

Modeling of Diffusive Transport of Polymers Moments Using Limiting Cases of the Maxwell–Stefan Model

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A polymer distribution is usually represented by its moments. Thus, to calculate transport in a polymer system, a formulation for the transport of moments of the polymer is needed. This is only possible if the moments close or if there is a suitable closing condition. To archive this, two simplifications of the Stefan–Maxwell diffusion are derived, which convert the transport equation of polymeric species to a closed set of transport equations for the polymer moments. The first approach corresponds to an infinitely diluted polymer system, whereas the second one describes a highly concentrated polymer system. Both formulations are compared with the full Stefan–Maxwell model of a ternary mixture of a solvent and two polymer species of different chain length.

1. Introduction

The method of moments is a well-established technique for modeling polymerization reactions.^[1] Instead of solving the balance equations of a distributed polymer only the statistical moments of the chain length distribution are calculated. Under the assumption of ideal mixing, the simple case of a homogeneous polymerization can be expressed by three or more moments of the living and dead chains' distributions, respectively. Moments are calculated in units of concentrations. The balance equation for each polymer species can thus be easily converted into moment equations. In many types of polymer reactions the moments close, otherwise, a closing condition is required.

In cases where the assumptions of ideal mixing or a very simple flow field (plug flow) are inadequate, species transport by convective and diffusive transport must be accounted for. Velocity fields may be calculated by well-established CFD methods and can be directly applied to the transport of polymeric species and to the transport of moments of the polymer size distributions. While the convective transport of polymer species can be

converted to transport of moments directly, this is not the case for diffusive transport. Diffusive transport of moments is scarcely discussed in the literature. A rare example is provided by Arriola for convective and diffusive transport in a tubular reactor.^[2]

As we will show, limiting cases of the general Stefan–Maxwell diffusion for ideal mixtures allow to derive a closed form for the transport equation of polymer moments. The first limiting case assumes for infinite dilution of the polymer chain, which means that friction between polymer chain is completely neglected and only friction between polymer chain and solvent (or monomers) is considered. Since the Stefan–Maxwell diffusion coefficient between solvent and


polymer is relatively large, the diffusive fluxes of moments are usually overestimated. This might be irrelevant if diffusion is subordinate to convection. In special cases like spray polymerization,^[3–5] regions of low convective transport (i.e., behind mixing elements) or polymer fouling close to walls of micro reactors, the assumption of “No Polymer Friction” introduces large errors. This is especially true at high polymer content. In this case, we propose to use a different limiting case of the Stefan–Maxwell model, where we assume for infinite friction between the polymer chains, which means that a polymer chain cannot diffuse against other polymer chains. Thus, all polymer chains at a given location move as a whole against the solvent. As will be shown, this assumption also allows for closure of the transport model of polymer moments.

The outline of this paper is as follows: First, we derive the general transport equation for a homopolymer and Stefan Maxwell equations for diffusive transport. Two limiting cases are then derived which allow converting of the transport equation of polymeric species to a closed set of moment equations. Finally, we discuss the advantages and limitations of both limiting cases and compare results to simulations with the full Stefan–Maxwell model, for a simple system consisting of one solvent and two discrete polymer species of different chain length.

2. Multicomponent Transport

In polymer reaction processes, where ideal mixing is assumed for polymers are either treated in terms of their moments, or, if one is interested in details of size distribution, by adaptive numerical Galerkin methods.^[6] The latter is also preferred in cases where moment equations do not close. To study complicated polymeric structures, like cross-linked networks, Monte Carlo methods are

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applied. When the impact of a distributed flow field on a polymerization process shall be studied, the method of moments is preferred, since other methods become computationally infeasible for practical purposes.

Usually, the mass-averaged velocity, e.g. in a CFD simulation, is known. Therefore, we start with the development of the equations in a mass-averaged reference frame.

The mass-induced velocity arises from the component velocities v_i , where w_i denotes the mass fraction on species i

$$v = \sum_i w_i v_i \quad (1)$$

The mass balance for a species i then reads

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot v \rho_i + \nabla \cdot J_i = M W_i r_i^{\text{total}} \quad (2)$$

with diffusive fluxes J_i relative to the mass-averaged velocity v , ρ_i is the mass density, $M W_i$ denotes the molecular mass, r_i^{total} the total reaction rate of species i .

Since reaction rates are expressed in terms of concentrations, a molar reference system is preferred for treating the moments of polymer systems. The mole balance for a species i reads

$$\frac{\partial c_i}{\partial t} + \nabla \cdot v^N c_i + \nabla \cdot J_i^N = r_i^{\text{total}} \quad (3)$$

with diffusive fluxes J_i^N relative to the molar average velocity

$$v^N = \sum_i x_i v_i \quad (4)$$

with the mole fraction x_i and the concentration c_i . To distinguish between a mass and a mole-centered reference system, mole-centered quantities are indicated by superscript N .

A component's velocity v_i can be calculated from molar fluxes by^[7]

$$v_i = v^N + \frac{J_i^N}{c_i} \quad (5)$$

The molar average velocity can be calculated with Equations (1) and (5) and some math to

$$v^N = v - \sum_i \frac{J_i^N M W_i}{\rho_i} \quad (6)$$

With Equation (6) and the assumption of constant density, the balance Equation (3) becomes

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \left(c_i \left(v - \frac{1}{\rho} \sum_i J_i^N M W_i \right) \right) + \nabla \cdot J_i^N = r_i^{\text{total}} \quad (7)$$

From polymer size distribution given in terms of repeating units s of (homo) polymer P denoted by $P(s)$ the k^{th} -moment can be calculated by

$$\xi^k = \sum_{s=1}^{\infty} s^k c_{P(s)} \quad (8)$$

The transport equation of moments is derived by multiplication of Equation (7) with s^k and summation over all polymer species $P(s)$ to

$$\frac{\partial \xi^k}{\partial t} + \nabla \cdot \left(\xi^k \left(v - \frac{1}{\rho} \sum_i J_i^N M W_i \right) \right) + \sum_{s=1}^{\infty} \nabla \cdot s^k J_{P(s)}^N = \sum_{s=1}^{\infty} s^k r_{P(s)}^{\text{total}} \quad (9)$$

The diffusive transport of moments of the polymer flux is denoted as

$$\sum_{s=1}^{\infty} s^k J_{P(s)}^N = J_{\xi^k}^N \quad (10)$$

While convective transport can be readily written in terms of moments, the diffusive transport of moments $J_{\xi^k}^N$ requires further consideration.

The molecular weight of the polymers can be expressed by the chain length s and the molecular weight of one repeating unit MW

$$M W_{P(s)} = s \cdot M W_{\text{seg}} \quad (11)$$

After splitting the sum for low-molecular species (index "low") and Polymer species, the balance equation develops to

$$\frac{\partial \xi^k}{\partial t} + \nabla \cdot \left(\xi^k \left(v - \frac{1}{\rho} \sum_i^{n_{\text{low}}} M W_i J_i^N - \frac{1}{\rho} M W_{\text{seg}} J_{\xi^1}^N \right) \right) + \nabla \cdot J_{\xi^k}^N = r_{\xi^k}^{\text{total}} \quad (12)$$

with the total reaction rate for the k^{th} moment

$$r_{\xi^k}^{\text{total}} = \sum_{s=1}^{\infty} s^k r_{P(s)}^{\text{total}} \quad (13)$$

and the total polymer flux of all polymer distributions $J_{\xi^1}^N$.

