ratio of permeabilities of two different types of molecules i and j is of high importance. The industrially important separation of carbon dioxide from methane is taken as an example. Two matrix materials are considered: 3,3’,4,4’-benzophenonetetraacarbonylecyanidine-4,4’-oxydianilin (BTDA-p,p’ODA), a highly selective polymer with low permeability [45,46]; and poly(1-trimethylsilyl-1-propyne) (PTMSP), a low-selectivity polymer with high permeability [46]. For the BTDA matrix, a hypothetical, highly CO2-permeable (\(P_{\text{CO}_2}/P_{\text{CH}_4} \gg 1\)) tubular filler with no CO2/CH4 selectivity is chosen in order to enhance the permeability of the membrane. On the other hand, for the PTMSP matrix, a hypothetical highly CO2-selective filler is embedded to enhance the selectivity. In both cases, the fillers have \(\alpha = 50\) and are randomly oriented. The transport parameters of both the polymers and the hypothetical tubular fillers are summarized in Table 1.

As shown in Fig. 8a, for the BTDA matrix with high selectivity (\(S_{\text{CO}_2/\text{CH}_4} = 57\)) but low permeability (\(P_{\text{m,CO}_2} = 0.625\) Barrer), the incorporation of a highly permeable tubular filler increases the effective permeability of the membrane. Consistent with the results in Section 4.1, a higher volume fraction of the filler improves the effective permeability, which however begins to plateau when \(P_{\text{f,CO}_2}/P_{\text{m,CO}_2} > 100\). At the same time, the membrane selectivity is not dramatically lowered. When the permeability of the filler is close to that of the matrix (\(P_{\text{f,CO}_2}/P_{\text{m,CO}_2} < 100\)), there is an observable drop in selectivity compared to the pure polymeric membrane, since the filler is non-selective (\(S_{\text{CO}_2/\text{CH}_4} = 1\)). However, when the filler is much more permeable than the matrix (\(P_{\text{f,CO}_2}/P_{\text{m,CO}_2} > 100\)), the selectivity is dominated by the low-permeability matrix and is maintained at the level of the pure polymer (\(S_{\text{CO}_2/\text{CH}_4} = 60\)). Generally, when the filler is less selective than the matrix, a highly permeable filler always benefits the membrane permeability and does not appreciably lower the selectivity. For the matrix with high permeability (\(P_{\text{m,CO}_2} = 18,000\) Barrer) but low selectivity (\(S_{\text{CO}_2/\text{CH}_4} = 4.8\)), one can reasonably expect an enhancement of overall selectivity by using a highly selective filler (\(S_{\text{CO}_2/\text{CH}_4} = 30\)). However, as summarized in Fig. 8b, a significant improvement of selectivity is only observed when the selective filler has a lower permeability than the matrix (\(P_{\text{f,CO}_2}/P_{\text{m,CO}_2} < 1\)). At the same time, the enhancement of selectivity sacrifices the effective permeability, resulting in \(P_{\text{f,CO}_2}/P_{\text{m,CO}_2} < 1\). However, the model prediction may not be valid when \(P_{\text{f,CO}_2}/P_{\text{m,CO}_2}\) is much smaller than unity, since gas molecules would mainly transport through the continuous-phase matrix without entering into the relatively impermeable fillers. On the other hand, when the permeability of the selective filler is much larger than that of the matrix (\(P_{\text{f,CO}_2}/P_{\text{m,CO}_2} > 10\)), the selectivity shows no improvement. However, for the case of \(P_{\text{f,CO}_2}/P_{\text{m,CO}_2} > 10\), the incorporation of filler shows no enhancement in selectivity but an improvement in permeability is observed. In general, when the filler is more selective than the matrix, there is a trade-off between the improvement of selectivity and permeability. A filler that is more selective than the matrix can only improve either the selectivity or the permeability, depending on the relative permeability (\(P_{\text{f,CO}_2}/P_{\text{m,CO}_2}\)). A similar trade-off has also been discovered for composite membranes with isotropic spherical fillers [30,47,48].

