

# **Modeling of Polymer Swelling and Drying Using PC-SAFT for Highly Cross-Linked Networks**

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# Kurzfassung

Hochvernetzte Polymere spielen eine zentrale Rolle bei der Verkapselung empfindlicher Elektronik, da sie als Barriere gegenüber Flüssigkeiten und Dampf wirken. Gleichzeitig können diese Materialien selbst Lösungsmittel aufnehmen, wodurch eine Beeinträchtigung der Funktion elektronischer Bauteile verursacht wird. Vor diesem Hintergrund befasst sich die vorliegende Arbeit mit der experimentellen und theoretischen Untersuchung von Quellung, Diffusion und Trocknung in hochvernetzten Polymernetzwerken für die Anwendung in Elektronik in Kontakt mit verschiedenen Lösungsmitteln.

Zur Beschreibung der thermodynamischen Gleichgewichte wird die Kombination aus der Zustandsgleichung PC-SAFT mit einem Netzwerkterm zur Berücksichtigung elastischer Beiträge des Polymernetzwerks genutzt. Der Stofftransport wird auf dieser Grundlage mithilfe eines Maxwell-Stefan-Ansatzes modelliert. Für alle untersuchten Systeme zeigt sich eine gute Übereinstimmung zwischen experimentellen Daten und Modellrechnungen, wodurch die Eignung des entwickelten Modellrahmens zur Beschreibung der Lösungsmittelaufnahme in hochvernetzten Polymeren bestätigt wird. Darüber hinaus zeigt sich, dass die Lösungsmittelaufnahme stark von der Wechselwirkung zwischen Polymer und Lösungsmittel abhängt. Insbesondere führt eine ähnliche Polarität von Polymer und Lösungsmittel zu einer erhöhten Aufnahme.

Ein weiterer Schwerpunkt der Arbeit liegt auf der Analyse geometrischer Einflüsse auf den Stofftransport. Es konnte gezeigt werden, dass die bestimmten Diffusionskoeffizienten stark von der zugrunde gelegten Geometrie abhängen und eindimensionale oder zweidimensionale Vereinfachungen zu deutlichen Abweichungen gegenüber einer realistischeren dreidimensionalen Beschreibung führen können. Die Berücksichtigung der Probengeometrie ist daher wesentlich für eine zuverlässige Modellierung und Bewertung des Diffusionsverhaltens.

Zusätzlich wurde Wärme- und Stofftransport gekoppelt, um Diffusion in elektronischen Verkapselungen während des Betriebes zu beschreiben. Dabei konnte gezeigt werden, dass Wärmequellen innerhalb elektronischer Bauteile das Quellungsverhalten beeinflussen. Gleichzeitig wurde deutlich, dass Trocknung und Quellung nicht mit identischen Diffusionskoeffizienten beschrieben werden können. Dies weist darauf hin, dass die der Trocknung zugrunde liegenden Transportmechanismen nicht vollständig im Modell berücksichtigt wurden.

Die Arbeit liefert damit einen wichtigen Beitrag zum Verständnis von Lösungsmittelaufnahme, Diffusion und Trocknung in hochvernetzten Polymernetzwerken unter praxisrelevanten Bedingungen.



# Abstract

Highly crosslinked polymers play a central role in the encapsulation of sensitive electronics, as they act as barriers against liquids and vapors. At the same time, these materials themselves can absorb solvents, which may impair the functionality of electronic components. Against this background, the present work deals with the experimental and theoretical investigation of swelling, diffusion, and drying in highly crosslinked polymer networks for application in electronics in contact with various solvents.

To describe the thermodynamic equilibria, a combination of the PC-SAFT equation of state with a network term to account for elastic contributions of the polymer network is used. Based on this, mass transport is modeled using a Maxwell–Stefan approach. For all investigated systems, good agreement between experimental data and model calculations is observed, confirming the suitability of the developed modeling framework for describing solvent uptake in highly crosslinked polymers. Furthermore, it is shown that solvent uptake strongly depends on the interaction between polymer and solvent. In particular, a similar polarity of polymer and solvent leads to increased uptake.

Another focus of the work is the analysis of geometric influences on mass transport. It was shown that the determined diffusion coefficients strongly depend on the underlying geometry and that one-dimensional or two-dimensional simplifications can lead to significant deviations compared with a more realistic three-dimensional description. Therefore, consideration of the sample geometry is essential for reliable modeling and evaluation of diffusion behavior.

In addition, heat and mass transport were coupled in order to describe diffusion in electronic encapsulations during operation. It was shown that heat sources within electronic components influence the swelling behavior. At the same time, it became clear that drying and swelling cannot be described using identical diffusion coefficients. This indicates that the transport mechanisms underlying drying were not fully accounted for in the model.

Thus, this work makes an important contribution to the understanding of solvent uptake, diffusion, and drying in highly crosslinked polymer networks under practically relevant conditions.



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# List of Symbols

## *Abbreviations*

ARD — average relative deviation

ATR-FTIR — Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy

CFL — Courant–Friedrichs–Lewy constant

EOS — Equation of State

IUPAC — International Union of Pure and Applied Chemistry

LLE — Liquid-Liquid equilibrium

MS — Maxwell–Stefan diffusion

SAFT — Statistical Associating Fluid Theory

PC-SAFT — Perturbed-Chain Statistical Associating Fluid Theory

PCP-SAFT — Perturbed-Chain Polar Statistical Associating Fluid Theory

VLE — Vapor-Liquid equilibrium

## *Latin Symbols*

$a$  — Helmholtz free energy

$A$  — surface area

$B_{i\alpha i\beta}$  — bonding fraction

$c$  — concentration

$D_{ij}$  — diffusion coefficient

$D_{MS}$  — Maxwell-Stefan diffusion coefficient

$D_{MS,\infty}$  — amplitude factor of the Maxwell–Stefan diffusion coefficient regarding temperature

$E$  — elasticity constant

$E_{A,D}$  — growth rate of the Maxwell–Stefan diffusion coefficient regarding temperature

$E_{A,\eta}$  — second parameter for the damper constant

$E_{A,t}$  — growth rate of the damper constant regarding temperature

$J_i$  — molar flux of component i

$k_{ij}$  — binary interaction parameter

$k_\phi$  — slope of the critical volume fraction regarding temperature

m — segment number

$m_{i,\alpha}$  — segment number of segment  $\alpha$

$\bar{m}$  — average segment number

$n_i$  — molar amount of substance

$J_i$  — molar flux of component i

$p_{elastic}$  — osmotic pressure in the polymer network

$Q'_k$  — Onsager coefficients

t — time

u — greatest change per time step

V — volume

$\vec{v}_i$  — flux velocity of component i

v — molar volume

$X^{A_{i\alpha}}$  — fraction of molecules that are not bonded to the association site

$x_i$  — mole fraction of component

x,y,z — spatial coordinates

Z — compressibility factor

$z_{i,\alpha}$  — segment fraction

$\Delta z$  — grid length

### *Greek Symbols*

$\alpha_{max}$  — ratio of the maximum volume to the reference state volume

$\delta_{km}$  — Kronecker delta

$\Delta$  — Laplace operator

$\Delta^{A_{i\alpha}B_{j\beta}}$  — association strength

$\varepsilon$  — dispersion energy

$\varepsilon$  — strain

$\varepsilon^{AB}$  — association energy

$\zeta_n$  — reduced segment density

$\eta$  — damper constant

$\eta$  — packing fraction

$\eta_0$  — amplitude factor of the damper constant regarding temperature

$\kappa^{AB}$  — association volume

$\mu$  — chemical potential

$\mu^a$  — dipole moment

$\phi$  — network functionality

$\vec{\nabla}$  — Nabla operator

$\rho$  — molar density

$\sigma$  — stress

$\sigma$  — segment diameter

$\phi$  — network functionality

$\phi_{solv}$  — volume fraction of the solvent

$\phi_{solv,c}$  — critical volume fraction at which swelling starts

Subscripts

assoc — association

disp — dispersion

dipole — dipole

elastic — elastic contribution

hc — hard chain

id — ideal gas

max — maximum

mix — mixture

pol — polymer

sol — solvent

# 1 Introduction

Solvent absorption, often referred to as swelling, is central to many polymer based technologies, ranging from drug delivery systems to moisture barrier coatings for sensitive electronics. Hydrogels, for example, can take up several times their own weight in liquid, whereas thermoset resins typically absorb only small amounts. The extent and rate of swelling are governed by temperature, pressure, polymer chemistry, and the nature of the solvent. Because performance depends on these factors, selecting an appropriate polymer-solvent pair is critical. In protective coatings even minimal swelling can allow solvent to reach conductive traces, causing short circuits and ultimately device failure. Therefore, the goal is to use a polymer with relatively slow solvent-diffusion kinetics, or generally low solvent uptake, for the intended application environment. In contrast, for controlled drug release, the carrier must swell just enough to deliver the active ingredient at a predictable rate while remaining chemically and mechanically stable.

Material selection generally relies on two complementary approaches. Laboratory swelling experiments are straightforward to design and reveal both the kinetics and equilibrium uptake, but tests can become time-consuming when solvents diffuse slowly. Thermodynamic models, once parameterized with experimental or literature data, can predict swelling behavior and thereby reduce the need for additional experiments. Combining targeted experiments with validated modelling therefore provides an efficient path to identifying polymers that meet the stringent demands of each application. Therefore, predictive and transferable modeling approaches are required to describe swelling behavior beyond isolated experimental observations. These can be used to optimize the coating thickness of electronics to increase lifetime and reduce manufacturing costs.

Modeling polymer swelling can be challenging because of their complexity and the addition of solvents. Krenn et al.<sup>1</sup> were able to describe this behavior for an epoxy resin by adding a network term to the PC-SAFT equation of state, with good agreement with experimental data. In this way, the diffusion behavior of an epoxy resin could also be described with good agreement to experimental observations. Although this framework has produced satisfying results, several areas remain unexplored. Since swelling experiments are very time-consuming, previous studies have focused mainly on epoxy resins, leaving a significant gap in the investigation of other polymer classes beyond thermoset resins. In addition, diffusion has generally been modeled in one dimension because of the simpler implementation and significantly lower computational cost, while geometric effects on the polymer have been neglected entirely. Although initial steps

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<sup>1</sup> P. Krenn, P. Zimmermann, M. Fischlschweiger and T. Zeiner, *Ind. Eng. Chem. Res.*, vol. 59, no. 11, pp. 5133-5141, 2020.

have been taken toward implementation in application-oriented fields, important areas with high industrial relevance still remain unexplored.

Despite these promising developments, a systematic and application-oriented description of swelling and drying in highly cross-linked polymer networks is still missing. Therefore, this work aims to address these questions. In particular, it remains unclear whether the existing framework can be transferred to additional polymer classes and, if so, whether it can provide a reliable basis for simulating swelling processes in electronic materials and devices. So, the main objective of this thesis is the extension and validation of a thermodynamically consistent framework for the description of swelling and drying in highly cross-linked polymer systems. The model should be capable of representing swelling equilibrium, diffusion kinetics, and the influence of viscoelastic effects for different polymer classes, while simultaneously accounting for multidimensional geometry and inhomogeneous temperature conditions. Furthermore, it should provide a first basis for the investigation of drying processes and for the transfer of the developed approach to realistic technical applications. Thereby, the relevance of thermodynamic, geometric, and thermal effects on solvent transport in highly cross-linked polymers should be clarified in order to contribute to a more comprehensive understanding of these systems. Based on this objective, the following research questions are addressed.

The first objective is to investigate whether the existing thermodynamic framework can be transferred to other swelling systems with different polymer and solvent combinations and to identify the factors that govern its applicability. Since highly cross-linked polymers may differ substantially in polarity and crosslink density, it must be assessed whether the existing model is sufficient to describe these effects or whether adaptation or extension is required. To answer this question, a systematic experimental study is required that covers relevant polymer classes used in electronic encapsulation, namely epoxy resins, phenolic resins, polyurethanes, and silicones, which represent a range of polarity and crosslink density, in combination with selected solvent systems. The experimental program must therefore be designed such that the influence of polymer type, solvent type, and temperature can be evaluated in a comparable manner and on a sufficiently broad database. In addition, the diffusion behavior must be analyzed more carefully, since Maxwell–Stefan and viscoelastic stress-based approaches describe different transport mechanisms whose relevance may vary depending on the polymer–solvent system. It must therefore be determined whether a coupled description is generally required or whether, in specific cases, one mechanism alone is sufficient.

Another important question concerns the transferability of the previously observed effects to multidimensional systems. So far, the investigations have been limited to one-dimensional descriptions, which cannot adequately represent either the geometry of the experimental samples or that of polymer components in real applications. It must therefore be clarified whether the effects identified in one dimension remain valid in higher dimensions or whether their interpretation changes once multidimensional transport is taken into account. For this purpose, two- and three-dimensional simulations are required in order to evaluate to what extent higher-dimensional descriptions

improve the representation of the actual diffusion process. Particular attention must be paid to the diffusion parameters, since these are typically fitted to experimental data and can therefore be critically examined by means of multidimensional modeling. At the same time, it must be determined whether the increased implementation complexity and computational cost of higher-dimensional simulations are justified by a corresponding gain in descriptive accuracy.

A further research question of this thesis is how heat transfer influences solvent transport and drying behavior in highly cross-linked polymer systems under application-relevant conditions. In encapsulated electronic components, heat and mass transport are inherently coupled, since both the equilibrium solvent uptake and the diffusion kinetics depend on temperature. In addition, internal or externally imposed heat fluxes may generate spatially non-uniform temperature fields, which can alter local transport conditions and thus affect both solvent penetration and solvent release. It must therefore be clarified how temperature gradients influence the spatial and temporal distribution of solvent within the polymer, whether they promote or retard transport into sensitive inner regions, and how they affect the kinetics and mechanisms of drying. A particular question is whether drying in highly cross-linked polymers can be described on the basis of diffusion parameters derived from swelling experiments, or whether solvent uptake and solvent release follow different transport behavior that requires separate consideration. In this context, it must also be evaluated whether the model is capable of representing the processes with sufficient accuracy.

Overall, the successful completion of this work would show whether the developed methodology can be transferred to different highly cross-linked polymer systems. In doing so, the thesis would not only extend the applicability of PC-SAFT-based swelling models to different polymer classes, but also clarify the role of diffusion mechanisms, sample geometry, and temperature gradients in solvent transport. The expected outcome is therefore a more comprehensive and application-oriented understanding of solvent uptake and release in polymer networks.



## 2 State of the Art

*In this chapter, the fundamental principles of polymer physics and swelling are presented and discussed. We first review the basic concepts of polymer physics and the thermodynamic principles necessary for calculating swelling equilibria. Next, we move from Fickian diffusion kinetics to Maxwell–Stefan diffusion in liquid systems, highlighting the influence of inhomogeneous temperature fields. Finally, we examine the available methods for measuring the swelling and drying of polymers.*

### 2.1 Fundamentals of Solvent Uptake in Polymers

Polymers constitute a vast field in both research and application, with various classifications and diverse utilization aspects. It is easy to distinguish between natural polymers, such as cellulose or caoutchouc, and synthetic polymers, whose utilization ranges from simple packaging materials to highly advanced technologies. Nevertheless, there are further additional classification schemes based on either fabrication, thermal behavior, chemistry, or other factors. These topics are well explained in many textbooks [1, 2]. Generally, a polymer is a substance composed of multiple very large molecules, known as macromolecules. The IUPAC [3] defines a macromolecule as ‘a molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass’. These molecules are often made up of repeating smaller units called monomers.

Here, the molar mass, along with the chain length, is a crucial parameter as it significantly influences various polymer properties, such as melting point and glass transition temperature [1, 2]. The melting point is the temperature at which a polymer transitions from a solid to a liquid state. In contrast, the glass transition temperature is the characteristic temperature at which an amorphous or semi-crystalline polymer shifts from a hard, glassy state to a softer, rubbery state (1; 2). Equally important as molar mass is the polymer architecture, which defines the polymer’s unique characteristics [1, 2]. Among the different polymer architectures, the most common are linear, branched, and cross-linked polymers as illustrated in Figure 1. A linear macromolecule consists of continuous chains of repeating units. In contrast, a branched macromolecule has smaller side chains attached to the main chain. A cross-linked macromolecule features linking points, known as crosslinks, between polymer chains, forming a large, interconnected network.

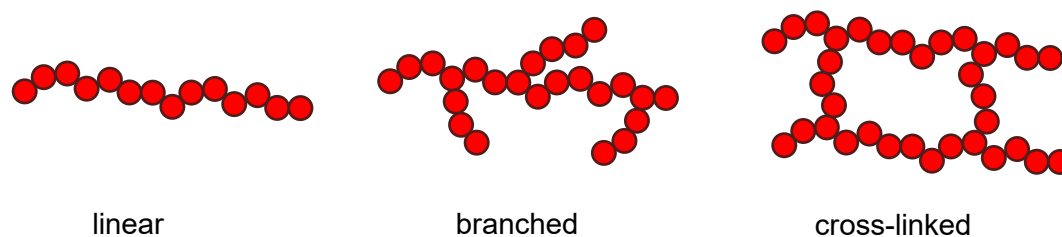


Figure 1: Macromolecular Architectures – Linear, Branched, and Cross-Linked

Polymer architecture is also crucial for the behavior of polymers in combination with solvents. Linear and branched polymers are sometimes capable of dissolving in suitable solvents, whereas cross-linked polymers can only absorb solvent into their network, a process known as swelling [4]. It is important to note that linear and branched polymers can also be insoluble in certain solvents and may only swell rather than fully dissolve [5].

Polymer swelling was first investigated over 70 years ago by Staudinger et al. [6] for polystyrene, Gee [7] for vulcanized rubber, and Flory et al. [8] for polyamides. Since then, various polymers have been studied regarding the amount of solvent uptake in relation to temperature and crosslinking degree. Notable polymer types investigated in the last few decades include hydrogels [9, 10] and thermosets [11].

Hydrogels are polymer systems that can absorb large amounts of water without dissolving. These polymers can take up solvents up to 1000 times their own weight. They consist of hydrophilic polymer chains that are either chemically crosslinked with covalent bonds or physically crosslinked with hydrogen bonds. Common properties of such polymers include a soft and elastic mechanical behavior, high biocompatibility, and reversible swelling behavior. Therefore, these polymers are commonly used for drug delivery in medicine, as well as in cosmetics and hygiene products. A famous example of such a hydrogel used in these fields is the Poly(N-isopropylacrylamide) polymer. Because of the vast variety of applications these polymers have, their swelling behavior has been extensively investigated and is well understood. [12, 13]

In contrast, the swelling behavior of thermosets has been significantly less researched and understood, despite its relevance in protective applications [14, 15, 16]. Since these polymers are characterized by their high chemical, thermal, and mechanical resistance, they are commonly used to protect sensitive components such as electronics [14, 16]. However, thermoset polymers are still capable of swelling, which can potentially damage delicate internal ingredients [14]. Fortunately, the swelling of thermosets occurs much more slowly and to a lesser extent compared to hydrogels [17]. Though, this makes experimental investigations of their swelling behavior more challenging due to the extended experimental durations required [17]. Thermosets are polymers that can only be transformed into a solid, crosslinked structure once through heat or chemical curing [18]. After this process, they can neither be melted nor reformed [18]. This is because, during the curing process, irreversible covalent bonds

form between the polymer chains, creating a highly crosslinked network [18]. Examples of such polymers include epoxy resins, phenolic resins, polyurethanes, and thermoset silicones [18].

The swelling of crosslinked polymer networks can be described by thermodynamic and elastic principles, as it essentially arises from the same mechanisms that govern polymer–solvent mixing. Mixing is driven by various solvent-polymer interactions, and in the case of swelling, by network effects of the polymer, such as elasticity and the availability of free volume into which the solvent can diffuse [4]. Elasticity effects arise from the fact that polymer chains in a swollen network cannot move freely. As the chains are stretched into unfavorable elongated configurations, additional repulsive forces develop. These forces increase as swelling continues and increasingly counteract the further swelling process until an equilibrium state is reached, where no further solvent uptake occurs. These forces can also be interpreted as a sort of osmotic pressure acting on the invading solution, thereby increasing its chemical potential [4].

Generally, for the polymer, these properties include the polymer's elastic behavior, degree of cross-linking, and the glass transition temperature [4]. Additionally, the swelling degree decreases with an increasing degree of cross-linking and polymer molar mass [4]. Another crucial aspect is the glass transition temperature in relation to polymer swelling, as diffusion kinetics change significantly when it is surpassed [19]. At the glass transition temperature, interactions between the polymer and solvents change, affecting physical properties such as elasticity, heat capacity, and viscosity [19]. It is also notable that swelling induces stress in the network, such as by breaking bonds, which can lead to a degradation of the mechanical behavior [4, 19].

## 2.2 Modeling of Equilibrium Conditions

Phase equilibria are a fundamental concept in thermodynamics and are crucial in various fields of process engineering. [20] Beginning with the fundamental laws of thermodynamics, a system refers to the part of the universe under investigation, while the environment is everything else outside the system, separated by the system boundary. A system can be considered open when there is an exchange of both matter and energy, closed when only energy is exchanged, and isolated when neither matter nor energy is exchanged. The total energy of the system ( $E$ ) is described by the first law of thermodynamics as the sum of heat ( $Q$ ) and work ( $W$ ). This law, also known as the law of conservation of energy, states that the total energy of a system remains constant unless altered by heat exchange or work performed on or by the system. The inherent part of a system's energy that is neither kinetic nor potential is referred to as the internal energy ( $U$ ). Since, for most thermodynamic processes, the difference between  $E$  and  $U$  can be considered negligible, the following relation can be derived:

$$dU = \partial Q + \partial W = TdS + PdV \quad \text{Eq. 1}$$

Here,  $\partial Q$  is written as  $TdS$  by definition of entropy  $S$  for a reversible process, and  $\delta W$  is written as  $P dV$ , representing reversible volumetric work. A reversible process in ther-

modynamics is an idealized process that proceeds through a continuous sequence of equilibrium states and can be reversed by an infinitesimal change in external conditions, leaving both the system and the surroundings unchanged. An irreversible process, in contrast, involves finite gradients (e.g., in temperature or pressure), cannot be exactly reversed, and is accompanied by internal entropy production.

The symbol  $\partial$  indicates that  $Q$  and  $W$  are process quantities and  $U$  is a state, quantity meaning that internal energy  $U$  cannot be written directly as a function of  $Q$  and  $W$ . (20) A thermodynamic system may also be described in terms of the enthalpy  $H$ , obtained from the internal energy  $U$  by a Legendre transformation. Since  $H = U + PV$ , and  $d(PV) = PdV + VdP$ , the fundamental relation becomes

$$d(H) = d(U + PV) = TdS + VdP \quad \text{Eq. 2}$$

Similarly, the expressions for Gibbs energy ( $G$ ) and Helmholtz energy ( $A$ ) are derived as follows:

$$d(G) = d(H - TS) = -SdT + VdP \quad \text{Eq. 3}$$

$$d(A) = d(U - TS) = -SdT - PdV \quad \text{Eq. 4}$$

For a multicomponent system, the internal energy depends on the molar amounts of each constituent. Taking this into account, Eq. 1 becomes:

$$dU = TdS + PdV + \sum_i \mu_i dn_i \quad \text{Eq. 5}$$

Here, the chemical potential  $\mu_i$  is introduced, defined as the partial derivative of the internal energy with respect to the number of moles ( $n$ ) of component  $i$ :

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}} \quad \text{Eq. 6}$$

The chemical potential therefore quantifies how the internal energy changes with composition and is a key parameter for describing mass transfer and chemical equilibrium.

The direction of spontaneous processes is determined by the second law of thermodynamics, which states that the total entropy of the system and its surroundings must increase, or remain constant in the limiting case of a reversible process. Consequently, equilibrium is the final state of any spontaneous process. (20)

Based on the work of **Josiah Willard Gibbs** this statement was reformulated, stating that, in a closed system, any spontaneous process occurring at constant pressure and volume results in a decrease in the system's energy [21]. By applying extreme value calculations with appropriate constraints, this criterion allows us to derive simplified expressions for equilibrium in terms of temperature ( $T$ ), pressure ( $P$ ), and chemical potential ( $\mu$ ) for arbitrary compounds and phases, as follows:

$$T^I = T^{II} = \dots = T^\pi \quad \text{Eq. 7}$$

$$P^I = P^{II} = \dots = P^\pi \quad \text{Eq. 8}$$

$$\mu_i^I = \mu_i^{II} = \dots = \mu_i^\pi \quad \text{Eq. 9}$$

Therefore, equilibrium conditions are described for N Compounds and  $\pi$  phases.

The relationship between each parameter in Eq. 7 – Eq. 9 for a single phase can be described by the **Gibbs-Duhem equation** [20]. This equation is derived by integrating Eq. 5 from a reference state where  $U = S = V = n_i = 0$ , to a state defined by  $U, S, V, n_1, \dots, n_N$ . Afterward, the resulting expression is differentiated and rearranged to yield the Gibbs-Duhem equation:

$$SdT - VdP + \sum_i n_i d\mu_i = 0 \quad \text{Eq. 10}$$

where  $S$  denotes the entropy,  $V$  the volume, and  $n_i$  the molar amount of species  $i$ . This equation implies that for the description of a single phase,  $N+2$  intensive variables are necessary (e.g.,  $T, P, \mu_1 \dots \mu_N$ ), where  $N+1$  are independent, and one is determined via the Gibbs-Duhem equation. Thus, one single phase has  $N+1$  degrees of freedom.

In a multicomponent and multi-phase system, the degrees of freedom ( $F$ ) are given analogously by the difference between the number of intensive variables required to describe the system. This is described by the phase rule:

$$F = N - \pi + 2 \quad \text{Eq. 11}$$

While the phase rule specifies how many intensive variables are required to define thermodynamic equilibrium, it does not by itself describe how the chemical potentials depend on composition. For mixtures, this dependence is of central importance, since the variation of chemical potential with composition governs phase equilibria and mixing behavior. A particularly important reference case is provided by the ideal mixture, for which the thermodynamic description takes a particularly simple form.

In thermodynamics, a mixture is referred to as ideal when the intermolecular interactions between unlike molecules are, on average, equivalent to those between like molecules, such that mixing occurs without any change in enthalpy or volume. Accordingly, for an ideal mixture, the enthalpy and volume of mixing satisfy  $\Delta H_{mix} = 0$  and  $\Delta V_{mix} = 0$ , respectively, and the driving force for mixing is exclusively the increase in entropy. As a consequence, the Gibbs free energy of mixing is determined solely by the entropic contribution and, for a multicomponent system, is given by  $\Delta G_{mix} = RT \sum_i n_i \ln x_i$  denotes the mole fraction of component  $i$ . For ideal liquid mixtures, this behavior directly leads to Raoult's law, according to which the partial vapor pressure of each component is proportional to its mole fraction in the liquid phase,  $p_i = x_i p_i^*$ . Equivalently, the chemical potential of component  $i$  in an ideal mixture can be written as  $\mu_i = \mu_i^* + RT \ln x_i$ . The concept of the ideal mixture therefore provides a fundamental thermodynamic reference state from which real mixtures deviate as a result of non-ideal intermolecular interactions, finite enthalpies of mixing, and activity coefficients differing from unity.

### 2.2.1 g<sup>E</sup>-Models

Thermodynamic properties can be calculated with g<sup>E</sup>-models [22, 23], where the expression for the chemical potential can be derived by taking the partial derivative of the total Gibbs energy with respect to the number of moles of component  $i$ , while keeping temperature, pressure, and the amounts of all other components constant [23]:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}} = \mu_i^{pure} + RT \ln(x_i) + RT \ln(\gamma_i) \quad \text{Eq. 12}$$

For an ideal mixture, the excess part is zero, since the activity coefficient is equal to 1. Therefore, the non-ideal contribution is considered as the excess Gibbs energy, which is clearly related to the activity coefficient as follows:

$$\left( \frac{\partial G^E}{\partial n_i} \right)_{T,P,n_{j \neq i}} = \left( \frac{\partial n_T \sum_i x_i \bar{\mu}_i^E}{\partial n_i} \right)_{T,P,n_{j \neq i}} = \bar{\mu}_i^E = RT \ln \gamma_i \quad \text{Eq. 13}$$

Famous g<sup>E</sup>-models are Wilson, Non-Random-Two-Liquid (NRTL) and Universal Quasi-chemical (UNIQUAC) [20, 23]. [23]. The disadvantage of these models is that the pressure dependence of a mixture is neglected, as these models assume an incompressible system in which the density is constant [20, 23]. Consequently, these models are not suitable for calculations at elevated pressures or for (P–V–T) relations in which pressure effects cannot be neglected.

## 2.2.2 Equation of State (EOS)

Thermodynamic properties, as well as phase equilibria such as VLE and LLE, can also be described using an equation of state (EOS). The first EOS was the ideal gas law, developed through the work of **Robert Boyle**, **Joseph Louis Gay-Lussac**, and **Benoît Paul Émile Clapeyron** in the 17th and 19th centuries. It is given by

$$Pv = RT \quad \text{Eq. 14}$$

The ideal gas law is the most simplified EOS, as it does not account for the individual properties of real gases. Like all equations of state, it provides a direct mathematical expression for the relationship between thermodynamic state variables and how they change in response to variations in others. Since the development of the ideal gas law, more than a hundred different EOS have been developed to more accurately model real substances [20].

A notable equation of state for describing gas properties is the famous van der Waals equation, developed in 1873. [24]. This equation introduced the concept of intermolecular attractive forces and was capable of qualitatively describing both gas and liquid phases. It is given as:

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \quad \text{Eq. 15}$$

The equation includes two substance-specific parameters,  $a$  and  $b$ . It is based on two main assumptions. First, unlike the ideal gas law, which assumes that gas particles have no volume, Van der Waals introduced the term  $(v - b)$  to represent the available volume for molecular movement, accounting for the finite volume occupied by gas molecules. Second, based on the experimental work of Joule and Thomson, the parameter  $a$  was introduced to account for the attractive forces between gas molecules.

To describe the behavior of a real gas compared to that of an ideal gas, it is common to use the compressibility factor ( $Z$ ) as an important thermodynamic parameter, which is defined as:

$$Z = \frac{Pv}{RT} \quad \text{Eq. 16}$$

Where  $Z = 1$  represents an ideal gas, and deviations from 1 indicate the degree of non-ideal behavior.

Common types of EOS include cubic EOS, virial equations; EOS based on statistical thermodynamics [20].

Cubic EOS are named as such because they always expand into a cubic expression with respect to volume. They are very popular in process simulation due to their robustness and their straightforward applicability to mixtures. These EOS are based on the Van der Waals equation, where famous examples include Redlich-Kwong, Soave-Redlich-Kwong and Peng-Robinson. [23]

Virial equations can be derived using statistical mechanics or regarded as a series expansion of the compressibility factor in terms of density:

$$Z = 1 + B'(T)P + C'(T)P^2 + \dots \quad \text{Eq. 17}$$

or in terms of pressure:

$$Z = 1 + B(T)\rho + C(T)\rho^2 + \dots \quad \text{Eq. 18}$$

Here, the ideal gas state at  $P \rightarrow 0$  or  $\rho \rightarrow 0$  is used as the reference point of the series. The virial coefficients  $B, C$  or  $B', C'$  depend per definition solely on temperature. Their main advantage lies in their strong theoretical foundation, as they can be linked to intermolecular potential functions. However, they are only valid for gases at low or moderate densities. [23]

Statistical thermodynamics is the connection between microscopic and macroscopic properties [20]. According to this, if the physical relation between a small number of molecules is known, statistical thermodynamics can extend it to a large number of molecules [20]. Functional relationships can be derived using thermodynamic potentials such as  $G(T, p, n_i)$ ,  $A(T, V, n_i)$ , and  $U(S, V, n_i)$ , which contain thermodynamic information about the system [23].

## 2.3 Polymer Thermodynamics

The thermodynamics of polymeric systems differs fundamentally from that of low-molecular-weight mixtures. The underlying reason is the macromolecular nature of polymers, in particular their chain architecture, high molar masses, restricted conformational freedom, and the resulting coupling of entropic and enthalpic contributions. These characteristics strongly influence phase behavior, miscibility, glass-transition and melting temperatures, as well as the mechanical and rheological properties of polymeric materials.