However, to derive an expression for the diffusive fluxes of polymer moments simplifications are needed. The treatment of the reaction rate in terms of moments is well-established and can be found in.^[8]

2.1. Stefan–Maxwell Equations for Multicomponent Mixtures

To derive an expression for the diffusive transport of moments we start with the rigorous treatment of multicomponent mixture by the Stefan-Maxwell equation. The general Stefan-Maxwell equations for isothermal diffusion in J -component systems are^[9]

$$d_i = \frac{x_i}{RT} \nabla \mu_i = - \sum_{j=1}^J \frac{x_i x_j (v_i - v_j)}{\mathfrak{D}_{ij}} \quad (14)$$

with the driving force d_i for species i , the ideal gas constant R , the temperature T , the chemical potential μ_i of species i , its molar fraction x_i , its overall transport velocity v_i and the Stefan–Maxwell diffusion coefficient \mathfrak{D}_{ij} for interactions between species i and j .

Using Equation (5) the general Stefan-Maxwell equation can be expressed by molar fluxes

$$d_i = - \sum_{j=1}^J \frac{x_i x_j (v_i - v_j)}{\mathfrak{D}_{ij}} = - \sum_{j=1}^J \frac{x_j J_i^N - x_i J_j^N}{c \mathfrak{D}_{ij}} \quad (15)$$

The overall concentration c can be calculated by

$$c = \sum_i^{n_{\text{low}}} c_i + \xi^0 \quad (16)$$

where ξ^0 is the 0th moment of all polymer distributions. To line out the basic ideas it is sufficient to consider a ternary mixture consisting of a small molecule like solvent or monomer (S) and two polymeric components of the same type but with different molecular mass resp. chain length ($P1 = P(4000)$ and $P2 = P(2000)$). The two discrete polymer species may represent two very narrow distributions of the same type of polymer. The ternary system will be used for comparison of the limiting cases with the full Stefan–Maxwell model.

For a ternary mixture the Stefan–Maxwell equations read:

$$\begin{aligned} d_S &= \frac{x_S}{RT} \nabla \mu_S = - \sum_{j=S}^J \frac{1}{c} \cdot \frac{x_j J_S^N - x_S J_j^N}{\mathfrak{D}_{Sj}} \\ &= - \frac{1}{c} \cdot \left(\frac{x_{P1} J_S^N - x_S J_{P1}^N}{\mathfrak{D}_{SP1}} + \frac{x_{P2} J_S^N - x_S J_{P2}^N}{\mathfrak{D}_{SP2}} \right) \end{aligned} \quad (17)$$

$$\begin{aligned} d_{P1} &= \frac{x_{P1}}{RT} \nabla \mu_{P1} = - \sum_{j=P1}^J \frac{1}{c} \cdot \frac{x_j J_{P1}^N - x_{P1} J_j^N}{\mathfrak{D}_{P1j}} \\ &= - \frac{1}{c} \cdot \left(\frac{x_S J_{P1}^N - x_{P1} J_S^N}{\mathfrak{D}_{P1S}} + \frac{x_{P2} J_{P1}^N - x_{P1} J_{P2}^N}{\mathfrak{D}_{P1P2}} \right) \end{aligned} \quad (18)$$

With the closing condition that all fluxes need to add up to zero,^[9] the J-th (resp 3rd in our example) flow can be calculated from

$$J_J^N = - \sum_i^{J-1} J_i^N. \quad (19)$$

For a ternary mixture with the elimination of J_3^N follows

$$\begin{aligned} d_S &= - \frac{1}{c} \cdot \left(\frac{x_{P1} J_S^N - x_S J_{P1}^N}{\mathfrak{D}_{SP1}} + \frac{x_{P2} J_S^N + x_S (J_S^N + J_{P1}^N)}{\mathfrak{D}_{SP2}} \right) \\ &= - \frac{1}{c} \cdot \left(\left(\frac{x_{P1}}{\mathfrak{D}_{SP1}} + \frac{x_{P2} + x_S}{\mathfrak{D}_{SP2}} \right) J_S^N + \left(\frac{x_S}{\mathfrak{D}_{SP2}} - \frac{x_S}{\mathfrak{D}_{SP1}} \right) J_{P1}^N \right) \end{aligned} \quad (20)$$

$$\begin{aligned} d_{P1} &= - \frac{1}{c} \cdot \left(\frac{x_S J_{P1}^N - x_{P1} J_S^N}{\mathfrak{D}_{SP1}} + \frac{x_{P2} J_{P1}^N + x_{P1} (J_S^N + J_{P1}^N)}{\mathfrak{D}_{P1P2}} \right) \\ &= - \frac{1}{c} \cdot \left(\left(- \frac{x_{P1}}{\mathfrak{D}_{SP1}} + \frac{x_{P1}}{\mathfrak{D}_{P1P2}} \right) J_S^N + \left(\frac{x_S}{\mathfrak{D}_{SP1}} + \frac{x_{P2} + x_{P1}}{\mathfrak{D}_{P1P2}} \right) J_{P1}^N \right) \end{aligned} \quad (21)$$

This example suggests the compact form

$$-c d_i = \sum_{j=1}^{J-1} B_{ij} J_j^N \quad (22)$$

with

$$\begin{aligned} B_{ii} &= \left(\frac{x_i}{\mathfrak{D}_{ij}} + \sum_{k=1; i \neq k}^J \frac{x_k}{\mathfrak{D}_{ik}} \right); \\ B_{ij} &= -x_i \left(\frac{1}{\mathfrak{D}_{ij}} - \frac{1}{\mathfrak{D}_{ij}} \right), \end{aligned} \quad (23)$$

where the index J describes the nth component (resp 3rd in our example) in the system.

Any formulation for the chemical potential in Equation (14) is applicable. The simplest case for the chemical potential (isothermal and ideal mixture) is used for the model development. Its gradient develops to

$$\begin{aligned} \nabla \mu_i &= \nabla (\mu_i^0 + RT \cdot \ln(x_i \gamma_i)) = RT \nabla (\ln(x_i) + \ln(\gamma_i)) = \\ &RT \frac{1}{x_i} \nabla x_i + RT \sum_{i=1}^J \frac{\partial \ln(\gamma_i)}{\partial x_j} \nabla x_j = RT \frac{1}{x_i} \sum_{i=1}^J \left(\delta_{ij} + x_i \frac{\partial \ln(\gamma_i)}{\partial x_j} \right) \nabla x_j \end{aligned} \quad (24)$$

with the chemical potential at a reference state μ_i^0 and the activity coefficient γ_i for species i . In the case of an ideal mixture in which $\gamma_i = 1$, the chemical potential simplifies to

$$\nabla \mu_i = RT \frac{1}{x_i} \sum_{i=1}^J \delta_{ij} \nabla x_i = RT \frac{1}{x_i} \nabla x_i \quad (25)$$

By inserting Equation (25) in Equation (22), the expression develops to

$$- \frac{c_i}{RT} RT \frac{1}{x_i} \nabla x_i = -c \nabla x_i = \sum_{j=1}^{J-1} B_{ij} J_j^N \quad (26)$$

