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The solution-diffusion model: "Rumors of my death have been exaggerated"

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ABSTRACT

The solution-diffusion (SD) model has been instrumental in the advancement of membrane science, due to its simplicity, transparency, and utility in process engineering. However, some doubts have recently been raised, concerning the fundamental validity of SD. These have largely been based on apparent discrepancies between molecular dynamics simulations and several features, deemed inherent to SD, that appeared in early reports — namely, the exact nature of the pressure and concentration distributions within the membrane. Herein, we re-visit the underlying physics of SD in the context of composite membranes, making no a-priori assumptions and, particularly, highlighting the role of polymer thermodynamics and the mechanics of a loaded, swollen film, supported by a porous substrate. The analysis provides a coherent view, linking the solvent concentration profile within the film and the resultant flux-pressure relations with the polymer rigidity and, importantly, the way in which the film is supported. It is shown that, although the flux may generally vary non-linearly with the feed pressure and depend on the film-support geometry, for rigid films – most common in real operations – SD predicts a linear behavior, virtually independent of specific geometry and pressure distribution. Moving forward, we stress the importance and need for further refinements of the SD model, driven by insight from molecular dynamics, thermodynamics and mechanics, while maintaining its applicability to process design.

0. Introduction

Polymeric, perm-selective thin films have been at the forefront of desalination and water purification for over 50 years, particularly the asymmetric and thin-film composite membranes that dominate today's markets of reverse osmosis (RO) and nanofiltration, as well as other processes, such as gas separation, pervaporation and diffusion dialysis.

Much of the progress made in utilizing this technology for large-scale processes is indebted to the advent of easy-to-apply models, beginning with the Kedem–Katchalsky (KK) model (Kedem and Katchalsky, 1958), derived from irreversible thermodynamics and, particularly, the so-called solution-diffusion (SD) model, first put forward by Lonsdale et al. (1965) and since then revisited and elaborated (Paul and Ebra-Lima, 1970, 1971; Paul, 1976; Wijmans and Baker, 1995; Paul, 2004). These simple, straightforward equations describing transport in membranes have received exceptionally wide use and have been incorporated into software employed by engineers designing RO-based desalination plants worldwide. Beyond its simplicity — why such widespread use of SD? Because it works. However, recently, questions have been raised on its physical foundations, and examining these is at the core of the forthcoming letter.

We begin by noting that, while not derived as such – a fact that is very likely at the root of the current debate on its validity – the final result represented by the SD model is rooted in the thermodynamics and physics of diffusion and is readily shown to be a limiting, weak-coupling case of the celebrated KK model, derived from the general theory of irreversible processes (Kedem and Katchalsky, 1958). The recent studies, adding molecular dynamics (MD) simulations to the picture, mainly reopen the question of how (and if) pressure affects solute transport (Song et al., 2021; Heiranian et al., 2022, 2023; Wang et al., 2023; Fan et al., 2024). Hereinafter, we wish to primarily relay and bring under scrutiny this aspect, which is intimately related to the more general question of what defines the SD model. Particularly, we aim to place both mechanical and thermodynamic principles in clear context, as the absence of such a view is a likely cause for misconception of the framework behind SD and, consequently, its potential flaws. The recent work by Hegde et al. (2022) offers a reconciled view of the pore-flow vs SD question but it, too, neglects to fully consider the mechanics of the system.

Finally, as there is no perfect model – strictly speaking, for molecular-scale membrane transport, both SD and pore-flow are likely to be approximate representations of transport — we outline several points that can be used as guides into future work with the goal of providing better insight, and possibly design tools, for membrane separation.

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Nomenclature

Greek

Δ	Difference between feed and permeate
δ	Difference or variation
γ	Activity coefficient
μ	Chemical potential
ϕ	Solvent volume fraction in polymer
Π	Osmotic pressure

Latin

D	Diffusion coefficient
E	Young's modulus
J	Solvent flux
L	Spacing of support pores
P	Pressure
P_e	Elastic pressure
P_T	'Thermal' pressure $= R_gT/V$
R	Support pore radius
R_g	Gas constant
T	Temperature
t	Active layer thickness
V	Partial molar volume
x	Spatial coordinate across active layer (along streamlines)

Other symbols

eq	Equilibrium
f	Feed
m	Membrane
p	Permeate
s	Solution

Apparent discrepancies and main points The recent questioning of the SD model can be divided into the following three observations arising from recent MD simulations of transport in polyamide films (Heiranian et al., 2022; Wang et al., 2023):

1. The solvent (water) concentration profile within a selective layer, subject to a pressure gradient, shows a negligible variation across the film, while SD assumes a gradual change.
2. The SD model predicts a non-linear dependence of the solvent permeation rate on the pressure as it approaches the "thermal" pressure, P_T,[1] while MD simulations show that linearity still holds at such and even higher pressures.
3. MD simulations show a linear pressure profile across the selective film, while SD assumes a constant pressure within the film, equal to that of the feed.