The driving force governing mixing and phase behavior in polymeric systems is the Gibbs free energy of mixing,  $\Delta G_{mix}$ , which in general consists of an entropic and an enthalpic contribution.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad \text{Eq. 19}$$

In contrast to low-molecular-weight liquids, the entropy of mixing in polymer solutions is strongly reduced, because a polymer molecule, due to its chain structure, diffuses as a single entity. This reduction is one of the main reasons for the frequently observed limited miscibility of polymeric systems.

### 2.3.1 Flory–Huggins theory

The classical Flory–Huggins theory [4, 25] represents the historical starting point of polymer thermodynamics and continues to form the basis of many modern models. It is based on a lattice model in which polymer segments and solvent molecules occupy lattice sites of equal size. The free energy density of mixing is formulated on a segment-normalized basis:

$$\frac{f(\phi)}{k_B T} = \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \quad \text{Eq. 20}$$

Here,  $N$  is the length of the polymer species, and  $\phi$  is the volume fraction of the polymer. The first two terms represent the combinatorial entropic contribution to mixing, whereas the term containing  $\chi$  accounts for the non-combinatorial enthalpic interaction between polymer and solvent.

The volume fraction  $\phi$  is defined as the ratio of the fluid volume  $V_f$  to the total volume  $V_{\text{tot}}$ , as:

$$\phi = \frac{V_f}{V_{\text{Tot}}} \quad \text{Eq. 21}$$

In this description, the volume fractions of the components, the number of segments (corresponding to the degree of polymerization for polymers), and the Flory–Huggins interaction parameter  $\chi$  are the key variables. The Flory–Huggins parameter  $\chi$  is often interpreted as a measure of the energetic interaction between polymer and solvent. In the original theory,  $\chi$  is treated as a purely enthalpic quantity that depends on temperature but is independent of concentration and molar mass. Experimental studies, however, show that in real systems  $\chi$  frequently depends on concentration, temperature, and molar mass [25].

These deviations arise from conformational changes of polymer chains upon mixing, differences in free volume, specific interactions such as hydrogen bonding, and the neglect of chain connectivity in the original formulation [25]. Despite these limitations, the Flory–Huggins theory provides valuable qualitative insights into phase behavior, critical points, and the influence of molar mass [25]. The Flory–Huggins theory is primarily applicable to incompressible systems, real polymeric materials exhibit pronounced pressure and volume dependencies.

### 2.3.2 Sanchez–Lacombe theory

The Sanchez–Lacombe theory [26] represents one of the most important approaches within the class of lattice-fluid theories developed for the thermodynamic description of polymeric systems [25]. It combines fundamental concepts of lattice models with an explicit treatment of free volume, thereby overcoming key limitations of incompressible lattice theories such as the classical Flory–Huggins model [25]. Within this framework, pressure, temperature, and density are related through an equation of state formulated in terms of reduced variables, allowing a unified description of both polymer melts and polymer-containing mixtures [25, 27].

The Sanchez–Lacombe equation of state is commonly expressed as

$$P = -RT \left( \frac{r-1}{v} \right) - RT \frac{1}{v^*} \ln \left( 1 - \frac{rv^*}{v} \right) - \frac{\varepsilon^* v^* r^2}{v^2} \quad \text{Eq. 22}$$

where  $r$ ,  $v^*$  and  $\varepsilon^*$  are the characteristic equation-of-state parameters, representing the component segment number, the segment volume, and energy parameter, respectively.

The characteristic parameters of the Sanchez–Lacombe theory can be determined from experimental pressure–volume–temperature (PVT) data. Their values possess a clear physical interpretation, as they are directly related to the compressibility, thermal expansivity, and cohesive behavior of polymeric systems. This feature distinguishes the Sanchez–Lacombe approach from purely phenomenological models and enables a consistent description of thermodynamic properties over wide ranges of temperature and pressure.

The applicability of the Sanchez–Lacombe theory extends well beyond pure polymer melts. It has been successfully employed to describe the thermodynamic behavior of polymer solutions, polymer blends, gas–polymer equilibria, and high-pressure systems [27]. By explicitly accounting for compressibility and free volume effects, the theory allows for a consistent calculation of phase equilibria and volumetric properties in systems where classical incompressible models fail. As such, the Sanchez–Lacombe equation of state constitutes an important complement to the Flory–Huggins theory, particularly for the quantitative description of polymer-containing systems under non-ambient conditions.

## 2.4 Free Energy of Polymer Networks

Polymeric networks can be modeled using either a  $g^E$  model or an EOS, as their behavior can be described in terms of free energy changes. The free energy ( $A$ ) during swelling is considered the sum of the free mixing energy ( $A_{id}$ ), the free energy of mixing ( $A_M$ ) and the elastic free energy ( $A_{el}$ ), such that [4]:

$$A = A_M + A_{el} + A_{id} \quad \text{Eq. 23}$$

This equation might serve as a good starting point for extending an equation of state to describe polymer swelling. In the case of highly crosslinked networks, it is advantageous to virtually cut off the polymer chains at the crosslinks, as graphically represented in Figure 2. In this way, free energy is represented by the interactions between these cut-up chains, while the elastic free energy is considered separately. For example, this is done for swelling calculations using the Flory-Rehner model [28] the Flory-Huggins model for low-swelling polymers such as polystyrene [29, 30]. In this context, Poschlad and Enders used the Koningsveld-Kleintjens and UNIQUAC models together with an affine network term from Flory [31].

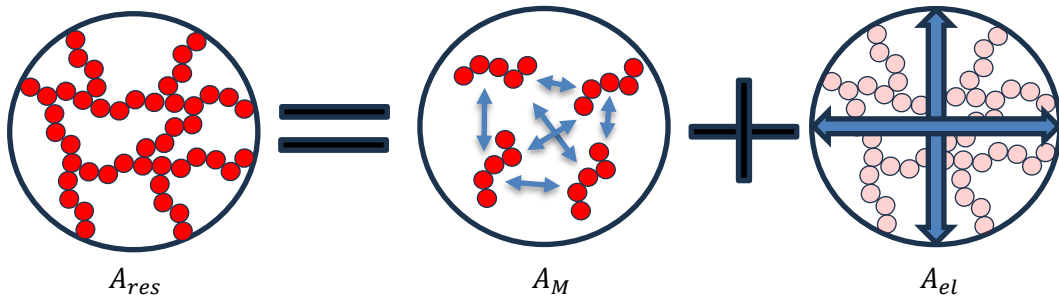


Figure 2: Illustration of mixing free energy and elastic free energy

The first network term was proposed by Flory and Rehner, based on the Gaussian stretching energies of affine networks [4, 32, 33]. It was assumed that polymers deform affinely, meaning that local deformations are identical to macroscopic deformations, while fluctuations between crosslinks are completely neglected [32]. As a result, polymer chains behave like harmonic springs that can be stretched infinitely, since monomer interactions are not considered.

Another expression based on Gaussian stretching was proposed by James and Guth [34] and is known as the phantom network theory. They assumed that polymer chains can move freely and that crosslinking points can fluctuate around their mean positions. Therefore, while macroscopic deformation is affine, the vector between the two ends of the chains, known as the end-to-end vector, does not deform affinely.

Both fully affine and phantom networks assume an ideal tetrafunctional polymer network, but real networks possess defects such as unreacted functionalities, cyclic structures, and entanglements. Therefore, Maurer and Prausnitz [35]. introduced an elasticity parameter to account for these network defects and their effects on swelling. Since elastic effects influence the amount of solvent absorbed by the polymer. Furthermore, Miao et al. [36] proposed a non-Gaussian model in which the stretching of the chains is considered finite.

## 2.5 Fick's Laws of Diffusion

The first general diffusion law was proposed in 1855 by **Adolf Fick**, who stated, based on experimental observations, that flux always moves from a region of high concentration to a region of lower concentration, with a magnitude proportional to the concentration gradient. This is well known as **Fick's first law**:

$$\vec{J}_1 = -D_{12} \vec{\nabla} c_1 \quad \text{Eq. 24}$$

This equation introduces the diffusion coefficient  $D_{12}$ , which is a proportionality constant between species within the system. Generally, the higher the diffusion coefficient, the faster the diffusion occurs. Despite the simplicity of this approach, one downside of Fick's model is that the diffusion coefficient is temperature and concentration dependent, which makes Fick's model highly dependent on experimental data. By inserting Fick's first law into the continuity equation (Eq. 33), **Fick's second law** is derived:

$$\frac{\partial c_1}{\partial t} = D_{12} \Delta c_1 \quad \text{Eq. 25}$$

This equation describes the diffusion of a substance over time in relation to its concentration. Both Fick's first and second laws were originally formulated for binary mixtures, where the diffusion of one species relative to another is considered. While Fick's second law has the same mathematical form as the heat equation, it governs mass diffusion driven by concentration gradients, whereas the heat equation describes energy transport driven by temperature gradients. Accordingly, its fundamental solution for the one-dimensional case is derived in a similar manner:

$$c_1(t, x) = \frac{1}{\sqrt{4\pi D_{12} t}} e^{\left(-\frac{x^2}{4D_{12} t}\right)} \quad \text{Eq. 26}$$

While Fick's laws are relatively simple for two-component systems, the complexity increases significantly for multicomponent diffusion. The first general formulation of Fick's diffusion laws for multicomponent systems was proposed in 1945 by **Onsager**:

$$\vec{J}_i = \sum_{k=1}^{n-1} D_{ik} \vec{\nabla} c_k \quad \text{Eq. 27}$$

This equation describes the diffusion in a system with  $n$  components, incorporating the diffusion coefficient  $D_{i,k}$ , which represents the interaction between species  $i$  and  $k$ , respectively.

## 2.6 Modeling of Diffusion Kinetics

Every system tends to achieve or maintain an equilibrium state. In this context, diffusion is a process that drives the system toward equilibrium by redistributing components on molecular level. It is characterized by the net movement of molecules, ions, atoms, or other entities within the system. Diffusion is commonly described using molar flux ( $J_i$ ), which is defined as:

$$\vec{J}_i = c_i \vec{v}_i \quad \text{Eq. 28}$$

where  $c_i$  is the molar concentration and  $\vec{v}_i$  is the flux velocity of component  $i$ . Flux describes the amount of a substance transported per unit area. Therefore, the total molar amount of a substance ( $\dot{n}_i$ ) passing through an area ( $A$ ) can be calculated as:

$$\dot{n}_i = \int \vec{J}_i \cdot d\vec{A} \quad \text{Eq. 29}$$

This integral represents the total transport of a quantity across a closed surface, while in contrast the change of the total amount of substance with time is  $\dot{n}_i(t) = \int c_i dV$  the total molar quantity ( $\dot{n}_i$ ) within that is represented as:

$$\dot{n}_i = - \frac{\partial}{\partial t} \int c_i dV \quad \text{Eq. 30}$$

The volume is noted as  $V$  and time as  $t$ . In order to be consistent with the conservation of mass, the change in mass must be equal to the mass flux:

$$\int \vec{J}_i \cdot d\vec{A} + \frac{\partial}{\partial t} \int c_i dV = 0 \quad \text{Eq. 31}$$

By applying the Gauss's theorem, the total molar flux ( $\dot{n}_i$ ) can also be expressed as a volume integral:

$$\int \vec{\nabla} \cdot \vec{J}_i dV + \frac{\partial}{\partial t} \int c_i dV = 0 \quad \text{Eq. 32}$$

This equation is also known as the **continuity equation**. Since the volume can be arbitrarily chosen, we obtain:

$$\vec{\nabla} \cdot \vec{J}_i + \frac{\partial}{\partial t} c_i = 0 \quad \text{Eq. 33}$$

Note that the derivatives in each of the spatial directions  $x$ ,  $y$ , and  $z$  are taken together in the Nabla ( $\vec{\nabla}$ ) or Laplace ( $\Delta$ ) operator, respectively.

$$\vec{\nabla} = \vec{e}_x \frac{\partial}{\partial x} + \vec{e}_y \frac{\partial}{\partial y} + \vec{e}_z \frac{\partial}{\partial z} \quad \text{Eq. 34}$$

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \text{Eq. 35}$$

Here,  $\vec{e}_x$ ,  $\vec{e}_y$ ,  $\vec{e}_z$  denote the unit vectors of the coordinate system.

## 2.7 Polymer diffusion kinetics

In contrast to diffusion in low-molecular-weight liquids or gases, diffusion in polymers is considerably more complex. This complexity arises from the dense packing of polymer chains and the strong coupling between molecular transport and the thermal motion of polymer segments. As a result, the mobility of penetrant molecules is not only governed by thermodynamic driving forces but is also strongly constrained by the polymer microstructure and its dynamic state.

A key structural parameter influencing diffusion in polymeric systems is the crosslinking density. An increase in crosslink density leads to a reduction in the mobility of the polymer network due to the formation of a more tightly connected three-dimensional structure [37]. Highly crosslinked networks are characterized by a smaller mesh size and reduced segmental mobility, which in turn limits the number of accessible free-volume pathways available for penetrant molecules [37]. Consequently, the diffusion coefficient generally decreases with increasing crosslink density.

From a mechanistic perspective, crosslinks act as additional topological constraints or obstacles within the polymer matrix. These constraints restrict polymer chain rearrangements and reduce the probability of cooperative segmental motions that are necessary to accommodate molecular diffusion. As polymer chain mobility is a critical factor in overcoming kinetic barriers, reduced segmental dynamics result in higher resistance to penetrant transport [37].

Experimentally, diffusion in polymers is commonly characterized by determining self-diffusion or mutual diffusion coefficients, both of which exhibit a strong temperature dependence. This behavior reflects the intimate coupling between diffusion and polymer segmental dynamics. In crosslinked systems, the temperature dependence of diffusion is often associated with changes in the activation energy for diffusion, which may increase with rising crosslink density due to enhanced energetic barriers for segmental rearrangement [37].

## 2.7.1 Free-volume Theory

The concept of free-volume theory in connection with diffusion was first proposed by Cohen and Turnbull (1959). The central concept of this theory is the free volume, defined as the fraction of the total polymer volume that is not occupied by polymer segments and is therefore available for molecular motion. Physically, free volume originates from inefficient chain packing, thermal fluctuations, and the incomplete filling of space by polymer chains. [38, 39] The free-volume fraction is commonly expressed as the ratio of the free volume to the total system volume, where the latter is composed of the intrinsic volume of the polymer molecules and the unoccupied volume [38].

In amorphous polymers, the diffusion of small molecules is not governed solely by an energetic activation barrier, as assumed in classical Arrhenius-type models. Instead, diffusion is strongly controlled by the availability of free-volume elements that are sufficiently large to accommodate a penetrant molecule and allow its displacement [38, 39]. The probability of a successful diffusive jump therefore increases with increasing free volume. On this basis, the self diffusion coefficient is frequently described by an exponential relationship of the form:

$$D \propto \exp(-\gamma f) \quad \text{Eq. 36}$$

where  $f$  is the free-volume fraction and  $\gamma$  is a material-specific parameter. This expression reflects the fact that diffusion is only possible when suitable free-volume cavities are available.

The strong temperature dependence of diffusion in polymers can be directly explained within the free-volume framework. As temperature increases, thermal expansion and enhanced segmental motion lead to an increase in free volume [39]. This, in turn, results in an exponential increase in molecular mobility and thus in the diffusion coefficient.

The free-volume theory is particularly successful in explaining the pronounced change in diffusion behavior observed in the vicinity of the glass transition temperature [38, 39]. Upon cooling, the free volume in a polymer decreases continuously. Below the glass transition temperature, the free-volume fraction becomes so small that molecular motion beyond localized vibrational movements is effectively suppressed. In this glassy state, polymer chain segments are frozen on experimental time scales, and only very small, transient free-volume elements remain available.

Above the glass transition temperature, the situation changes fundamentally. The free volume increases rapidly with temperature, enabling cooperative segmental motions and local structural rearrangements of the polymer chains [38, 39]. Especially near the glass transition temperature, even small temperature changes can lead to disproportionately large increases in free volume [38, 39]. This results in a dramatic rise in molecular mobility and, consequently, in diffusion coefficients, often spanning several orders of magnitude over a narrow temperature range [38, 39]. This temperature regime corresponds to the transition of the polymer from a glassy state to a rubbery or viscoelastic state, where long-range segmental dynamics become possible.

## 2.8 Maxwell-Stefan Approach

From a thermodynamic perspective, the diffusion of each component from one phase to another is driven by the difference in its chemical potential ( $\mu_i$ ) at constant temperature and pressure. Therefore, for non-ideal mixture the driving force is defined as [40].

$$d_i = \frac{x_i}{RT} \bar{\nabla} \mu_i \quad \text{Eq. 37}$$

This force must be balanced by the forces ( $F_f$ ), which arise from interactions between components  $i$  and the other components  $j$ . They are graphically illustrated in Figure 3. [41, 42]

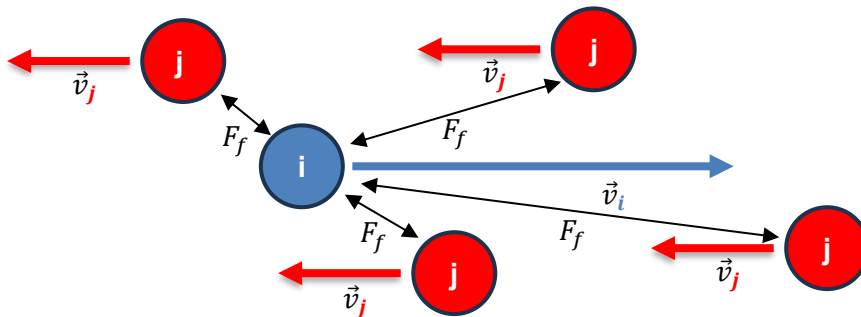


Figure 3: Relative motion ( $\vec{v}$ ) between species  $i$  and  $j$  gives rise to inhibiting forces ( $\vec{F}_f$ ).

These interactions, causing collisions between molecules are proportional to the velocity difference ( $\vec{v}_i - \vec{v}_j$ ) and to the molar quantities of components  $i$  and  $j$ , respectively, with a proportionality constant  $\varphi_f$  [41, 42, 43]. Thus, the driving force is related to:

$$d_i = - \sum_{j \neq i} \varphi_f x_i x_j (\vec{v}_i - \vec{v}_j) \quad \text{Eq. 38}$$

Here, the diffusion coefficient is introduced as  $D_{ij} = 1/\varphi_f$ . This coefficient, also known as the Maxwell–Stefan diffusivity, reflects the contribution of a binary pair  $i$  and  $j$  in a multicomponent system. It can also be interpreted as an inverse friction coefficient, and satisfies the symmetry  $D_{ij} = D_{ji}$  [40].

By inserting Eq. 37 into Eq. 38 and we obtain the Maxwell-Stefan (MS) diffusion equation:

$$-\frac{1}{RT} \vec{\nabla} \mu_i = \sum_{j \neq i} \frac{x_j}{D_{ij}} (\vec{v}_i - \vec{v}_j) \quad \text{Eq. 39}$$

This equation is based on the work of **James Clerk Maxwell** [44], who established its foundation using physical gas kinetics, and **Jožef Štefan** [45], who investigated multi-component diffusion. By inserting Eq. 28 in Eq. 39, the MS equation can be rewritten in terms of flux:

$$\frac{1}{RT} \vec{\nabla} \mu_i = \sum_{j \neq i} \frac{x_j}{D_{ij}} \left( \frac{\vec{J}_j}{c_j} - \frac{\vec{J}_i}{c_i} \right) \quad \text{Eq. 40}$$

This equation describes a linear system of equations that must be solved to obtain each flux, respectively. However, similar to the multicomponent Fick's diffusion law, Eq. 40 alone is not invertible for the fluxes, as they are linearly dependent. This dependency arises because the sum of all fluxes must be equal to zero to ensure mass conservation:

$$0 = \sum_i \vec{J}_i \quad \text{Eq. 41}$$

Nevertheless, by eliminating  $\vec{J}_n$  we treat  $\vec{J}_n$  as the only linearly dependent flux. This transformation leads to a reduced system:

$$-\frac{c_{tot}}{RT} \vec{\nabla} \mu_i = \vec{J}_i \left( \frac{1}{D_{in}} + \frac{1}{x_i} \sum_{j \neq i}^n \frac{x_j}{D_{ij}} \right) + \sum_{j \neq i}^{n-1} \vec{J}_j \left( \frac{1}{D_{in}} - \frac{1}{D_{ij}} \right) \quad \text{Eq. 42}$$

This can be written in the form of a system of linear equations:

$$-\frac{c_{tot}}{RT} \begin{bmatrix} \vec{\nabla} \mu_0 \\ \vdots \\ \vec{\nabla} \mu_{n-1} \end{bmatrix} = B \begin{bmatrix} \vec{J}_0 \\ \vdots \\ \vec{J}_{n-1} \end{bmatrix} \quad \text{Eq. 43}$$

where  $c_{tot}$  is the total concentration of the mixture and B is a  $(n-1) \times (n-1)$  matrix defined as:

$$B_{ij} = \begin{cases} \frac{1}{D_{in}} + \frac{1}{x_i} \sum_{k \neq i}^n \frac{x_k}{D_{ik}} & \text{for } i = j \\ \frac{1}{D_{in}} - \frac{1}{D_{ij}} & \text{for } i \neq j \end{cases} \quad \text{Eq. 44}$$

It can be mathematically proven that invertibility is guaranteed for up to four compounds due to the constraint  $x_i > 0$  and the condition  $\sum x_i = 1$ . Solving Eq. 43 yields:

$$\vec{J}_i = -\frac{c_{tot}}{RT} \sum_j^{n-1} B_{ij}^{-1} \vec{\nabla} \mu_j \quad \text{Eq. 45}$$

Finally, inserting the continuity equation (Eq. 33) yields the change in concentration over time for the  $i$ -th species:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \left( \frac{c_{tot}}{RT} \sum_j^{n-1} B_{ij}^{-1} \vec{\nabla} \mu_j \right) \quad \text{Eq. 46}$$

The change of  $c_n$  over time is then calculated by taking  $\vec{\nabla} \cdot \vec{J}_n$  and applying  $\vec{J}_n = -\sum_i^{n-1} \vec{J}_i$  in accordance with Eq. 41.

Revisiting this, both Maxwell-Stefan and Fickian diffusion models are commonly used to describe solvent diffusion kinetics. In Fick's laws, the diffusion coefficient is often concentration-dependent, for example, in the case of polymer swelling [17]. However, it is possible to calculate the Fickian diffusion coefficient from the Maxwell-Stefan model by considering that the fluxes in both models must be equal. The Fickian diffusion coefficient for the binary case is then given by

$$D_{Fick} = D_{MS} \underbrace{\frac{x_1}{RT} \frac{\partial \mu_1}{\partial x_1}}_{\Gamma} \quad \text{Eq. 47}$$

where the transformation factor  $\Gamma$  is referred to as the thermodynamic correction factor.

## 2.9 Inhomogeneous Temperature Fields

Heat transfer is a fundamental physical process that governs energy transport in solids, fluids, and gases. Among the three classical modes of heat transfer—conduction, convection, and radiation—heat conduction describes the transport of thermal energy through a material medium as a result of microscopic interactions between particles.

Heat conduction arises from temperature gradients within a material. On a microscopic scale, thermal energy is transferred through lattice vibrations (phonons) in solids and through molecular collisions in fluids. When a temperature difference exists, energy flows spontaneously from regions of higher temperature to regions of lower temperature, in accordance with the second law of thermodynamics.

In continuum thermodynamics, heat conduction is treated as a macroscopic phenomenon, characterized by averaged material properties. This approach enables the formulation of constitutive laws that relate heat flux to measurable quantities such as temperature and spatial gradients.

The fundamental constitutive relation governing heat conduction is Fourier's law, which establishes a linear relationship between the heat flux vector and the temperature gradient. In its most general vector form, Fourier's law is expressed as

$$\mathbf{q} = -k\nabla T \quad \text{Eq. 48}$$

where  $\mathbf{q}$  is the heat flux vector,  $k$  is the thermal conductivity of the material, and  $\nabla T$  is the temperature gradient. The negative sign indicates that heat flows in the direction of decreasing temperature.

Thermal conductivity is a material-specific property that quantifies the ability of a substance to conduct heat and may depend on temperature, pressure, and material structure. Fourier's law is based on several fundamental assumptions. First, it assumes local thermal equilibrium, meaning that temperature is well-defined at every point within the medium. Second, it presumes a linear relationship between heat flux and temperature gradient, which is valid for most engineering materials under moderate temperature gradients. While Fourier's law accurately describes heat conduction in a wide range of materials and conditions, deviations may occur at very low temperatures, extremely high heat fluxes, or at length scales comparable to the mean free path of energy carriers. In such cases, non-Fourier heat conduction models may be required.

By combining Fourier's law with the principle of energy conservation, the heat conduction equation can be derived. For an isotropic, homogeneous medium with constant thermal properties and no internal heat generation, the transient heat conduction equation is given by

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T \quad \text{Eq. 49}$$

$$\alpha = \frac{k}{\rho c_p} \quad \text{Eq. 50}$$

where  $\alpha$  is the thermal diffusivity,  $\rho$  is the density, and  $c_p$  is the specific heat capacity at constant pressure.

## 2.9.1 Coupling mass and heat fluxes

In the presence of a non-uniform temperature field, the temperature gradient leads to the coupling of both mass and heat fluxes. This coupling must be described within the framework of non-equilibrium thermodynamics, where a linear relationship exists between the independent thermodynamic fluxes and the thermodynamic forces responsible for entropy production, particularly near equilibrium [46]. For an isotropic,  $n$ -component mixture, the flux of species  $\vec{J}_i$  and the reduced heat flux  $\vec{J}_q$  can be expressed using linear phenomenological laws as [46]:

$$\vec{J}_q = -L_{qq} \frac{1}{T^2} \vec{\nabla} T - \sum_k^{n-1} \sum_{j=1}^{n-1} L_{qk} \frac{A_{kj}}{T} \vec{\nabla} \mu_j \quad \text{Eq. 51}$$

$$\vec{J}_i = -L_{iq} \frac{1}{T^2} \vec{\nabla} T - \sum_k^{n-1} \sum_{j=1}^{n-1} L_{ik} \frac{A_{kj}}{T} \vec{\nabla} \mu_j \quad \text{Eq. 52}$$

This law includes the phenomenological coefficients:  $L_{qq}$ , which is related to thermal conductivity;  $L_{ik}$ , which corresponds to the diffusion coefficients; and  $L_{iq}$ , which characterizes thermal diffusion, describing the flow of matter caused by temperature gradients — a phenomenon also known as the Soret effect in liquids. Conversely, the Dufour effect, which refers to heat flow induced by concentration gradients, depends on the coefficient  $L_{qk}$ . All four phenomenological constants are temperature and/or concentration dependent [46]. Additionally, this equation introduces the variable  $A_{km}$ , which is defined as:

$$A_{jk} = \delta_{jk} + \frac{x_k}{x_n} \quad \text{Eq. 53}$$

with  $\delta_{km}$  being the Kronecker delta, and Eq. 53 inverse is given by:

$$A_{jk}^{-1} = \delta_{jk} - x_k \quad \text{Eq. 54}$$

Since the phenomenological coefficient  $L_{ik}$  is related only to diffusion, and therefore also the right-hand side of Eq. 52 pertains only to diffusion, the following relation can be derived by inserting Eq. 45 [46]:

$$L_{ik} = \frac{c_{tot}}{R} \sum_j^{n-1} B_{ij}^{-1} A_{jk}^{-1} \quad \text{Eq. 55}$$

The constant  $L_{qq}$  is related to the heat flux and introduces the heat conductivity  $\lambda$  as:

$$L_{qq} = \lambda T^2 \quad \text{Eq. 56}$$

The Dufour and thermal diffusion effects are connected to each other by the Onsager relation [46]:

$$L_{qi} = L_{iq} \quad \text{Eq. 57}$$

Although temperature flux of mixtures containing more than two components is not commonly investigated, the mass and temperature fluxes are related there through a vector of Onsager coefficients, given in J/mol [46, 47, 48]:

$$Q'_i = \sum_{k=1}^{n-1} L_{k,i}^{-1} L_{qk} \quad \text{Eq. 58}$$

This formula can be rearranged as:

$$L_{qi} = \sum_{k=1}^{n-1} L_{i,k} Q'_k \quad \text{Eq. 59}$$

However, in most cases, the contributions of  $L_{iq}$  can be neglected, as they are typically found to be irrelevant in liquid systems [47].

## 2.10 Diffusion Kinetics in Polymers

The diffusion kinetics of liquids into a polymer matrix are much more complex than the mixing of gases and liquids, as additional repulsive forces from the stretched polymer chains act upon the invading fluid. [49] However, both MS and Fick's laws are still suitable for describing diffusion-controlled swelling processes where the stretching rates are much faster than the diffusion speed [50, 49]. This type of polymer diffusion is commonly described in the literature as Case I diffusion [51]. In contrast, Case II diffusion is mostly controlled by the elongation of polymer chains, termed relaxation. The diffusion types are illustrated in Figure 4.

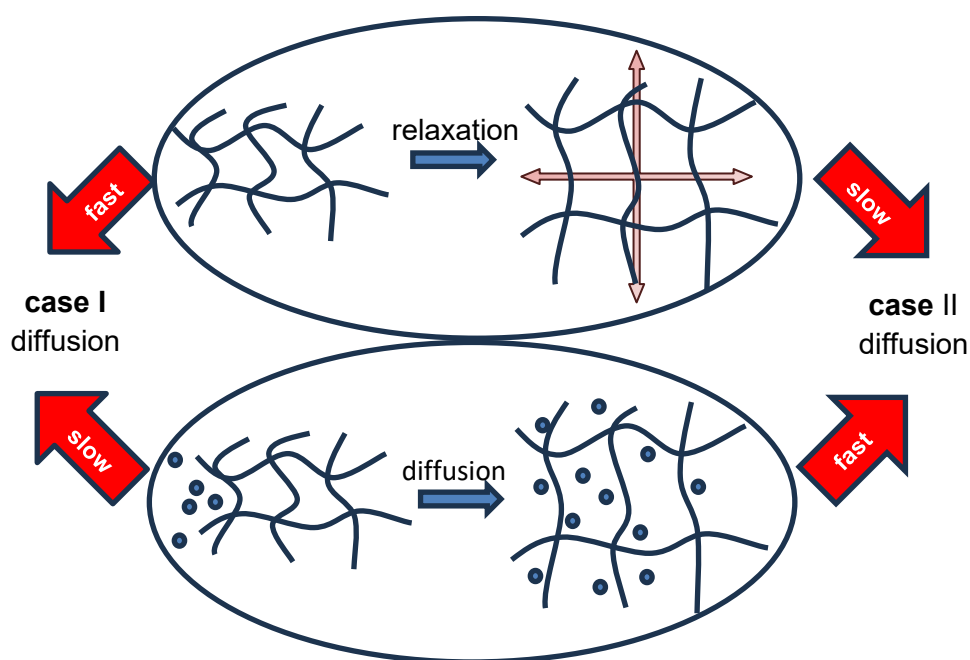


Figure 4: Illustration of Case I and Case II diffusion

Phenologically, both chases can be distinguished experimentally. Chase I diffusion shows a logarithmic-like diffusion curve, while Chase II exhibits a strong linear region in the middle. Toward the end, both phenomena approach a maximal value — the equilibrium where mass uptake ceases. Between the two diffusion types, there is also anomalous diffusion, which represents an overlap of both processes and exhibits an intermediate shape between the two. This occurs when the relaxation and diffusion speeds are of comparable magnitude.

The flux of the polymer itself must be set to zero during swelling, since the polymer chains are not capable of freely diffusing [17]. They are locally fixed due to chain entanglement, strong physical interactions between chains, or cross-linking [4]. Despite being stretched and displaced by the invading compound, the chains show no flux. Instead, this resistance acts against the invading compound [4].