Therefore, a formulation follows, which is explicit in the fluxes J_j^N and suitable for numerical simulation codes based on molar concentrations, by inverting the matrix B containing the elements B_{ij} as

$$J_j^N = \sum_{i=1}^{J-1} -c (B^{-1})_{ji} (\nabla x_i) \quad (27)$$

3. Limiting Cases of Stefan–Maxwell Diffusion in Polymer Systems

The rigorous treatment of an infinite number of polymer species $P(s)$, $s [1..∞]$ and corresponding number of equations for the diffusive transport is infeasible. As already stated, representation in terms of moments is sufficient in most cases, but a closed set of expression for the diffusive transport of moments is required. The simplest way to obtain a closed expression would be

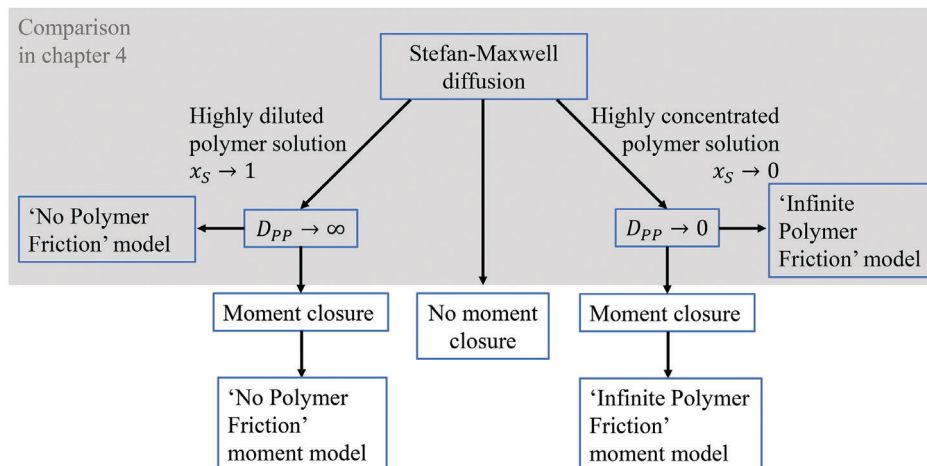


Figure 1. Overview of the developed models and simplifications.

to take the same diffusion coefficients between solvent and polymer and between polymer and polymer. In this case, however, the transport of the polymers would be greatly overestimated. With a choice of different diffusion coefficients, we do not obtain a closure conditions for the diffusive transport of moments.

For this reason, we have taken a closer look at two limiting cases for Stefan–Maxwell diffusion. A simplification can be archived by assuming for an infinitely diluted solution. Then the sum on the right side of the Stefan–Maxwell Equation (14) for a component i can be interpreted as friction terms between species i and all other species j . If the solvent is abundant, only the friction between the solvent and all polymer chains are of interest, while the friction between polymer chains is neglected. This is the first limiting case called “No Polymer Friction” for diffusive transport.

If the polymer content is high, friction between different polymer chain becomes the dominating mechanism, which restricts the movement of polymer chains. This is also a reliable assumption if the polymer is of high molecular weight, crosslinked or branched, such that entanglement considerably restricts the mobility of the polymer chains. In this case, the Stefan–Maxwell equation can be simplified by assuming for the limiting case of infinite friction between polymer chains. The polymer then moves as a whole relative to the solvent; thus, gradients of polymeric species will not equilibrate. Consider a polymer, consisting of two layers I and II , being infiltrated by a solvent (S). Both layers are of the same polymer but of different chain length distributions. The solvent will equilibrate, but if the solvent fraction is not high it takes a very long time for the polymers to equilibrate. In many practical applications, equilibration is not achieved even on the long term.

An overview about the simplifications and the resulting models is shown in **Figure 1**.

3.1. Stefan–Maxwell diffusion

Let’s consider a polymer membrane with a total depth of $L = 200 \mu\text{m}$, consisting of two layers I and II , being infiltrated by a solvent (S). Both layers are of the same polymer, but of different chain

Table 1. Physical data of solvent and two polymers of different molar weight.

	S	P1	P2
Density $\rho [\frac{\text{kg}}{\text{m}^3}]$	1000	1000	1000
Molar weight $M_w [10^{-3} \frac{\text{kg}}{\text{mol}}]$	18	400 000	200 000
Degree of polymerization		4000	2000

lengths. The degree of polymerization in the first layer is twice the one of layer two, which means that the chain length of Polymer P1 is twice as the chain length of Polymer P2. The assumed physical properties of this example are provided in **Table 1**. The solvent concentration in layer I (left side) is smaller than in layer II (right side). The binary diffusion coefficient of both is in the order of $\mathfrak{D}_{SP1} = \mathfrak{D}_{SP2} = \mathfrak{D}_{SP} = 10^{-9} \frac{\text{m}^2}{\text{s}}$. No outer forced convection is imposed, and no chemical reactions are taking place.

The polymer concentration is the same in both membranes, whereas the first moment is higher in layer I . Hence, solvent concentration and mole fraction are lower there, and the polymer fraction is higher. The solvent is therefore driven from layer II into layer I . The results presented here are based on balance equations for the individual components as presented in chapter 2.1. A diffusion coefficient of $\mathfrak{D}_{P1P2} = 10^{-12} \frac{\text{m}^2}{\text{s}}$ was assumed between both polymer species. This is three orders smaller than that of the solvent against both polymers. Thus, the friction between the polymer chains is high and they are almost unable to move against each other but only against the solvent. The equilibration progress during the first 20 s is plotted in **Figure 2**. After 20 s only the solvent is fully equilibrated ($\nabla x_S = 0$) and the two polymers are not due to the smaller diffusion coefficients. Of course, after sufficiently long times the polymers will equilibrate as well. The final state ($t \rightarrow \infty$) of the system is shown in dashed red.

The total polymer concentration is shown as the 0th chain length moment in Figure 2 as well as the 1st chain length moment, which represents the concentration of repeat units within polymer chains. From **Figure 3**, where the detailed course of the 0th chain length moment is shown, it can be concluded that the

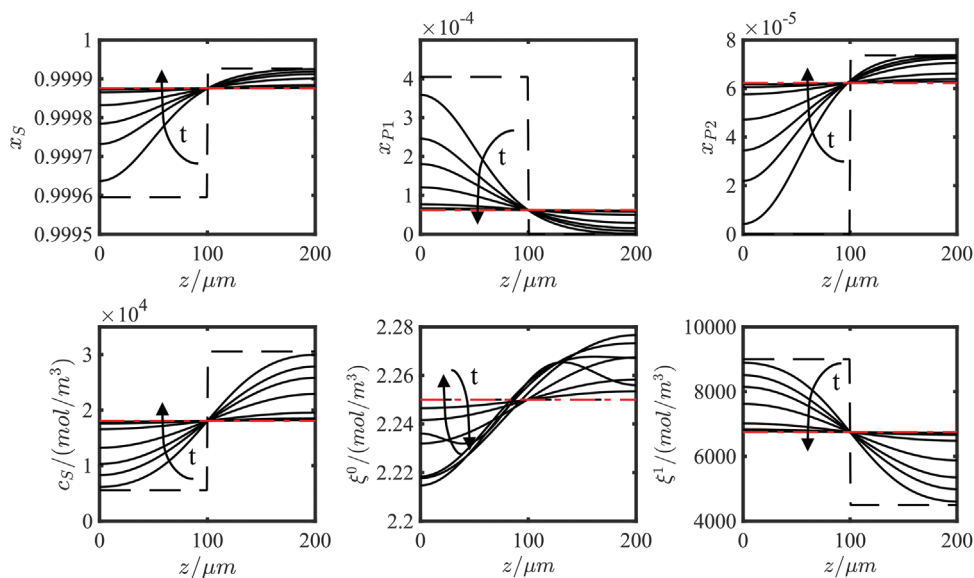


Figure 2. Results for [1,2,3,5,10,15,20] s for the Stefan–Maxwell approach with a diffusion coefficient between the polymers of $\mathfrak{D}_{P_1P_2} = 10^{-12} \frac{\text{m}^2}{\text{s}}$ and between solvent and polymer $\mathfrak{D}_{SP} = 10^{-9} \frac{\text{m}^2}{\text{s}}$. The initial conditions are dashed. The final state is dashed in red.