We maintain that these apparent discrepancies result from misinterpretations of SD (rather than its in-applicability), due to incorrect relations describing the distributions of solvent concentration and pressure within the film. In what follows, we wish to recap the essential thermodynamic basis for transport in a dense membrane, and emphasize the way these relations should comply with mechanical coupling between the fluid and solid phases and how these may vary, dependent on the manner in which the selective layer is supported.

Fundamental diffusive transport relations

In order to establish these ideas, we first present the relations for the solvent flux and concentration, at a given pressure distribution, $P(x)$. In general, the solvent volume flux is given by (Paul, 1976; Mulder, 2012)

$$\mathbf{J} = -\frac{D(x)\phi(x)}{1-\phi(x)}\frac{\nabla\mu(x)}{R_gT}, \tag{1}$$

where x is the coordinate across the film and $D(x)$, $\phi(x)$ and $\mu(x)$ denote the solvent diffusivity, volume fraction (concentration), and chemical potential, respectively. The factor $1-\phi$ in the denominator is the bulk-flow correction (Paul, 1976). Further, the chemical potential, μ, is defined as (Hill, 2012; Rubinstein and Colby, 2003)

$$\mu - \mu_0 = R_gT\ln(\gamma\phi) + V P_e + V P = V\left(-\Pi + P_e + P\right), \tag{2}$$

where the subscript 0 refers to the pure solvent as a reference state, γ is the solvent activity coefficient, P_e is the elastic pressure within the polymer (due to swelling), and Π is the osmotic pressure. The sum $-\Pi + P_e$ depends on ϕ, i.e., solvent uptake or swelling.[2]

We note that, in an ideal case, $\nabla\mu = R_gT\nabla\ln\phi$ and $\phi \ll 1$, so that Eq. (1) becomes the Fick equation. The formulation here is intentionally kept generalized, thus μ includes the pressure-dependent part as well, so as to permit inclusion of important model aspects that relate to mechanics, as will be elaborated in the forthcoming sections. It is also important to note that, while the osmotic pressure is lumped together with the elastic and hydraulic pressures, it is not a mechanical stress but, rather, the most convenient representation of the solvent activity within the polymer or, equivalently, the concentration-dependent part of its chemical potential.

Eq. (2) is written for the polymer, while in a solution (subscript s), $\mu = V_s\left(-\Pi_s + P\right)$. Equating the chemical potential in the solution and membrane (subscript m) phases gives the implicit relation between ϕ and Π_s at equilibrium, for a given P (see section S1 in the Supplementary Material for further details),

$$\hat{\Pi}(\phi) = \Pi_s\frac{V_s}{V_m} - P\frac{V_s - V_m}{V_m}, \tag{3}$$

where $\hat{\Pi}(\phi) = \Pi(\phi) - P_e(\phi)$ represents an 'effective' osmotic pressure within the polymer, incorporating the elastic pressure — defined in this manner, it equals the solution's osmotic pressure, Π_s, when the two phases are at equilibrium. Eq. (3) indicates that the actual effect of the mechanical pressure on $\hat{\Pi}$, via $P(V_s - V_m)/V_m$, is very small due to the low compressibility of both solvent and polymer.[3] The approximation $\hat{\Pi}(\phi) \approx \Pi_s$ is, therefore, reasonable in any practical case.

Given $P(x)$ and $\hat{\Pi}(\phi)$, the concentration profile, $\phi(x)$, and the flux, $\mathbf{J}$, are obtained by substituting Eqs. (2) and (3) into Eq. (1) and solving it with appropriate boundary conditions at the membrane-solution interfaces. It is important to note, that it is the system of Eqs. (1)–(3) that constitutes the SD model, rather than specific distributions of ϕ and P, or resultant dependence of $\mathbf{J}$ on the feed pressure.

[1] We define the 'thermal pressure', P_T as a convenient short-hand notation for R_gT/V, where R_g, T and V are the gas constant, absolute temperature and partial molar volume of the solvent (for water at 293 K, with $V = 18\cdot10^{-6}$ m^3/mol, $P_T = 135$ MPa). P_T appears in many relations here, e.g., the osmotic pressure is the product of P_T and dimensionless logarithm of solvent activity, which makes it a reference value for the osmotic pressure.