4.6. Effects of interfacial voids and pinholes

The examples in the previous section are used as a basis for assessing the impact of defects such as interfacial void spaces and pinholes on the membrane performance. To represent typical defects of this nature, average channel sizes of 5 nm and 50 nm

---

**Table 1**

<table>
<thead>
<tr>
<th>Material or defect</th>
<th>Permeation property</th>
<th>(P_{\text{CO}_2}) (Barrer)</th>
<th>(P_{\text{CH}_4}) (Barrer)</th>
<th>(S_{\text{CO}_2/\text{CH}_4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDB-p,p’ODA</td>
<td></td>
<td>0.625</td>
<td>0.011</td>
<td>57</td>
</tr>
<tr>
<td>PTMSP</td>
<td></td>
<td>18,000</td>
<td>4190</td>
<td>4.3</td>
</tr>
<tr>
<td>Hypothetical low-selectivity tubular filler</td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>Hypothetical low-selectivity tubular filler</td>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Void space with average diameter of 5 nm</td>
<td></td>
<td>15,200</td>
<td>25,200</td>
<td>0.6</td>
</tr>
<tr>
<td>Pinhole with average diameter of 50 nm</td>
<td></td>
<td>152,000</td>
<td>252,000</td>
<td>0.6</td>
</tr>
</tbody>
</table>
are assumed for the interfacial voids and pinholes, respectively. The permeability of the void space and the pinhole at 25 °C can be estimated by Eq. (18), and the results are summarized in Table 1. The effect of nanoscale voids surrounding the tubular fillers is summarized in Fig. 9. In the case of Fig. 9a, a non-selective tubular filler ($S_{\text{CO}_2/\text{CH}_4} = 1$) is incorporated to enhance the permeability of the highly selective ($S_{\text{CO}_2/\text{CH}_4} = 57$) but low-permeability ($P_{m_{\text{CO}_2}} = 0.625$ Barrer) matrix. The presence of voids significantly increases the membrane permeability for any given $P_{T_{\text{CO}_2} / P_{m_{\text{CO}_2}}}$. This is due to several factors, including the high permeability of the void space and its isotropic nature (which intrinsically provides higher permeability than a tubular filler). Furthermore, the presence of voids at low $P_{T_{\text{CO}_2} / P_{m_{\text{CO}_2}}}$ also improves the selectivity. When the permeability of the tubular filler is close to that of the low-permeability matrix, the highly permeable void space dominates the molecular transport in the region around the filler. The composite membrane now resembles a combination of only the matrix and the void space, which has roughly a five orders-of-magnitude higher permeability than the matrix. Hence, the selectivity is now close to the matrix selectivity of 57, depending on the volume fraction of the void space. On the other hand, the presence of voids in the case of a highly selective tubular fillers $S_{\text{CO}_2/\text{CH}_4} = 30$ incorporated in a low-selectivity ($S_{\text{CO}_2/\text{CH}_4} = 4.8$) but highly permeable matrix ($P_{m_{\text{CO}_2}} = 1.80 \times 10^4$ Barrer), monotonically improves the effective permeability for reasons similar to those discussed in the previous case. However, the void space significantly lowers the selectivity in comparison to a defect-free composite membrane, by allowing molecules to bypass the highly selective tubular filler. An interesting phenomenon in Fig. 9b is the maximum in the membrane selectivity with respect to the relative permeability $P_{T_{\text{CO}_2} / P_{m_{\text{CO}_2}}}$. At low $P_{T_{\text{CO}_2} / P_{m_{\text{CO}_2}}}$, the highly permeable void space dominates the molecular transport rate in the region of the void space/filler. The selectivity of the composite membrane is then dominated by the matrix. On the other hand, at high $P_{T_{\text{CO}_2} / P_{m_{\text{CO}_2}}}$, the permeability of the tubular filler is higher than that of the void space. Hence, the filler dominates the transport in the region of the void space/filler, since the mass transport in the void space around the filler can be modeled by the resistances of the void space and the filler in parallel (Fig. 3). Similar to the findings of Section 4.5, the overall selectivity of the composite membrane is now determined by the relatively low-permeability matrix. In general, interfacial voids can enhance both selectivity and permeability when fillers are incorporated to enhance permeability of a highly selective matrix; but their presence does not benefit the case wherein fillers are embedded to improve the selectivity of a highly permeable matrix.