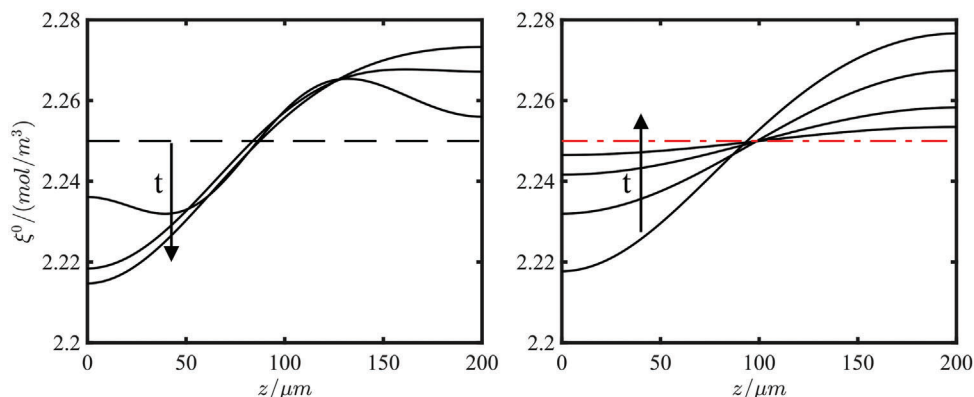


Figure 3. Detailed course of ξ^0 over the domain for different times according to Figure 2. Left side shows results for [1,2,3] s and right side results for [5,10,15,20] s. The initial condition is dashed. The final state is dashed in red.

total concentration of polymer shifts to layer II within the first three seconds. Later the diffusion of the polymers against each other compensates for this shift (5–20s).

The non-equilibrated state of ξ^0 after 20 s can be explained with the help of **Figure 4**, where the mole based averaged velocity v^N and the different fluxes are shown. The course of v^N shows the direction of the total mean transport of the components. As time progresses, the total transport becomes smaller. In the beginning, the solvent equilibrates from layer II into layer I due to the driving force of the chemical potential. The molar flux of the solvent is therefore negative. In contrast, polymer P1 must compensate for this flux and thus diffuses against the solvent into layer II (flux of P1 is positive). Polymer P2 diffuses with the solvent into layer I but tries to compensate the force of the solvent with the flux of the polymer P2. After 20 s the diffusive flux of polymer I is still not zero, which means that it still diffuses

against the polymer in layer II. Therefore, the overall molar flux J_p^N of polymer P1 and P2 is positive but stops after the equilibration of the solvent. After that, only small fluxes of each polymer components occur due to the small diffusion coefficient.

For distributed polymer systems, it is useful to describe the transport of moments. To derive the equations for such a transport, the polymer moments must close or a suitable closure condition must be applied. Next, two limiting cases are presented, in which this closure of the moments transport can be achieved by simplifications.

3.2. Stefan–Maxwell Model for Highly Diluted Polymer Solutions (“No Polymer Friction” Model)

The first limiting case describes diffusive polymer transport in a system with a high solvent content $x_s \rightarrow 1$. In this chapter,

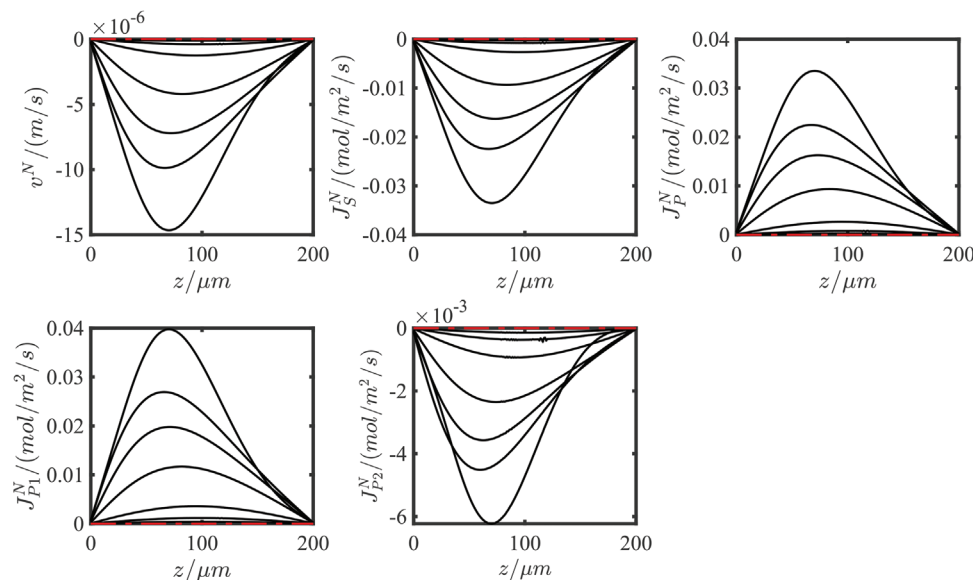


Figure 4. Velocities and Fluxes for [1,2,3,5,10,15,20] s for the Stefan-Maxwell approach with a diffusion coefficient between the polymers of $\mathfrak{D}_{P1P2} = 10^{-12} \frac{m^2}{s}$ and between solvent and polymer $\mathfrak{D}_{SP} = 10^{-9} \frac{m^2}{s}$. The final state is dashed in red.

the derivation for this limiting case for the previously presented ternary mixture with solvent S, polymer P1, and P2 is presented. A detailed derivation for distributed polymer systems can be found in the Supporting Information.

Starting from the Maxwell–Stefan equation for the polymer P1

$$d_{P1} = -\frac{1}{c} (B_{P1P1}J_{P1}^N + B_{P1S}J_S^N) \quad (28)$$

B_{P1P1} and B_{P1S} simplifies to

$$B_{P1P1} = \left(\frac{x_{P1}}{\mathfrak{D}_{P1P2}} + \frac{x_S}{\mathfrak{D}_{P1S}} + \frac{x_{P2}}{\mathfrak{D}_{P1P2}} \right), \quad (29)$$

$$B_{P1S} = -x_{P1} \left(\frac{1}{\mathfrak{D}_{P1S}} - \frac{1}{\mathfrak{D}_{P1P2}} \right).$$