It is important to note that all the models mentioned above are not capable of describing relaxation-based diffusion, commonly referred to as Case II diffusion [50]. The first attempt to address this was proposed by Thomas and Windle [51], who assumed complete viscous relaxation. The stress-strain rate relationship for a viscous compound is given by:

$$\frac{\partial \varepsilon}{\partial t} = \frac{\sigma}{\eta} \quad \text{Eq. 60}$$

where  $\varepsilon$  is the strain,  $\sigma$  is the stress, and  $\eta$  is a constant that correlates with the shear modulus at time  $t$ . To obtain an expression for the time-dependent uptake of solvent, the one-dimensional strain is expressed as the volumetric strain, which corresponds to the increase in volume. By assuming ideal mixing between the polymer and the solvent, the volumetric strain can be directly related to the volume fraction ( $\phi_{solv}$ ) [51]. Furthermore, by assuming isotropic strain, the one-dimensional stress is replaced by the unidirectional osmotic pressure ( $p_{elastic}$ ) [51], caused by the solvent absorption. The change in solvent volume over time is then expressed as:

$$\frac{\partial \phi_{solv}}{\partial t} = \frac{p_{elastic}}{\eta} \quad \text{Eq. 61}$$

The major disadvantage of this model is that diffusion is assumed to be completely relaxation-controlled, which limits its applicability to only specific cases of Case II diffusion. It does not accurately describe Fickian or anomalous diffusion, where both diffusion and relaxation jointly define the mass transport kinetics. Furthermore, the model has limited predictive capability, as the damping constant is dependent on the solvent, polymer, and temperature, requiring re-adjustment whenever any of these parameters change.

Nevertheless, it is beneficial to assume viscoelastic stretching instead of purely viscous behavior when describing relaxation-controlled diffusion. A viscoelastic approach is much more representative of the stretching behavior of polymer chains. In polymers, part of the deformation is reversible because it involves only elastic chain elongation. This can be captured with a Kelvin–Voigt. Consequently, the polymer is treated more like a solid than a liquid

By incorporating both viscous and elastic deformations, a better representation of time-dependent stress is achieved, allowing for the consideration of non-linear strain responses as well. Fortunately, the validity of the Thomas–Windle approach can be readily extended to a viscoelastic framework by treating one-dimensional stress as osmotic pressure and one-dimensional strain as volumetric strain, analogously [52]. However, a viscoelastic approach alone is not sufficient to describe Case I diffusion, since it does not account for mass transfer too. To simultaneously capture both phenomenon's accurately, diffusion and polymer relaxation must be coupled.

There are various viscoelastic models available, with the most common being the simple Maxwell and Kelvin-Voigt approaches [52]. More complex models, such as the Zener model (also known as the Standard Linear Solid model), are also suitable [52]. Note that the Zener model can be represented in two forms: the Maxwell-based form ( $Zener_M$ ) and the Kelvin-based form ( $Zener_K$ ). This is illustrated in Figure 5.

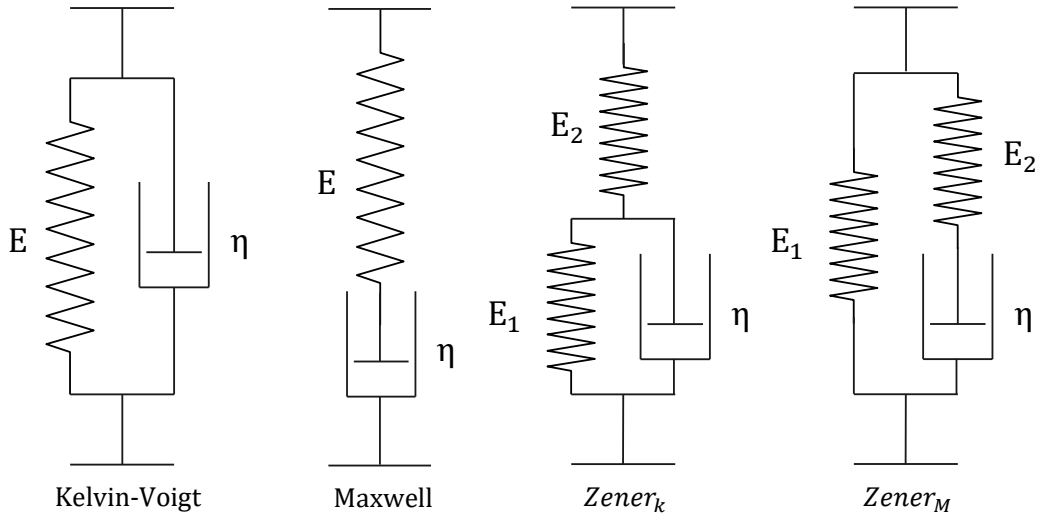


Figure 5: Viscoelastic models for relaxation based swelling.

The Kelvin-Voigt model consists of a Newtonian damper and a Hookean elastic spring connected in parallel and describes reversible deformation over a short period of time. Under constant tension, the deformation rate decreases while asymptotically approaching a stationary state. After the load is removed, the material gradually returns to its original condition. The model is well-suited for describing the creep behavior of polymers but is less accurate in representing stress relaxation [52]. It is particularly appropriate for solid-like polymers, and its stress–strain rate relationship with an elasticity constant  $E$  is given by the following first-order differential equation [52]:

$$\frac{\partial \epsilon}{\partial t} = \frac{1}{\eta} (\sigma - E\epsilon) \quad \text{Eq. 62}$$

In contrast, the Maxwell model consists of a Newtonian damper and a Hookean elastic spring connected in series. The key difference compared to the Kelvin-Voigt model is that deformation is irreversible, as even a small amount of tension applied over an infinite period results in infinite elongation. In this model, tension decreases exponentially. However, a limitation of the Maxwell model is that it inaccurately represents the creep behavior of polymers, as it predicts a linear increase in deformation [52]. In reality, the creep rate decreases over time [52]. The Maxwell model is best suited for liquid-like polymers. The model is described by the following equation:

$$\frac{\partial \varepsilon}{\partial t} - \frac{1}{E} \frac{\partial \sigma}{\partial t} = \frac{\sigma}{\eta} \quad \text{Eq. 63}$$

A physically more realistic representation of viscoelastic materials is achieved with the Zener model, which combines features of both the Maxwell and Kelvin-Voigt models [52]. Although it may yield mathematically uncertain results under specific conditions, it effectively accounts for instantaneous deformation, representing the immediate elastic portion of the strain [53]. Additionally, it can describe stress relaxation under constant strain as well as inelastic recovery.

The Zener<sub>M</sub> representation is given by:

$$\sigma + \frac{\eta}{E_2} \frac{\partial \sigma}{\partial t} = \varepsilon E_1 + \eta \frac{(E_1 + E_2)}{E_2} \frac{\partial \varepsilon}{\partial t} \quad \text{Eq. 64}$$

and the Zener<sub>K</sub> representation is expressed as:

$$\sigma + \frac{\eta}{E_1 + E_2} \frac{\partial \sigma}{\partial t} = \varepsilon \frac{E_1 E_2}{E_1 + E_2} + \eta \frac{E_1}{E_1 + E_2} \frac{\partial \varepsilon}{\partial t} \quad \text{Eq. 65}$$

## 2.11 Measurement of Swelling and Drying

The key difference between measuring drying and swelling is that swelling starts with a completely dry polymer sample surrounded by the solvent of interest, whereas drying starts with a swollen sample surrounded by air or vacuum. Both methods then monitor the change in the amount of absorbed solvent over time. There are two primary approaches to measuring the swelling and drying of polymers: spectroscopic [10, 54, 55, 56, 57, 58, 59] and gravimetric methods [17, 29, 11]. On the one hand, spectroscopic approach tracks specific polymer or solvent signals over time to calculate solvent uptake. This method may provide also a snapshot of the swelling profile at a given moment [55]. The gravimetric approach, on the other hand, measures weight changes during swelling. Its key advantage is high accuracy, especially when polymers absorb only minimal amounts of solvent. Gravimetric methods can detect even the smallest changes and directly determine the weight of the absorbed solvent, avoiding issues with spectral interference.

However, some measurements techniques may require removing the polymer from the solvent for example weighing, leading to brief drying periods that could distort the measured swelling kinetics. However, the error caused by drying decreases when diffusion kinetics are slower. This means that for long swelling periods, the error becomes negligible, as the time the polymer is exposed to air is minimal compared to the time it remains immersed in the solvent. In cases involving highly volatile solvents and/or high temperatures, where drying distortions are not negligible, in situ measurements are advantageous. This can be achieved using a magnetic levitation scale, which allows continuous monitoring of weight changes. Furthermore, this approach eliminates issues related to different solvents and room temperature variations. Such a

method was used by Krüger and Sadowski [29] to measure the absorption of toluene by glassy polystyrene at temperatures up to 115 °C.

In literature [54, 56], infrared spectroscopy is commonly used for measuring polymer swelling. This method measures changes in the molecular environment of certain functional groups. For example, in ATR-FTIR [54, 56], the intensity of OH and COOH bands is commonly analyzed. Changes in band intensity or peak shifts provide information about the swelling process. Its biggest advantage is the possibility of in situ measurement of the swelling process, allowing real-time observation.

An approach similar to infrared spectroscopy is based on Raman spectroscopy, which was used to measure the swelling of poly(ethylene glycol) in water [57]. This is achieved by monitoring the superposition of the spectra of bulk and hydration water. Information about the degree of swelling is provided by the contributions of both bands, as they are temperature- and concentration-dependent.

A notable spectroscopic method applying Rutherford backscattering spectrometry was used, for example, by Hui et al. [58] to measure transient swelling of polystyrene in iodohexane. The swelling was measured using a  $\text{He}^{2+}$  ion beam to irradiate the polymer sample, while an energy-sensitive detector measured the backscattered ions from nuclei below the polymer surface. Information about the composition was obtained from the spectrum of the backscattered ion's energy. This approach is suitable for measuring uptake at the surface up to a few micrometers deep.

Other spectroscopic methods for determining volume changes include monitoring the sample thickness using a camera, microscope, or caliper [10]. Techniques such as ellipsometry can also be useful for determining sample thickness by measuring changes in the polarization state of light [11]. Interferometric methods can be employed as well, which involve continuously measuring changes in the refractive index of thin films to gather information about swelling [55]. Additionally, swelling behavior can be studied using turbidity measurements, where light scattering is analyzed [59].



## 3 Theory

*Starting with the main concept of PC-SAFT, each term in the PC-SAFT equation of state will be examined briefly but in greater detail. We will then consider polymer-diffusion kinetics and the implementation of the Maxwell–Stefan framework in conjunction with PC-SAFT. Finally, we will explain how multidimensional modeling is treated and how heat flux is coupled with mass transfer.*

### 3.1 PC-SAFT

The thermodynamic model used for representing all relevant properties in this work is the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) EOS, developed by Gross and Sadowski more than 20 years ago [60]. PC-SAFT is a recognized extension of the SAFT model, which was developed by Chapman et al. [61]. One of the key strengths of PC-SAFT lies in its ability to accurately model a wide range of compounds, from highly nonpolar to strongly polar substances, including water, with good agreement to experimental data. Additionally, PC-SAFT has proven effective in modeling polymeric systems, including both polymer solutions [62] and swollen polymer networks [63].

SAFT and its extensions, including PC-SAFT, are grounded in Barker-Henderson Perturbation Theory [64] and Wertheim’s Thermodynamic Perturbation Theory [65]. In these models, molecules are treated as coarse-grained chains of spherical segments, with various interactions occurring both between and within these chains. The pair potential  $u(r)$ , which defines whether an interaction is attractive or repulsive, was proposed in generalized form by Chen and Kreglewski [66]:

$$u(r) = \begin{cases} \infty & r \leq 0.88\sigma \\ 3\varepsilon & 0.88\sigma < r \leq \sigma \\ -\varepsilon & \sigma < r \leq 1.5\sigma \\ 0 & 1.5\sigma < r \end{cases} \quad \text{Eq. 66}$$

Here,  $\sigma$  denotes the diameter of a segment,  $r$  is the distance between segments, and  $\varepsilon$  represents the dispersion energy, which corresponds to the depth of the square-well potential.

Thermodynamic properties within PC-SAFT are derived from the residual Helmholtz energy, given by:

$$a_{\text{res}} = \frac{A^{\text{res}}}{RT} \quad \text{Eq. 67}$$

It consists of the sum of various energy contribution terms:

$$a_{\text{res}} = a_{\text{hc}} + a_{\text{disp}} + a_{\text{assoc}} + a_{\text{dipole}} + a_{\text{elastic}} \quad \text{Eq. 68}$$

Here,  $a_{hc}$  denotes the repulsive interactions between molecular chains, while  $a_{disp}$  accounts for the dispersive (attractive) interactions. Associative interactions between functional groups are described by  $a_{assoc}$ , and dipole-dipole interactions are captured by  $a_{dipole}$ . For a polymeric system, the network contribution is represented by the elastic term  $a_{elastic}$ . All of these contributions are discussed in detail in the following chapters.

### 3.1.1 Hard Chain

The hard chain-contribution term represents the repulsive interaction of each segment within the chain, based on the Barker-Henderson Perturbation Theory [64]. These hard chain terms account for the volume occupied by the molecules. Since overlapping would cause an infinite repulsion, no overlapping occurs. The free energy term is given as:

$$a_{hc} = \bar{m}a_{hs} - \sum_i x_i(m_i - 1) \ln g_{ii}^{hs}(d_{ii}) \quad \text{Eq. 69}$$

$$\bar{m} = \sum_i x_i m_i \quad \text{Eq. 70}$$

Here, the  $a^{hs}$  term is the dimensionless Helmholtz energy of a number of  $\bar{m}$  hard spheres, described as:

$$a^{hs} = \frac{1}{\zeta_0} \left[ \frac{3\zeta_1\zeta_2}{(1-\zeta_3)} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left( \frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1-\zeta_3) \right] \quad \text{Eq. 71}$$

The reduced segment density  $\zeta_n$  is a commonly used quantity in the PC-SAFT framework. The packing fraction, represented by  $\zeta_3$ , is especially useful for estimating a suitable initial density when solving Eq. 68.

$$\zeta_n = \frac{\pi}{6} \rho \sum_i x_i m_i d_i^n \quad \text{Eq. 72}$$

The temperature-dependent Barker-Henderson diameter is obtained by introducing a modified square-well potential:

$$d_i = \sigma_i \left( 1 - 0.12 \exp \left( -3 \frac{\epsilon_i}{kT} \right) \right) \quad \text{Eq. 73}$$

The remaining term in Eq. 69 is based on Wertheim's perturbation theory and incorporates the formation of a chain of hard spheres:

$$g_{ii}^{hs}(d_{ij}) = \frac{1}{(1-\zeta_3)} + \left( \frac{d_i d_j}{d_i + d_j} \right) \frac{3\zeta_2}{(1-\zeta_3)^2} + \left( \frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2\zeta_2^2}{(1-\zeta_3)^3} \quad \text{Eq. 74}$$

### 3.1.2 Dispersion

The dispersive contribution represents a perturbation to the hard chain reference fluid, introduced by adding attractive interactions modeled through a square-well pair potential, with the well depth defined by the parameter  $\epsilon$ . This is based on the Barker–Henderson perturbation theory [64], where dispersive perturbations are considered up to the second order and expressed as:

$$\begin{aligned}
 a_{\text{disp}} = & -2\pi\rho I_1(\eta, \bar{m}) \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{kT}\right) \sigma_{ij}^3 \\
 & - \pi\rho\bar{m} \left(1 + Z^{hc} + \rho \frac{\partial Z^{hc}}{\partial \rho}\right)^{-1} I_2(\eta, \bar{m}) \\
 & \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{kT}\right)^2 \sigma_{ij}^3
 \end{aligned} \tag{Eq. 75}$$

In this equation, the first term represents the first-order perturbation, while the second term corresponds to the second-order perturbation. The expression for the compressibility factor of the hard chain reference fluid is given by:

$$\left(1 + Z^{hc} + \rho \frac{\partial Z^{hc}}{\partial \rho}\right) = \left(1 + \bar{m} \frac{8\eta - 2\eta^2}{(1 - \eta)^4} + (1 - \bar{m}) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1 - \eta)(2 - \eta)]^2}\right) \tag{Eq. 76}$$

The surface integrals  $I_1(\eta, \bar{m})$  and  $I_2(\eta, \bar{m})$  are approximated using sixth-order power series expansions as functions of the reduced segment density  $\eta$

$$I_1(\eta, \bar{m}) = \sum_{i=0}^6 a_i(\bar{m}) \eta^i \tag{Eq. 77}$$

$$I_2(\eta, \bar{m}) = \sum_{i=0}^6 b_i(\bar{m}) \eta^i \tag{Eq. 78}$$

The coefficients  $a_i(\bar{m})$  and  $b_i(\bar{m})$  are expressed as functions of the mean segment number  $\bar{m}$  by the following relations:

$$a_i(\bar{m}) = a_{0,1} + \frac{\bar{m} - 1}{\bar{m}} a_{1,i} + \frac{\bar{m} - 1}{\bar{m}} \frac{\bar{m} - 2}{\bar{m}} a_{2,i} \tag{Eq. 79}$$

$$b_i(\bar{m}) = b_{0,1} + \frac{\bar{m} - 1}{\bar{m}} b_{1,i} + \frac{\bar{m} - 1}{\bar{m}} \frac{\bar{m} - 2}{\bar{m}} b_{2,i} \tag{Eq. 80}$$

The regression coefficients  $a_{0,1}$ ,  $a_{1,i}$ ,  $a_{2,i}$ ,  $b_{0,1}$ ,  $b_{1,i}$  and  $b_{2,i}$  can be found in the appendix.

Mixtures of components are treated according to the van der Waals one-fluid theory [67]. In this approach, the expressions for the unlike dispersion energy  $\epsilon_{ij}$  and the unlike segment diameter  $\sigma_{ij}$ , between a component  $i$  and a component  $j$ , are obtained by applying the Berthelot–Lorentz combining rules [68] as follows:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} (1 - k_{ij}^{disp}) \quad \text{Eq. 81}$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad \text{Eq. 82}$$

Here,  $k_{ij}^{disp}$  is a binary interaction parameter for the dispersion energy, which can be temperature dependent:

$$k_{ij}^{disp} = k_{ij}^a + k_{ij}^b \frac{1}{T} + k_{ij}^c \frac{1}{T^2} \quad \text{Eq. 83}$$

### 3.1.3 Association

The directed interactions between functional groups are described using the association contribution. This approach is derived from the Wertheim perturbation theory of first order, with the perturbative contribution expressed as:

$$a_{assoc} = \sum_i x_i \sum_{A_i} N_{i,A} \left( \ln X^{A_i} - \frac{1 - X^{A_i}}{2} \right) \quad \text{Eq. 84}$$

Here,  $X^{A_i}$  denotes the fraction of molecules that are not bonded to the association site of type A. Determining  $X^{A_i}$  is the most computationally intensive part, as it requires solving a system of nonlinear mass balance equations:

$$\frac{1}{X^{A_i}} = 1 + \rho \sum_j x_j \sum_B X^{B_j} \Delta^{A_i B_j} \quad \text{Eq. 85}$$

This balance includes the association strength  $\Delta^{A_i B_j}$ , which describes the interaction between an association site of type A of component  $i$ , and an association site of type B of component  $j$ . It is defined as:

$$\Delta^{A_i B_j} = g_{ij}^{hs}(d_{ij}) \kappa^{A_i B_j} \sigma_{ij}^3 \left( \exp \left( \frac{\epsilon^{A_i B_j}}{kT} \right) - 1 \right) \quad \text{Eq. 86}$$

This equation includes the unlike association energy  $\epsilon^{A_i B_j}$  and the unlike association volume  $\kappa^{A_i B_j}$ , which describe the interaction between each type of site of different components. These are calculated using the combining rules proposed by Wolbach and Sandler [69]:

$$\epsilon^{A_i B_j} = \frac{1}{2} (\epsilon^{A_i B_j} + \epsilon^{A_i B_j}) \quad \text{Eq. 87}$$

$$\kappa^{A_i B_j} = \sqrt{\kappa^{A_i B_i} \kappa^{A_j B_j}} \left( \frac{\sqrt{\sigma_{ii} \sigma_{jj}}}{1/2 (\sigma_{ii} + \sigma_{jj})} \right)^3 \quad \text{Eq. 88}$$

Both the association energy and association volume are model parameters that describe the association behavior of self-associating compounds. However, one limitation of this approach is that the association of non-self-associating compounds—such as ketones, tertiary amines, etc.—is not included. This limitation was addressed by Kleiner and Sadowski [70], who proposed an induced-association interaction approach, which showed good agreement with experimental data. In this method, for non-self-associating compounds, the association energy is set to zero, while the association volume parameter is set equal to that of the associated component.

### 3.1.4 Dipole Interactions

Accounting for dipolar interactions within PC-SAFT significantly improves the modeling of phase behavior in real mixtures, without the need for additional fitting parameters, since the dipole moment is experimental measurable. An EOS contribution suitable for the PC-SAFT framework was developed by Gross and Vrabec [71], based on third-order perturbation theory and written in the Padé approximation, as given below:

$$a_{dipole} = \frac{a_2^{DD}}{1 - a_3^{DD}/a_2^{DD}} \quad \text{Eq. 89}$$

The second-order ( $a_2^{dipole}$ ) and third-order ( $a_3^{dipole}$ ) perturbation terms are given by:

$$a_2^{DD} = -\frac{\pi\rho}{(k_B T)^2} \sum_i \sum_j \frac{x_i x_j}{m_i m_j} \frac{n_{\mu,i} n_{\mu,j} \mu_i^2 \mu_j^2}{\sigma_{ij}^3} \cdot J_{2,ij}^{DD} \quad \text{Eq. 90}$$

$$a_3^{DD} = \frac{4(\pi\rho)^2}{3(k_B T)^3} \sum_i \sum_j \sum_k \frac{x_i x_j x_k}{m_i m_j m_k} \frac{n_{\mu,i} n_{\mu,j} n_{\mu,k} \mu_i^2 \mu_j^2 \mu_k^2}{\sigma_{ij} \sigma_{ik} \sigma_{jk}} \cdot J_{3,ijk}^{DD} \quad \text{Eq. 91}$$

In Eq. 90 and Eq. 91,  $n_{\mu,i}$  is the number of dipole moments  $\mu_i$  for component  $i$ . The integrals  $J_{2,ij}^{DD}$  and  $J_{3,ijk}^{DD}$  represent two-body and three-body correlation functions, respectively. These are approximated by power series as follows:

$$J_{2,ij}^{DD} = \sum_{n=0}^4 \left( a_{n,ij}^{DD} + b_{n,ij}^{DD} \frac{\epsilon_{ij}}{kT} \right) \eta^n \quad \text{Eq. 92}$$

$$J_{2,ij}^{DD} = \sum_{n=0}^4 c_{n,ijk}^{DD} \eta^n \quad \text{Eq. 93}$$

The regression coefficients  $a_{n,ij}^{DD}$ ,  $b_{n,ij}^{DD}$ , and  $c_{n,ijk}^{DD}$  are correlated as:

$$a_{n,ij}^{DD} = a_{0n}^{DD} + \frac{m_{ij} - 1}{m_{ij}} \cdot a_{1n}^{DD} + \frac{m_{ij} - 1}{m_{ij}} \cdot \frac{m_{ij} - 2}{m_{ij}} \cdot a_{2n}^{DD} \quad \text{Eq. 94}$$

$$b_{n,ij}^{DD} = b_{0n}^{DD} + \frac{m_{ij} - 1}{m_{ij}} \cdot b_{1n}^{DD} + \frac{m_{ij} - 1}{m_{ij}} \cdot \frac{m_{ij} - 2}{m_{ij}} \cdot b_{2n}^{DD} \quad \text{Eq. 95}$$

$$c_{n,ijk}^{DD} = c_{0n}^{DD} + \frac{m_{ijk} - 1}{m_{ijk}} \cdot c_{1n}^{DD} + \frac{m_{ijk} - 1}{m_{ijk}} \cdot \frac{m_{ijk} - 2}{m_{ijk}} \cdot c_{2n}^{DD} \quad \text{Eq. 96}$$

The coefficients in Eq. 94 — Eq. 96 can be found in the appendix. The abbreviations  $m_{ij}$  and  $m_{ijk}$  are defined as:

$$m_{i\alpha j\beta} = (m_{i\alpha} m_{j\beta})^{1/2} \quad \text{Eq. 97}$$

$$m_{i\alpha j\beta k\gamma} = (m_{i\alpha} m_{j\beta} m_{k\gamma})^{1/3} \quad \text{Eq. 98}$$

With the restriction  $m_{i\alpha j\beta} \leq 2$  and  $m_{i\alpha j\beta k\gamma} \leq 2$ , the dipole moment is not allowed to extend over more than two segments.

### 3.1.5 Elastic Contribution

The effect of the polymeric network can be included through the elastic contribution. As discussed in Chapter 2.3, this term describes the elastic behavior of the network, in contrast to the other previously discussed terms, which represent the interactions between the virtual cut-ups, as well as their interactions with the invading solvent.

The chosen network term was first proposed by Miao et al. [36], and was later utilized in similar works by Arndt and Sadowski [72] for hydrogel swelling, and by Krenn et al. [15, 17] for thermoset polymers. In these studies, the swelling behavior of the hydrogel Poly(N-isopropylacrylamide) was successfully described, and the used framework was subsequently extended to thermoset polymers. The network energy contribution is given as:

$$a_{elastic} = x_{pol} \cdot \frac{\phi - 2}{\phi} \left[ \frac{3}{2} \cdot \frac{\left(\frac{v_{pol}}{v_0}\right)^{2/3} - 1}{1 - \left(\frac{1}{\alpha_{max}} \cdot \frac{v_{pol}}{v_0}\right)^{2/3}} - \ln\left(\frac{v_{pol}}{v_0}\right) \right] \quad \text{Eq. 99}$$

This term introduces two additional model parameters: the network functionality ( $\phi$ ) and the ideal maximum volume ( $\alpha_{max}$ ). The maximum volume is defined as the ratio between a reference state—where no elastic forces are present—and the theoretical limit to which the polymers can be stretched in a tetrahedral network [72].

Both parameters must be fitted to match the swelling behavior of the polymer. However, they remain independent of the solvent, as they represent only the stretching behavior of the network itself [15]. The network functionality is physically defined as the number of cross-links per polymer chain, although in this framework, it serves more as a representation of the overall elasticity [15]. In this way, it also accounts for deviations from the ideal cross-linking structure, such as network defects, loops, dangling chains, and variations from monodispersity [15]. It is worth noting that Maurer et al. [73, 74] even used a single adjustable parameter instead.

### 3.2 Modeling Solvent Diffusion in Polymers

Diffusion in polymers was modeled using a combination of a viscoelastic approach and the MS diffusion model to account for fully relaxation-controlled, diffusion-controlled, and anomalous diffusion behavior — the latter being a combination of both mechanisms.

To represent relaxation-controlled diffusion, a viscoelastic approach based on the Kelvin–Voigt model was chosen. Relaxation-controlled stretching becomes relevant only when the stretching of polymer chains is slower than mass transport; in that case, it becomes the rate-determining step of the overall transport process. This is particularly important at the edge of the polymer matrix, where mass uptake is highest, while the solvent concentration in the interior is always lower.

Based on this observation, the polymer matrix can be considered as consisting of a relaxation-controlled zone near the edge with a thickness of  $z_{rel}$ , where diffusion is primarily governed by polymer relaxation, and a diffusion-controlled zone in the interior, where diffusion follows the MS-diffusion model. This concept was also used by Krenn et al. [17] to model solvent diffusion in an epoxy resin and is graphically illustrated in Figure 6.

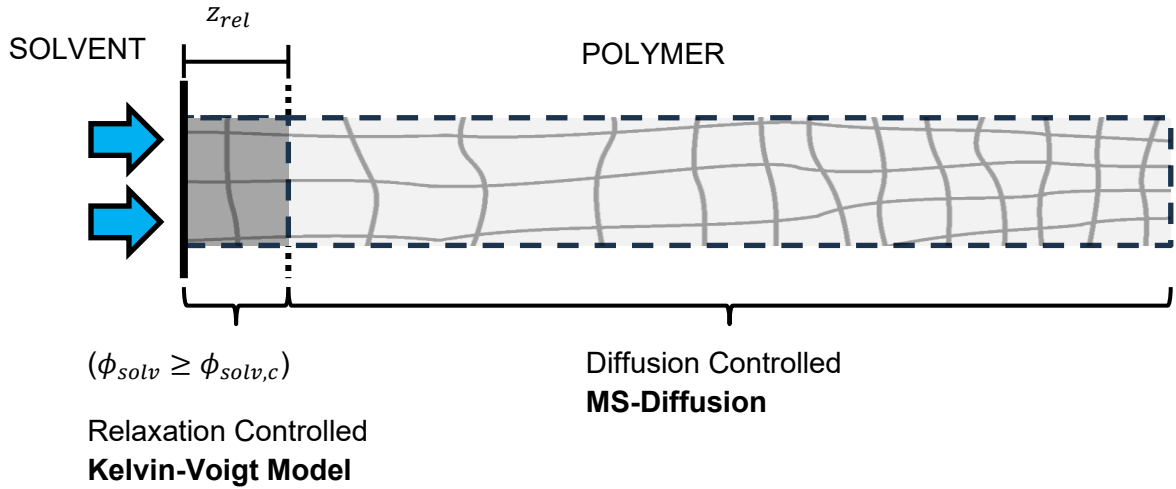


Figure 6: Illustration of modeling simultaneously using viscoelastic and MS-diffusion approaches

Since polymer networks always contain some free volume between chains, solvent can diffuse into these regions without requiring polymer stretching. However, viscoelastic stretching begins once a critical solvent volume fraction ( $\phi_{solv,c}$ ) is reached. Below this threshold, solvent diffusion can be modeled solely by the MS approach.

By defining the thickness of the relaxation-controlled zone as infinitesimally small, the solvent volume fraction at the start of the simulation is set equal to  $\phi_{solv,c}$ . From this point on, concentration changes are simulated exclusively using the viscoelastic model. In this way, polymer relaxation is treated as a boundary condition. However, in cases where relaxation is irrelevant for diffusion, this boundary can be treated as a Dirichlet boundary condition by setting the polymer concentration equal to the swelling equilibrium value.

Starting with the framework for MS-diffusion of solvents in polymers, the system of equations must be built under the assumption that the net flux of the polymer is zero, due to the fact that polymers are not capable of freely diffusing — as discussed in the previous chapter. This contrasts with liquids and gases, where the flux of one component is calculated based on the condition that the sum of all fluxes must equal zero.

Starting with Eq. 40, the formulation can be expanded as follows:

$$-\frac{1}{RT}c_{mix}\vec{\nabla}\mu_i = -\frac{1}{D_{in}}\vec{J}_n + \frac{1}{D_{in}}\left(\frac{x_n}{x_i}\vec{J}_i\right) - \sum_{j \neq i}^{n-1} \frac{1}{D_{ij}}\left(\vec{J}_j - \frac{x_j}{x_i}\vec{J}_i\right) \quad \text{Eq. 100}$$

By defining the polymer as the  $n$ -th component, due to  $\vec{J}_n = 0$  this equation becomes:

$$-\frac{1}{RT}c_{mix}\vec{\nabla}\mu_i = \frac{\vec{J}_i}{x_i}\left(\sum_{j \neq i}^n \frac{x_j}{D_{ij}}\right) - \left(\sum_{j \neq i}^{n-1} \frac{\vec{J}_j}{D_{ij}}\right) \quad \text{Eq. 101}$$

Therefore, the  $(n-1) \times (n-1)$  matrix  $B$  in Eq. 43 becomes, for a polymer swelling systems:

$$B_{ij} = \begin{cases} \frac{1}{x_i} \sum_{k \neq i}^n \frac{x_k}{D_{ik}} & \text{for } i = j \\ -\frac{1}{D_{ij}} & \text{for } i \neq j \end{cases} \quad \text{Eq. 102}$$

For the special case of a binary mixture, this simplifies to:

$$\vec{J}_s = c_{mix}D_{sp} \frac{1}{RT} \frac{x_s}{x_p} \vec{\nabla}\mu_s \quad \text{Eq. 103}$$

where  $s$  indicates the solvent and  $p$  the polymer.

According to Chapter 2.10, relaxation-controlled diffusion was modeled using a viscoelastic approach based on the Kelvin–Voigt model, where the one-dimensional stress  $\sigma$  is replaced by the unidirectional elastic pressure  $p_{elastic}$ . The current strain is defined as:

$$\epsilon = \frac{L - L_0}{L_0} \quad \text{Eq. 104}$$

Where  $L$  is the current length of the polymer chains and  $L_0$  is the length in the initial stress-free state. This can also be expressed in terms of the polymer volume ( $V$ ) or volume fraction ( $\phi_{solv}$ ) of the solvents:

$$\varepsilon = \frac{V - V_0}{V_0} = \frac{1 - \phi_{solv,c}}{1 - \phi_{solv}} - 1 \quad \text{Eq. 105}$$

where  $\phi_{solv,c}$  is the critical solvent volume fraction at which polymer chain stretching begins.