[2] The use of an osmotic pressure instead of activity is widely used in polymer physics, as it has the same units as pressure, thus the swelling equilibrium is expressed simply as $\Pi = P_e$ in a pure solvent ($\Pi_s = 0$) or $\Pi - \Pi_s = P_e$ in general.

[3] e.g., at 100 MPa, V_s changes by only $\sim 4\%$, based on the compressibility of water, $4\cdot10^{-10}$ Pa^{-1}. Hence, $(V_s - V_m)/V_m$ is at most a few percent for $P/P_T < 1$, typical of MD simulations, and much less for pressures of a few MPa, or $P/P_T < 0.1$, typical of real operation.

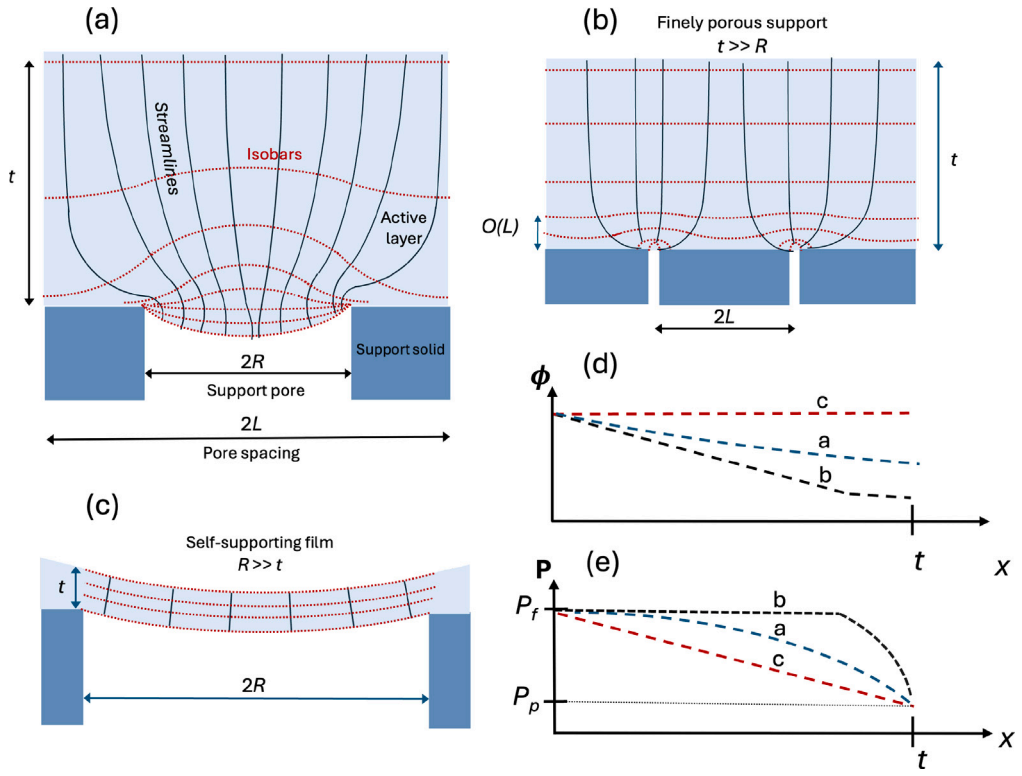

Fig. 1. Pressure and flux within a thin-film composite membrane, under mechanical equilibrium. (a) Schematic representation of a general case, where the active layer, of thickness t, is supported from below by a porous substrate with pore size R. (b) The limiting case of a thick active layer. Here, the flux and pressure contours are unaffected by the support, except for a small region near the pore-film interface.(c) The limiting case of a thin active layer (relative to the support pore size), illustrating the self-supporting nature of this scenario, and the resultant, evenly distributed flux. (d) Sketch of the distribution of the solvent volume fraction, ϕ, across the active layer, for cases a–c described in the previous figures. (e) Sketch of the pressure distribution across the active layer, for cases a–c described in the previous figures. As the support pores and their spacing become smaller compared with the thickness, the pressure drop becomes increasingly more pronounced in a region adjacent to the pore.