The effect of pinholes on the membrane performance is evaluated in Fig. 10. In analogy to the void spaces, the case of highly permeable but non-selective ($S_{\text{CO}_2/\text{CH}_4} = 1$) fillers incorporated to improve the permeability of a highly selective ($S_{\text{CO}_2/\text{CH}_4} = 57$) but low-permeability ($P_{m_{\text{CO}_2}} = 0.625$ Barrer) matrix is considered in Fig. 10a. Even a trace volume of pinholes causes
a dramatic increase of permeability, and also greatly reduces the high selectivity that would normally be derived from the matrix, lowering it to that of the pinhole \((S_{\text{CO}_2/\text{CH}_4} = 0.6)\). These phenomena clearly occur because the pinhole provides a low-selectivity but high-permeability channel for molecules to bypass the membrane from the feed side to the permeate side. In comparison, the void spaces only allow molecules to bypass the filler but not the matrix, since the voids are embedded in the matrix as a discrete phase. For the case of highly selective fillers \((S_{\text{CO}_2/\text{CH}_4} = 30)\) embedded in a permeable but low-selectivity matrix, the presence of pinholes monotonically increases the effective permeability as the volume fraction of the pinhole increases (Fig. 10b). However, even a trace volume of pinholes \((\phi_p = 10^{-2})\) leads to a complete loss of selectivity of the membrane, and hence pinholes should obviously be avoided during membrane fabrication. There also exists a maximum in selectivity with respect to \(P_{f,\text{CO}_2}/P_{m,\text{CO}_2}\); for reasons similar to the case of voids.

Fig. 11. Effects of fillers on permeability and selectivity of composite membranes with Cellulose Acetate as a matrix. (a)–(c) show predictions of the KJN model for tubular fillers with selectivities of 1, 10, and 50 respectively; whereas (d)–(f) show predictions of the Maxwell model for spherical isotropic fillers with filler selectivity of 1, 10, and 50 respectively. In these plots, the filler volume fraction (\(\phi_f\)) is the independent variable.
4.7. Filler effects on cellulose acetate membranes for CO\textsubscript{2}/CH\textsubscript{4} separations

Cellulose acetate is one of the state-of-the-art polymers for natural gas separation, due to its good selectivity (S\textsubscript{CO\textsubscript{2}/CH\textsubscript{4}} up to 25) and robustness [49,50]. However, the efficiency of current cellulose acetate-based natural gas separation membranes is limited by its low permeability (P\textsubscript{m,CO\textsubscript{2}} = 3 Barrer). Fig. 11a-c summarizes the tubular filler effect for different filler permeabilities, selectivities, and volume fractions. For a non-selective filler (S\textsubscript{CO\textsubscript{2}/CH\textsubscript{4}} = 1) (Fig. 11a) of much higher permeability than the matrix (e.g., P\textsubscript{f,CO\textsubscript{2}} > 300 Barrer), the effective permeability of the resulting composite membrane is more enhanced and the high selectivity from the matrix is being preserved, in comparison to fillers with low permeability (P\textsubscript{f,CO\textsubscript{2}} < 30 Barrer). On the other hand, when a somewhat selective tubular filler is used (S\textsubscript{CO\textsubscript{2}/CH\textsubscript{4}} = 10) (Fig. 11b), the composite membrane selectivity becomes closer to that of the pure cellulose acetate membrane if the filler permeability is low (P\textsubscript{f,CO\textsubscript{2}} < 30 Barrer). If highly selective tubular fillers (e.g., S\textsubscript{CO\textsubscript{2}/CH\textsubscript{4}} = 50) (Fig. 11c) are prepared and embedded into the cellulose acetate matrix, the enhancement of the selectivity is only observed when the permeability of the fillers is close to the matrix permeability, i.e., the two phases are “well matched”. No significant selectivity improvement is observed when the permeability of the tubular fillers is much higher than that of the matrix, and this observation supports the discussion in Section 4.5. Comparisons of spherical isotropic fillers, whose effective permeabilities are estimated by the Maxwell model, with the same intrinsic permeability and selectivity are summarized in Fig. 11d–f. When the filler selectivity is lower than that of the matrix (Fig. 11d and e), spherical fillers can better enhance the permeability but lead to a greater loss in selectivity, in comparison to tubular fillers. On the other hand, when the fillers have higher selectivity (Fig. 11f) than the matrix, spherical fillers show a more significant enhancement of both permeability and selectivity than tubular fillers. This observation agrees with the results of Section 4.4, in that isotropic fillers can more efficiently improve the effective permeability of composite membranes than anisotropic tubular fillers.