Inserting this into Eq. 62 yields:

$$\frac{\partial \phi_{solv}}{\partial t} = \frac{(1 - \phi_{solv})^2}{\eta(1 - \phi_{solv,c})} \left( p_{elastic} - E \left( \frac{1 - \phi_{solv,c}}{1 - \phi_{solv}} - 1 \right) \right) \quad \text{Eq. 106}$$

Since the free volume is increasing almost linearly with the temperature critical solvent volume fractions temperature dependency is given as [17]:

$$\phi_{solv,c} = d_\phi + T \cdot k_\phi \quad \text{Eq. 107}$$

where  $d_\phi$  and  $k_\phi$  are constants specific to the current solvent-polymer system.

The temperature dependence of the damper constant is based on the thermal activation of the mobility of the glassy chains. For this, an experimentally validated correlation, commonly used for the viscosity of liquids, is applied [17]:

$$\eta = \eta_0 \cdot e^{E_{A,t}/T} \quad \text{Eq. 108}$$

With  $\eta_0$  as the amplitude factor and  $E_{A,t}$  as the growth rate.

Due to the space demand of the invading solvent, the volume of the polymer grid increases. As the number of grid points remains constant, the width of each grid point expands. This relationship is expressed as [17]:

$$\Delta z^3 = (1 - \phi_{fillers}) \cdot \frac{(1 - \phi_{solv,c})}{(1 - \phi_{solv})} \cdot \Delta z_0^3 \quad \text{Eq. 109}$$

where  $\Delta z_0^3$  is the grid size of the dry polymer, and  $\phi_{fillers}$  is the volume fraction occupied by the filler material. This value is assumed to be constant during swelling, as the filler material is typically based on inorganic silicate compounds, which are unaffected by the invading solvent. Therefore, the filler portion retains a constant volume and weight.

Another system parameter that is temperature-dependent is the Maxwell–Stefan diffusion constant. It can be described by a classical exponential correlation:

$$D = D_\infty \cdot e^{-\frac{E_{A,D}}{RT}} \quad \text{Eq. 110}$$

where  $D_\infty$  is the diffusion constant at infinite temperature, and  $E_{A,D}$  is the activation energy for diffusion.

### 3.3 Modeling Heat flux

Based on the framework outlined in Chapter 2.9, heat flux can also be coupled with the diffusion of solvents in a polymer network [75, 46]. In this context, the phenomenological coefficients  $L_{q1}$ ,  $L_{1q}$  are replaced by the Dufour coefficient ( $D'_T$ ) and the thermal diffusion coefficient ( $D_T$ ) for the binary case, as follows (72; 36):

$$L_{q1} = D'_T x_1 x_2 T^2 \quad \text{Eq. 111}$$

$$L_{1q} = D_T x_1 x_2 T^2 \quad \text{Eq. 112}$$

According to the Onsager reciprocal relation,  $D'_T$  must be equal to  $D_T$  [46].

From Eq. 55 and Eq. 102, the phenomenological diffusion coefficient becomes, for a binary system:

$$L_{11} = \frac{c_{tot}}{R} \cdot D_{MS} \quad \text{Eq. 113}$$

Using these relations, the heat and mass fluxes can be modeled by inserting all constraints into Equations Eq. 51 and Eq. 52:

$$\vec{J}_s = -\frac{c_{tot}}{RT} \cdot \frac{x_s}{x_p} \cdot D_{MS} \cdot \vec{\nabla} \mu_s - c_{tot} \cdot x_s \cdot x_p \cdot D_T \cdot \vec{\nabla} T \quad \text{Eq. 114}$$

$$\vec{J}_q = -\lambda \cdot \vec{\nabla} T - c_{tot} \cdot x_s \cdot T \cdot D'_T \cdot \vec{\nabla} \mu_s \quad \text{Eq. 115}$$

By including the mass conservation law, this becomes:

$$\frac{\partial c_i}{\partial t} = \frac{c_{tot}}{RT} \cdot \frac{x_s}{x_p} \cdot D_{MS} \cdot \Delta \mu_s + \nabla (c_{tot} \cdot x_s \cdot x_p \cdot D_T \cdot \nabla T) \quad \text{Eq. 116}$$

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho \cdot c_p} \cdot \Delta T + \frac{1}{\rho \cdot c_p} \nabla (c_{tot} \cdot x_s \cdot T \cdot D'_T \cdot \nabla \mu_s) \quad \text{Eq. 117}$$

Here,  $\rho$  is the density and  $c_p$  the specific heat capacity. With density derived from the PC-SAFT EOS, these parameters are evaluated using the following mixing rules [76]:

$$\frac{1}{\lambda} = \sqrt{\frac{w_1}{\lambda_1^2} + \frac{w_2}{\lambda_2^2}} \quad \text{Eq. 118}$$

$$c_p = w_1(c_p)_1 + w_2(c_p)_1 \quad \text{Eq. 119}$$

### 3.4 Spatial Discretization

Spatial discretization is a fundamental step in the numerical solution of partial differential equations. Many physical processes are naturally described by continuous functions defined over continuous spatial domains. These include fluid flow, structural deformation, electromagnetic wave propagation, and in the context of this work heat conduction and mass flux. However, computers cannot calculate infinitely many points in space, nor can they directly manipulate continuous functions or their derivatives. To make such problems computationally tractable, the spatial domain must be transformed into a finite set of discrete elements, points, or volumes. This process, known as spatial discretization, converts continuous equations into algebraic or ordinary differential equations that can be solved numerically.

In a continuous setting, a function  $f(x)$  is defined for all spatial locations  $x$  within a domain. Spatial discretization replaces this continuous description with a discrete approximation  $F(x_i)$ , where each index  $i$  corresponds to a specific point, node, element, or control volume. The continuous domain is partitioned into a mesh or grid, which may be structured or unstructured, made up of irregularly shaped elements that allow complex geometries to be represented. Regardless of the specific mesh type, the objective is the same: to represent the spatial variation of the unknown field with a finite number of degrees of freedom.

The core challenge of spatial discretization lies in approximating spatial derivatives. Different numerical methods achieve this in different ways. The finite difference method (FDM) approximates derivatives using difference quotients on a structured grid. For example, the first and second derivative can be approximated by a central difference formula involving values at neighboring grid points:

$$\frac{\partial f(x)}{\partial x} = \frac{F(x_{i-1}) - F(x_{i+1}))}{2\Delta x} \quad \text{Eq. 120}$$

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{F(x_{i-1}) + 2F(x_i) - F(x_{i+1}))}{\Delta x^2} \quad \text{Eq. 121}$$

Where  $\Delta x$  is the grid length. This method is conceptually simple and computationally efficient, but its reliance on structured grids makes it less suitable for complex geometries.

The finite element method (FEM) takes a more flexible, variational approach. The domain is divided into elements, and the solution is approximated as a linear combination of basis functions that are locally supported within each element. Instead of directly approximating derivatives at specific points, FEM constructs a weak or integral form of the governing equations. This leads to a system of algebraic equations that relate the nodal values of the solution. Because the method naturally accommodates irregular meshes and higher-order basis functions, it is widely used in structural mechanics and multiphysics simulations.

The finite volume method (FVM) centers its discretization strategy on conservation principles. The domain is subdivided into control volumes, and the governing equations are integrated over each of them. By applying the divergence theorem, fluxes across the boundaries of each control volume become the central quantities. This ensures that the numerical scheme conserves mass, momentum, and energy at the discrete level. FVM is therefore especially popular in computational fluid dynamics, where the preservation of conservation laws is crucial for physical accuracy.

Regardless of the chosen method, spatial discretization transforms a continuous partial differential equation into a finite-dimensional system. The continuous operator acting on the unknown function becomes a discrete operator acting on a vector of nodal or elemental values. For time-dependent problems, this often results in a system of ordinary differential equations of the form:

$$\frac{\partial \mathbf{x}}{\partial t} = F(\mathbf{x}) \quad \text{Eq. 122}$$

where  $\mathbf{x}$  is the vector of discretized spatial values. Time discretization techniques can then be applied to march this system forward in time.

The quality of a spatial discretization depends on several factors, including mesh resolution, element shape, and the order of approximation. A finer mesh generally captures more detailed spatial features but increases computational cost. The accuracy of the discretization typically improves as the mesh spacing decreases, and under suitable conditions, the numerical solution converges to the exact solution of the continuous partial differential equation. Stability considerations also play a crucial role, especially when spatial discretization is combined with explicit time-integration schemes. In such cases, restrictions linking spatial resolution to allowable time-step sizes, such as the Courant–Friedrichs–Lewy (CFL) condition, must be satisfied to ensure numerical stability.

### 3.5 Numerical Approach

To solve the MS equation, the spatial cubic domain must be discretized into a three-dimensional grid according to Eq. 123 - Eq. 126, where the indices  $x$ ,  $y$ , and  $z$  represent coordinates in space [77]. Here, the grid size  $\Delta z$  is set to be equal in all directions of the room but depends on the current solvent concentration. To perform 2D calculations within this framework, the terms  $N_{x,y,z+0.5}$  and  $N_{x,y,z-0.5}$  are set to zero. In the 1D case, the terms  $N_{x,y+0.5,z}$  and  $N_{x,y-0.5,z}$  are also set to zero.

$$\frac{\partial c_i}{\partial t} = \frac{1}{\Delta z} (N_{x+0.5,y,z} - N_{x-0.5,y,z} + N_{x,y+0.5,z} - N_{x,y-0.5,z} + N_{x,y,z+0.5} - N_{x,y,z-0.5}) \quad \text{Eq. 123}$$

$$N_{x+0.5,y,z} = \frac{(c_{tot})_{x+0.5,y,z}}{RT} \sum_j^{n-1} (B_{ij}^{-1})_{x+0.5,y,z} \left[ \frac{(\mu_{solv})_{x,y,z} - (\mu_{solv})_{x+1,y,z}}{\Delta z} \right] \quad \text{Eq. 124}$$

$$(c_{tot})_{x+0.5,y,z} = \frac{(c_{tot})_{x+1,y,z} + (c_{tot})_{x,y,z}}{2} \quad \text{Eq. 125}$$

$$(B_{ij}^{-1})_{x+0.5,y,z} = \frac{(B_{ij}^{-1})_{x+1,y,z} + (B_{ij}^{-1})_{x,y,z}}{2} \quad \text{Eq. 126}$$

Time integration was performed using an explicit 4th-order Runge–Kutta method to ensure numerical stability and accuracy. The Runge–Kutta scheme was chosen instead of the forward Euler method because it proved to be more stable on a multidimensional grid, avoiding numerical oscillations under certain conditions. Despite the simplicity of the Euler method and its requirement of only one time-step evaluation, the Runge–Kutta method allows for larger time steps with adequate accuracy, outweighing the cost of performing four intermediate function evaluations per step. Each time step of a function  $f$  is calculated as:

$$y_{n+1} = y_n + \frac{h}{6}(k_1 + 2k_2 + 2k_3 + k_4) \quad \text{Eq. 127}$$

$$t_{n+1} = t_n + \Delta t \quad \text{Eq. 128}$$

with:

$$k_1 = f(t_n, y_n) \quad \text{Eq. 129}$$

$$k_2 = f\left(t_n + \frac{\Delta t}{2}, y_n + \frac{k_1}{2}\right) \quad \text{Eq. 130}$$

$$k_3 = f\left(t_n + \frac{\Delta t}{2}, y_n + \frac{k_2}{2}\right) \quad \text{Eq. 131}$$

$$k_4 = f(t_n + \Delta t, y_n + \Delta t \cdot k_3) \quad \text{Eq. 132}$$

The size of the time step ( $\Delta t$ ) was determined based on the maximum change ( $u$ ) per grid step, following the Courant–Friedrichs–Lewy (CFL) condition described in Eq. 133. A CFL number Below 0.5 was chosen to maintain appropriate accuracy and ensure numerical stability.

$$CFL \geq \frac{u\Delta t}{\Delta z} \quad \text{Eq. 133}$$

## 3.6 Solver Algorithm

In order to solve a mathematical problem that cannot be solved analytically, a numerical solver is required. In this work, three types of solvers were utilized for solving nonlinear systems of equations or for parameterization. These were Powell-Dogleg-Solver [78], which is capable of solving nonlinear problems very efficiently; Bi-Conjugate Gradient Stabilized (BiCGSTAB) Algorithm [79], a robust method for solving linear systems with sparse matrices; and the Particle Swarm Optimizer (PSO) [80], which is a relatively simple yet highly robust approach for the parameterization of complex models.

### 3.6.1 Powell-Dogleg

The standard approach for solving nonlinear equations in this work was the Powell–Dogleg solver. This algorithm is a nonlinear least-squares optimizer that combines the advantages of Newton-type methods, which converge rapidly but can be numerically unstable, and gradient-descent methods, which are more robust but typically converge slowly.

By merging both concepts within a trust-region framework, the Powell–Dogleg method achieves a balance between speed and stability, making it particularly suitable for complex nonlinear parameter estimation problems.

The Powell–Dogleg method is designed to solve nonlinear least-squares problems of the form

$$\min_x \frac{1}{2} \|f(x)\|^2 \quad \text{Eq. 134}$$

where  $f(x)$  is a vector-valued function representing the residuals between calculated value and the desired value. The goal is to determine the parameter vector  $x$  that minimizes the sum of squared residuals. Within each iteration, the algorithm searches for an approximate solution inside a trust region with radius  $\Delta$ . This region defines the maximum step size considered reliable, based on the local validity of the linear approximation of  $f(x)$ .

Inside this trust region, the algorithm determines a step vector  $p$  that minimizes the quadratic model of the objective function:

$$m(p) = \frac{1}{2} \|Jp + f(x)\|^2 \quad \text{Eq. 135}$$

where  $J$  is the Jacobian matrix of partial derivatives of  $f(x)$  with respect to the parameters. The ideal step would be the Gauss-Newton step, which is obtained by solving the linearized normal equations:

$$(J^T J)p = -J^T f(x) \quad \text{Eq. 136}$$

The Gauss-Newton step is taken if it lies within the trust region. In the case that even the Cauchy step lies outside the trust region, it is reduced to the boundary of this region. Otherwise, an intermediate step is taken along the connection between both directions, known as the dogleg step.

This combination provides a powerful compromise between stability and efficiency. The gradient direction ensures convergence even when the initial guess is far from the true solution, while the Newton-type correction accelerates convergence as the solution is approached. Consequently, the Powell–Dogleg solver often converges faster than purely gradient-based methods, yet is less sensitive to ill-conditioning or poor initial estimates than pure Newton or Gauss–Newton algorithms.

### 3.6.2 BiCGSTAB

The numerical solution of large linear systems of the form

$$Ax = b \quad \text{Eq. 137}$$

plays a central role in scientific computing, particularly in the discretization of partial differential equations arising in fluid dynamics, structural mechanics, and transport phenomena. When the system matrix  $A \in \mathbb{R}^{n \times n}$  is large, sparse, and nonsymmetric, direct solution techniques such as Gaussian elimination or LU decomposition quickly become impractical due to their prohibitive computational cost and memory requirements. In such cases, iterative Krylov subspace methods provide an efficient and scalable alternative.

Among these methods, the BiConjugate Gradient Stabilized (BiCGSTAB) algorithm represents a significant development. Introduced by van der Vorst [79], BiCGSTAB was designed as a robust and smoothly convergent variant of the BiConjugate Gradient (BiCG) and Conjugate Gradient Squared (CGS) methods, specifically targeting nonsymmetric and indefinite linear systems.

Unlike direct solvers, BiCGSTAB belongs to the class of iterative projection methods, in which the solution vector is not computed in a single step. Instead, the algorithm constructs a sequence of approximations  $x_k$  that converges to the exact solution by successively minimizing the residual over appropriately chosen Krylov subspaces. The iteration is initialized with an initial guess  $x_0$ , from which the initial residual is defined as

$$r_0 = b - Ax_0 \quad \text{Eq. 138}$$

This residual serves as the starting point for generating the Krylov subspace and measuring convergence.

A key advantage of BiCGSTAB lies in its ability to handle general nonsymmetric matrices without requiring the explicit transpose of  $A$ , while retaining short recurrence relations and linear memory complexity. This makes the method particularly attractive for large-scale sparse problems, where both storage and computational efficiency are critical. In exact arithmetic, BiCGSTAB is a finite method, meaning that convergence can be achieved in at most  $n$  iterations. In practice, however, rounding errors and ill-conditioning often limit performance, necessitating careful algorithmic design.

The development of BiCGSTAB was motivated by shortcomings observed in the CGS method. While CGS can exhibit very rapid convergence, its residual norms often show highly irregular behavior, including large intermediate growth that may lead to severe cancellation effects and loss of accuracy. Van der Vorst [79] demonstrated that this behavior originates from the implicit squaring of the BiCG residual polynomial, which can amplify unfavorable spectral components of the matrix. BiCGSTAB addresses this issue by introducing an additional local residual minimization step, which stabilizes the iteration and results in a significantly smoother convergence history.

At each iteration, BiCGSTAB updates the approximate solution using a combination of two directions: a BiCG-like search direction and an additional correction direction obtained by minimizing the residual in the Euclidean norm. The update can be written in the form

$$x_{k+1} = x_k + \alpha p_k + \omega s_k \quad \text{Eq. 139}$$

where  $p_k$  denotes the search direction inherited from the BiCG framework,  $s_k$  is an intermediate residual correction, and  $\alpha$  and  $\omega$  are scalar coefficients determined through inner products. The parameter  $\omega$  plays a central role in stabilizing the iteration by minimizing the norm of the residual after the BiCG step, thereby damping oscillations and preventing excessive growth of rounding errors.

The corresponding residual update is given by

$$r_{k+1} = b - Ax_{k+1} \quad \text{Eq. 140}$$

although, for efficiency reasons, the residual is typically updated recursively rather than recomputed explicitly. Convergence is monitored by the norm of the residual, and the iteration is terminated once a prescribed tolerance is reached.

Despite its advantageous properties, the BiCGSTAB method is still susceptible to convergence difficulties. As with all Krylov subspace methods, its performance is strongly influenced by the spectral properties and conditioning of the matrix  $A$ . In poorly conditioned problems, the method may stagnate or even diverge. Consequently, preconditioning is essential for practical applications. Van der Vorst [79] discusses several preconditioning strategies, including left, right, and split preconditioning, and shows that incomplete LU (ILU) and Jacobi preconditioners are particularly effective in improving convergence rates for sparse systems. Extensive numerical experiments presented in the original study demonstrate that BiCGSTAB generally converges more smoothly than CGS and often requires fewer iterations to reach a given accuracy. More im-

portantly, the method tends to produce residuals that reliably reflect the true error of the computed solution, reducing the risk of misleading convergence diagnostics. These properties make BiCGSTAB a robust and widely adopted solver in modern numerical linear algebra.

In summary, BiCGSTAB combines the efficiency of short-recurrence Krylov methods with enhanced numerical stability through local residual minimization. Its ability to handle large, sparse, nonsymmetric systems with moderate memory requirements has established it as a standard tool in computational science and engineering, particularly when coupled with effective preconditioning techniques.

### 3.6.3 Particle Swarm Optimizer

Particle Swarm Optimization (PSO) is a population-based stochastic optimization technique originally developed to model collective learning and adaptive behavior observed in social organisms. The method was first introduced by Kennedy and Eberhart [80] as an abstraction of social interaction mechanisms rather than a biologically exact imitation, with inspiration drawn primarily from the coordinated movement patterns of bird flocks and fish schools. The fundamental idea underlying PSO is that complex and intelligent global behavior can emerge from simple local interaction rules among individuals, without the need for centralized control or explicitly imposed problem-specific heuristics

In contrast to classical gradient-based optimization methods, PSO does not rely on derivative information and therefore remains applicable to highly nonlinear, discontinuous, or multimodal objective functions. This characteristic makes the algorithm particularly well suited for problems characterized by complex response surfaces, such as the calibration and parameter identification of advanced thermodynamic and physical models. By maintaining a population of candidate solutions and exploiting both individual experience and collective knowledge, PSO exhibits a strong capability to explore the search space globally while simultaneously refining promising regions, thereby reducing the likelihood of premature convergence to local optima.

Within the PSO framework, a finite number of particles is initialized and randomly distributed throughout the multidimensional search space defined by the parameters to be optimized. Each particle represents a potential solution and is characterized by its current position and velocity. During the iterative optimization process, particles move through the search space by updating their velocities and positions according to simple mathematical rules that encode social learning mechanisms.

Two key memory components govern the behavior of each particle. The first is the personal best position, commonly referred to as *pbest*, which stores the best solution encountered by the particle itself over the course of its trajectory. This component reflects an individual learning process analogous to autobiographical memory, encouraging particles to return toward regions of the search space that have previously yielded favorable objective function values. The second component is the global best posi-

tion, denoted as  $gbest$ , which represents the best solution discovered by any particle in the swarm. This global information is shared implicitly among all particles and acts as a form of collective knowledge or social norm, guiding the swarm toward the most promising region identified so far.

The dynamical evolution of each particle is typically described by a velocity update equation followed by a position update equation:

$$v_i(t + 1) = \omega v_i(t) + c_1 r_1 (pbest_i - x_i(t)) + c_2 r_2 (gbest - x_i(t)) \quad \text{Eq. 141}$$

$$x_i(t + 1) = x_i(t) + v_i(t + 1) \quad \text{Eq. 142}$$

Here,  $v_i(t)$  denotes the velocity of particle  $i$  at iteration  $t$ , and  $x_i(t)$  represents its current position in the search space. The parameter  $\omega$  is the inertia weight that controls the particle's momentum, while  $c_1$  and  $c_2$  are the cognitive and social acceleration coefficients, respectively. The random numbers  $r_1$  and  $r_2$ , each uniformly distributed within the interval  $[0, 1]$ , introduce stochastic behavior into the system, ensuring diversity in the search process and preventing premature convergence.

The velocity update incorporates three distinct contributions: an inertia term, which preserves part of the particle's previous motion; a cognitive term, which attracts the particle toward its personal best position; and a social term, which pulls the particle toward the global best position. The relative influence of these components is controlled by algorithmic parameters, including the inertia weight and acceleration coefficients, which balance exploration and exploitation during the search process. Random factors are introduced into both the cognitive and social terms through uniformly distributed random variables, ensuring stochasticity in the particle trajectories. This randomness plays a critical role in maintaining population diversity, enabling particles to overshoot promising regions and explore unexplored areas of the search space.

Once the velocity has been updated, the particle's position is advanced accordingly. Through repeated application of these update rules, the swarm collectively searches the parameter space, with particles dynamically adjusting their trajectories based on both individual experience and shared information. Importantly, PSO achieves this behavior using only primitive mathematical operations, resulting in a computationally efficient algorithm with modest memory requirements.

The conceptual simplicity of PSO is one of its defining strengths. Unlike evolutionary algorithms that rely on complex operators such as crossover and mutation, PSO directly manipulates candidate solutions in continuous space. This mechanism has been shown to yield robust performance across a wide range of optimization tasks, including highly nonlinear benchmark functions and real-world engineering problems. The tendency of particles to overshoot optimal regions, combined with momentum effects introduced by the inertia term, enables effective exploration of unknown areas while still converging reliably toward global optima.

## 4 Experimental

*This chapter summarizes all experimental methodologies and materials used in this work for measuring polymer swelling and drying.*

### 4.1 Materials

Four commercially available polymers were investigated in this study. The first two were a phenol-formaldehyde thermoset (phenoplast) and an epoxy resin, both supplied by Raschig as black sheets 1 mm and 2 mm thick; these sheets were cut into smaller pieces to obtain specimens of convenient size. The third material was an addition-cure silicone elastomer, produced from two precursor mixtures provided by CHT Group in Tübingen, Germany. Equal masses of the two components were mixed, repeatedly evacuated to remove air, and cured for one hour at 105 °C to yield flexible, transparent cuboids. The fourth polymer was a polyurethane prepared from a kit supplied by Easy Composites in Beneluxbaan, Netherlands.

Degassing of silicone and polyurethane was carried out in an exicator vessel, where the uncured polymer mixture had been placed in a mould. Under vacuum, bubbles formed during mixing of the starting materials were removed. This procedure had to be repeated several times at room temperature until no bubbles remained. Afterwards, the produced plates were cut into smaller samples, similar to the epoxy and phenol resin. However, the thickness of both the silicone and polyurethane had to be measured each time with a vernier caliper, since it varied slightly between each sample.

#### 4.1.1 Epoxy resin

Epoxy resins constitute one of the most important and versatile subclasses of thermosetting polymers. They are defined by the presence of one or more epoxide (oxirane) functional groups, which are highly strained three-membered rings capable of reacting with a wide range of curing agents [81]. In strict chemical terms, the designation epoxy resin refers to uncured monomeric or oligomeric compounds containing epoxide groups; however, in practical and industrial usage, the term is commonly extended to include the corresponding cured thermoset systems.

The vast majority of industrially relevant epoxy resins are bi- or multifunctional epoxides, as monofunctional epoxides are primarily employed as reactive diluents or viscosity modifiers rather than as structural matrix materials [81]. Commercial epoxy resins are available with aliphatic, cycloaliphatic, or aromatic backbones and span a wide range of molecular weights, from low-viscosity liquid resins to high-molecular-weight solid resins. Among these, diglycidyl ethers of bisphenol A (DGEBA) represent by far the most dominant resin type, accounting for more than 75 % of global epoxy resin

consumption [81]. This dominance is attributed to the favorable balance between cost, processability, and mechanical performance offered by bisphenol A-based systems. Most commercially important epoxy resins are synthesized via the reaction of epichlorohydrin with compounds containing active hydrogen atoms, most commonly phenolic hydroxyl groups [81]. This process yields glycidyl-based epoxy resins, which form the backbone of modern epoxy technology. The reaction proceeds through formation of chlorohydrin intermediates followed by dehydrohalogenation, producing the epoxide functionality. Alternative synthesis routes include the direct epoxidation of olefins using peracids, which is primarily employed for cycloaliphatic epoxy resins.

In addition to standard DGEBA systems, multifunctional epoxy resins, such as epoxy novolacs and aromatic glycidyl amines, have been developed for applications requiring higher thermal stability, increased cross-link density, and enhanced chemical resistance [81]. These resins are particularly relevant in demanding environments such as aerospace composites and semiconductor encapsulation, where elevated service temperatures and long-term reliability are critical.

The primary industrial utility of epoxy resins lies in their ability to form highly cross-linked thermosetting networks upon reaction with suitable curing agents [81]. Common curing systems include amines, anhydrides, phenolic resins, polyamides, and mercaptans, each producing networks with distinct architectures and property profiles. During curing, the epoxide rings undergo ring-opening reactions, leading to the formation of covalent crosslinks and transforming the initially processable resin into an insoluble and infusible thermoset. The resulting cured epoxy networks are typically amorphous and exhibit a unique combination of properties, including high mechanical strength and stiffness, excellent adhesion to a wide range of substrates, low shrinkage upon cure, and outstanding resistance to moisture, chemicals, and corrosion [81]. These attributes, together with good electrical insulation and dimensional stability, distinguish epoxy resins from most other polymeric materials and underpin their widespread industrial adoption.

This wide variety of specialized resins, whose properties are tailored to specific applications, makes the development of generalized predictive models for solvent diffusion challenging, as swelling behavior is strongly influenced by the polarity, functionality, and network structure of the individual resin formulations. Nevertheless, many epoxy systems share key characteristics that are particularly relevant for electronics, including thermal stability, chemical resistance, and mechanical toughness. Because many of the detailed chemical formulations are proprietary and protected by patents, the epoxy resin investigated in this study is used primarily as a benchmark to characterize general swelling behavior. A systematic investigation of the influence of varying cross-linking densities would have been prohibitively time-intensive and experimentally costly. However, since swelling of epoxy resins has rarely been studied in the context of electronic applications, the results obtained here remain valuable as a reference point for comparing swelling behavior across different polymer classes.

In many technical applications, epoxy resins are not used in their neat form but contain fillers that improve thermal, mechanical, or electrical performance. Common fillers such as silica or alumina are particularly relevant in electronic materials. These additives may also affect solvent diffusion and swelling by changing the effective polymer volume, introducing tortuous transport pathways, and influencing the filler–matrix interphase. As a result, filled epoxy systems can exhibit swelling behavior that differs markedly from that of unfilled networks.

#### 4.1.2 Phenol resin

Phenolic resins are long-established thermosetting polymers that are valued for their combination of thermal stability, chemical resistance, and favorable fire-related properties. In practical applications, phenolic resins are rarely used as neat materials; instead, they are predominantly formulated as compound systems in which fillers and reinforcing agents are incorporated to tailor mechanical, thermal, electrical, and processing characteristics. Commonly used fillers include wood flour, mineral fillers, mica, and glass fibers, which may be combined depending on the intended application and performance requirements [82].

The cross-linking density of phenolic resins is comparatively high and is strongly influenced by resin type, curing conditions, and formulation. During curing, methylene and ether bridges are formed between aromatic rings, resulting in a rigid three-dimensional network with limited segmental mobility [82]. This dense network structure governs key macroscopic properties such as stiffness, heat resistance, and chemical durability. Owing to the irreversible nature of the cross-linking reactions, cured phenolic resins are infusible and insoluble, which fundamentally distinguishes them from thermoplastic polymers [82].

In comparison with epoxy resins, phenolic resins likewise form highly cross-linked thermoset networks; however, significant differences arise from their chemical structures and curing mechanisms. Phenolic resins undergo condensation reactions that may involve the formation of low-molecular-weight byproducts [82, 81]. Within the family of thermosetting resins used in electrical and structural applications, phenolic resins are commonly selected where flame resistance, thermal stability, and economic efficiency are critical. [82, 81].

Phenolic resins are employed in a wide range of industrial applications, including molded components, laminated materials, friction products, and electrically insulating parts [82]. In electrical engineering, phenolic-resin-based laminates and molded articles are used for components that demand dimensional stability and reliable insulating behavior. Further application areas include binders for abrasives and friction materials, composite systems, foams, and coatings, where the inherent thermal and chemical resistance of phenolic networks is advantageous [82].

### 4.1.3 Polyurethane

Polyurethanes represent a highly versatile class of polymeric materials formed through step-growth polyaddition reactions between multifunctional polyols and di- or polyisocyanates [83]. Any polymer containing urethane linkages within its backbone is classified as a polyurethane, irrespective of additional functional groups or copolymer structures [83]. This broad definition reflects the structural and compositional diversity of polyurethane materials, which cannot be adequately described by a single repeating unit in the manner of conventional commodity polymers.

The exceptional tunability of polyurethane systems arises from the wide selection of available building blocks. Polyols may be based on polyether, polyester, polycarbonate, acrylic, or polybutadiene backbones and may exhibit a broad range of functionalities, molecular weights, and architectures [83]. Isocyanates may be aromatic or aliphatic, with significant consequences for reactivity, ultraviolet stability, mechanical behavior, and long-term durability [83]. In practical formulations, non-isocyanate components frequently constitute the majority of the polymer volume, making the choice of polyol chemistry a primary lever for tailoring material properties [83].

During polymerization, the dominant reaction pathway involves nucleophilic addition of hydroxyl groups to isocyanate functionalities, leading to the formation of urethane bonds [83]. However, polyurethane chemistry is inherently complex, and several secondary reactions may occur simultaneously or sequentially. These include allophanate formation through reactions between urethane groups and excess isocyanates, biuret formation via reactions between urea groups and isocyanates, and isocyanurate formation through isocyanate trimerization [83]. The extent to which these reactions contribute to the final network structure depends not only on temperature and catalyst concentration, but also critically on stoichiometry, local isocyanate excess, and curing history [83].

Crosslinked polyurethane networks typically exhibit a favorable combination of toughness, elasticity, abrasion resistance, and chemical stability [83]. Their mechanical performance is strongly governed by microphase-separated morphologies consisting of soft segments derived from polyols and hard segments formed by isocyanate–chain extender domains [83]. This phase structure is often kinetically trapped during curing, resulting in materials whose properties depend not only on chemical composition but also on processing conditions [83]. Although polyurethanes display excellent mechanical resilience, their thermal stability is generally lower than that of epoxy or phenolic resins. This limitation arises primarily from the intrinsic thermal lability of urethane linkages rather than from aromatic content alone [83].