So, what seems to be the problem here? We now turn our attention to possible causes of controversy. First, as elaborated below, in order to include a complete mechanical description, the boundary conditions at both feed- and permeate-membrane interfaces require that the normal stress in the polymer is equal to the liquid pressure (Landau et al., 2012; Doi, 2009). This differs from the "classical" approximation, where the feed side complies with this mechanical equilibrium, but at the permeate side there is a jump from the feed pressure P_f within the polymer to $P_p < P_f$ in the permeate (Paul and Ebra-Lima, 1970; Paul, 1973). The consequence of this approximation is an exaggerated effect of the feed pressure on the solvent chemical potential within the membrane at the permeate side, which is artificially increased by $V(P_f - P_p)$. As elaborated below, this approximation is often reasonable in practice; however, it may lead to major misinterpretations for systems considered in molecular simulations.

The pressure distribution and mechanical considerations

The pressure distribution, $P(x)$, is mostly generated via load transmission between the feed surface and the solid support, but is also affected by the solvent flux. An excellent account of this was recently provided by Hegde et al. (2022), who modeled membrane transport as a fluid–solid mixture, considering the stress distributions and displacements of both phases. In the present context of dense membranes, the pressure variations due to solvent transport are small compared with the load transmission.

Consider the general case of a film with thickness t extending over circular pores of radius R, spaced at a distance L, and uniformly loaded with a feed pressure P_f, while the pressure is P_p on the pore side (Fig. 1a). The normal stress is transmitted through the membrane to the solid fraction of the support, whereby, at equilibrium, the stress integrated over the solid support area must equal the total load at the feed side, i.e., P_f times the 'footprint' area. Far from the pore, the pressure due to the loading stress within the film will tend to be virtually uniform and close to P_f, ignoring a small gradient due to the solvent flux, superimposed over the much larger loading stresses. However, as already stated, at the interface between the membrane and the pore fluid, the normal stress must be equal to P_p. In order for the normal stress to equal P_p, there will be a rapid change within the membrane, becoming anisotropic in the vicinity of the pore, over distances $O(R)$ or $O(L)$ (see Fig. 1a).[4] Specifically, the membrane surface will deform and bulge into the pore, such that the pressure gradient within the curved region will be countered by tangential stresses (Timoshenko and Woinowsky-Krieger, 1959). Since the solvent flux, $\mathbf{J}(x)$, is driven by the pressure gradient, its direction or streamlines will follow the gradient of the principal normal stress, connecting the feed and permeate, perpendicular to the isobar lines, as schematically depicted in Fig. 1a (refer to sections S2.1 and S3 in the Supplementary Material for a more elaborate description). The streamlines begin perpendicular to the membrane surface and at first stay approximately parallel to each other but will bend and funnel towards the pore (Ramon et al., 2012; Mondal et al., 2019) and, ultimately, within the pore, will terminate at the membrane-permeate interface. The local flux will remain approximately constant near the feed side but, upon approaching the pore, will increase, reaching its maximum within the pore (Ramon et al., 2012; Mondal et al., 2019). The trajectory and variation of $P(x)$ and $\mathbf{J}(x)$ from the feed to permeate will, therefore, largely be dictated by geometry,

[4] Since the problem has 3 length-scales, namely t, R and L, these may be reduced to 2 scaled lengths, with which one may define the region of influence at the pore (Ramon et al., 2012). Only one scale length remains, if – as often the case – R and L are not far apart.

i.e., t, R, and L. Given these variations, $\phi(x)$, along each 'streamline', will follow from Eqs. (1)–(3), i.e., obey the following relation

$$\mathbf{J} = -D\frac{\hat{\phi}(\Pi_s, P)}{1-\hat{\phi}(\Pi_s, P)}\frac{\nabla(P-\Pi_s)}{P_T}, \tag{4}$$

in which $\hat{\phi}$ represents the concentration ϕ that satisfies Eq. (3) for given Π_s and P. Note that Π_s should be understood as the actual osmotic pressure in the solution phases, while, within the membrane, it is 'virtual', i.e., that of a hypothetical solution in equilibrium with the local state of the polymer comprising the membrane. Under this definition, it varies continuously across the membrane-solution interfaces.