Due to high dilution, the friction between two polymer molecules approaches zero, which means that the diffusion coefficient leads to $\mathfrak{D}_{P1P2} \rightarrow \infty$ and $\frac{1}{\mathfrak{D}_{P1P2}} \rightarrow 0$. Thus, simplifications can be made for the previously derived Stefan–Maxwell diffusion in Equation (29). B_{P1j} simplifies to

$$B_{P1P1} = \left(\frac{x_{P1} + x_{P2}}{\mathfrak{D}_{P1P2}} + \frac{x_S}{\mathfrak{D}_{P1S}} \right) = \frac{x_S}{\mathfrak{D}_{P1S}}, \quad (30)$$

$$B_{P1S} = -x_{P1} \left(\frac{1}{\mathfrak{D}_{P1S}} - \frac{1}{\mathfrak{D}_{P1P2}} \right) = -\frac{x_{P1}}{\mathfrak{D}_{P1S}}$$

and Equation (28) to

$$d_{P1} = -\frac{1}{c} \left(\frac{x_S}{\mathfrak{D}_{P1S}} J_{P1}^N - \frac{x_{P1}}{\mathfrak{D}_{P1S}} J_S^N \right) \quad (31)$$

Multiplication by c^2 and by the diffusion coefficient, it follows

$$c^2 \mathfrak{D}_{P1S} d_{P1} = (c x_{P1} J_S^N - c x_S J_{P1}^N) = (c_{P1} J_S^N - c_S J_{P1}^N) \quad (32)$$

After rearranging the equation, an expression for the polymer flux is obtained,

$$J_{P1}^N = \frac{-c^2 \mathfrak{D}_{P1S} d_{P1} + c_{P1} J_S^N}{c_S} = \frac{-c^2 \mathfrak{D}_{P1S} \nabla x_{P1} + c_{P1} J_S^N}{c_S} \quad (33)$$

This expression can be written in general terms for chains of length s with any number of low molecular weight species (solvents) as

$$J_{Ps}^N = \sum_{j=1}^{n_{low}} \frac{-c^2 \mathfrak{D}_{P(s)j} \nabla x_{P(s)} + \zeta^0 J_j^N}{c_j} \quad (34)$$

After applying the moment approach $\xi^k = \sum_{s=1}^{\infty} s^k c_{P(s)}$, the diffusive flux for moments becomes

$$J_{\xi^k}^N = \sum_{s=1}^{\infty} s^k J_{P(s)}^N = \sum_{j=1}^{n_{low}} \frac{\xi^k J_j^N - \mathfrak{D}_{P(s)j} (c \nabla \xi^k - \xi^k \nabla c)}{c_j} \quad (35)$$

From Equation (35), the diffusive flux of moments depends only on the diffusion of the low molecular species, the moment itself, and the total concentration.

3.3. Stefan–Maxwell Model for Concentrated Polymer Solutions (“Infinite Polymer Friction” Model)

The second limiting case describes the diffusive transport of polymers which are in a system with a low solvent content $x_S \rightarrow 0$. A simplification can be made by assuming that the Stefan–Maxwell diffusion coefficients between polymers of different

chain length are identical, thus $\mathfrak{D}_{P(s)P(r)} = \mathfrak{D}_{PP}$. We start again with the Maxwell-Stefan equation for the polymer P1

$$d_{P1} = -\frac{1}{c} (B_{P1P1}J_{P1}^N + B_{P1S}J_S^N) \quad (36)$$

with B_{P1P1} and B_{P1S}

$$B_{P1P1} = \left(\frac{x_{P1}}{\mathfrak{D}_{P1P2}} + \frac{x_S}{\mathfrak{D}_{P1S}} + \frac{x_{P2}}{\mathfrak{D}_{P1P2}} \right), \quad (37)$$

$$B_{P1S} = -x_{P1} \left(\frac{1}{\mathfrak{D}_{P1S}} - \frac{1}{\mathfrak{D}_{P1P2}} \right).$$

Assuming high polymer content, we take the limit $\mathfrak{D}_{P1P2} \rightarrow 0$, which implies that all polymers are transported with the same diffusive velocity and the friction between the polymer chains is infinite.

Multiplication of Equation (36) with this diffusion coefficient leads to

$$\mathfrak{D}_{P1P2}d_{P1} = -\mathfrak{D}_{P1P2} \frac{1}{c} (B_{P1P1}J_{P1}^N + B_{P1S}J_S^N) \quad (38)$$

with B_{P1P1} and B_{P1S}

$$D_{P1P2} B_{P1P1} = \left(\frac{\mathfrak{D}_{P1P2}(x_{P1} + x_{P2})}{\mathfrak{D}_{P1P2}} + \frac{\mathfrak{D}_{P1P2}x_S}{\mathfrak{D}_{P1S}} \right) = x_{P1} + x_{P2}, \quad (39)$$

$$D_{P1P2} B_{P1S} = -x_{P1} \left(\frac{\mathfrak{D}_{P1P2}}{\mathfrak{D}_{P1S}} - \frac{\mathfrak{D}_{P1P2}}{\mathfrak{D}_{P1P2}} \right) = x_{P1}.$$

Inserting Equation (39) into Equation (38) and multiplication with c^2 , it follows a relation for the flux of the polymer P1

$$J_{P1}^N = -\frac{c_{P1}}{c_{P2} + c_{P1}} J_S^N = \frac{c_{P1}}{c_{P2}} J_{P2}^N \quad (40)$$

and analogous for P2

$$J_{P2}^N = -\frac{c_{P2}}{c_{P2} + c_{P1}} J_S^N = \frac{c_{P2}}{c_{P1}} J_{P1}^N \quad (41)$$

The total polymer flux J_P^N arises from the summation of both terms to

$$J_P^N = J_{P1}^N + J_{P2}^N = J_{P1}^N + \frac{c_{P2}}{c_{P1}} J_{P1}^N = \frac{c_{P1} + c_{P2}}{c_{P1}} J_{P1}^N \quad (42)$$

J_{P1}^N follows with the total polymer concentration c_P resp. the 0th moment ξ^0 and the total polymer flux

$$J_{\xi^0}^N = J_P^N \quad (43)$$

to

$$J_{P1}^N = \frac{c_{P1}}{c_P} J_P^N = \frac{c_{P1}}{\xi^0} J_{\xi^0}^N \quad (44)$$

After applying the definition of moments, $\xi^k = \sum_{s=1}^{\infty} s^k c_{P1}$, the diffusive flux for moments becomes

$$J_{\xi^k}^N = \sum_{s=1}^{\infty} s^k J_{P1}^N = \frac{\sum_{s=1}^{\infty} s^k c_{P1}}{\xi^0} J_P^N = \frac{\xi^k}{\xi^0} J_P^N \quad (45)$$

Generalization to homo polymer distributions with segment number s the following expression applies

$$c x_{P(s)} \sum_{P(r)=1}^{\infty} J_{P(r)}^N = \left(\sum_{P(r)=1}^{\infty} c_{P(r)} \right) J_{P(s)}^N = \xi^0 J_{P(s)}^N \quad (46)$$

respectively

$$J_{P(s)}^N = \frac{c_{P(s)}}{\xi^0} \sum_{P(r)=1}^{\infty} J_{P(r)}^N = \frac{c_{P(s)}}{\xi^0} J_P^N \quad (47)$$

A more detailed deviation can be found in the Supporting Information. After applying the moment definition again, $\xi^k = \sum_{s=1}^{\infty} s^k c_{P(s)}$, the diffusive flux for moments develops to

$$J_{\xi^k}^N = \sum_{s=1}^{\infty} s^k J_{P(s)}^N = \frac{\sum_{s=1}^{\infty} s^k c_{P(s)}}{\xi^0} J_P^N = \frac{\xi^k}{\xi^0} J_{\xi^0}^N \quad (48)$$

Finally, the flux of higher polymer moments only depends on the flux of the 0th polymer moment

$$J_{\xi^k}^N = \frac{\xi^k}{\xi^0} J_{\xi^0}^N \quad (49)$$

In other words, the diffusive transport of higher moments is related to the diffusive flux of the 0th moment. If the total concentration of polymers is constant, no equilibration of higher moments will take place. This preserves spatial inhomogeneities of the polymer and is a realistic physical behavior for polymer solutions with low solvent content. It is also physically consistent as all polymer moments have the same species velocity, regardless of the degree of the polymer moment.