4.8. Advanced configuration of composite membranes with tubular fillers

In Sections 4.4 and 4.7, it was demonstrated that spherical isotropic fillers generally enhance the permeability of composite membranes to a greater extent than tubular fillers. However, the focus was on membranes whose thickness is much larger than the individual filler length. The fillers do not provide “direct” channels for molecules from the feed to the permeate side, and the effective permeability is thus limited by the matrix. Hence, although previous studies have shown that nanotubes possess superior transport properties, they cannot be exploited fully by conventional composite membranes. On the other hand, a composite membrane has been conceived in which all the fillers span the membrane thickness and serve as direct channels from the feed to permeate side for molecules [4,23]. Such a membrane may be quite thin (< 1 μm). Transport in this membrane can be modeled by two resistances in parallel, and the effective permeability can be written as:

\[
P_{\text{eff}} = (1 - \Phi_f)P_m + \Phi_f P_f
\]

The permeability and selectivity of “conventional” and “advanced” composite membranes with tubular fillers are compared in Fig. 12a-b, with parameters from Section 4.7. The advanced membrane shows substantially higher permeability, since transport is no longer limited by the matrix. For tubular fillers with lower selectivity than the matrix, the advanced membrane does not preserve the high matrix selectivity (Fig. 12a) as efficiently as the conventional membrane because the highly permeable tubular fillers dominate the mass transport in the “advanced” composite membranes. As a consequence, when the fillers have high selectivity and permeability, large performance enhancements can be realized as long as the fillers possess both good permeability and good selectivity (e.g., the red solid circle in Fig. 12b). (For interpretation of the references to color in this paragraph, the reader is referred to the web version of the article.)

5. Conclusions

An analytical model has been developed for describing molecular transport in composite membranes with tubular fillers. It includes the key microstructural parameters, namely the filler volume fraction (\(\Phi_f\)), filler aspect ratio (\(\alpha\)), an arbitrary filler orientation distribution function (\(f(\theta)\)), the permeability ratio of the filler and the matrix (\(P_f/P_m\)), and the presence of voids and pinholes. The model is first validated for several limiting cases, and then used to predict the permeability and selectivity of several composite membranes containing tubular fillers with a range of
properties and embedded in different polymers. A number of general conclusions can be drawn from our predictions. First, a high filler volume fraction \( \Phi_f \) always benefits the membrane permeability. Second, a relative permeability \( \Phi_f / \Phi_m \) larger than unity can improve membrane permeability, but little further enhancement occurs after \( \Phi_f / \Phi_m > 100 \). Third, a composite membrane with randomly oriented fillers provides practically equal performance to membrane in which the fillers are aligned in the desired orientation (\( \theta = 0 \)). However, a membrane with fillers aligned at the undesired orientation (\( \theta = \pi/2 \)) has a dramatically lower permeability. Fourth, the aspect ratio (\( \alpha \)) does not impact the permeability of a membrane with fillers aligned at the desired orientation. For a membrane with randomly oriented fillers, a high aspect ratio is preferred since it provides a higher effective permeability. Fifth, the current models for isotropic fillers (Maxwell and Hamilton–Crosse) strongly deviate from the predictions of the present KJN model, since they do not account for the highly anisotropic transport in the tubular filler.