When can we expect linearity of flux versus pressure? Paul and Ebra-Lima (1971) reported a non-linear pressure–flux relation measured for solvents driven through soft, highly-swollen rubber films, which they explained using the "classical" approximation (i.e., that the pressure is constant in the film), adding a term $V(P_f - P_p)$ to the chemical potential within the membrane at the membrane-permeate interface. Real-world membranes, even rubbery films used for pervaporation and particularly ones used for RO, are far from being that soft; nevertheless, the fundamental question is valid. Integration of Eq. (4) across the film yields

$$\langle J\rangle = \frac{1}{t}\left\langle\int_{x=0}^{t} J\,dx\right\rangle = \frac{1}{tP_T}\left\langle\int_0^t \frac{D\phi}{1-\phi}d(P-\Pi_s)\right\rangle = \left\langle\frac{D\phi}{1-\phi}\right\rangle\frac{\Delta(P-\Pi_s)}{tP_T}. \tag{5}$$

Here, in general, $J(x) = |\mathbf{J}(x)|$ is the flux variation along streamlines, dictated by the geometry and thus different for each streamline (as shown in Fig. 1a), while Δ is the difference between feed and permeate and $\langle\cdots\rangle$ designates averaging over all streamlines, i.e., over the footprint area. Eqs. (4) and (5) indicate that non-linearity stems from the variation of ϕ and its generally nonlinear relation to the osmotic pressure $\phi = \hat{\phi}(\Pi_s)$ (e.g., as given by the Flory–Huggins or other models) and its averaging across the film. The averaging becomes fairly straightforward in the limiting cases considered next.

First, for $t \gg R$ (Fig. 1b), the pressure and local flux vary significantly only over distances $O(R)$ or $O(L) \ll t$ (see Section S2.2 in the Supplementary Material). In this case, the film is uniformly compressed with $P(x) \approx P_f$, approximately constant throughout the film, as is the local flux $J = |\mathbf{J}|$, except for the small near-pore region, where the pressure rapidly drops to P_p at the permeate interface. This small region contributes negligibly to the integral in Eq. (5) and, in this specific case, the result becomes indistinguishable from the 'classical' approximation of a film uniformly compressed with the feed pressure all way down to the substrate (Lonsdale et al., 1965; Paul and Ebra-Lima, 1970). The important point here is that, excluding this small region, given that $\mathbf{J}$ must be constant across the film and $\nabla P = 0$, Π_s must increase linearly from feed to permeate to keep the driving force $\nabla(P-\Pi_s)$ (and, therefore, the flux), constant. Eq. (5) indicates that the linearity of the relation between $\langle J\rangle$ and ΔP is dependent on whether ϕ varies substantially with Π_s. Note that, since both P and $P-\Pi_s$ vary monotonically along the streamlines as does, consequently, Π_s, their variations are expected to be of the same order of magnitude, i.e., $\delta\Pi_s \sim \Delta P$. Essentially, it is this variation of Π_s, equivalent to the chemical potential changing by $V\delta\Pi_s \sim V\Delta P$, rather than the non-physical pressure jump across the membrane-permeate interface, that is responsible for the pressure-dependence of the permeability in supported films.

To leading order, $\delta\phi \approx \delta\Pi_s/(\partial\Pi_s/\partial\phi)_{\Pi_s=0}$ expresses the variation of ϕ with Π_s. To estimate the derivative, we can use several approximations. First, as concluded above, $\Pi_s \approx \hat{\Pi} = \Pi - P_e$. Then, for $\Pi_s = 0$, i.e., swelling in a pure solvent, $\Pi = P_e$. Next, as follows from thermodynamics of polymer swelling, $P_e \sim E$ and $\partial P_e/\partial\phi \sim E$, i.e., both must be on the order of E, the elastic modulus of the polymer (Hill, 2012; Rubinstein and Colby, 2003; Doi, 2009), which also makes $\Pi \sim E$. We further approximate the membrane phase as an ideal solution, so that $\Pi \sim -P_T\ln\phi$, equilibrium swelling in a pure solvent is $\phi_{eq} \sim \exp(-\Pi/P_T) \sim \exp(-E/P_T)$ and $(\partial\Pi/\partial\phi)_{\Pi_s=0} \sim -P_T/\phi_{eq} \sim -P_T\exp\left(E/P_T\right)$. Ultimately, we have

$$\frac{\delta\phi}{\phi_{eq}} \sim \frac{\delta\Pi_s}{\phi_{eq}\left(\partial\Pi_s/\partial\phi\right)_{\Pi_s=0}} \sim \frac{\Delta P}{\phi_{eq}\left(\partial\Pi/\partial\phi - \partial P_e/\partial\phi\right)_{\Pi_s=0}} \sim \frac{\Delta P/P_T}{1+\phi_{eq}E/P_T}, \tag{6}$$

an estimate of the relative variation of ϕ, indicating that the concentration variation is small when either $\Delta P/P_T \ll 1$ or $\phi_{eq}E/P_T \gg 1$. Both conditions were violated in the classical experiments by Paul and Ebra-Lima (1970, 1971), who employed ΔP of a few MPa, close to $P_T \sim$ 10–20 MPa for the organic liquids used, and included polymer elongation data that indicate $E \sim 0.1$ MPa. Eq. (6) then yields $\delta\phi \sim \phi_{eq}$, i.e., substantial de-swelling under pressure resulting in a contractile lateral stress (which was noted by Paul and Ebra-Lima, 1970). As expected, this also resulted in a non-linear flux-pressure relationship, approaching, at very high pressures, a limiting flux corresponding to $\phi \to 0$ on the permeate side (pervaporation) (Paul and Ebra-Lima, 1971).