Polyurethanes are widely employed in coatings, adhesives, elastomers, flexible and rigid foams, sealants, and electronic encapsulation materials [83]. In many of these applications, processing involves the controlled mixing of reactive liquid components rather than melt processing of preformed pellets. For composite and functional formulations, fillers are commonly incorporated at concentrations ranging from approximately

10 to 60 % in weight to enhance stiffness, abrasion resistance, dimensional stability, or thermal conductivity [83]. Such systems demand precise control over formulation, mixing, and curing to achieve reproducible performance.

Moisture sensitivity represents a critical aspect of polyurethane processing. Water reacts readily with isocyanate groups to form unstable carbamic acid intermediates, which decompose into carbon dioxide and amines [83]. The evolved carbon dioxide can generate bubbles, voids, or unwanted porosity, while the amines may further react with isocyanates to form urea linkages, thereby altering the intended network architecture and material properties [83].

The polyurethane used in this study was synthesized according to the manufacturer's recommended mass ratio of 1:1.2. After degassing, the mixture was cured at temperatures above 105 °C to obtain rigid, transparent cuboids. All samples were dried at 105 °C for at least two weeks until no further mass loss was observed, and their final thicknesses were measured using a vernier caliper.

#### 4.1.4 Silicone

Silicone resins constitute a distinct class of hybrid organic–inorganic polymeric materials whose fundamental structural motif is the polysiloxane backbone, composed of alternating silicon and oxygen atoms ( $-\text{Si}-\text{O}-\text{Si}-$ ), with organic substituents covalently bound to the silicon atoms. This unique backbone architecture is responsible for the extraordinary physicochemical properties of silicone resins, which clearly distinguish them from purely organic polymer systems. [84]. The exceptional thermal and oxidative stability of silicone resins originates from the high bond dissociation energy of the siloxane linkage, which significantly exceeds that of typical carbon–carbon bonds found in organic polymers. Consequently, silicone materials maintain structural integrity and functional performance over a remarkably broad temperature range, typically from  $-50$  °C up to  $250$  °C, while silicone resins and resin-based laminates can withstand temperatures of  $350$  °C or even higher under specific conditions [84]. In addition, their inorganic backbone confers outstanding resistance to ultraviolet radiation and oxidative environments, including exposure to ozone and peroxide-rich atmospheres, conditions under which many organic polymers undergo rapid degradation [84].

Depending on the chemical functionality of the precursor silanes and the processing route employed, cross-linking in silicone resins can proceed through several distinct mechanisms, including hydrolytic polycondensation of chlorosilanes or alkoxysilanes, hydrosilylation reactions involving Si–H groups, and radical-initiated processes. The resulting three-dimensional networks are characterized by a high degree of structural flexibility, a property that is atypical for cross-linked polymers. This flexibility arises from the long Si–O bond length and the low rotational barrier of the siloxane chain, which together lead to extremely low glass transition temperatures and only minor changes in mechanical and dielectric properties with increasing temperature [84]. As a consequence of their molecular architecture, cured silicone resin networks exhibit very low

surface energy, pronounced hydrophobicity, and excellent chemical resistance toward aqueous solutions of acids, bases, salts, and many organic media. Even thin silicone layers impart strong water-repellent and anti-adhesive properties to modified surfaces, a feature widely exploited in protective coatings and release systems [84]. Although the intrinsic mechanical strength of silicone resins is generally lower than that of highly cross-linked organic thermosets, their mechanical performance remains sufficient for a broad spectrum of applications, particularly where flexibility, thermal stability, and environmental resistance are of greater importance than high modulus or tensile strength.

In modern electronics, silicone resins are regarded as indispensable materials due to their unique combination of thermal stability, electrical insulation performance, flexibility, and resistance to moisture and radiation [85]. The inorganic–organic hybrid backbone ensures stable dielectric behavior over a wide temperature range, enabling reliable operation in demanding environments. As noted in the literature, silicone materials retain their dielectric and mechanical properties even under prolonged thermal stress, making them especially suitable for high-temperature electronic components and outdoor systems [84]. Accordingly, silicone resins are widely used in power electronics, LED encapsulation, sensors, control units, and other applications requiring long-term reliability under harsh operating conditions [85].

Silicone-based potting compounds and gels are particularly valuable for the protection of sensitive electronic assemblies [85]. After curing, these materials remain elastomeric and effectively buffer mechanical vibrations, thermal expansion mismatches, and external mechanical stresses, thereby protecting delicate microstructures from damage [85]. To tailor mechanical, rheological, and thermal properties for specific applications, silicone resins are commonly compounded with inorganic fillers such as silica, alumina, or glass fibers [85]. Moreover, due to the flexible nature of the siloxane network, silicone-based systems often exhibit relatively rapid equilibration in diffusion and sorption experiments compared to more rigid polymer networks [85].

### 4.1.5 Solvents

Details about the solvents used, including their CAS numbers, suppliers and purities, are provided in Table 1. All solvents were employed as received, without further purification. Deionized water served both as the liquid medium and, in vapor form, for swelling experiments in steam.

Table 1. Chemicals used in this work

| chemical    | CAS Reg. No. | supplier            | purity (mass fraction) |
|-------------|--------------|---------------------|------------------------|
| heptane     | 142-82-5     | Honeywell           | 99.0 %                 |
| toluol      | 108-88-3     | Lactan GmbH & Co KG | > 99.8 %               |
| isopropanol | 67-63-0      | Honeywell           | 99.9 %                 |
| acetone     | 67-64-1      | Lactan GmbH & Co KG | > 99.8 %               |
| methanol    | 67-56-1      | Honeywell           | 99.9 %                 |
| cyclohexane | 110-82-7     | Honeywell           | ...99.9%               |

## 4.2 Experimental Procedure

Swelling behavior was quantified gravimetrically using a Sartorius Secura 26-1CEU microbalance with a linearity error of  $\pm 0.01$  mg. Prior to immersion, all polymer specimens were thoroughly dried at 105 °C under ambient pressure until no further change in mass was detected, corresponding to a mass variation of less than 0.1 % of the total sample weight. This process typically required two to three weeks. All investigated polymers were thermally stable within this temperature range, as indicated by the manufacturers' data, which reported either decomposition temperatures above 250 °C or cured at comparable temperatures to the measurements. The resulting constant mass was taken as the dry reference mass  $m_0$ .

Following drying, the samples were immersed in the solvent noted in Table 1. For each solvent and temperature condition, at least three samples with identical geometry and thickness were analyzed in parallel to ensure statistical reliability. For the phenol and epoxy resin experiments, the supplied material had to be cut into smaller rectangular specimens measuring 2 cm  $\times$  1.5 cm with a thickness of 1 mm and 2 mm, as provided by the supplier. In contrast, the silicone and polyurethane samples were synthesized manually. As a result, their thickness varied depending on the respective batch and is therefore reported individually in the Results section for each experiment. Although these materials were synthesized as plates, they were likewise cut into rectangular specimens measuring 1.5 cm  $\times$  2 cm prior to the measurements.

The samples were placed in small, tightly sealed glass vessels (shot glasses) equipped with Teflon-coated silicone gaskets to prevent contamination and evaporation. The vessels were kept completely filled with solvent to avoid the formation of headspace and were stored in thermostatic water baths that ensured uniform temperature distribu-

tion. For most solvents, the bath temperatures were adjusted to the respective boiling points of the solvents and maintained at 50 °C, 65 °C, or 80 °C, as these conditions provided stable and reproducible results. For water, however, slightly modified temperatures of 55 °C, 65 °C, and 85 °C were used. The sealing quality of the vessels represented a critical experimental factor; therefore, lids were replaced approximately every 1000 h to avoid leakage or diffusion of moisture. Furthermore, small amounts of solvent were continuously lost during the measurements and had to be replenished continuously throughout the experiment.

During weighing, each specimen was briefly removed from its vessel, rapidly blotted with a fresh tissue to remove excess liquid, and immediately placed on the balance. A new tissue was used for every measurement cycle to prevent cross-contamination, and care was taken to ensure that no fibers or residues adhered to the specimen surface. The total weight  $m_t$  of each specimen was recorded, and the solvent uptake was calculated per 1000 mg of polymer according to

$$q = \frac{(m_t - m_0)}{m_0} \cdot 1000 \text{ mg/g} \quad \text{Eq. 143}$$

expressed as milligrams of solvent absorbed per 1 g of polymer. Measurement temperature effects on weighing accuracy were not considered, as the measurement step was brief compared with the overall experimental duration. Any abrupt changes in mass that deviated from the typical swelling trend were classified as outliers or attributed to chemical degradation of the sample. An antistatic device was employed throughout all measurements to suppress electrostatic forces and thereby improve precision.

Initially, measurements were carried out daily to capture the early kinetics of swelling. As equilibrium approached, the measurement intervals were gradually extended—typically to weekly or biweekly intervals—to minimize experimental disturbance and reduce cumulative handling errors. The total duration of the experiments varied widely depending on the polymer system, ranging from several days to multiple months or even years. The experiment was considered complete once no further mass increase was detected over at least three consecutive measurements, or when a mass decrease indicated chemical degradation. All specimens remained in their original vessels throughout the experiment to ensure consistent boundary conditions.

In addition to liquid immersion tests, vapor exposure experiments were conducted for selected materials—specifically epoxy and phenol resins—using a CertoClav MultiControl 2 autoclave. Samples were placed on a grid basket above deionized water inside the autoclave, which was heated to 125 °C and maintained at this temperature for the entire duration of the experiment. The experimental setup is shown schematically in Figure 7. This generated an overpressure corresponding to the vapor–liquid equilibrium (VLE) of water. For weighing, the autoclave was briefly cooled to moderate temperatures. Because the required cooling and transport steps would have significantly distorted transient uptake data, vapor experiments were limited to equilibrium measurements only. Equilibrium was confirmed once no further change in sample mass was

observed over several consecutive days, with mass fluctuations remaining within the experimental uncertainty.

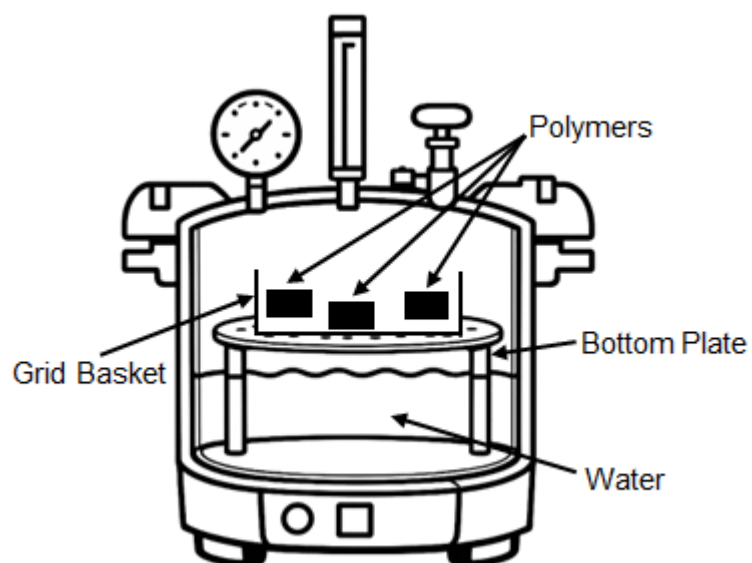


Figure 7: Schematic representation of the autoclave setup used for the vapor exposure experiments.

### 4.3 Density Measurement

Polymer densities were determined using pycnometry based on liquid displacement. Two calibrated pycnometers with nominal volumes of 100 mL and integrated thermometers were used to ensure reproducibility. The exact vessel volume was established by weighing the clean, dry pycnometer  $m_1$ , filling it completely with the working fluid, removing any air bubbles by gentle tapping or ultrasonic treatment, and inserting the thermometer until excess liquid escaped through the overflow capillary. After carefully drying the exterior, the filled pycnometer was weighed ( $m_2$ ), and the temperature of the liquid was recorded. The pycnometer volume was calculated from the mass difference and the density  $\rho_{solv}$  of the working fluid, which was determined at the same temperature using an Anton Paar SVM 3000 Stabinger viscometer. The temperature inside the viscometer was adjusted to match that measured with the pycnometer to eliminate temperature-related errors.

For the measurement of polymer densities, a known amount of finely cut polymer fragments was introduced into the dry pycnometer and weighed again  $m'_1$ . The vessel was then filled with the same working fluid, degassed in an ultrasonic bath to eliminate trapped air, and closed with the thermometer stopper until overflow occurred. After drying the outside, the filled pycnometer was weighed  $m'_2$ , and the temperature was noted. This temperature was also measured with the viscometer to ensure consistency between the fluid density and the measurement conditions. The temperature during all experiments was approximately  $22 \pm 2$  °C

The polymer density  $\rho_{sample}$  was calculated from the mass  $m_{sample}$  of the pure sample using the following relations:

$$V_1 = \frac{m_2 - m_1}{\rho_{solv}} \quad \text{Eq. 144}$$

$$V_2 = \frac{m'_2 - m'_1}{\rho'_{solv}} \quad \text{Eq. 145}$$

$$\rho_{sample} = \frac{m_{sample}}{V_1 - V_2} \quad \text{Eq. 146}$$

Distilled water served as the reference liquid for dry samples, while the swelling solvent was used as the working fluid for measurements of swollen polymers to ensure thermodynamic consistency with the swelling state. All measurements were conducted at room temperature. Each determination was performed twice, using both pycnometers to verify reproducibility and minimize systematic error.

## 5 Results and Discussion

*This chapter presents all results from the experimental and modeling work conducted in this study. The data are compared and interpreted to highlight different aspects of polymer swelling. The model results are based on the theoretical framework outlined in Chapter 3, while the experimental results follow the methodology described in Chapter 4.*

*We begin by analyzing the influence of temperature, polarity, and solvent structure on the swelling equilibrium. Based on these results, swelling behavior will be theoretically predicted. The discussion then extends to diffusion kinetics for the same set of solvents, emphasizing the relevance of incorporating multi-dimensional geometries - especially under inhomogeneous temperature fields.*

*Building on this framework, a 3D simulation of swelling in a real electronic component is presented. Finally, the opposite process of swelling -drying- is addressed to complete this work.*

*Since parts of this work have already been published, they are cited as ,Wagner et al. (2024)' [86] and ,Wagner et al. (2025)' [87].*

### 5.1 Swelling Equilibrium<sup>1</sup>

Swelling equilibrium was measured gravimetrically as described in the previous chapter and modeled using an EOS by applying standard thermodynamics. The mass change was measured over time until equilibrium was reached, specified as the point at which no further changes in mass occurred. This behavior was modeled using PC-SAFT, which requires model parameters that are either taken from literature or fitted to experimental data. The PC-SAFT parameters for the solvents were typically fitted to experimental VLE data and were taken from the literature [60, 70, 88], as summarized in **Table 2**.

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<sup>1</sup> This chapter contains results that have already been published in Wagner et al. (2024) and Wagner et al. (2025).

**Table 2.** Physical data and PC-SAFT parameters of the solvents used in this work

| general parameters                        |                  |               |                     |                 |                 |                |                       |
|-------------------------------------------|------------------|---------------|---------------------|-----------------|-----------------|----------------|-----------------------|
|                                           | methanol         | water         | isopropanol         | acetone         | heptane         | toluol         | cyclo-<br>hexane      |
| M [g/mol]                                 | 32.042           | 18.015        | 60.096              | 58.08           | 100.203         | 78.114         |                       |
| PC-SAFT parameters and network parameters |                  |               |                     |                 |                 |                |                       |
|                                           | methanol<br>[88] | water<br>[88] | isopropanol<br>[88] | acetone<br>[70] | heptane<br>[60] | toluol<br>[60] | cyclo-<br>hexane [89] |
| $\sigma$ [Å]                              | 3.2300           | 3.0007        | 3.2085              | 3.2742          | 3.8049          | 3.6478         | 3.8499                |
| $\epsilon/k_B$ [K]                        | 188.90           | 366.51        | 208.42              | 232.99          | 238.40          | 287.35         | 278.11                |
| $m$ [-]                                   | 1.5255           | 1.0656        | 3.0929              | 2.7448          | 3.4831          | 2.4653         | 2.5303                |
| $\epsilon^{AB}/k_B$ [K]                   | 2899.5           | 2500.7        | 2253.9              |                 |                 |                |                       |
| $\kappa^{AB}$ [-]                         | 0.035176         | 0.034868      | 0.024675            |                 |                 |                |                       |
| assoc.<br>mod. [-]                        | 2B               | 2B            | 2B                  | ind. ass.       |                 |                |                       |
| $\mu^a$                                   |                  |               |                     | 2.88            |                 |                |                       |

Since polymers possess no vapor pressure, their model parameters cannot be derived from VLE data. Instead, the parameters were fitted to experimental density values, which were measured using the pycnometer method or provided by the manufacturer. The dry polymer densities at room temperature are as follows: polyurethane – 1185 kg/m<sup>3</sup>, phenol-formaldehyde resin – 1915 kg/m<sup>3</sup>, epoxy resin – 2018 kg/m<sup>3</sup>, and silicone – 1014 kg/m<sup>3</sup>. The theoretical results then deviated only minimal from experimental data with: less than 1.0 % for polyurethanes, less than 1.0 % for phenoplasts, less than 1.0 % for epoxy resin, and less than 4.5 % for silicones.

Since the dry polymer density was only measured at room temperature, temperature effects on the pure polymer were not taken into account. However, to improve the quality of the pure polymer parameters, swelling data at different temperatures were additionally included. In this first step, the binary interaction parameter was set to zero, as it was later defined individually for each solvent. This ensured that the pure polymer parameters would provide the best possible representation of the swelling mixture in conjunction with accurately calculating the polymer density.

The advantage of this approach is that the obtained model parameters are well-suited for describing swelling behavior. However, the trade-off is that the pure polymer data may be slightly overfitted to the swelling behavior of these mixtures. This might limit the suitability of the parameter set to this specific type of silicone, since crosslinking density and additives in different silicones could additionally affect swelling behavior. Furthermore, errors caused by unknown degradation of the network, such as bond cleavage in response to network expansion, might remain undetected. Nonetheless, temperature effects on polymer density were kept within a realistic range. For example, the theoretical density of silicone decreased by 2.0% at 50 °C and by 4.3% at 80 °C relative to room temperature. These results are consistent with experimental observations [90] for long-chain polydimethylsiloxane, which showed a decrease of 1.9% at 55 °C and 5.2% at 80 °C.

The swelling density could also be described accurately. For silicone, the model slightly underestimated the density in isopropanol by 1.9% at 50 °C, 2.7% at 65 °C, and 2.2% at 80 °C compared to experimental values. In heptane, the measured density of swollen silicone at 50 °C was 853 kg/m<sup>3</sup>, with the model slightly overestimating it by 6.2%. The observed decrease in sample density was a result of the increase in its volume due to swelling.

All polymer PC-SAFT parameters were fitted using a particle swarm optimizer [80] and are listed in **Table 3**.

**Table 3.** Physical data, network parameters, and PC-SAFT parameters of the polymers determined in this work

|                            | general parameters                        |                                |             |                  |
|----------------------------|-------------------------------------------|--------------------------------|-------------|------------------|
|                            | polyurethane                              | phenol formalde-<br>hyde resin | epoxy resin | silicone         |
| M [g/mol]                  | 919.21                                    | 624                            | 800         | 600              |
|                            | PC-SAFT parameters and network parameters |                                |             |                  |
|                            | polyurethane                              | phenol formalde-<br>hyde resin | epoxy resin | silicone<br>[86] |
| $\sigma$ [Å]               | 2.6645                                    | 3.30166                        | 2.25871     | 4.83816          |
| $\varepsilon/k_B$ [K]      | 210.682                                   | 175.442                        | 187.669     | 355.71           |
| $m$ [-]                    | 56.8527                                   | 11.4582                        | 46.0544     | 7.59905          |
| $\varepsilon^{AB}/k_B$ [K] |                                           | 22.1824                        | 152.535     |                  |
| $\kappa^{AB}$ [-]          |                                           | 0.0145391                      | 0.00241971  |                  |
| assoc.mod. [-]             | ind. ass.                                 | 2B                             | 2B          |                  |
| $N_{assoc}$ [-]            | 1                                         | 6 · 2                          | 2 · 2       |                  |
| $\phi$ [-]                 | 2.76842                                   | 2.00791                        | 2.82414     | 3.74966          |
| $\alpha_{max}$ [-]         | 1.79279                                   | 2.16271                        | 1.74338     | 3.75793          |

The binary interaction parameters were close to zero for all polymer–solvent combinations, indicating that the interaction energy between polymers and solvents was accurately described without requiring significant adjustment through these parameters. Furthermore, some polymer–solvent systems were modeled as temperature-independent, using only a single parameter  $k_{ij}^a$ , which implies that the model is capable of accounting for temperature effects without relying solely on binary interaction parameters.

For most systems, a linear relationship with temperature was observed, represented by the additional parameter  $k_{ij}^b$  described in Eq. 83. In these cases, the systems were found to be only weakly temperature-dependent, as indicated by the relatively small values of this parameter. Only the combination of silicone in isopropanol exhibited a more complex temperature dependence, requiring a total of three parameters. The binary interaction parameters are provided in **Table 4**.

**Table 4.** Binary interaction parameters determined in this work.

| Component i | Component j  | $k_{ij}^a$ [-] | $k_{ij}^b$ [K] | $k_{ij}^c$ [K] |
|-------------|--------------|----------------|----------------|----------------|
| methanol    | epoxy resin  | -0.0658243     | 0              | 0              |
| water       | epoxy resin  | 0.020628       | 0              | 0              |
| acetone     | epoxy resin  | -0.135542      | 0              | 0              |
| heptane     | epoxy resin  | 0.177188       | -30.2708       | 0              |
| water       | Phenoplast   | -0.1035        | -16.7805       | 0              |
| heptane     | Phenoplast   | 0.191286       | -31.1969       | 0              |
| toluol      | Phenoplast   | 0.22255        | -40.0958       | 0              |
| methanol    | polyurethane | -0.0455184     | 0              | 0              |
| water       | polyurethane | -0.0152422     | 0              | 0              |
| isopropanol | polyurethane | -0.006613      | 0              | 0              |
| acetone     | polyurethane | -0.00505948    | 0              | 0              |
| toluol      | polyurethane | 0.0643232      | 0              | 0              |
| acetone     | silicone     | 0.08658        | -8.3575        | 0              |
| toluol      | silicone     | -0.164         | 40.0           | 0              |
| water       | silicone     | 0.67713        | -210.712       | 0              |
| isopropanol | silicone     | -0.2569        | 207.75         | -33543         |
| heptane     | silicone     | 0.069580       | -48.899        | 0              |
| cyclohexane | silicone     | -0.42327       | 104.74         | 0              |

Using this parameter set, the PC-SAFT model was capable of describing the experimental swelling behavior with very good correlation. The theoretical and measured swelling equilibria for each mixture are illustrated in Figure 8.

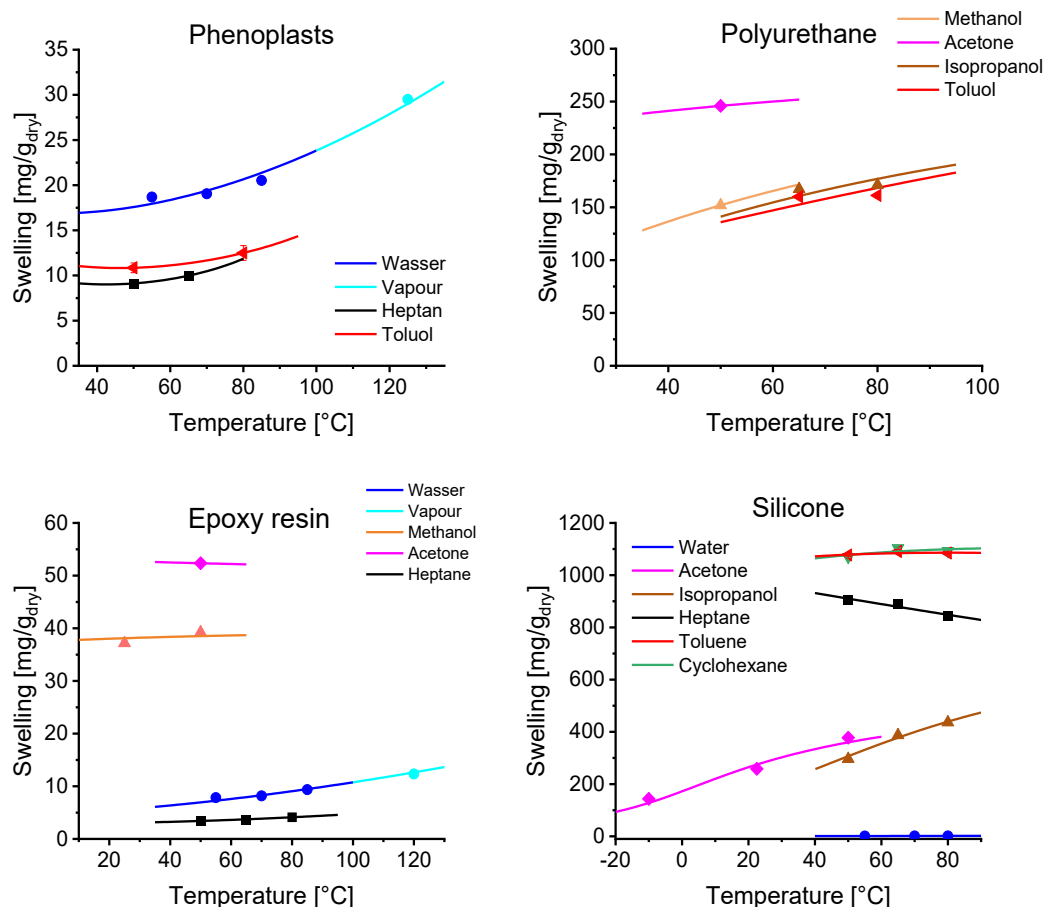


Figure 8: Swelling equilibria of phenoplasts, polyurethane, epoxy resins, and silicone<sup>2</sup>

In the discussion, the main factor influencing total solvent uptake was identified as the difference in polarity between the solvent and the polymer, with similar polarity leading to higher uptake. Silicone is a very nonpolar polymer, as it possesses no functional groups. This leads to a high uptake of nonpolar solvents such as toluene and heptane. In contrast, high polar solvents like water cause only minimal swelling, while solvents of medium polarity result in moderate swelling. The other polymers phenoplast, polyurethane, and epoxy resin contain some functional groups, making them moderately polar. For this reason, medium-polarity solvents such as acetone, isopropanol, or methanol were most readily absorbed, while in comparison, both highly polar and nonpolar solvents were absorbed to a lesser extent.

For most polymer-solvent mixtures, the swelling increased with temperature. The only exception was heptane in silicone, where swelling decreased with rising temperature, likely due to the system approaching its upper critical solution temperature. Additional-

<sup>2</sup> This figure have already been published in Wagner et al. (2025)

ly, polyurethane and silicone showed significantly higher solvent uptake compared to epoxy resin and phenoplast. This is because polyurethane and silicone were synthesized during this work without fillers. In contrast, the epoxy resin and phenoplast samples were assumed to contain approximately 75% filler by weight. These fillers are typically silicon oxide-based and add weight but do not swell, and therefore do not contribute to the swelling behavior. Consequently, they were treated as additional mass that remains constant during swelling but does not participate in the swelling process.

Considering polyurethane more specifically, measuring the uptake of water was not feasible due to the degradation of the samples into a white, sticky mass. This most likely resulted from a polyaddition reaction between residual components from the polymer's starting materials and the invading water. This reaction is commonly utilized in the production of polyurethane foams [91]. Similarly, the uptake of heptane could not be measured due to side reactions between the solvent and the polymer, as the samples gradually became increasingly sticky. Swelling of polyurethane in acetone was challenging but feasible, as the samples became increasingly brittle over time. The specimens had to be handled very carefully until equilibrium was reached, and multiple attempts were necessary since the samples often broke during the process.

The phenoplast presented a different kind of challenge due to the extremely long experimental durations required to reach equilibrium. In some cases, measurements could not be carried out until equilibrium, as continuing the experiments would have been extremely difficult due to various complications. Extended experimental durations increase the likelihood of variations in results, potentially caused by slow chemical reactions between the polymer and the solvent. Moreover, repeated measurements raise the risk of contamination of either the solvent or the polymer surface. Therefore, careful and clean working conditions are crucial to obtaining reliable long-term results. Additionally, residual substances from the polymer synthesis might slowly diffuse out of the material, thereby altering the chemical potential of the surrounding solvent. Such effects were recently observed in swelling experiments involving salted solutions [92]. Swelling of the phenoplast in methanol stopped after 15,000 hours, with a non-equilibrium uptake of 55 mg/g at 50 °C and 10 mg/g at 25 °C. Similarly, swelling in acetone was interrupted after 7,000 hours, showing a total uptake of 4.3 mg/g at 50 °C and 1.01 mg/g at 25 °C. In the case of isopropanol, no measurable uptake was observed after three weeks. It is reasonable to assume that isopropanol was absorbed by the polymer to some extent, but the diffusion rate was so low that no uptake was noticeable within this time frame.

## 5.2 Dimensional Dependence of Swelling Kinetics<sup>3</sup>

Starting from diffusion kinetics in polymers, the influence of the spatial dimensionality of the polymer sample is discussed. In all experiments, the samples were macroscopic and had the shape of a cuboid. The main assumption in this work is that, during swelling or drying, solvent transport occurs only at the boundaries of the sample, which is visualized in Figure 9.

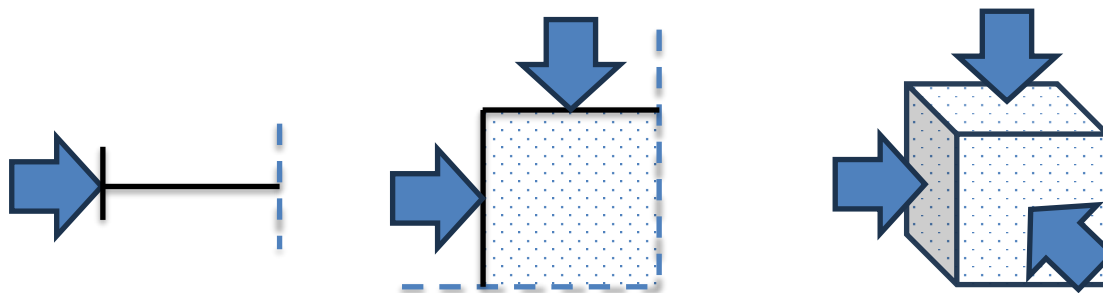


Figure 9: Comparison between diffusion modeling in 1D, 2D, and 3D. The arrows indicate solvent entering the polymer during swelling. Solid lines represent the boundaries, and dotted lines indicate mirror planes.

The simplest case considered is one-dimensional (1D) diffusion. In this case, solvent can enter or leave the polymer only at the outermost grid points. These grid points therefore define the boundary conditions for mass transport between the environment and the polymer matrix. To reduce computational cost, symmetry can be exploited by mirroring the system at one boundary. This effectively doubles the accuracy of the simulation, as the mirrored boundary represents the interior of the polymer rather than an additional external surface.

When extending the model from 1D to two dimensions (2D), the simulation becomes significantly more complex. In 1D, the concentration gradient can only point in two directions, either toward the center or toward the boundary. In contrast, in 2D the gradient can point in any direction within the plane, depending on the local chemical potential at each grid point. From a numerical perspective, the number of neighboring grid points also increases: each grid point is influenced not only by its left and right neighbors, but also by its upper and lower neighbors.

As a consequence, the diffusion behavior near the boundaries differs substantially from the 1D case. Instead of a single boundary point, entire arrays of boundary grid points exist along each side of the sample. In particular, grid points near the corners experience faster changes in solvent concentration, as they are influenced by two boundary surfaces rather than one. During swelling, solvent uptake at these locations is therefore

<sup>3</sup> This chapter contains results that have already been published in Wagner et al. (2024)

significantly faster, while the flux in the center of each plane remains similar to that observed in 1D simulations.