The performance of membranes containing tubular fillers in mixture separations was explored, and several conclusions were reached. Non-selective but highly permeable fillers in a selective but low-permeability matrix can enhance membrane permeability and maintain selectivity. Highly selective fillers in a permeable but low-selectivity matrix can enhance selectivity only when \( \Phi_f / \Phi_m \leq 1 \), whereas a highly selective filler possessing high permeability can only enhance the effective permeability. Additionally, void spaces or pinholes prevent selectivity improvement even when \( \Phi_f / \Phi_m \leq 1 \). The membrane performance is more sensitive to the presence of pinholes, which cause a precipitous decrease in selectivity. Furthermore, case studies were performed to understand how tubular and spherical isotropic fillers affect the performance of state-of-the-art polymeric membranes. For conventional composite membranes of much larger thickness than the filler dimensions, the tubular filler must have far superior intrinsic transport properties than spherical fillers in order to obtain the same performance enhancement. On the other hand, the fabrication of advanced composite membranes with selective tubular fillers spanning the membrane thickness is seen to be highly advantageous.

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Appendix A.

A.1. Derivation of Maxwell-type model for tubular fillers

In this section, the derivation of a Maxwell-type model for composite membranes with tubular fillers is outlined, analogous to the conventional Maxwell model for membranes with isotropic spherical fillers [31,51]. It includes derivation of the pressure profile of a matrix with one tubular filler, and the extension of this pressure profile to a matrix with a given amount of tubular filler.

A.1.1. Pressure profile of a matrix with one tubular filler

First, a two-dimensional matrix with one tubular filler is considered, as illustrated in Fig. A1a. The governing equation for the pressure profile for the matrix and the filler is:

\[
\nabla^2 p_f = \nabla^2 p_m = 0 \tag{A.1}
\]

where \( p_f \) and \( p_m \) are the pressures in the filler and the matrix as functions of position. The membrane usually has a significantly larger length in \( x \) direction than in \( y \) direction, and the applied pressure gradient is only in the \( y \) direction. Hence it is reasonably assumed that there is negligible pressure gradient in \( x \) direction for the matrix. On the other hand, due to the geometrical constraint, mass transport in the interior of the filler can be considered, so that the pressure gradient of the filler in \( y \) direction can be artificially projected to simplify the mathematics. A "pseudo-one-dimensional" model is obtained, and the two governing equations (A.1) become two second-order ODEs in a single variable \( y \).

Assuming a given pressure, \( p_0 \), at the center of the tubular filler:

\[
p_f(y = 0) = p_0 \tag{A.2}
\]

A known constant pressure gradient \( A \) in \( y \) direction is considered to be applied on the matrix:

\[
dp_m/dy = A \tag{A.3}
\]

Continuity of pressure and mass flux at the filler–matrix interface leads to:

\[
p_f \left( y = \frac{l}{2} \cos \theta \right) = p_m \left( y = \frac{l}{2} \cos \theta \right) \tag{A.4}
\]

\[
p_f \frac{dp_f}{dy} \left( \frac{l}{2} \cos \theta \right) = p_m \frac{dp_m}{dy} \left( y = \frac{l}{2} \cos \theta \right) \tag{A.5}
\]

where \( p_f \) and \( p_m \) are the permeability of the filler and matrix, and \( \xi \) is the axis along which the filler is oriented. The relation between \( dy \) and \( d\xi \) is \( d\xi = \cos \theta \cdot dy \). Eq. (A.5) can thus be rewritten as:

\[
p_f \frac{dp_f}{dy} \left( y = \frac{l}{2} \cos \theta \right) \cdot \cos^2 \theta = p_m \frac{dp_m}{dy} \left( y = \frac{l}{2} \cos \theta \right) \tag{A.6}
\]

With the above specifications, the ODEs are solved to yield:

\[
p_m(y) - p_0 = A \frac{l \cdot \cos \theta}{2} \left[ \frac{p_m}{p_f} \cos^2 \theta - 1 \right] + Ay \tag{A.7}
\]

A.1.2. Pressure profile for a matrix with a given amount of tubular filler

Next, tubular fillers, \( n_f \) in number, and at the same orientation, dispersed in a matrix as illustrated in Fig. A1b are considered. As in the conventional Maxwell model, the fillers have a fairly dilute concentration so that they do not interact. Hence the pressure profiles derived in step 1 can be summed to yield the pressure at any location in the matrix:

\[
p_m(y) - p_0 = A \frac{n_f l \cdot \cos \theta}{2} \left[ \frac{p_m}{p_f} \cos^2 \theta - 1 \right] + Ay \tag{A.8}
\]