However, for polyamide films used for RO, $E \sim 1-3\ GPa$, four orders of magnitude larger (Freger and Ramon, 2021), which may render the water concentration variations far smaller. A subtle point here is that, if $\phi_{eq} \sim exp(-E/P_T)$, as approximated above for an ideal gel, $\phi_{eq}E/P_T$ will always be small and ϕ will vary substantially. For instance, a recent paper has shown that a concentration gradient can be measured even in a relatively stiff polymer, for a thick sample that permitted such resolution (Anon, 2024). However, RO polyamide possesses an intrinsic microporosity (Gorgojo et al., 2014; Freger and Ramon, 2021), which makes $\phi_{eq} \sim 0.1$ (Dražević et al., 2014) independent of E, therefore $\phi_{eq}E/P_T$ is large and $\delta\phi \ll \phi_{eq}$ even at $\Delta P = 100$ MPa, close to P_T of water. For modeling purposes, Eq. (5) may be integrated, to a good approximation, by assuming a constant $\phi = \phi_{eq}$, even though Π_s will vary throughout the film. Importantly, the resultant linear dependence on feed pressure fully conforms with purely diffusive transport and does not necessarily imply viscous flow.

Diffusion or viscous flow? The phenomenological nature of equations describing diffusion and D'arcy-scale 'pore flow' result in an analogous functional form, which can lead to similar values for the permeance, dependent on the parameters used in the calculation. As an illustration, we can make an order-of-magnitude estimate for the water permeance of RO membranes using $t = 100$ nm, $\phi \sim 0.1$, and water diffusivity $D \sim 10^{-10}$ m^2 s^{-1}, robustly reproduced in several MD studies (Kolev and Freger, 2014),

$$\frac{J}{\Delta P} \sim \frac{D\phi}{(1-\phi)P_T t} \sim \frac{10^{-10}\cdot 0.1}{0.9\cdot 1.35\cdot 10^8\cdot 10^{-7}} \sim 10^{-12}\ \left[\frac{\text{m}}{\text{s Pa}}\right],$$

agreeing well with the permeance found for seawater RO membranes (Dražević et al., 2014).

The D'arcy (pore-flow) model yields a similar estimate for the permeance, based on the same ϕ and bulk water viscosity, using a pore size of 0.2 nm. However, an important distinction exists — while the parameters used to estimate the diffusive flux are only weakly dependent of the actual structure (other than swelling/porosity, ϕ, and t), a viscous flow estimate is highly sensitive to the choice of *a-priori* unknown pore size that is, in fact, often deduced from the measured permeance itself itself (Bason et al., 2010). Moreover, the common pore size estimate of 0.2 nm is close to the molecular radius of water (0.14 nm), placing uncertainty on the use of viscosity as a valid continuum parameter at this scale, while diffusivity generally remains a valid molecular characteristic.

The curious case of the self-supporting film. Following the previous analysis, we wish to emphasize that the condition $t \gg R$ neither exhausts all possibilities nor defines the SD model. As an illustration, consider the opposite limiting case, $t \ll R$ - a thin, self-supporting film extending over a large pore (Fig. 1c). Here, unlike the previous case, the

membrane will curve to counter the load, therefore, the normal stress will *not* be uniform across the film. Rather, as in a thin shell, it will decrease linearly from P_f to P_p (Timoshenko and Woinowsky-Krieger, 1959) (see section 2.3 in the Supplementary Material). As $\nabla P = \Delta P/t$ now stays constant throughout, it is no longer required that Π_s varies such that the driving force, $\nabla(P - \Pi_s)$, and the flux are constant across the film. Figs. 1d and 1e display the differences expected in the pressure and concentration profiles for all cases considered. Most remarkably, as Π_s is now constant, ϕ will not vary either, thus Eq. (5) predicts a linear flux-pressure dependence that extends to pressures far above P_T, regardless of polymer rigidity. In full agreement with this prediction, recent MD studies, where the modeled film was implicitly self-supported, found a linear flux-pressure relationship and a negligible water concentration variation (cf. Fig. 1d), which was *misinterpreted as a violation of the SD model* (Heiranian et al., 2022; Wang et al., 2023).