If the diffusion coefficient is kept constant, the overall solvent uptake appears faster in higher dimensions because solvent can enter the polymer through a larger number of boundary surfaces. However, this geometric effect may lead to an apparent overestimation of the diffusion coefficient when fitting simulation results to experimental data. This effect becomes even more pronounced when extending the simulation to three dimensions (3D), where additional surfaces allow solvent to enter the polymer. In 3D, each grid point has six neighboring points instead of four. The boundary now consists of entire planes of grid points, which most accurately represent the real experimental situation, as physical samples are inherently three-dimensional objects. Although the computational cost increases significantly—scaling with the third power of the number of grid points—the 3D model provides the most realistic representation of solvent diffusion in polymer samples.

The dimensional error in this study is determined for the silicone samples by fitting the simulation results to the experimentally measured solvent uptake. The sample matrix is discretized into a multidimensional grid, where the solvent amount at each grid point is calculated, and the total weight is determined by computing the arithmetic mean across the entire sample. For this discussion, silicone is particularly well suited as the model material, because it exhibits only type I diffusion; meaning no linear diffusion occurs. Therefore, only the Maxwell–Stefan diffusion model is required. This may be advantage, as type II diffusion is largely independent of the polymer geometry and is only relevant at the surface, as specified.

All measured samples are rectangular cuboids with dimensions of  $x = 20$  mm,  $y = 20$  mm, and  $z = 8.5$  mm. These need to be represented in 1D, 2D, and 3D simulations accordingly. In the 1D case, only the shortest side is considered as the length; in the 2D case, the two shortest sides are used; and the 3D case reconstructs the complete geometry of the polymer sample. Numerically, the shortest side is always set to 50 grid points, while the other sides are scaled proportionally (124 grid points) to reflect the actual dimensions of the samples.

In Figure 10, the simulation of the swelling at 80 °C of isopropanol and heptane in 1D, 2D, and 3D is compared to the experimental behavior.

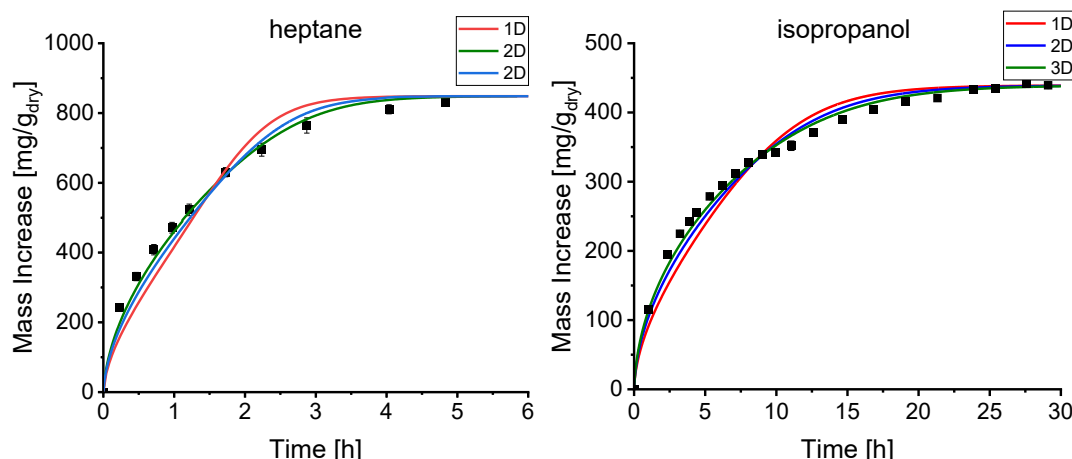


Figure 10. Comparing measured (■) and calculated solvent uptake of silicone in heptane and isopropanol at 80 °C over time in 1D, 2D, and 3D.<sup>4</sup>

Based on the correlation between the experimental and theoretical progression of the curve, the diffusion coefficients were determined and are listed in Table 5. The best agreement was achieved in the 3D model, which is therefore considered the most accurate representation, as it captures all relevant geometric effects and shows only minimal deviation from the experimental data. Reducing the model to 2D and 1D leads to increasing deviations, highlighting the importance of including dimensional effects for accurately modeling the swelling behavior.

**Table 5:** Comparison of the diffusion coefficient at different dimensions.

| dimension | heptane                                    | isopropanol                                |
|-----------|--------------------------------------------|--------------------------------------------|
| 1D        | $2.45 \cdot 10^{-10} \text{ m}^2/\text{s}$ | $3.95 \cdot 10^{-10} \text{ m}^2/\text{s}$ |
| 2D        | $1.85 \cdot 10^{-10} \text{ m}^2/\text{s}$ | $3.00 \cdot 10^{-10} \text{ m}^2/\text{s}$ |
| 3D        | $1.45 \cdot 10^{-10} \text{ m}^2/\text{s}$ | $2.34 \cdot 10^{-10} \text{ m}^2/\text{s}$ |

The diffusion coefficient decreased with higher dimensionality, showing deviations of 28% in 2D and 69% in 1D compared to 3D. This indicates that diffusion coefficients tend to be overestimated when spatial effects are overly simplified. The deviation in 1D was particularly high, as it does not account for geometric effects beyond sample thickness. Notably, these deviations are influenced by the sample shape, with the largest discrepancies occurring at the corners where mass increases faster than at the central face. For thin foils, however, 1D calculations can still be sufficient, offering significant reductions in computational time. In contrast, 3D simulations, despite utilizing 30 CPU cores at 2.10 GHz, required several days to complete and were by far the most time-consuming compared to 2D and 1D.

<sup>4</sup> This figure have already been published in Wagner et al. (2025)

Since the dimensional deviations for both heptane and isopropanol mixtures were similar, the effect appears to be independent of solvent polarity. Dimensional deviations were greatest at the beginning and just before equilibrium, where the theoretical curve intersects the experimental data. This occurs because the diffusion coefficient was fitted to minimize the mean deviation, resulting in this curve progression. Volume changes during diffusion were not included here, as all deviations were assumed to arise solely from the sample geometry. In addition, the quotient between the 3D and 1D cases was found to be nearly identical for both solvent systems. This suggests that the 1D case may be sufficient for fitting purposes, which would be numerically simpler.

The next step is a detailed investigation of the geometric influence on diffusion-driven swelling. For this purpose, the swelling behavior of a cuboid polymer sample is modeled in two dimensions. The initial geometry consists of a cuboid discretized with 25 grid points in each spatial direction, which represents a total polymer thickness of 8.5 mm. A mirror plane is applied on one side to represent symmetry conditions. Following, the cuboid is then extended by adding 25 grid points to one side, while the thinnest dimension is kept constant at 25 grid points. This approach allows the systematic investigation of how the swelling behavior changes as the sample becomes progressively thinner relative to its lateral dimensions. The polymer under consideration is a silicone elastomer immersed in isopropanol. The investigated geometries are illustrated in Figure 11.

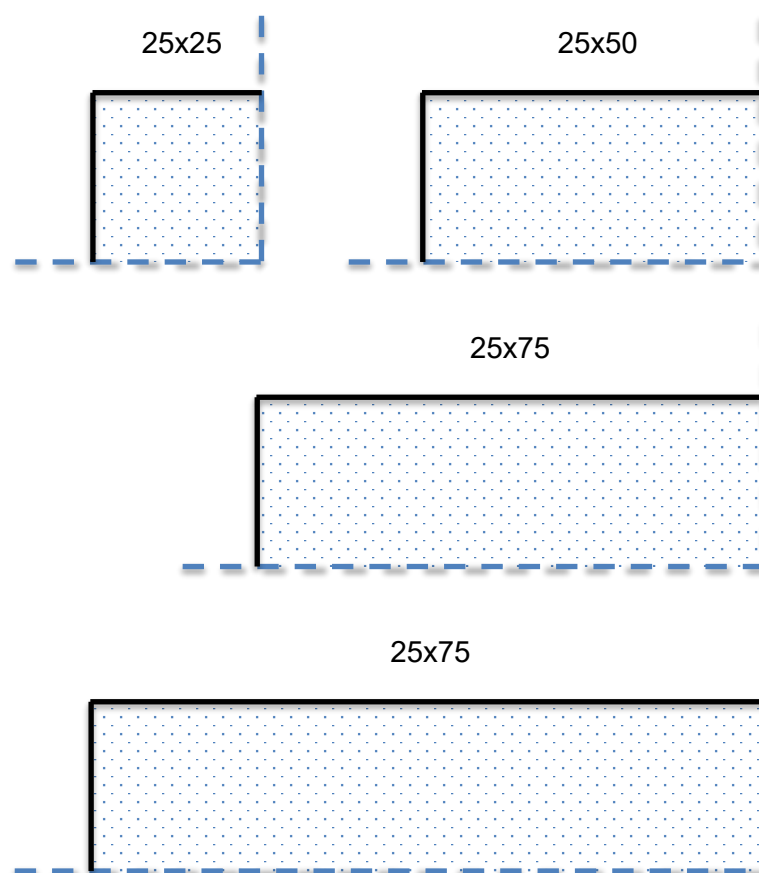


Figure 11: Illustration of the shape of the two-dimensional sample used to model the geometric influence on swelling. The solid black line represents the boundary between the polymer and the solvent, and the dotted blue line indicates a mirror plane.

The results show that, as the sample becomes thinner, the influence of the additional spatial dimensions becomes increasingly negligible. Consequently, the swelling behavior approaches that of a one-dimensional diffusion process. This transition is particularly evident when comparing thicker samples to thinner ones, where strong changes in the swelling kinetics can be observed. This is illustrated in Figure 12.

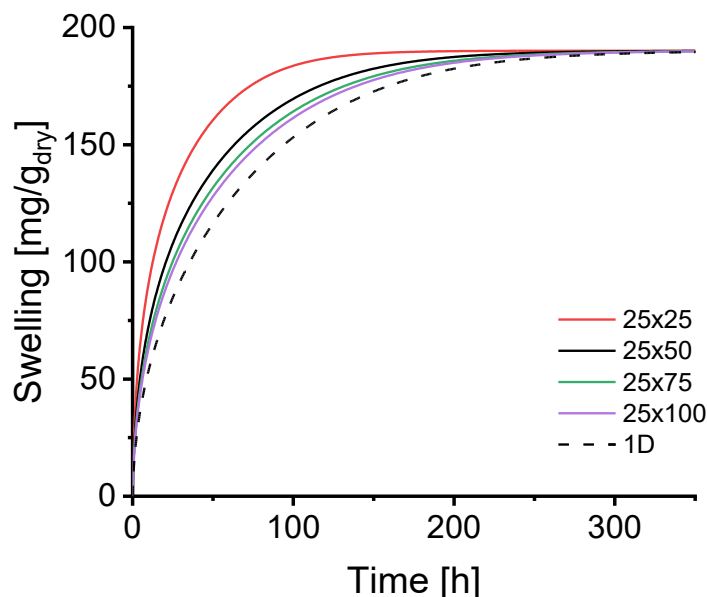


Figure 12: Results of the benchmark study modeling the geometric influence on swelling. Silicone was used as the polymer, and isopropanol at 50 °C served as the solvent environment. The solvent geometry in two dimensions is characterized by the number of grid elements up to the mirror plane. A thickness of 8.5 mm is represented by 25 grid points. The diffusion coefficient of isopropanol was taken as specified in the following chapter, and volume change was taken into account.

The underlying reason for this behavior lies in the geometric distribution of grid points. In a perfectly cubic geometry, the relative number of grid points located near edges and corners is maximized compared to those in the interior. These corner and edge regions experience diffusion from multiple directions, leading to strong multidimensional effects. In contrast, grid points located far from the boundaries are less affected by diffusion from other dimensions, as discussed previously.

As the sample becomes thinner, the proportion of grid points that are sufficiently far from the lateral boundaries increases, meaning that the distance from the center to the corners increases. These interior points predominantly experience diffusion in almost only one direction. As a result, the overall swelling behavior increasingly resembles that of a one-dimensional diffusion process.

This analysis implies that very thin samples, such as polymer foils, can often be accurately described using one-dimensional diffusion models, since multidimensional geometric effects play only a minor role.

## 5.3 Temperature Dependence of Absorption Kinetics<sup>5</sup>

The temperature effect on swelling was analyzed for all investigated polymers. Diffusion I and Diffusion II were distinguished to model the curve progression accurately, with the latter associated with linear uptake behavior. Since Case II diffusion is relaxation-controlled and less dependent on the sample's geometry, it was modeled one-dimensionally to reduce computational cost. Additionally, all samples were significantly thinner than silicone, which further minimized potential spatial effects. In contrast, Case I diffusion, which is influenced by the sample's spatial form, was modeled in two dimensions as a compromise between computational effort and parameter accuracy. In every simulation, the shorter edge was discretized into 50 grid points, and the number of points along the longer edge was adjusted to preserve the sample's aspect ratio.

For Case I diffusion, only the diffusion coefficient needs to be fitted to the experimental data. In contrast, Case II diffusion also requires adjustment of the Kelvin-Voigt parameters. Since two of these parameters are affected by temperature, a total of three parameters must be fitted for each polymer-solvent mixture at a given temperature, in addition to the diffusion coefficient.

The diffusion coefficient was fitted to the initial swelling behavior, up to the point where the curve transitions to a linear trend. This transition is determined by the critical solvent fraction, while the damping constant defines the slope of the linear region. The elasticity constant was used as an additional fitting parameter. The best correlation with experimental data was achieved with an elasticity constant of  $2.0 \cdot 10^7 \text{ Pa}$  for polyurethane and  $3.0 \cdot 10^5 \text{ Pa}$  for phenoplast. A sensitivity analysis of the elasticity constant showed that small variations ( $\pm 25\%$ ) had minimal impact on the swelling gradient compared to the other parameters. However, significantly higher or lower values resulted in unrealistic outcomes, such as negative swelling gradients below the LLE or poor correlation with experimental data.

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<sup>5</sup> This chapter contains results that have already been published in Wagner et al. (2024) and Wagner et al. (2025).

All determined Maxwell-Stefan and Kelvin-Voigt parameters are summarized in **Table 6**

**Table 6:** MS- and Kelvin-Voigt-parameter determined in this work.

| Polyurethane |                      |                      |                     |                    |                       |                    |
|--------------|----------------------|----------------------|---------------------|--------------------|-----------------------|--------------------|
|              | $d_\phi$             | $k_\phi$             | $\eta_0$            | $E_{A,t}$          | $D_{MS,\infty}$       | $E_{A,D}$          |
| toluene      | $1,37 \cdot 10^{-3}$ | $1,53 \cdot 10^{-3}$ | $3,06 \cdot 10^4$   | $7,73 \cdot 10^3$  | $5,07 \cdot 10^{-5}$  | $4,63 \cdot 10^4$  |
| isopropanol  | -0.17                | $4,00 \cdot 10^{-3}$ | $4,38 \cdot 10^4$   | $7,57 \cdot 10^3$  | $7,47 \cdot 10^{-10}$ | $1,35 \cdot 10^4$  |
| acetone      |                      |                      |                     |                    | $5,8 \cdot 10^{-13}$  |                    |
| methanol     |                      |                      |                     |                    | $2,79 \cdot 10^{-12}$ |                    |
| Phenoplast   |                      |                      |                     |                    |                       |                    |
|              | $d_\phi$             | $k_\phi$             | $\eta_0$            | $E_{A,t}$          | $D_{MS,\infty}$       | $E_{A,D}$          |
| heptane      | 0.038                | $4,0 \cdot 10^{-4}$  | $3,7 \cdot 10^{13}$ | 0                  | $1,07 \cdot 10^{-10}$ | $1,63 \cdot 10^4$  |
| toluene      | 0.032                | 0                    | $1,95 \cdot 10^6$   | $5,12 \cdot 10^3$  | $1,18 \cdot 10^{-11}$ | $1,28 \cdot 10^4$  |
| water        |                      |                      |                     |                    | $1,01 \cdot 10^{-8}$  | $2,55 \cdot 10^4$  |
| Epoxy Resin  |                      |                      |                     |                    |                       |                    |
|              | $d_\phi$             | $k_\phi$             | $\eta_0$            | $E_{A,t}$          | $D_{MS,\infty}$       | $E_{A,D}$          |
| heptane      | $1,13 \cdot 10^{-4}$ | $3,33 \cdot 10^{-4}$ | $2,3 \cdot 10^{16}$ | $-9,39 \cdot 10^2$ | $5,41 \cdot 10^{-10}$ | $1,72 \cdot 10^4$  |
| water        | 0.024                | $4,70 \cdot 10^{-4}$ | $1,8 \cdot 10^{14}$ | 0                  | $6,61 \cdot 10^{-9}$  | $1,64 \cdot 10^4$  |
| acetone      | 0.295                | 0                    | $8,0 \cdot 10^{14}$ | 0                  | $3,50 \cdot 10^{-14}$ | 0.0                |
| methanol     | 0.295                | 0                    | 0.526               | $1,13 \cdot 10^4$  | 4.56                  | $7,74 \cdot 10^4$  |
| Silicone     |                      |                      |                     |                    |                       |                    |
|              | $d_\phi$             | $k_\phi$             | $\eta_0$            | $E_{A,t}$          | $D_{MS,\infty}$       | $E_{A,D}$          |
| toluene      |                      |                      |                     |                    | $2,98 \cdot 10^{-9}$  | $9,56 \cdot 10^3$  |
| acetone      |                      |                      |                     |                    | $1,57 \cdot 10^{-10}$ | $-3,94 \cdot 10^3$ |
| isopropanol  |                      |                      |                     |                    | $3,18 \cdot 10^{-10}$ | 0.0                |
| heptane      |                      |                      |                     |                    | $1,64 \cdot 10^{-8}$  | $1,28 \cdot 10^4$  |

Deriving this parameter can be challenging, as each variable influences multiple aspects of solvent progression. This becomes especially critical when predicting swelling behavior in electronic applications, where the time required for a solvent to penetrate the material is primarily governed by MS-diffusion, while the point at which a critical condition is exceeded may be described by relaxation-controlled diffusion. Achieving reliable modelling depends on a critical evaluation of the experimental data. It is essential to measure multiple samples for each solvent-polymer combination to enhance accuracy and determine the mean deviation. Fine-tuning parameters can be hindered by experimental variability. Unexpected trends, such as an unanticipated increase or decrease in mass, may be associated with experimental errors. These may result from contamination during the measurement procedure or from leaky sample vessels. Consequently, repeated trials are often necessary to obtain consistent results while closely monitoring the swelling progression.

### 5.3.1 Silicone

The swelling behavior of silicone in toluene, acetone, isopropanol, and heptane is illustrated in Figure 13. All calculations were performed in two dimensions as a compromise between result quality and the computational time required. Furthermore, silicone possesses no functional groups, eliminating associative interactions between solvent and polymer, such as hydrogen bonding, and reducing the system to purely non-polar interactions.

#### Silicone

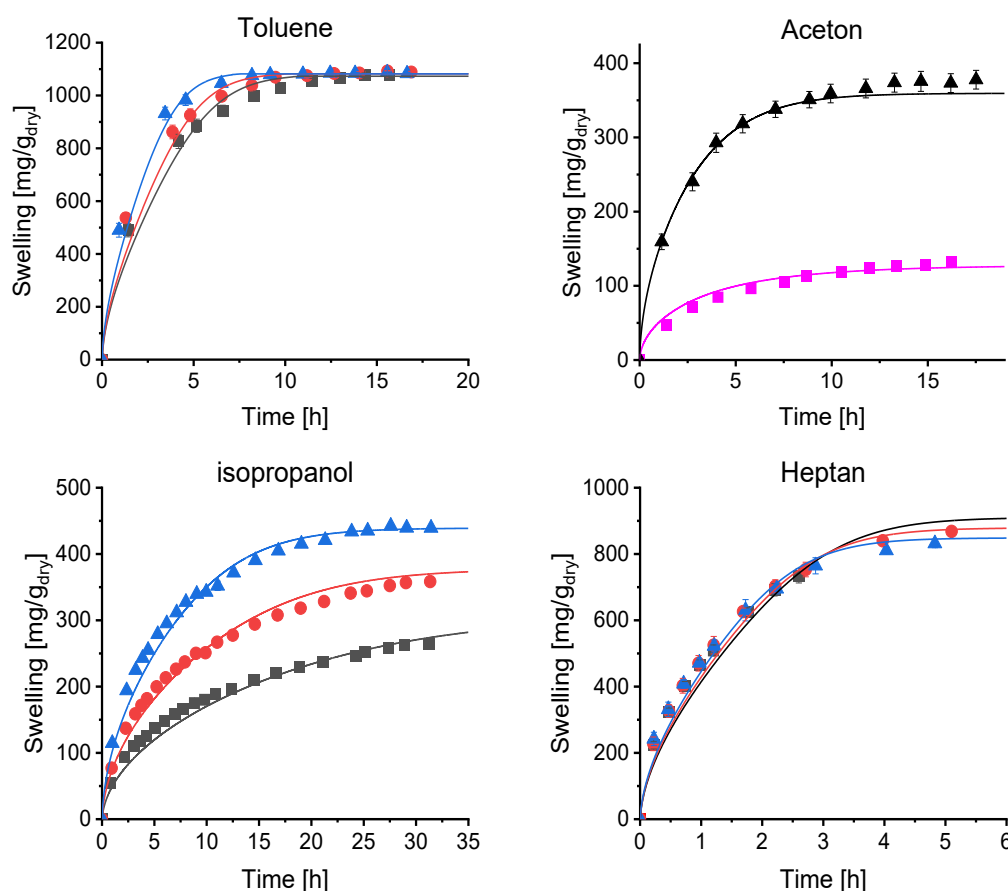


Figure 13: Swelling of silicone in various solvents at different temperatures. For silicone immersed in acetone, the mean sample thicknesses were 8.91 mm / 20.7 mm at -10 °C and 7.65 mm / 22.2 mm at 50 °C. In toluene, the thicknesses were 8.27 mm / 22.7 mm at 50 °C and 8.84 mm at 65 °C. Samples swollen in isopropanol and heptane showed thicknesses of 8.5 mm / 20 mm. Measurements were performed at -10 °C (magenta, —), 50 °C (black, —), 65 °C (red, —), and 80 °C (blue, —).<sup>6</sup>

<sup>6</sup> Parts of his figure have already been published in Wagner et al. (2025).

Modeling the diffusion behavior of silicone produced excellent agreement between experiment and theory: every experimental data point was closely reproduced by the simulation. For silicone, only the MS-diffusion model was required, because all swelling systems exhibited Case I diffusion. This is attributable to silicone's glass-transition temperature of roughly  $-60\text{ }^{\circ}\text{C}$  [93, 94]; the swelling experiments were performed at much higher temperatures, so polymer-chain relaxation can be neglected. The absence of relaxation effects lets us isolate the influence of temperature on the MS-diffusion coefficient.

Unlike (Wagner et al. (2023)), isopropanol and heptane was modeled with a variable-volume mesh so the results would be comparable with those for toluene and acetone, which were also simulated with volume expansion. The change improved the fit slightly: the fitted diffusion coefficient rose by 8 % for isopropanol and 14 % for heptane relative to a static grid. The comparison shows that neglecting volume growth introduces a smaller error than the dimensional error, discussed in the previous chapter. As the specimen swells, the numerical grid expands and the diffusion path lengthens; the fitted coefficient must therefore increase to reproduce the measured uptake.

In general, diffusion accelerates with temperature, since faster molecular motion increases the diffusion coefficient. Silicone in isopropanol, however, showed an almost temperature-independent coefficient. Heptane displayed the opposite trend: its coefficient decreased as temperature rose. This inverse behavior likely results from the lower compatibility of heptane with silicone at higher temperatures. The swelling-equilibrium data already suggest this effect. With reduced solubility, diffusion slows down.

Solvent polarity had only a minor effect on the diffusion constant: coefficients increased slightly with polarity, and all systems remained within the same order of magnitude. Temperature sensitivity likewise depended more on each solvent's individual nature than on polarity. For example, although heptane and toluene are both strongly non-polar, heptane was more temperature sensitive. Similar polarity can yield similar uptake curves, but the resemblance mainly reflects comparable swelling equilibria; non-polar solvents show closely spaced equilibrium values, whereas polar solvents diverge more strongly.

Overall, diffusion appears to be governed more by molecular size than by polarity. In the present solvent set, the larger molecules also happen to be less polar, so the observed trends likely represent a superposition of molecular-size and polarity effects.

### 5.3.2 Polyurethane

Similar to silicone, polyurethane was also synthesized without any filler material, allowing the swelling behavior to be controlled solely by polymer-solvent interactions. Figure 14 illustrates the swelling behavior of polyurethane in toluene, acetone, methanol, and isopropanol.

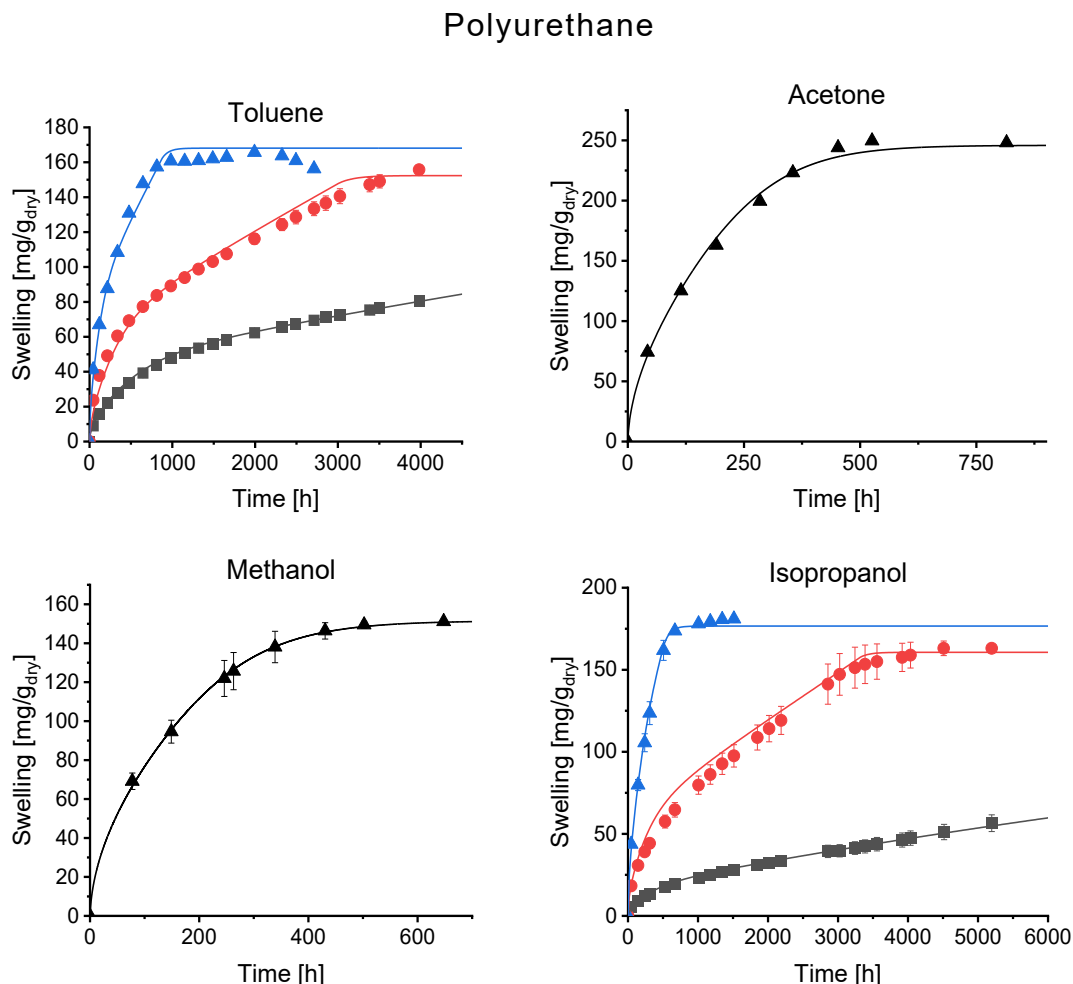


Figure 14: Swelling of polyurethane in various solvents at different temperatures. The mean sample thickness in toluene was 2.95 mm at 50°C, 3.2 mm at 65°C, and 3.19 mm at 80°C. In isopropanol, the thickness was 3.60 mm at 50°C, 3.20 mm at 65°C, and 2.92 mm at 80°C. Measurements were performed at 50 °C (black, —), 65 °C (red, —), and 80 °C (blue, —).<sup>7</sup>

Polyurethane exhibited both diffusion behaviors, namely Case I for methanol and acetone, and Case II for toluene and methanol (see Chapter 2.10). Although acetone still showed a weak linear behavior, to avoid overfitting, the modeling was effectively carried out using MS-diffusion only. This suggests that the diffusion type is not solely

<sup>7</sup> This figure have already been published in Wagner et al. (2025)

determined by the polymer itself, but also by solvent-polymer interactions. No clear correlation was observed between solvent polarity and the resulting diffusion type. Instead, the effect appears to be influenced by the molecular shape of the solvent, which notably differs between methanol and isopropanol.

Additionally, the diffusion type was affected by temperature. Higher temperatures favored MS-diffusion behavior, likely due to changes in the polymer's relaxation. At elevated temperatures, polymer chain stretching increases, which accelerates relaxation. Alongside faster relaxation, the critical solvent volume also increases with temperature, further enhancing MS-diffusion contributions. The critical solvent concentration was more strongly influenced by the solvent type, whereas the damping constant remained nearly the same for both toluene and isopropanol.

After approaching equilibrium in toluene and isopropanol, slight changes in weight were still observed. These may be attributed to unknown side reactions between the solvent and the polymer, or to slow chain degradation. However, these changes were considered negligible. Further measurements after 500 hours indicated that isopropanol at 65 °C had reached equilibrium. The equilibrium for both isopropanol and toluene at 50 °C could not be measured due to the extended experimental duration. Instead, it was predicted using PC-SAFT, and the Kelvin-Voigt parameters were fitted to the available experimental data.

### 5.3.3 Phenoplast

The phenoplast was provided by the manufacturer as a thin polymer plate. Information about the crosslinker, filler, and additives was not accessible. However, it was assumed that the filler constituted 75% by weight, and the crosslinker was presumed to consist of simple phenol monomer units, as the simplest representative of this polymer class.

Figure 15 illustrates the experimental and theoretical swelling behavior of the phenoplast in water, heptane, and toluene.