3.4. Model Summary

To summarize the previously described findings, **Table 2** shows an overview of the different simplifications to describe the transport of moments in a respective system.

An extension to multiple polymer distributions can be made by calculating the diffusive fluxes for all distributions separately. From this the overall diffusive fluxes for all polymer distributions $J_{\xi^k}^N$ can be calculated. Finally, the balance equations can be calculated for each species and polymer distribution.

4. Results

The results presented here are based on the calculation of the balance equations for the individual components as mentioned according to Equation (33) resp. (40). Note that the moments are an exact

Table 2. Overview of equations to be implemented in a polymer system with constant density.

Balance equation for low-molecular species

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \left(c_i \left(\nu - \frac{1}{\rho} \sum_i^{n_{low}} MW_i J_i^N - \frac{1}{\rho} MW_{seg} J_{\xi_1}^N \right) \right) + \nabla \cdot J_i^N = r_i^{total}$$

Balance equation for polymer moments of a representative polymer distribution P

$$\frac{\partial \xi_p^{jk}}{\partial t} + \nabla \cdot \left(\xi_p^{jk} \left(\nu - \frac{1}{\rho} \sum_i^{n_{low}} MW_i J_i^N - \frac{1}{\rho} MW_{seg} J_{\xi_1}^N \right) \right) + \nabla \cdot J_{\xi_p^{jk}}^N = r_{\xi_p^{jk}}^{total}$$

With the flux $J_{\xi_1}^N$, which is the summation of the 1st moment over all polymer distributions.

$$J_{\xi_1}^N = \sum_p^J J_{\xi_1^p}^N$$

Molar average velocity

$$\nu^N = \nu - \frac{1}{\rho} \sum_i J_i^N MW_i$$

Highly diluted polymer solution $x_S \rightarrow 1$ (“No Polymer Friction” model)

Transport of low molecular species

$$J_j^N = \sum_{i=1}^{J-1} -c(B^{-1})_{ji} (\nabla x_i)$$

$$J_{\xi_p^{jk}}^N = \sum_{j=1}^{n_{low}} \frac{\xi_p^{jk} J_j^N - \mathfrak{D}_{pSj} (c \nabla \xi_p^{jk} - \xi_p^{jk} \nabla c)}{c_j}$$

Transport of polymer moments of a representative polymer distribution P

Highly concentrated polymer solution $x_S \rightarrow 0$ (“Infinite Polymer Friction” model)

Transport of low molecular species

$$J_j^N = \sum_{i=1}^{J-1} -c(B^{-1})_{ji} (\nabla x_i)$$

Transport of polymer moments of a representative polymer distribution P

$$J_{\xi_p^{jk}}^N = \frac{\xi_p^{jk}}{\xi_p^0} J_{\xi_p^0}^N$$

solution and not an approximation. The same results can thereby be obtained with the “No Polymer Friction” moment model and the “Infinite Polymer Friction” moment model. For comparison to the full model in terms of the molar mass fractions of the individual species, the component balance equations were chosen here. Validity of moment balances was checked.

4.1. Model Comparison for Polymers in Diluted Systems

This setup represents the diffusion of polymer chains in a system with high solvent content $x_S \rightarrow 1$. The results for the different mole fractions for the first 20 s can be seen in **Figure 5** for the full Stefan-Maxwell model and the “No Polymer Friction” model. The figure shows that the assumption $D_{P1P2} \rightarrow \infty$ shows good agreement to the full model for solutions with a very high solvent content. In systems with a high solvent content, two polymer molecules almost never touch. For this reason, it is a good assumption to assume a diffusion coefficient of $D_{P1P2} \rightarrow \infty$, which means that there is no friction between the two polymer chains. Figure 5 shows that after 20 s of simulation time the solvent and polymer fractions have balanced out.

Figure 6 shows the “Infinite Polymer Friction” model in comparison to the full model for highly diluted systems, whereas the assumption $D_{P1P2} \rightarrow 0$ is inappropriate for this case. The course can be explained as follows. The mole fraction for the solvent is equilibrated after that time, but the mole fractions for the polymers aren't. Since the driving force for the solvent tends to zero $\nabla x_S = 0$, the transport of the whole system stops. This can be explained by calculating the fluxes in this state

$$d_S = 0 = -\frac{1}{c} \cdot \left(\left(\frac{x_{P1}}{\mathfrak{D}_{SP1}} + \frac{x_{P2} + x_S}{\mathfrak{D}_{SP2}} \right) J_S^N + \left(\frac{x_S}{\mathfrak{D}_{SP2}} - \frac{x_S}{\mathfrak{D}_{SP1}} \right) J_{P1}^N \right) \quad (50)$$

which means that J_{P1}^N directly follows from J_S^N or vice versa. From the driving force for polymer P2 which is always zero

$$\mathfrak{D}_{P1P2} d_{P1} = 0 = x_{P2} J_{P1}^N - x_{P1} J_{P2}^N \quad (51)$$

follows that J_{P2}^N directly depends on J_{P1}^N and vice versa. Equation (19) follows a trivial linear equation system for the fluxes with all fluxes

$$J_i = 0 \quad (52)$$

4.2. Model Comparison for Polymers in Concentrated Systems

This setup represents the diffusion of polymer chains in a system with low solvent content $x_S \rightarrow 0$. The results for the different mole fractions for the first 20 s are depicted in **Figure 7** for the full model and the “No Polymer Friction” model. The figure shows that the assumption $D_{P1P2} \rightarrow \infty$ is inappropriate for this case. In systems with a low solvent content, the polymer molecules touch each other, which means that there is high friction between the molecules. Therefore, the assumption with a diffusion coefficient of $D_{P1P2} \rightarrow \infty$, which implies no friction between polymer molecules, is not suitable. In the “No Polymer Friction” model, the mole fractions of both the solvent and the polymers equalize, whereas in the full model, the fractions of the polymers do not equalize, at least not in the first 20 s. However, after an infinitely long simulation time, the mole fractions of the polymers are also balanced. In this context, we neglect the very slow interaction between polymer molecules because the friction between these molecules is much higher due to the lower diffusion coefficient.