The case $t \ll R$ is likely irrelevant for soft films, as they would deform[5] and possibly rupture under pressure. Under pressures on the order of MPa's, the deformation would likely be excessive for soft films with $E < 1$ MPa. However, we can speculate that polyamide films with $E \sim 1$ GPa may well be self-supported over lateral dimensions several times their thickness. Moreover, this may actually be the case for composite membranes, even when a substrate with pores a few nanometers large supports a 100–200 nm thick polyamide top layer. Recent studies, employing high-resolution imaging, indicate that the selective polyamide layer is often crumpled and forms dome-like structures, of which only a fraction rests on the support (Freger and Ramon, 2021). Remarkably, since the approximation of a constant $\phi = \phi_{eq}$ will still be valid for such rigid films, the result obtained for $t \gg R$ is virtually unchanged for $t \ll R$, except that the calculated flux will be per permeable area, rather than the membrane footprint.

Concluding remarks and outlook — where can we do better?

The main goal of the foregoing analysis has been to re-establish the general framework for SD and, consequently, provide a better understanding of its true scope. Of course, such a framework will not apply to a membrane with continuum-scale pores, such as used for ultrafiltration. The particular relevance of SD is for dense membranes, e.g., as used in RO/NF, gas separation, or pervaporation - i.e., polymers whose 'porous nature' is dependent on the degree of swelling by the penetrating molecules transporting through them.

Importantly, we show how careful consideration of thermodynamic and, particularly, mechanical principles of the thin-film composite membrane, i.e., including the support, provides a clear indication of the way in which "SD-behavior" is commonly manifested in practice, and why it may be misconstrued. As stated earlier, the strength of SD has been its remarkable applicability to real process design — but it is a simplified model. As such, our expectations of it should not exceed the amount of detail it contains and efforts should focus on improving it by refining its physical content. A particular point of contention has been the detailed view of the transport — diffusion vs viscous flow. Given the length-scales involved, these aspects lie at the point where the exact statistics of molecular motion – uncorrelated, purely 'Brownian' motion charactertic of molecular diffusion or highly correlated collective motion of viscous flow – can sometimes overlap and be neither, strictly speaking. Rather than attempting to reconcile this aspect within an inherently incomplete framework (be it SD or viscous flow), it is more useful to think of ways to broaden the physical scope of our models.

This may be achieved in a number of possible ways, and we offer the following points to consider. Firstly, molecular dynamics is proving to be an exceptionally useful tool for unraveling specific interactions that govern transport within polymer networks. However, MD simulations require extra care when employed, as they are difficult to link with experimentally measurable quantities. Moreover, the choices made within the MD simulations may have profound impact on the outcome of the simulations. A simple example has been illustrated here — the implicit mechanics of the film within the simulation. Just as important may be the choices made with respect to the force fields employed — many of which are under continued debate within the MD community. Further challenges include the ability to account for polymer elasticity, which is difficult to model by MD, especially for cross-linked materials (Yang and Qu, 2012), and coupling transport relations with mechanical equilibrium.

In conclusion, implementation of theoretical insight into practice – as part of process design – would still require continuum-scale models capable of incorporating the finer resolution in a computationally accessible, experimentally-validated, framework.

CRediT authorship contribution statement

Viatcheslav Freger: Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Conceptualization. **Guy Z. Ramon:** Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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References

Anon, 2024. Hydraulic permeation-induced water concentration gradients in ion exchange membranes. J. Membr. Sci. 705, 122858.
Bason, S., Kaufman, Y., Freger, V., 2010. Analysis of ion transport in nanofiltration using phenomenological coefficients and structural characteristics. J. Phys. Chem. B 114 (10), 3510–3517.
Doi, M., 2009. Gel dynamics. J. Phys. Soc. Japan 78 (5), 052001.
Dražević, E., Košutić, K., Freger, V., 2014. Permeability and selectivity of reverse osmosis membranes: Correlation to swelling revisited. Water Res. 49, 444–452.
Fan, H., Heiranian, M., Elimelech, M., 2024. The solution-diffusion model for water transport in reverse osmosis: What went wrong? Desalination 580, 117575.
Freger, V., Ramon, G.Z., 2021. Polyamide desalination membranes: Formation, structure, and properties. Prog. Polym. Sci. 122, 101451.
Gorgojo, P., Karan, S., Wong, H.C., Jimenez-Solomon, M.F., Cabral, J.T., Livingston, A.G., 2014. Ultrathin polymer films with intrinsic microporosity: anomalous solvent permeation and high flux membranes. Adv. Funct. Mater. 24 (30), 4729–4737.
Hegde, V.H., Doherty, M.F., Squires, T.M., 2022. A two-phase model that unifies and extends the classical models of membrane transport. Science 377 (6602), 186–191.
Heiranian, M., DuChanois, R.M., Ritt, C.L., Violet, C., Elimelech, M., 2022. Molecular simulations to elucidate transport phenomena in polymeric membranes. Environ. Sci. Technol. 56 (6), 3313–3323.