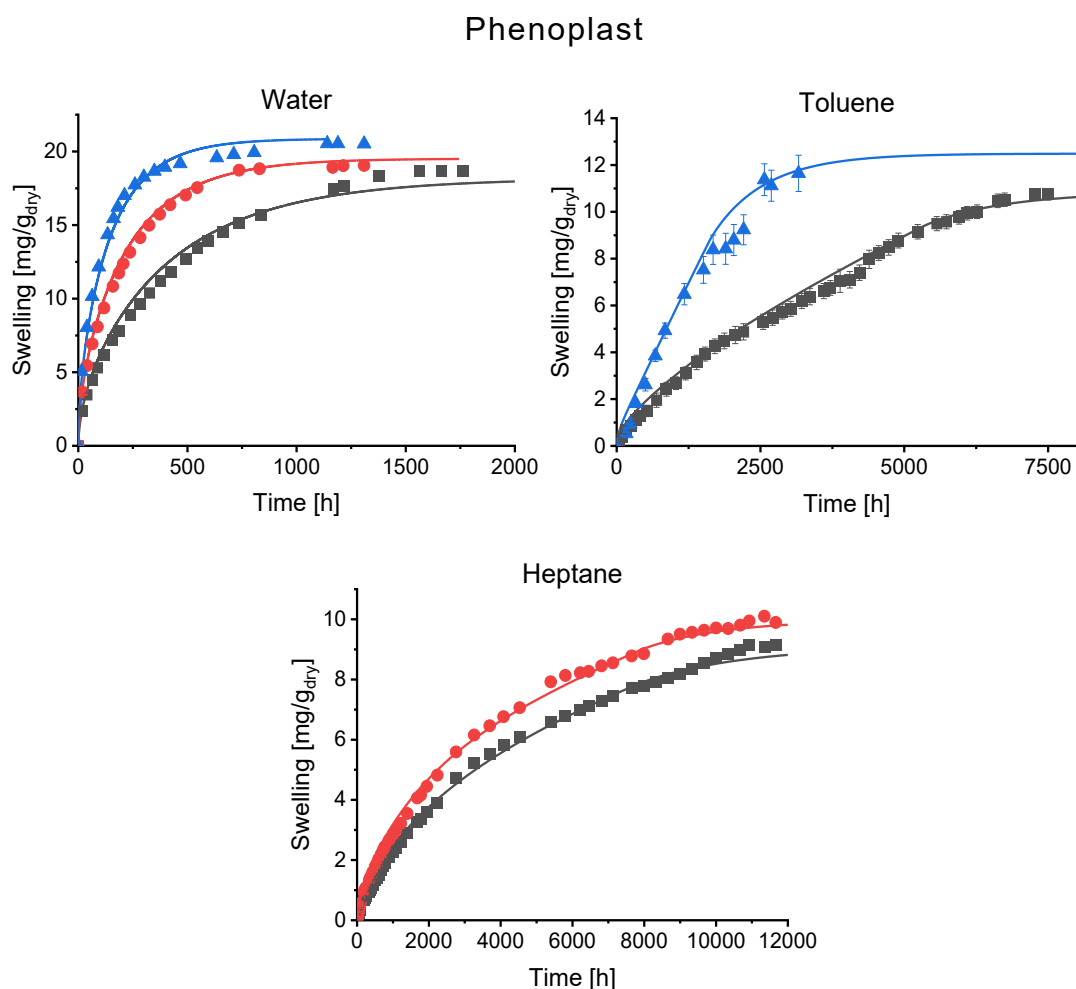


Figure 15: Swelling of the phenoplast in various solvents at different temperatures. The mean sample thickness was 2 mm for all polymer samples in heptane and water and 1 mm in toluene. Measurements were performed at 55 °C (black, —), 70 °C (red, —), and 85 °C (blue, —) for water and at 50 °C (black, —), 65 °C (red, —), and 80 °C (blue, —) for the other solvents.<sup>8</sup>

Among all investigated polymers, the phenoplast exhibited by far the slowest diffusion behavior. As a result, equilibrium could only be measured for three swelling systems (water, heptane, and toluene), while for methanol and acetone, only the initial swelling phase was captured. The long diffusion times are likely associated with a high crosslinking density, as it has been demonstrated in hydrogels that increased crosslinking density leads to reduced diffusion rates.

Furthermore, the high crosslinking density may also contribute to a significant portion of relaxation-controlled diffusion. Strong viscoelastic swelling behavior has been shown to increase with higher crosslinking [95]. All systems showed noticeable viscoelastic stretching effects, including methanol and acetone, where equilibrium was not reached

<sup>8</sup> This figure have already been published in Wagner et al. (2025)

due to the extended swelling duration. Even in water, a small deviation between theoretical and experimental diffusion at 50 °C was observed, likely caused by viscoelasticity. However, this deviation was considered negligible in favor of using a simpler parameter set, and the simulation remained highly accurate.

The increase in crosslinking slows relaxation, which also favors Case-II diffusion in nearly all systems [96]. Based on experimental data, heptane appeared to exhibit Case-I diffusion. However, modeling with an MS-diffusion approach alone proved insufficient, as a linear behavior was still visible between 500 and 11,000 hours. Notable deviations between the simulation and experimental data were observed for toluene at 50 °C, most likely due to experimental inaccuracies. Nevertheless, the modeling approach was capable of describing all solvent-polymer systems with high precision

Medium-polar solvents, which were expected to show the highest uptake, could not be measured until equilibrium due to the long experimental duration. These solvents also exhibited strong Case-II diffusion behavior. This is primarily because, in these systems, the equilibrium lies significantly above the critical solvent fraction compared to other systems, which drastically increases the linear diffusion time.

Furthermore, the swelling curve tended to shift toward Case-I diffusion when the critical solvent volume was close to the equilibrium state, indicating that this relationship is independent of the polymer type. In addition, Case-I diffusion behavior increased with temperature in these systems. Both the critical solvent volume and the damping constant were affected by temperature, as also observed for polyurethane.

#### **5.3.4 Epoxy Resin**

The diffusion properties of water and heptane for epoxy resin have already been investigated [15, 17]; therefore, here, the transferability to a different polymer is examined. Similar to these polymers, a filler amount of 75% by weight is assumed, with a crosslinker having a different molar mass of 800 mg/g. For the sake of clarity, the polymer measured here will be referred to as new, and the already published polymer will be referred to as old. Furthermore, the swelling kinetics of acetone and methanol are additionally provided in Figure 16.

## Epoxy Resin

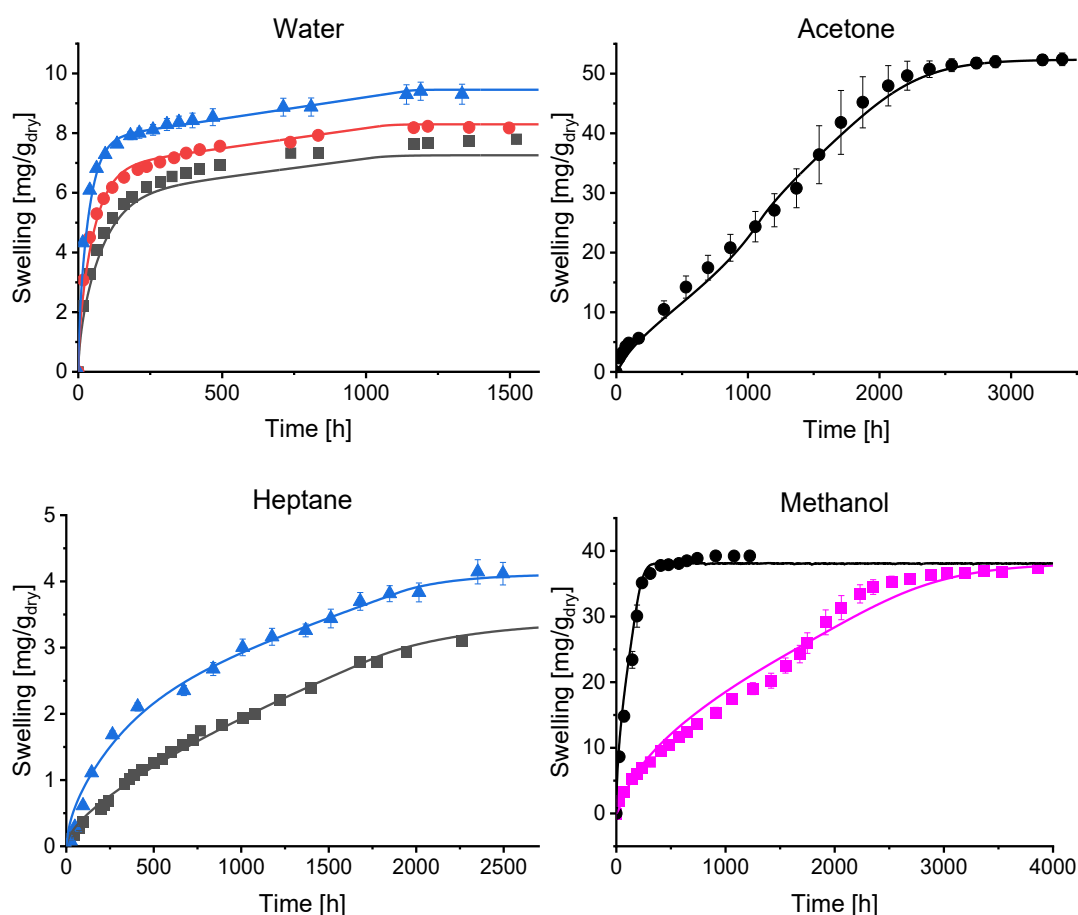


Figure 16: Swelling of the epoxy resin in various solvents at different temperatures. The mean sample thickness was 2 mm for all polymer samples. Measurements were performed at 55 °C (black, —), 70 °C (red, —), and 85 °C (blue, —) for water and at 25 °C (magenta, —), 50 °C (black, —), and 80 °C (blue, —) for the other solvents.<sup>9</sup>

Water, heptane, and isopropanol were found to diffuse much more slowly for the new polymer, with isopropanol never reaching the equilibrium state due to its significantly longer diffusion times. In connection with this, the lower equilibrium uptake of both heptane and water indicates that both solvents are less favored here. This may also be related to a higher crosslinking density, which reduces both the free space available for the solvent to penetrate and the relaxation speed of the polymer chains. However, the previously discussed trend that average-polar solvents favor Case-II diffusion is valid for both the new and old polymers. This is especially true for the initial measurements of toluene and methanol. Notably, for the new polymer, there is an increasing importance of viscoelastic stretching, which may also be related to the higher crosslinking density. [96]

<sup>9</sup> This figure have already been published in Wagner et al. (2025)

Experiment and simulation deviate slightly for water at 50 °C due to an underprediction of the equilibrium swelling. Although it would be possible to match the experimental diffusion much better by adding a term to the binary interaction parameter in PC-SAFT, this was not done in the interest of maintaining a broader range of fungibility across higher or lower temperatures. Mismatches to the experimental data for methanol at 50 °C were considered as experimental deviations.

In conjunction with polyurethane and phenoplasts, the trend of increasing MS contribution due to a higher critical volume fraction and faster relaxation, along with the influence of temperature, is also consistent. It was further observed that Type II behavior was evident for solvents that were absorbed the most, as they exceeded the critical volume fraction well before reaching equilibrium. This increased the diffusion time, as relaxation occurred much more slowly than the MS behavior.

## 5.4 Parameter Effects in MS Diffusion and Kelvin-Voigt

The objective of this chapter is to investigate how the individual model parameters influence the swelling behavior of the system. For this purpose, a material system is employed whose model parameters have already been identified in the preceding chapters. Based on this system, benchmark simulations are conducted to analyze the characteristics of Case I and Case II diffusion. The aim of these simulations is not to reproduce experimental swelling behavior quantitatively. Instead, they are intended to elucidate the specific influence of each model parameter and to clarify their underlying physical significance. In addition, the chapter demonstrates how targeted modifications of these parameters enable the adaptation and description of different material systems within the modeling framework.

For clarity, the models applied in this work are briefly revisited. Diffusion-driven mass transport is described using the Maxwell–Stefan model, which was theoretically introduced in Chapter 2.8 and is applied here to represent Case I diffusion. In contrast, the viscoelastic material response associated with Case II diffusion is captured using the Kelvin–Voigt model, also introduced in Chapter 3.2.

The relations derived from the model that are essential for understanding the governing mechanisms of the simulated swelling behavior. The inverse damping constant  $1/\eta$  and the term  $1/(1 - \phi_{solv,c})$  exhibit phenomenological similarities to a diffusion coefficient. Both quantities control the temporal evolution of the concentration and thus strongly influence the characteristic timescale of the process. The elastic pressure contribution  $p_{elastic}$  is obtained from the derivative of the elastic component of the Helmholtz free energy with respect to density. The corresponding derivation demonstrates that this term depends not only on the densities of the pure components but also on the local mixture density. These quantities are computed using the PC-SAFT

equation of state. Consequently,  $p_{elastic}$  does not constitute an independent model parameter; rather, it arises directly from the underlying thermodynamic model.

For the benchmark simulations, a polyurethane–isopropanol system is considered with a grid size of 25 grid points and mirrored at the polymer inner side, representing a sample diameter of 1.0 mm. The PC-SAFT parameters employed for this system are taken from chapter 5.1, and the diffusion parameters are likewise adopted from the same source. Any deviations from the parameter values used in chapter 5.3 are explicitly stated in the present chapter, while all remaining parameters are kept unchanged. This particular system was selected because it does not contain fillers, thereby eliminating the need for additional correction factors or supplementary model terms. In principle, however, any of the material systems investigated in this work could serve as a suitable reference for describing the behavior discussed here. All simulations are performed at a system temperature of 65 °C.

The analysis starts with a direct comparison between the Maxwell–Stefan diffusion coefficient  $D_{MS}$  and the inverse damping constant  $1/\eta$ . In the considered example, chain relaxation within the Kelvin–Voigt framework is kept constant. The analysis focuses on how the swelling behavior changes when the diffusion coefficient  $D_{MS}$  is varied. Both parameters accelerate one of the underlying physical processes. An increase in  $D_{MS}$  leads to faster mass transport, whereas an increase in  $1/\eta$  results in more rapid chain relaxation. For this reason,  $D_{MS}$  and  $1/\eta$  are directly compared, as illustrated in Figure 17. Case I behavior dominates when  $D_{MS}$  is large relative to  $\eta$ . In contrast, increasing values of  $1/\eta$  enhance the contribution of Case II behavior. Between these two limiting regimes lies the region of anomalous diffusion, which is characterized by the interplay of both mechanisms.

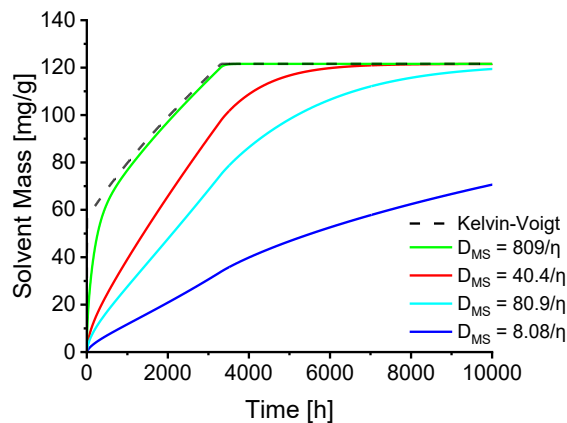


Figure 17: Influence of  $D_{MS}$  and  $1/\eta$  on swelling behavior. Since  $D_{MS}$  and  $\eta$  have different SI units, the relation is scaled by a factor of  $\text{m}^3/\text{kg}$  to ensure dimensional consistency.

Many swelling curves associated with anomalous diffusion exhibit an almost linear progression over extended intervals. Toward the end of the process, however, the curves increasingly flatten as  $D_{MS}$  becomes small relative to  $1/\eta$ . In the case of very

fast diffusion or when a pure Kelvin–Voigt model is applied, a sharp corner appears in the curve. This feature arises from the attainment of swelling equilibrium. Because the pure Kelvin–Voigt model does not explicitly describe this equilibrium state, a discontinuity emerges in the curve progression. In the combined modeling approach, this transition is represented continuously: although equilibrium is reached at the boundary, the interior of the material continues to be governed by diffusion-driven transport. The slower this subsequent transport proceeds, the flatter the transition region becomes.

When  $1/\eta$  is significantly larger than  $D_{MS}$ , the influence of the viscoelastic contribution diminishes, and swelling behavior is increasingly governed by the Maxwell–Stefan model. Furthermore, within the regime of anomalous diffusion, the slope of the linear section is also affected by the diffusion coefficient. In general, however, the slope can be most effectively adjusted via  $1/\eta$ , as it is directly proportional to this property. Beyond this, the Maxwell–Stefan model influences the curve shape both before and after the linear regime. Overall, essential characteristics of the swelling curves can already be controlled through targeted variation of these two parameters.

The influence of the elastic contribution is examined in the subsequent section. From a purely mathematical perspective, this contribution decreases with increasing swelling and may even become negative. As a result, the Kelvin–Voigt model can impose an upper limit on swelling that is independent of the swelling equilibrium predicted by the thermodynamic model. Although this allows for adjustment of the maximum swelling, it rarely leads to satisfactory results in practice. The reason is that the swelling behavior is strongly constrained as equilibrium is approached, which typically does not correspond to observations in real systems. More realistic results are obtained when this parameter is kept slightly below this limiting value.

Attempts to correlate the elastic contribution with classical elastic deformation coefficients, such as the Young’s modulus, were not successful. This finding highlights that the parameter represents a purely model-internal quantity. The effect of this parameter is illustrated in Figure 18, where two cases are shown: one dominated by Maxwell–Stefan or anomalous diffusion and another characterized by pronounced Kelvin–Voigt behavior. In diffusion dominated by the Maxwell–Stefan mechanism, this parameter primarily shifts the equilibrium toward lower swelling values and thereby distorted the final uptake. Since the equilibrium is already defined by the thermodynamic model, this additional effect should not arise in that regime. In the Kelvin–Voigt-dominated case, the elastic contribution mainly affects the slope of the curve. However, a similar effect can also be achieved by adjusting  $\eta$ , which suggests that omitting this parameter may be advantageous in certain situations. Nevertheless, the elastic contribution allows for a slight modification of the curve shape during the late stage of swelling.

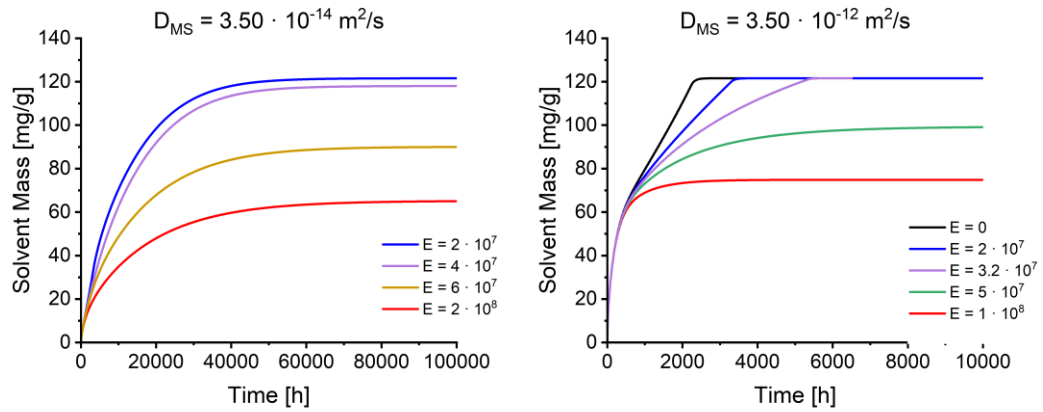


Figure 18: Influence of the elastic contribution  $E$  on swelling. The diffusion coefficient was chosen such that both strong Case I and Case II diffusion behavior can be illustrated.

Finally, the influence of the critical concentration  $\phi_{solv,c}$  is investigated, as shown in Figure 19. Because  $\phi_{solv,c}$  is directly proportional to the slope of the linear regime, the parameter  $\eta$  is adjusted such that the product  $\eta(1 - \phi_{solv,c})$  remains constant. This approach enables the isolated assessment of the effect of  $\phi_{solv,c}$ . The results indicate that  $\phi_{solv,c}$  determines the height of the corner at which the transition from Maxwell–Stefan diffusion to the linear swelling regime occurs. Importantly, this parameter does not affect the time step or the rate of the process, as is the case for the diffusion coefficient  $D_{MS}$ , but solely the extent of swelling in terms of absorbed mass. In addition, the curves increasingly flatten toward the end of the process as smaller values of  $\phi_{solv,c}$  are chosen. This flattening is caused by the elastic contribution of the model and primarily influences the late stage of swelling.

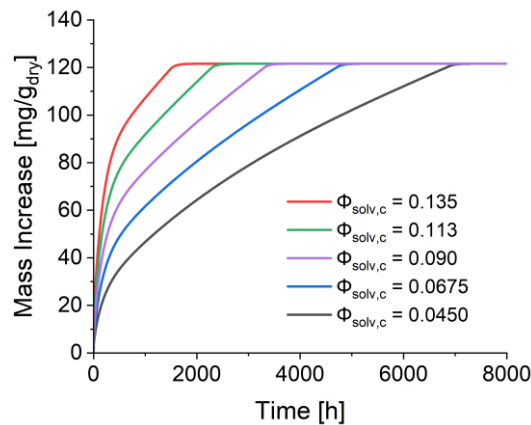


Figure 19: Influence of the critical concentration  $\phi_{solv,c}$ . The product  $\eta(1 - \phi_{solv,c})$  was kept constant, and the diffusion coefficient was set to  $3.50 \cdot 10^{-12} \text{ m}^2/\text{s}$ .

## 5.5 Drying<sup>10</sup>

Starting with a swollen sample in a solvent-free environment, the opposite of swelling can be modeled; namely, drying. Beginning with the simplest case for modeling, a Dirichlet boundary condition was chosen, with a solvent-free surface representing a vacuum-like release without any interfacial interaction.

A system temperature of 25 °C, matching the experimental conditions, was used. The diffusion coefficients were calculated using the Arrhenius parameters derived in Chapter 5.3. The diffusion coefficients were recalculated using the dimensional differences determined in Chapter 5.2, as the sample geometry remained the same as for the swelling case.

This prediction of the drying behavior is illustrated in Figure 20 for a silicone sample swollen with isopropanol. This is shown alongside an approach where the diffusion coefficients were directly adjusted to fit the measured drying behavior. Furthermore, the spatial effects were also investigated.

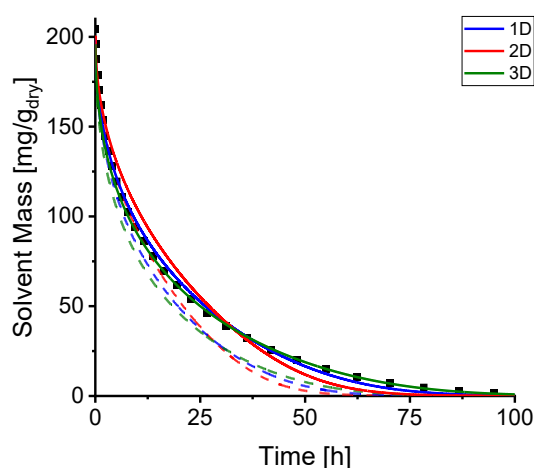


Figure 20. Comparison of measured (■), adjusted (—), and predicted (---) solvent evaporation from isopropanol-swollen silicone at room temperature (calc. 25 °C) over time represented in 1D, 2D, and 3D.<sup>11</sup>

Transitioning from a 1D to a 3D drying model affects the curve progression in much the same way as it does for swelling. However, the diffusion coefficients obtained by fitting to the experimental drying data are inconsistent with those predicted for swelling: the coefficients required for drying are lower by a factor of 1.33. Using the swelling-based coefficients for drying would therefore underestimate the drying rate. By adjusting these

<sup>10</sup> This chapter contains results that have already been published in Wagner et al. (2024)

<sup>11</sup> This figure have already been published in Wagner et al. (2024)

coefficients, the simulated drying profile aligns very closely with the experimental results. The diffusion coefficients used for these calculations are listed in Table 7

**Table 7:** Adjusted and predicted diffusion coefficient for drying.

| dimension | predicted                                  | adjusted                                   |
|-----------|--------------------------------------------|--------------------------------------------|
| 1D        | $3.69 \cdot 10^{-10} \text{ m}^2/\text{s}$ | $2.85 \cdot 10^{-10} \text{ m}^2/\text{s}$ |
| 2D        | $2.80 \cdot 10^{-10} \text{ m}^2/\text{s}$ | $2.10 \cdot 10^{-10} \text{ m}^2/\text{s}$ |
| 3D        | $2.18 \cdot 10^{-10} \text{ m}^2/\text{s}$ | $1.60 \cdot 10^{-10} \text{ m}^2/\text{s}$ |

The variation in the diffusion coefficient between drying and swelling can be influenced by several factors. In the present calculation, volume changes were neglected. During drying, the specimen shrinks, reducing the grid size and slightly accelerating the predicted drying rate, whereas the corresponding elongation during swelling would slow the swelling rate. Because this assumption was applied to both processes, it cannot account for the observed deviation.

Material degradation is also excluded in the model. Swelling can break polymer chains and generate micro-cracks or surface pores. Robinson et al. [97] reported that swelling stimulates pore formation and enlarges pore size in dense polydimethylsiloxane membranes; the resulting larger pores enhanced viscous solvent flow. Viscous flow is not considered here, as mass transfer is modeled solely with the Maxwell–Stefan framework, which depends only on chemical-potential gradients.

Another plausible explanation lies in the boundary conditions. Interfacial effects are neglected: both swelling and drying are simulated with a Dirichlet boundary condition that fixes the concentration at the outermost grid point. This corresponds to an ideal vacuum in which surface transport resistances are ignored. In contrast, the experiments were performed under ambient conditions, where external mass-transfer resistance slows drying. Because the internal polymer behavior is governed purely by diffusion, any apparent difference in the diffusion coefficient must be attributed to surface-transport effects.

Figure 21 presents snapshots of the drying profile. A rapid decrease in solvent concentration first appears at the surface and then progresses toward the center of the sample. Initially, the concentration in the core remains almost unchanged, being encased by an almost-dry polymer layer, being encased by an almost-dry polymer layer. During swelling, the diffusion behavior is reversed: the solvent concentration gradually increases from the surface toward the interior.

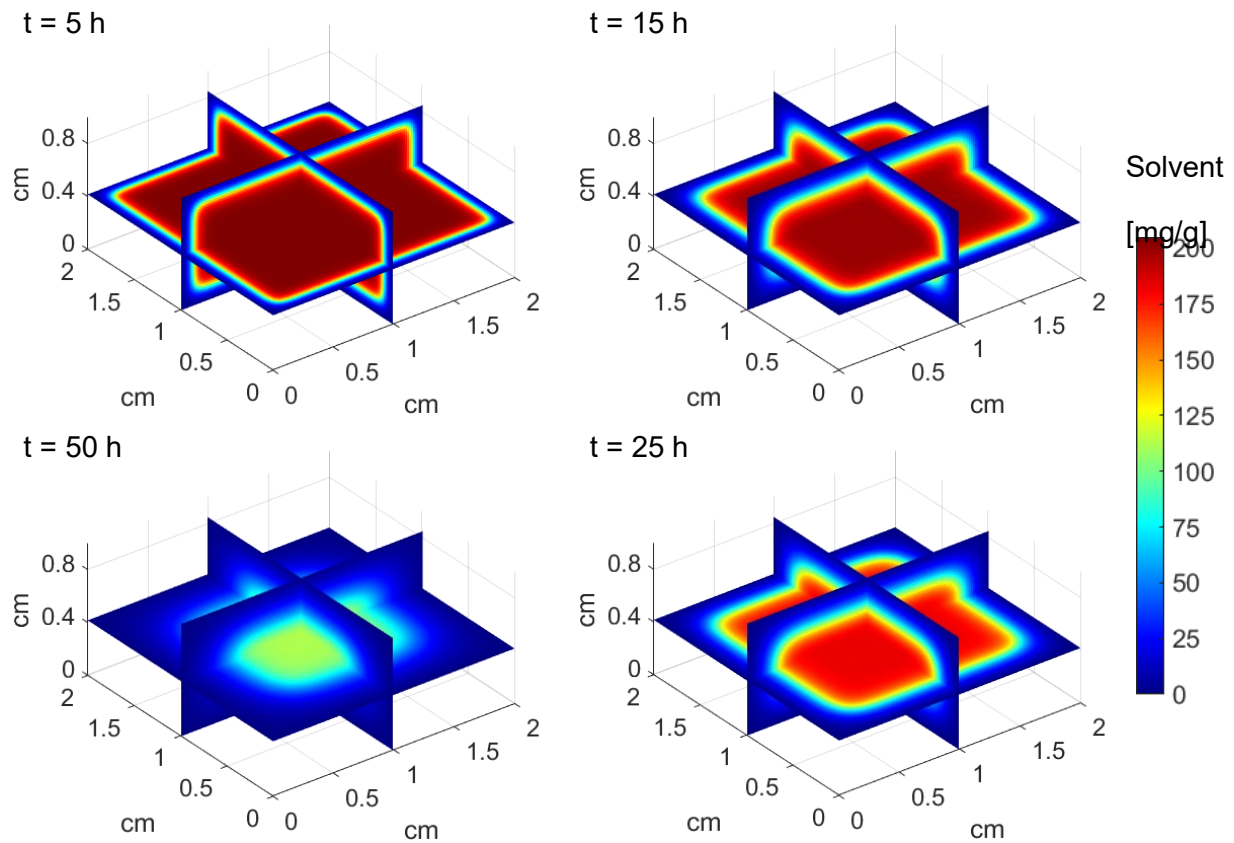


Figure 21: Snapshots of the 3D drying profile of the isopropanol-swollen silicone at 25 °C.<sup>12</sup>

## 5.6 Modeling of an Electronic Device with Heat Sources

In the next step, the diffusion model will be extended to real electronics. Real electronic assemblies are more complex than polymer samples, as they contain heat sources, diffusion barriers, and geometric aspects make it necessary to model them in at least two dimensions. Furthermore, incorporating an inhomogeneous temperature field is essential because such gradients dramatically affect diffusion behavior. The impact of temperature fields on the swelling of polymer matrices was previously studied in one dimension by Krenn et al. [75]; this work will now be extended to two dimensions, representing the architecture of real electronics.

In this study, the surrounding solvent is heptane. For simplicity, only the most critical part of the electronic system, where temperature generation occurs and temperature fields are most relevant, is simulated in two dimensions. The architecture of this section is illustrated in Figure 22.

<sup>12</sup> This figure have already been published in Wagner et al. (2024)

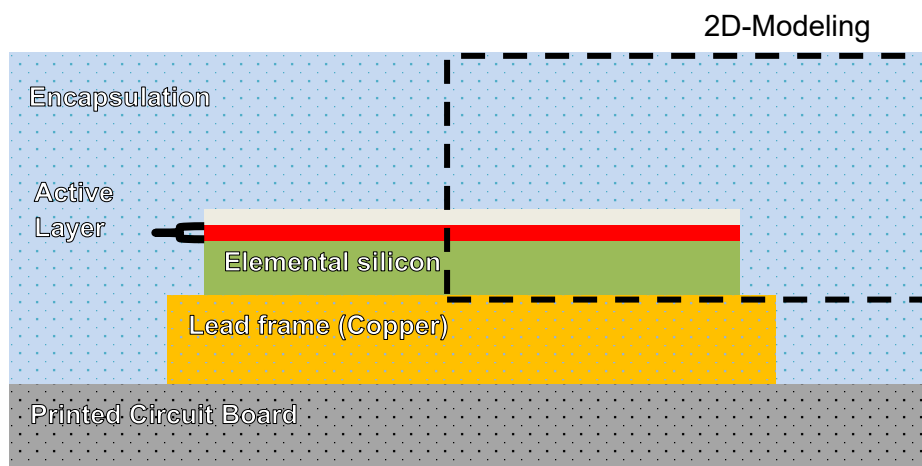


Figure 22: Graphical illustration of the model electronic compound

Because the thermal diffusion coefficient  $D_T$  was not determined, it was set to zero. The grid consists of 52 and 101 points in the x and y directions, respectively, covering the active layer where almost all electrical energy is converted into heat. This layer rests on a silicon substrate 0.23 mm thick, shown as the grey area in the figure. The entire system is encapsulated in 2 mm of epoxy resin, modelled with the same polymer used by Krenn et al. [75]. For the boundary conditions, one edge was mirrored, and the side farther inside the electronic system was simplified as a thin sheet of bulk copper, one grid point thick. This metal layer can release heat to the environment but blocks the solvent. The remaining sides were treated as pure solvent. The electronic system is assumed to generate heat continuously at  $7.71 \text{ W/cm}^2$  in the active layer, indicated by the thin, red band. On top of the active layer, a 20 nm thick aluminum metallization layer is placed, shown as the grey area. Because this layer is so thin, it was combined with the active layer in the simulation and represented by a single grid point thickness.

Table 2 lists the heat flux parameters used for the solvent and the polymer. The polymer contains a filler fraction of 75 % and a filler density of  $2\,330 \text{ kg m}^{-3}$ ; both values were included when calculating the overall density. Because thermal conductivity and heat capacity were reported only for the mixture, the filler was assumed to have the same thermal conductivity and heat capacity as the polymer matrix. Furthermore, the thermal diffusion parameters were kept constant for silicon and copper, as both materials were treated as diffusion barriers.