Figure 8 shows the comparison between the full Stefan-Maxwell model and the “Infinite Polymer Friction” model. The

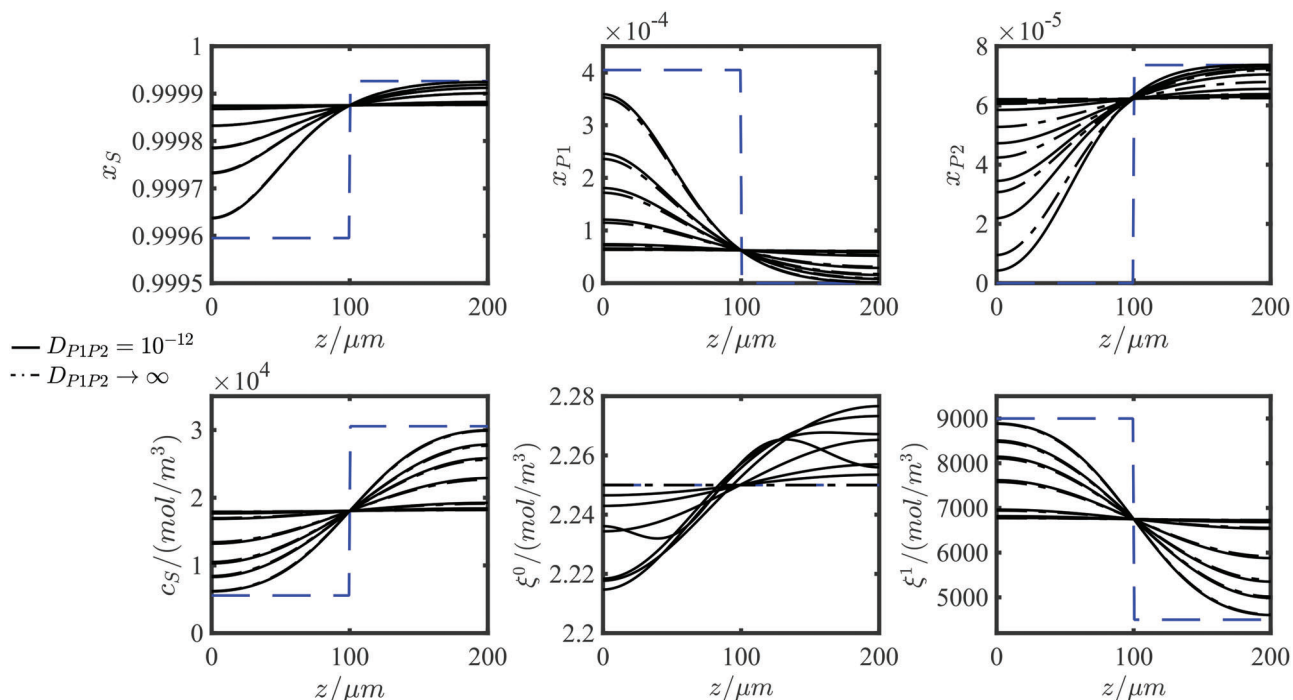


Figure 5. Results for [1,2,3,5,10,15,20] s for the full Stefan-Maxwell model (solid lines) with a diffusion coefficient between the Polymers of $\mathfrak{D}_{P1P2} = 10^{-12} \frac{\text{m}^2}{\text{s}}$ compared to the “No Polymer Friction” model (dashed lines) for highly diluted systems. The diffusion coefficient between solvent and polymer was chosen to $\mathfrak{D}_{SP} = 10^{-9} \frac{\text{m}^2}{\text{s}}$ in both the models. The initial conditions are dashed in blue.

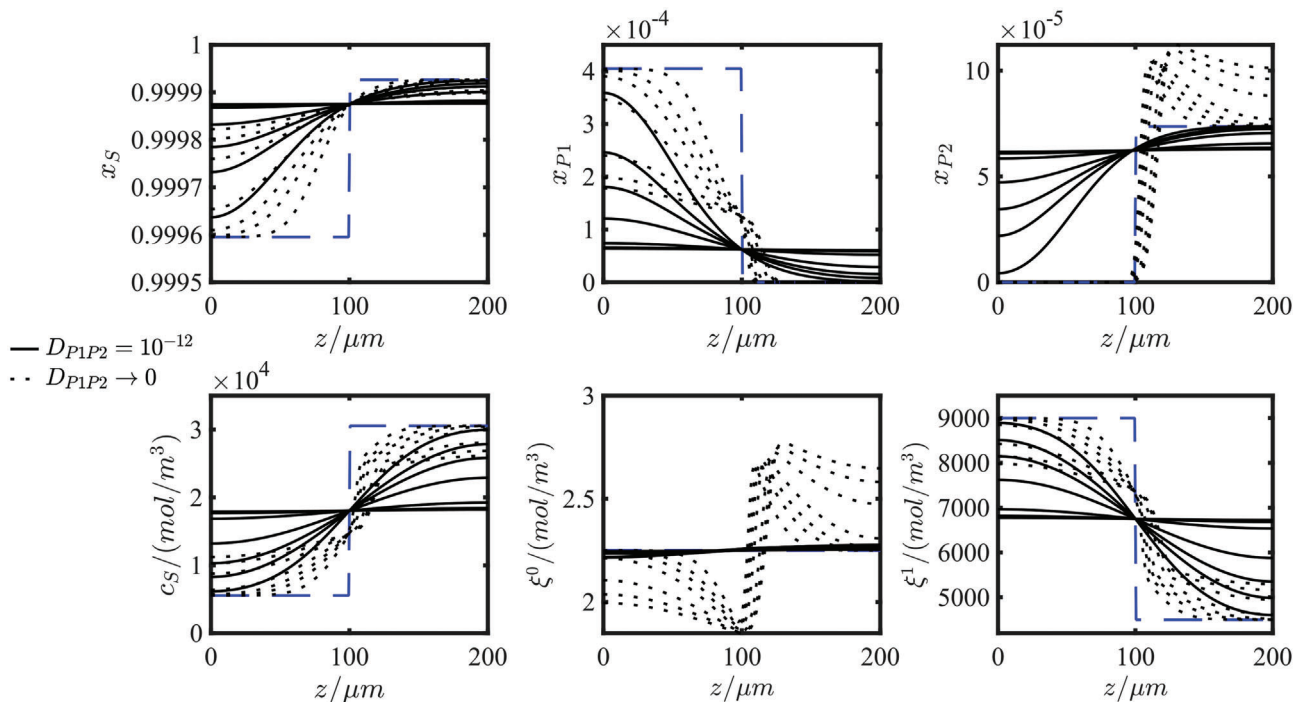


Figure 6. Results for [1,2,3,5,10,15,20] s for the full Stefan-Maxwell model (solid lines) with a diffusion coefficient between the Polymers of $\mathfrak{D}_{P1P2} = 10^{-12} \frac{\text{m}^2}{\text{s}}$ compared to the “Infinite Polymer Friction” model (dotted lines) for highly diluted systems. The diffusion coefficient between solvent and polymer was chosen to $\mathfrak{D}_{SP} = 10^{-9} \frac{\text{m}^2}{\text{s}}$ in both the models. The initial conditions are dashed in blue.