[5] the theory of plates predicts the film will displace at the center, into the pore, by a distance $\sim R^4\Delta P/Et^3$ (Timoshenko and Woinowsky-Krieger, 1959). For the film to be self-supporting, this displacement must be small compared with t or R, satisfying $R \ll (E/\Delta P)^{1/4}t$ or $(E/\Delta P)^{1/3}t$, respectively.

Heiranian, M., Fan, H., Wang, L., Lu, X., Elimelech, M., 2023. Mechanisms and models for water transport in reverse osmosis membranes: history, critical assessment, and recent developments. Chem. Soc. Rev..

Hill, T., 2012. An Introduction to Statistical Thermodynamics. Addison-Wesley, ISBN: 9780486130903, pp. 410–414, 1060.

Kedem, O., Katchalsky, A., 1958. Thermodynamic analysis of the permeability of biological membranes to non-electrolytes. Biochim. Biophys. Acta 27, 229–246.

Kolev, V., Freger, V., 2014. Hydration, porosity and water dynamics in the polyamide layer of reverse osmosis membranes: A molecular dynamics study. Polymer 55 (6), 1420–1426.

Landau, L.D., Pitaevskii, L., Kosevich, A.M., Lifshitz, E.M., 2012. Theory of Elasticity: Volume 7. Elsevier.

Lonsdale, H., Merten, U., Riley, R., 1965. Transport properties of cellulose acetate osmotic membranes. J. Appl. Polym. Sci. 9 (4), 1341–1362.

Mondal, S., Griffiths, I.M., Ramon, G.Z., 2019. Forefronts in structure–performance models of separation membranes. J. Membr. Sci. 588, 117166.

Mulder, M., 2012. Basic Principles of Membrane Technology. Springer science & business media.

Paul, D., 1973. Relation between hydraulic permeability and diffusion in homogeneous swollen membranes. J. Polym. Sci. Polym. Phys. Ed. 11 (2), 289–296.

Paul, D., 1976. The solution-diffusion model for swollen membranes. Sep. Purif. Methods 5 (1), 33–50.

Paul, D.R., 2004. Reformulation of the solution-diffusion theory of reverse osmosis. J. Membr. Sci. 241 (2), 371–386.

Paul, D., Ebra-Lima, O., 1970. Pressure-induced diffusion of organic liquids through highly swollen polymer membranes. J. Appl. Polym. Sci. 14 (9), 2201–2224.

Paul, D., Ebra-Lima, O., 1971. The mechanism of liquid transport through swollen polymer membranes. J. Appl. Polym. Sci. 15 (9), 2199–2210.

Ramon, G.Z., Wong, M.C., Hoek, E.M., 2012. Transport through composite membrane, part 1: Is there an optimal support membrane? J. Membr. Sci. 415, 298–305.

Rubinstein, M., Colby, R., 2003. Polymer Physics. OUP Oxford, ISBN: 9780198520597.

Song, L., Heiranian, M., Elimelech, M., 2021. True driving force and characteristics of water transport in osmotic membranes. Desalination 520, 115360.

Timoshenko, S., Woinowsky-Krieger, S., 1959. Theory of plates and shells. In: Engineering mechanics series, McGraw-Hill, ISBN: 9780070858206.

Wang, L., He, J., Heiranian, M., Fan, H., Song, L., Li, Y., Elimelech, M., 2023. Water transport in reverse osmosis membranes is governed by pore flow, not a solution-diffusion mechanism. Sci. Adv. 9 (15), eadf8488.

Wijmans, J.G., Baker, R.W., 1995. The solution-diffusion model: a review. J. Membr. Sci. 107 (1–2), 1–21.

Yang, S., Qu, J., 2012. Computing thermomechanical properties of crosslinked epoxy by molecular dynamic simulations. Polymer 53 (21), 4806–4817.