The local area of the matrix with \( n_f \) tubular fillers (dashed rectangle in Fig. A1b) is considered to be a homogeneous medium with effective permeability \( P_{eff} \). This medium has a characteristic length, \( t \), equivalent to the characteristic length \( l \cos \theta \) in step 1. The rectangle has no tilt angle, so \( \theta = 0 \). Therefore, the pressure profile far away from this medium can be expressed in analogy to Eq. (A.7):

\[
p_m(y) - p_0 = A \frac{t}{2} \left[ \frac{p_m}{p_f} \frac{1}{P_{eff}} - 1 \right] + Ay \tag{A.9}
\]

The characteristic length \( t \) can be related to \( n_f \) by the filler volume fraction \( \Phi_f \), as in Eq. (5):

\[
n_f = \frac{t}{l \cdot \cos \theta \cdot d \cdot \sin \theta} \Phi_f \tag{A.10}
\]

Eq. (A.9) can thus be rewritten as:

\[
p_m(y) - p_0 = A \frac{t \cdot \cos \theta \cdot \Phi_f}{2 (\cos \theta + \frac{t}{2} \sin \theta)} \left[ \frac{p_m}{p_f} \cos^2 \theta - 1 \right] + Ay \tag{A.11}
\]
Finally, (A.9) and (A.11) are equated to derive the effective permeability $P_{\text{eff}}$:

$$
\frac{P_{\text{eff}}}{P_m} = \left[ 1 + \frac{\cos \theta}{\cos \theta + \frac{1}{a} \cdot \sin \theta} \left( \frac{P_m}{P_f} \cdot \cos^2 \theta - 1 \right) \Phi_f \right]^{-1} \tag{A.12}
$$

Eq. (A.12) summarizes the Maxwell-type model for tubular fillers, wherein the permeability enhancement factor is described as a function of the orientation ($\theta$), aspect ratio ($a$), and volumetric fraction ($\Phi_f$) of the filler; as well as the relative permeability of the filler and the matrix ($P_f/P_m$).

**A.1.3. Limiting cases**

For the limiting cases of: (i) a membrane comprised of only matrix or fillers ($\Phi_f = 0$ or 1), and (ii) a membrane only containing fillers ($\Phi_f = 1$) with a desired orientation ($\theta = 0$), Eq. (A.12) correctly reduces to the expected permeability through single-phase membranes. For a composite membrane with fillers of volume fraction $\Phi_f$ aligned in the desired orientation ($\theta = 0$), the mass flux is obtained as:

$$
J = \frac{\Delta p}{t[(1/P_m)(1-\Phi_f) + (1/P_f)\Phi_f]} \tag{A.13}
$$

The flux is independent of the aspect ratio of the filler, and only the volume fraction ($\Phi_f$) and permeability ($P_f$) of the filler contribute. This result is in correct agreement with Eq. (21). For the membrane composed of only fillers ($\Phi_f = 1$) with the undesired orientation ($\theta = \pi/2$), Eq. (A.12) leads to a mass flux $J = 0$. This is due to the flux continuity boundary condition (Eqs. (A.4) and (A.5)), wherein transport in the filler and matrix are perpendicular to each other in this case. Hence, the flux in the tubular filler does not contribute to the flux in the matrix, leading to a zero bulk flux. Additionally, in this specific case wherein the tubular filler lies along $x$ direction and the bulk mass transport is along $y$, the pseudo-1D approximation as well as the resulting Maxwell-type model are no longer valid.

**Nomenclature**

- $D$ diameter of a spherical filler
- $D_{Kn}$ Knudsen diffusivity
- $d$ outer diameter of a tubular filler
- $\alpha$ aspect ratio of a tubular filler defined as $l/d$
- $f(\theta)$ fraction of fillers oriented at $\theta$ amongst all fillers present in the same composite membrane
- $g(\theta)$ orientation distribution function of fillers in a composite membrane
- $J$ molecular flux of permeation
- $l$ length of a tubular filler
- $M$ molecular weight of transported species
- $n$ shape factor in the Maxwell model
- $n_f$ number of fillers along the molecular path in a membrane from feed to permeate side
- $P_{\text{eff}}$ effective permeability of a membrane

**References**