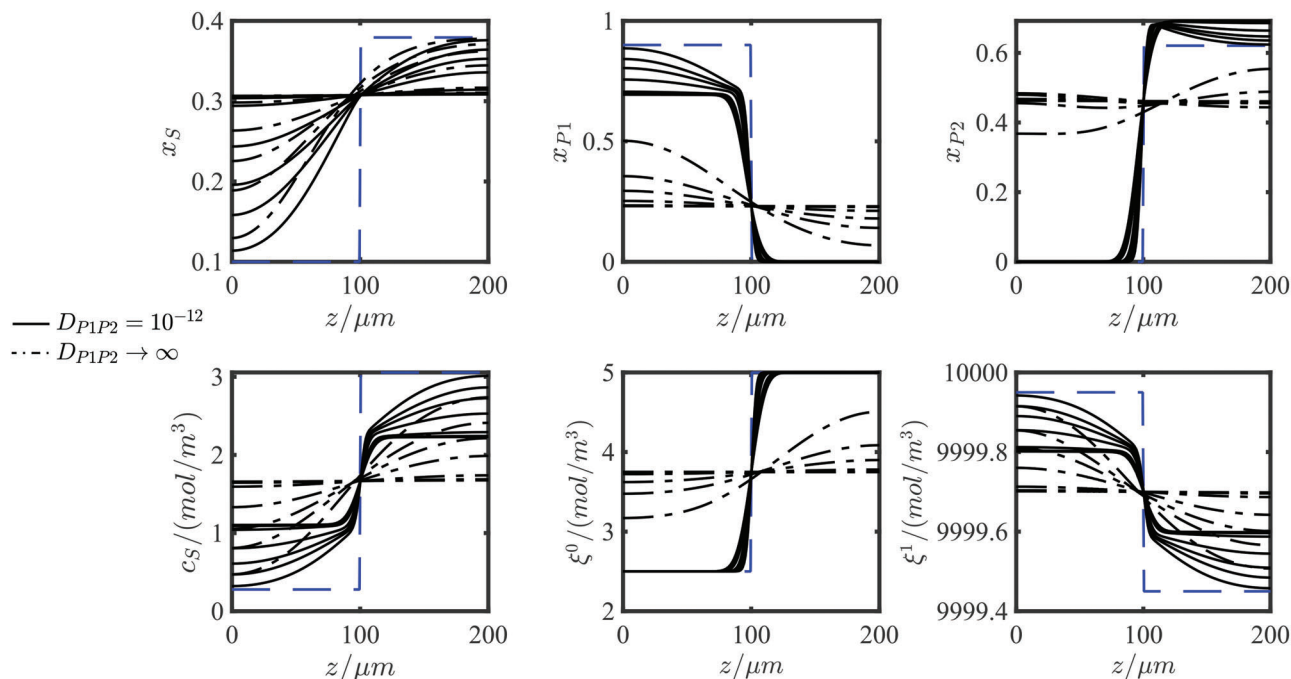


Figure 7. Results for [1,2,3,5,10,15,20] s for the full Stefan–Maxwell model (solid lines) with a diffusion coefficient between the Polymers of $\mathfrak{D}_{P1P2} = 10^{-12} \frac{\text{m}^2}{\text{s}}$ compared to the “No Polymer Friction” model (dashed lines) for concentrated systems. The diffusion coefficient between solvent and polymer was chosen to $\mathfrak{D}_{SP} = 10^{-9} \frac{\text{m}^2}{\text{s}}$ in both the models. The initial conditions are dashed in blue.

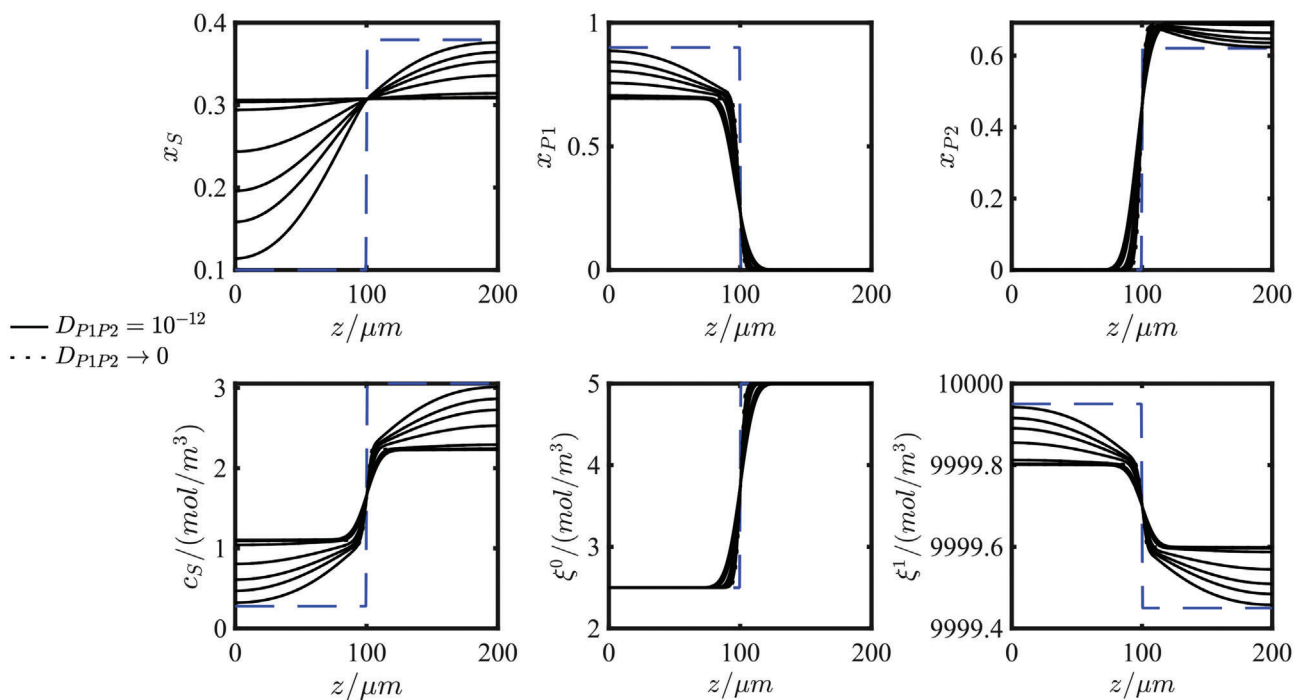


Figure 8. Results for [1,2,3,5,10,15,20] s for the full Stefan–Maxwell model (solid lines) with a diffusion coefficient between the Polymers of $\mathfrak{D}_{P1P2} = 10^{-12} \frac{\text{m}^2}{\text{s}}$ compared to the “Infinite Polymer Friction” model (dotted lines) for concentrated systems. The diffusion coefficient between solvent and polymer was chosen to $\mathfrak{D}_{SP} = 10^{-9} \frac{\text{m}^2}{\text{s}}$ in both the models. The initial conditions are dashed in blue.

assumption $D_{p1p2} \rightarrow 0$ for solutions with a high polymer content is in good agreement with the full model. Again, the mole fraction for the solvent is equilibrated after that time. But the mole fractions for the polymers aren't. Since the driving force for the solvent equals to zero $\nabla x_s = 0$, the transport of the whole system stops. For a system with a high polymer content, this behavior is certainly a good assumption.

5. Conclusion

To adequately describe a polymer system for example in a CFD simulation, a mathematical formulation for the transport of moments of polymer distributions is necessary. To derive such a formulation, the polymer moments must close or a suitable closing condition must be applied. In this paper, we first presented the full Stefan–Maxwell model, which does not close in the case of different binary diffusion coefficients. Then we presented two different limiting cases for the Stefan–Maxwell model, which do close. It was shown that each limiting case provides good agreement to the full model for the respective application. The “No Polymer Friction” model can be used when a highly dilute polymer solution is present and thus friction between polymer molecules can be neglected. Here excellent agreement can be observed. In contrast, at high polymer concentrations the “Infinite Polymer Friction” model can be used, since at high concentrations the friction between the polymers is extremely high, so that they virtually do not diffuse against each other but only with the solvent. For this reason, the system “solidifies” as soon as the solvent is equilibrated.

Using these limiting cases of the rigorous Stefan–Maxwell theory has the advantage that the transport equation for moments of polymer species close. Which of the two formulations is more suitable depends on the polymer content of the solution, the average chain length of the polymer, the degree of branching of the polymer, and the molecular weight.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request

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