**Table 8:** Heat flux parameters

|                                        | epoxy resin<br>+ filler [75] | heptane<br>[93] | silicone<br>[93] | copper<br>[93] |
|----------------------------------------|------------------------------|-----------------|------------------|----------------|
| $\lambda \text{ [W/(m}\cdot\text{K)]}$ | 1.125                        | 0.140           | 148              | 327.8          |
| $c_p \text{ [J/(kg}\cdot\text{K)]}$    | 857                          | 224             | 710              | 385            |
| $\rho \text{ [kg/m}^3\text{]}$         | Calc.                        | Calc.           | 2712             | 8940           |

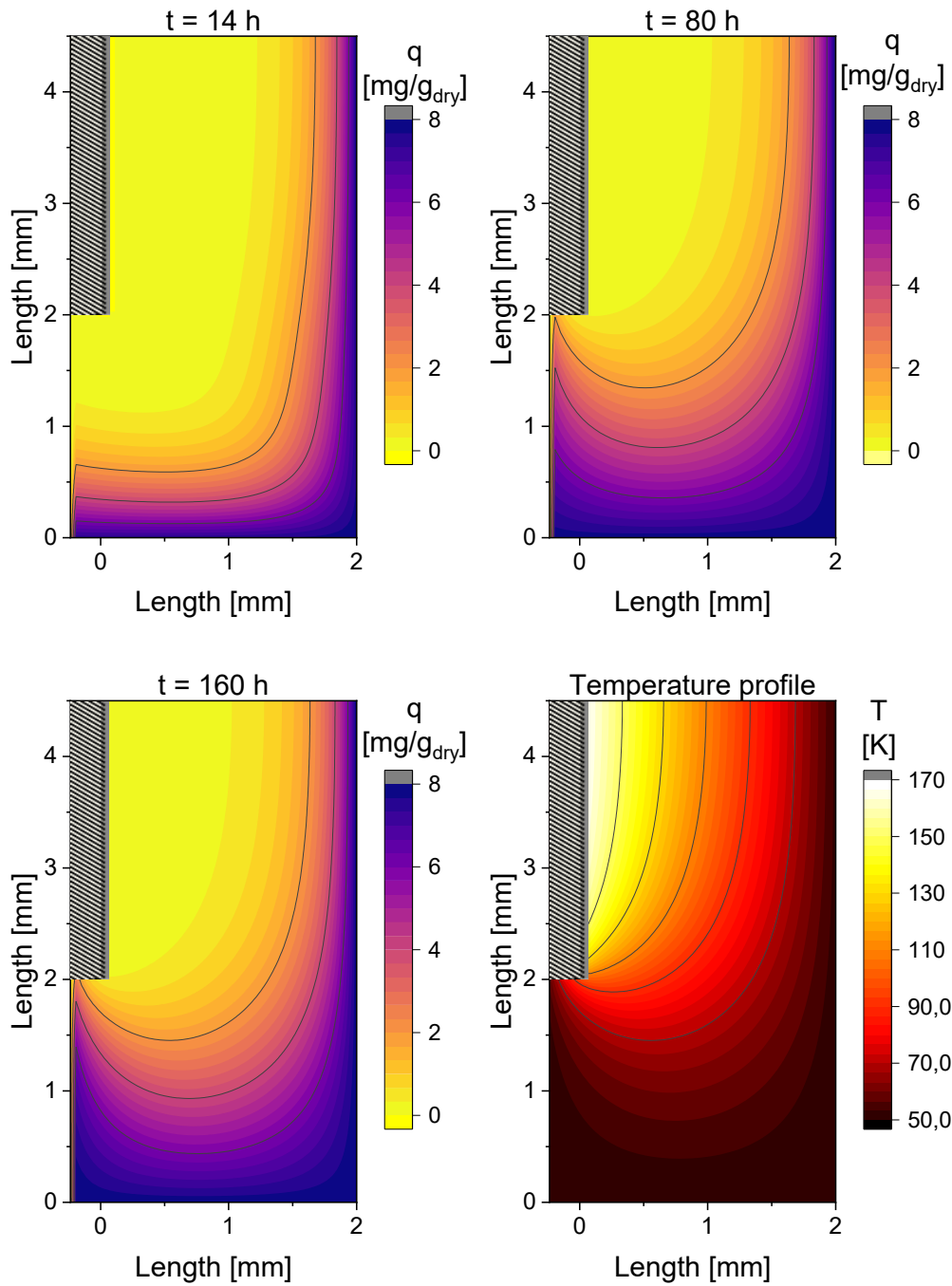


Figure 23: Modeling of electronic encapsulation: The grey area in the left upper corner indicates the bulk silicone region (0.2 mm, 2.5 mm), along with the slightly grey layer, which has a thickness of 40 μm and represents the active layer. A heating power of 7.14 W/cm<sup>2</sup> was assumed.

When the model was initialized with a uniform temperature of 50 °C, a nearly steady, inhomogeneous temperature profile formed within seconds. Over longer times, only minor adjustments occurred because the polymer's thermal properties changed slightly as it absorbed solvent; these variations were negligible for mass transfer. As expected, the hottest region lay close to the active layer, while cooler zones appeared at the surface and near the copper plane, since both released heat to the surroundings.

Although phase equilibrium and diffusion rate increase with temperature [17, 75], swelling is counteracted by thermo-osmosis [98]. The chemical potential rises with temperature, generating a gradient that opposes swelling. After 160 h this interplay produces a stationary swelling profile that is essentially the inverse of the temperature profile. Krenn et al. [75] previously identified the same stationary solvent profile in one dimension. The model also predicts that substantial amounts of solvent can penetrate to sensitive inner layers, potentially causing short circuits and shortening the device's lifetime.

These results underscore the need for multidimensional modelling: simple one-dimensional calculations cannot capture such effects. Extending the approach to three dimensions would likely yield even more accurate predictions, but at a high computational cost-2-D simulations already require much longer than comparable runs with uniform temperature fields. The methodology could also be applied to other problems, such as estimating the service life of chemical sensors in reactors where they face continuously harsh conditions.

## 5.7 Non-Uniform Temperature Fields

Coupling heat flux and mass transfer can be used to predict the drying of a polymer sample in an inhomogeneous temperature field. Assuming an initial thickness of 2.32 mm, the simulation models a swollen polymer sample on a heating plate supplied with a constant heat flux of  $5 \cdot 10^{-5}$  W. A heat source is placed at one edge of a one-dimensional epoxy-resin matrix swollen with heptane, and the calculation starts from a homogeneous temperature distribution. The computational grid comprises 50 nodes. A symmetry condition is imposed at the heat-source side, while a Dirichlet boundary condition is applied at the opposite side to represent a solvent-free polymer. The results are shown in Figure 24.

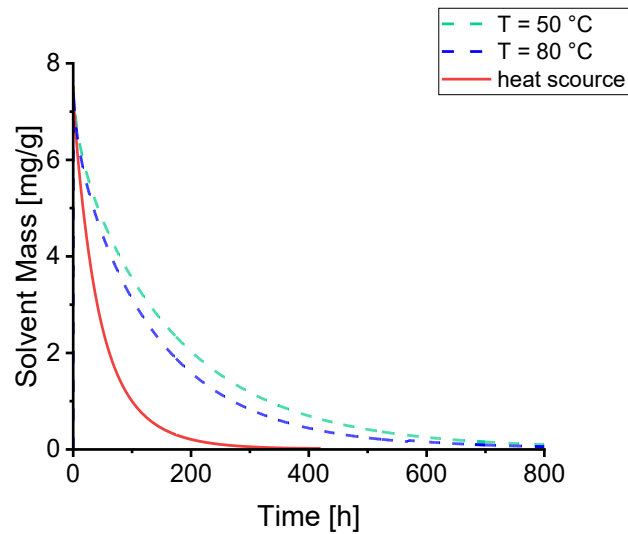


Figure 24: Drying of a polymer in an inhomogeneous temperature field.

An inhomogeneous temperature field markedly accelerates drying compared with a uniform temperature rise. Thermo-osmosis intensifies the chemical-potential gradient that drives the solvent out of the matrix. This effect is the opposite of swelling, where temperature gradients slow diffusion [75]. Temperature snapshots that illustrate the phenomenon are presented in Figure 25.

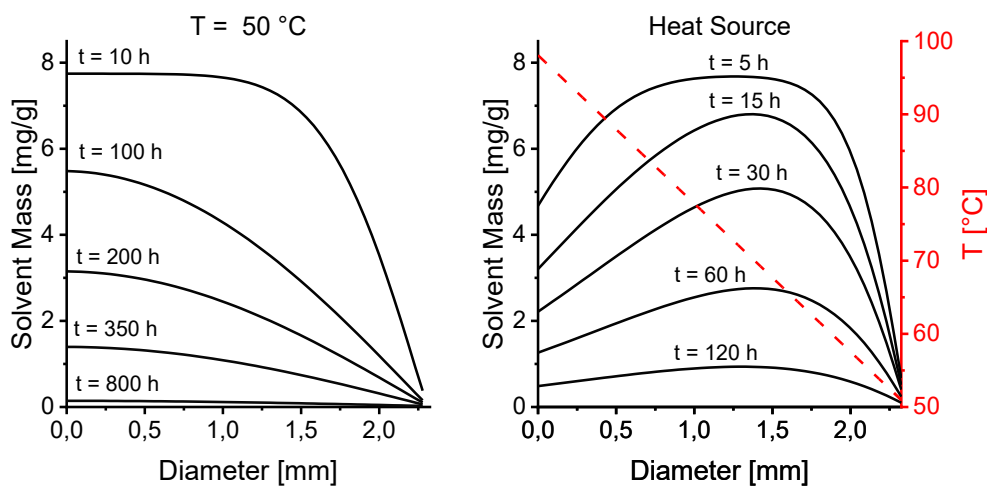


Figure 25: Concentration and temperature profiles at various times for an epoxy resin swollen with heptane.

Near the heat source the solvent content falls rapidly, whereas under isothermal conditions it hardly changes. The impact on mass flux is also apparent, because at certain times the solvent concentration is higher near the phase boundary than in simulations with a homogeneous temperature field.

Now, this study investigates heat flow in different spatial dimensions. As the simplest representative case, a single heat source embedded in a polymer matrix is investigated. Although the experimental realization in all cases technically consists of embedding only one heating element into a polymer, the effective experimental configuration and resulting heat transport behavior differ fundamentally depending on the spatial dimensionality considered.

The primary objective of this study is to elucidate how dimensional effects influence heat transport in systems of different spatial dimensions. In many existing studies, dimensionality is treated in a highly simplified manner. Using this elementary benchmark problem, the present work demonstrates the magnitude of the differences that arise from such simplifications and highlights the potential errors introduced when dimensional effects are neglected. The analysis is restricted exclusively to benchmark calculations, as discussed previously, and does not aim to reproduce specific experimental systems.

In the one-dimensional (1D) case, the configuration corresponds to a planar heating plate embedded in the polymer. Heat transport occurs unidirectionally through the polymer layer, with heat dissipation taking place at the opposite boundary. This setup represents the simplest possible heat conduction scenario and is often implicitly assumed in reduced models. In contrast, the two-dimensional (2D) case models the heat source as a cylindrical or pipe-like element within the polymer matrix. Heat spreads radially outward from the source, and thermal energy is dissipated through the lateral boundaries of the polymer. This geometry already introduces fundamentally different temperature profiles and heat flux distributions compared to the one-dimensional approximation. The three-dimensional (3D) case represents a point-like heat source that is completely surrounded by the polymer matrix. Heat is released uniformly into all spatial directions, corresponding to a localized hot spot within the material. This configuration most closely reflects situations in which heat generation is highly localized and spatial confinement effects become significant. The differences between these dimensional cases and their implications for heat transport behavior are discussed in detail in Figure 26.

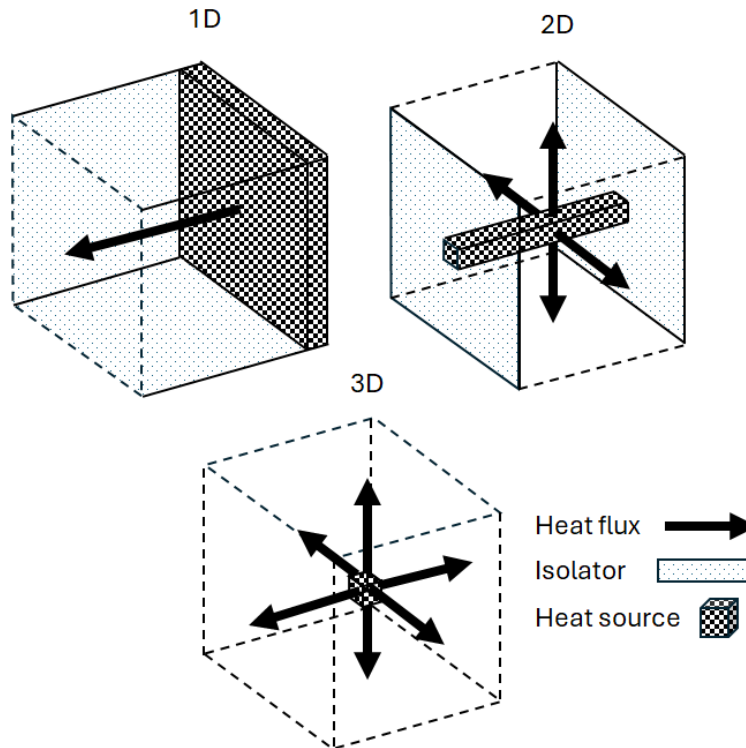


Figure 26: Schematic illustration of the one-, two-, and three-dimensional benchmark heat-transfer configurations

Despite being based on the same fundamental concept, the three configurations give rise to distinct physical systems. Consequently, the heat flux behavior depends strongly on the spatial dimension under consideration. Owing to the different dimensionalities, the manner in which thermal energy is released into the polymer matrix varies significantly. For an identical heating power, markedly different local temperatures are obtained, both in the immediate vicinity of the heat source and throughout the polymer matrix. Thus, the same heating power leads to substantially different temperature levels near the heat source as well as fundamentally different temperature distributions within the material. These differences become particularly pronounced when comparing the one-dimensional and three-dimensional cases, where the use of identical heating powers can result in unrealistically high local temperatures for the 1D case in the vicinity of the heat source. To avoid this issue and to enable a physically meaningful comparison between the different dimensional configurations, the heating power was not chosen to be identical in all cases. Instead, an approximately identical surface temperature was prescribed. Accordingly, the heating rate was adjusted in a dimension-dependent manner such that comparable surface temperatures were achieved for the one-, two-, and three-dimensional systems.

For a consistent comparison across all three spatial dimensions, a common comparison criterion was introduced. Specifically, the distance between the heat source and the polymer surface was fixed. This distance corresponds to 25 grid points, representing a physical length of 5.2 mm. The chosen discretization constitutes a compromise

between computational efficiency and numerical accuracy. The associated distance of 5.2 mm is not motivated by a specific physical system but was selected arbitrarily as a benchmark length scale. Importantly, this distance was chosen to be identical for all dimensional configurations, thereby ensuring a consistent basis for comparison between the 1D, 2D, and 3D cases. In the following, this characteristic distance is referred to as the diameter. Based on these parameters, heat transport is modeled for the different special cases. The simulations start from a fully swollen polymer and terminate once the solvent has completely diffused out of the polymer matrix. Simultaneously, the drying process of the polymer is investigated. The polymer is initially in thermal swelling equilibrium at a temperature of 65 °C and is subsequently dried at the same temperature. The system thus represents a swollen polymer, analogous to the previous example in which thermo-osmosis was discussed for the one-dimensional case.

As in the preceding analysis, heptane is used as the solvent. The polymer surface is maintained at a constant temperature of 65 °C and is subject to the same boundary condition as before, namely the instantaneous release of solvent to the surrounding environment. At the outer boundary of the system, a constant boundary condition with zero solvent concentration is imposed. This boundary condition ensures continuous solvent removal and provides a consistent framework for comparing the drying behavior across different spatial dimensions.

The heat source is operated at a constant heating rate. The heating rates were set to  $1.89362 \cdot 10^{-4}$  W for the one-dimensional case,  $4 \cdot 10^{-3}$  W for the two-dimensional case, and  $2.0 \cdot 10^{-2}$  W for the three-dimensional case. Numerically, the heat source is implemented as a point-like element acting on the corresponding grid point, where the prescribed heating rate is applied. The heat source operates with a constant heating rate throughout the simulation. At each time step, the imposed heating power is converted into a corresponding temperature increase. This conversion explicitly accounts for the material properties of the polymer, including its density, thermal conductivity, and specific heat capacity, thereby ensuring thermodynamically consistent heat generation within the numerical framework.

To reduce computational cost, a mirror plane is introduced directly adjacent to the heat source. The mirror plane is positioned such that it coincides with the system center and lies immediately next to the heat source. Owing to the symmetry of the problem, this approach effectively halves the number of required grid points without affecting the physical validity of the solution. In all dimensional configurations, the heat source is located at the center of the system and serves as the origin for the radial distance considered in the analysis. This consistent placement ensures that the spatial dependence of temperature and heat flux can be compared directly across the one-, two-, and three-dimensional cases.

To begin with, the temperature field and its evolution are investigated employing one-, two-, and three-dimensional simulations. For all considered dimensions, the benchmark simulations indicate that after approximately 400 hours, the temperature distribution no

longer exhibits any significant temporal variation. Beyond this point, the temperature profile remains effectively time-invariant and is independent of changes in the solvent distribution. This observation confirms that a steady-state thermal condition has been reached, and that subsequent variations in the solution composition do not measurably affect the temperature field. Figure 27 illustrates a direct comparison of the temperature distributions for the different dimensional models (1D, 2D, and 3D). In particular, the figure contrasts the temperature profiles obtained after one hour with those after 400 hours, thereby highlighting the transient thermal behavior at early times as well as the convergence toward a steady-state profile at later times.

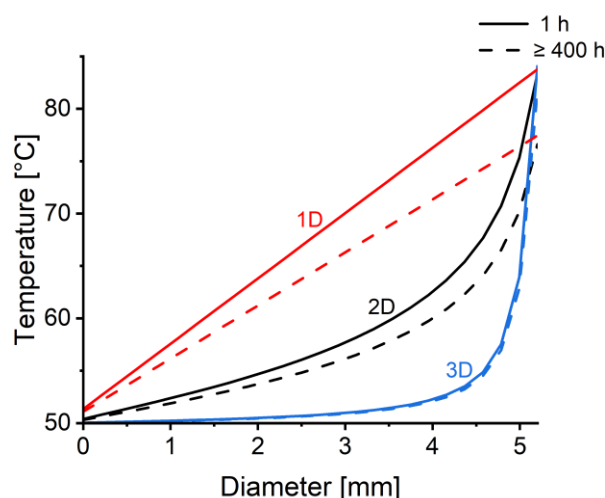


Figure 27: Comparison of Temperature Profiles in 1D, 2D, and 3D Models at Early and Steady-State Conditions

The temperature distributions differ significantly depending on the spatial dimension considered. These differences are evident both in the shape of the temperature profiles and in their temporal evolution. In the one-dimensional (1D) case, the temperature profile exhibits a linear behavior, with the temperature decreasing uniformly from the heat source toward the surface. Heat transport is restricted to a single spatial direction, resulting in a constant temperature gradient. Due to this constrained heat flow, thermal energy cannot dissipate laterally, which leads to comparatively higher temperatures throughout the domain.

In contrast, the two-dimensional (2D) case shows a nonlinear, approximately exponential temperature profile. A pronounced temperature drop occurs in the vicinity of the heat source, while the gradient becomes less steep farther away. In this configuration, heat can dissipate toward the lateral boundaries, providing additional pathways for heat transport. Along the third spatial direction (z-axis), the temperature remains constant, reflecting the reduced dimensional complexity compared to the fully three-dimensional case.

The three-dimensional (3D) model exhibits a strongly nonlinear temperature distribution, characterized by a particularly steep temperature decline near the heat source. In this case, heat can dissipate in all spatial directions, which significantly enhances the local heat flux away from the source. As a consequence, the temperature near the heat source decreases more rapidly than in the lower-dimensional models.

From a physical perspective, these differences can be explained by the increasing number of available heat transport pathways with each additional spatial dimension. Higher dimensionality introduces more degrees of freedom for heat transport, which enhances the local heat flux and leads to a stronger temperature decrease near the heat source. Even more pronounced differences between the models are observed in the temporal evolution of the temperature field.

In the one-dimensional case, the temperature profile exhibits the strongest temporal variation. The temperature distribution evolves significantly over time, indicating a slow approach toward a quasi-stationary state. This pronounced time dependence arises from the limited heat dissipation capacity inherent to the one-dimensional geometry. In the two-dimensional case, the temporal variation of the temperature field is reduced compared to the 1D model but remains clearly observable and relevant. Although lateral heat dissipation accelerates thermal equilibration, time-dependent effects still play an important role in the overall thermal behavior. In the three-dimensional case, the temperature field shows only minor temporal changes. The temperature profile is nearly time-invariant, indicating a rapid establishment of a quasi-stationary thermal state. The enhanced heat dissipation in all spatial directions results in a stronger initial temperature drop, which reduces the impact of later temporal effects.

This behavior can be explained by the interplay between spatial dimensionality, heat dissipation, and solvent transport. With increasing dimensionality, the relative surface area available for heat release decreases, while the efficiency of heat dissipation increases. As a result, the temperature near the heat source drops more rapidly, and the feedback effect of solvent flow becomes increasingly localized. Since the solvent is transported away relatively quickly and the region near the heat source becomes comparatively dry, temperature variations diminish faster in higher-dimensional systems ( $3D > 2D > 1D$ ). Consequently, the influence of late-time effects is reduced, and the system approaches a quasi-stationary state more rapidly.

It should be noted that the term stationary is not strictly accurate, as minor temporal changes persist. However, these changes are negligible with respect to their influence on solvent transport and can therefore be considered insignificant for the coupled thermal and mass flux behavior. As a consequence, higher-dimensional models lead to a faster establishment of a quasi-stationary temperature state, while time-dependent effects dominate primarily in dimensionally simplified systems. Lower-dimensional models may therefore distort the temperature distribution and should be applied with caution when transient thermal effects are of interest.

The results of the solvent concentration analysis as a function of spatial dimensionality are presented in Figure 28. Shown are the concentration profiles after 50 hours and after 400 hours, allowing the temporal evolution of the solvent distribution to be examined in detail.

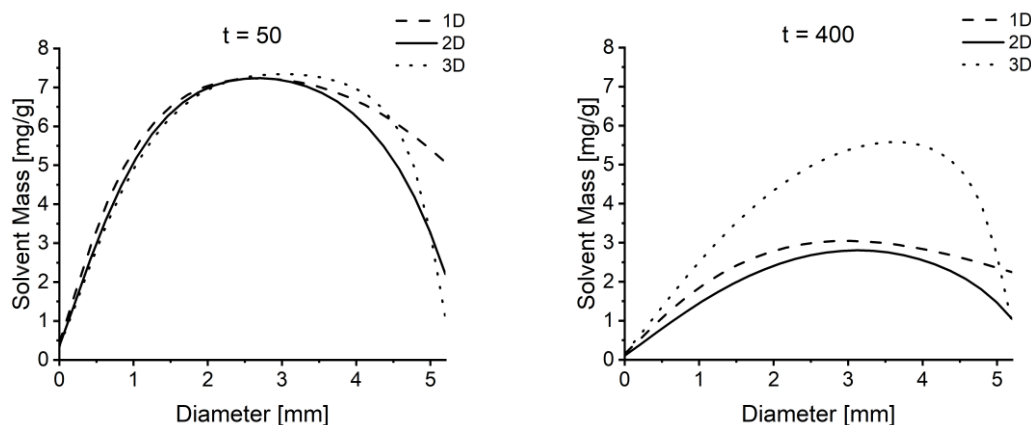


Figure 28: Solvent concentration profiles as a function of spatial dimension after 50 h and 400 h.

After 50 hours, two physical mechanisms act simultaneously. On the one hand, the solvent diffuses toward the polymer boundaries, leading to a gradual loss of solvent from the system. On the other hand, the presence of the heat source induces a thermal displacement of the solvent. At the polymer surface, a slight increase in the reduction of solvent concentration with increasing spatial dimensionality is observed, following the order  $1D < 2D < 3D$ . However, at this early time, this dimensional effect remains weak compared to the dominant influence of the heat source itself. In the immediate vicinity of the heat source, a clearer dependence on dimensionality becomes apparent. With increasing dimension, the solvent concentration decreases more strongly, with the effect being most pronounced in the three-dimensional case. Moving away from the heat source, the concentration profiles increased as the spatial dimension increases. In the one-dimensional case, the concentration rises relatively gradually and reaches a maximum at approximately 2 mm from the heat source. In contrast, the three-dimensional case exhibits a significantly steeper increase. From a physical perspective, the qualitative shape of the solvent concentration profile closely follows the temperature distribution. Temperature gradients give rise to gradients in the chemical potential,

which in turn drive solvent transport. As a consequence, temperature and concentration profiles exhibit qualitatively similar spatial behavior after 50 hours.

After 400 hours, the previously observed patterns change substantially, and the solvent distributions differ between the spatial dimensions. The overall remaining solvent content shows a clear ordering: the three-dimensional system retains the highest solvent amount, the two-dimensional system exhibits the lowest, and the one-dimensional system lies in between, with a slightly higher solvent content than in the two-dimensional case. This behavior results from the competition between two opposing processes: thermal displacement of the solvent induced by the heat source and diffusive transport of the solvent toward the polymer boundaries.

In the three-dimensional case, the relative influence of the heat source becomes the weakest, as the supplied thermal energy is distributed over a larger polymer volume. Consequently, the thermally induced displacement of the solvent is comparatively small. At the same time, diffusion toward the polymer boundaries is most efficient due to the higher number of available transport pathways. Overall, however, the weak influence of the heat source dominates, resulting in the highest remaining solvent content after 400 hours. In the two-dimensional case, the total solvent loss is largest. Here, the energy input from the heat source is higher than in three dimensions, while diffusive transport to the boundaries is more efficient than in one dimension. Both effects act simultaneously and most effectively in this geometry, leading to the strongest overall solvent depletion.

In the one-dimensional case, the energy input per polymer volume is highest, and the thermally induced solvent displacement is therefore particularly strong in principle. However, subsequent mass transport is severely limited by geometric constraints. Diffusion toward the boundaries can occur only along a single spatial direction, resulting in the smallest number of available transport pathways. As a consequence, the removal of the displaced solvent is significantly slowed. Compared to the two-dimensional case, the effective solvent flux toward the boundaries is smaller, leading to a higher remaining solvent content despite the stronger energy input.

In summary, the observed ordering of remaining solvent content after 400 hours, namely  $3D > 1D > 2D$ , arises from the interplay between the energy input from the heat source and the geometry-dependent diffusion pathways. Spatial dimensionality significantly influences both the strength and the temporal evolution of these competing effects.

These findings have important implications for the interpretation of dimension-dependent simulations and experiments. Without explicit consideration of geometric differences, comparisons between one-, two-, and three-dimensional models may lead to misleading conclusions. A careful, dimension-aware analysis is therefore essential when interpreting solvent transport phenomena in polymer systems.

Figure 29 provides a direct comparison between two-dimensional (2D) and three-dimensional (3D) simulations based on a representative cross-sectional view. The purpose of this figure is to complement the preceding analysis by directly contrasting the temperature and solvent mass distributions obtained from both modeling approaches.

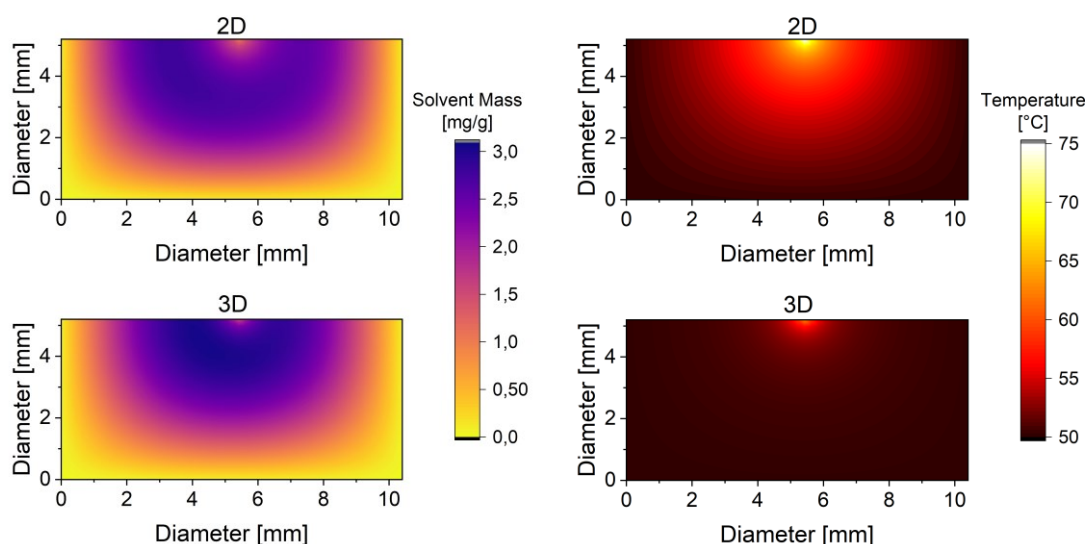


Figure 29: Comparison of the cross-sectional temperature distribution and solvent mass between the two-dimensional (2D) and three-dimensional (3D) models. The cross section represents a cut through the polymer matrix from the heat source to the outer surface at 400 h.

The selected cross section corresponds to a plane cutting transversely through the polymer matrix, allowing for a consistent spatial comparison between the 2D and 3D cases. This perspective enables a clear assessment of dimensional effects on the coupled transport phenomena.

The results shown in this comparison confirm and further substantiate the observations discussed previously. In terms of temperature distribution, the 2D simulation exhibits a noticeably broader spread of elevated temperatures in the immediate vicinity of the heat source. In contrast, the 3D simulation reveals a more pronounced temperature decay with increasing distance from the heat source, indicating enhanced spatial dissipation in three dimensions. The solvent distribution follows the temperature field qualitatively in both cases, reflecting the strong coupling between thermal and mass transport processes. The direct cross-sectional comparison clearly demonstrates that both temperature and solvent distributions are more strongly localized in the 2D case than in the 3D case.

Overall, these findings underscore the significant influence of spatial dimensionality on coupled heat and mass transport. The comparison highlights that reduced-dimensional models tend to overemphasize localization effects, whereas three-dimensional simulations capture a more realistic spatial attenuation of temperature and solvent concentration fields.



## 6 Conclusion and Outlook

In this thesis, a thermodynamic consistent framework for the description of swelling and drying in highly cross-linked polymer systems was extended and validated on the basis of experimental and theoretical investigations. The developed approach combines the PC-SAFT equation of state with Maxwell–Stefan diffusion and a viscoelastic description in order to represent equilibrium swelling, diffusion kinetics, geometric effects, and the influence of non-uniform temperature conditions within a unified framework. The methodology was applied to different polymer classes and transferred to multidimensional as well as application-oriented systems. Thereby, the work addressed the central objective formulated in the introduction, namely to assess whether solvent transport in highly cross-linked polymers can be described consistently across different material systems and increasingly realistic operating conditions.

The results show that the existing framework can be transferred to different highly cross-linked polymer classes as well as to different solvents and is capable of consistently describing the swelling and diffusion behavior of the investigated systems. The PC-SAFT-based model represented the measured swelling equilibria with high agreement, while the observed differences between the polymer–solvent systems were captured in a physically meaningful manner. In this context, polymers with a higher crosslink density exhibited, at least qualitatively, lower solvent uptake and slower diffusion, indicating that the framework also reflects the expected influence of network structure on transport and sorption behavior. The study shows that the transferability of the framework does not remove the need for a minimum experimental basis. In order to account reliably for temperature dependence, at least two experimental data points are required for swelling and at least two for diffusion for each polymer–solvent system. Overall, the investigation of all polymer–solvent systems revealed that a similar polarity of polymer and solvent results in increased solvent uptake, and that this trend can be reproduced by the model. Epoxy resins and phenolic resins generally showed lower solvent uptake than silicones and polyurethanes. This behavior is most likely associated with their filler content, although crosslink density also appears to play a crucial role. In particular, phenolic resins were likely more highly cross-linked than epoxy resins. However, because filler content also strongly affects the uptake behavior, the individual contributions of these factors cannot yet be clearly separated. The present study demonstrates that experimental investigations may be challenging, as the samples occasionally showed chemical and mechanical degradation, particularly in terms of volumetric expansion. This underlines the advantage of modeling approaches, which allow the behavior to be described over a broad temperature range even in cases where experiments are difficult to perform or evaluate reliably.

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Furthermore, the results demonstrated that the transfer of findings from one-dimensional descriptions to multidimensional systems is only possible to a limited extent and must always be evaluated in relation to the underlying transport mechanism and the actual sample geometry. The comparison of one-, two-, and three-dimensional models demonstrates that geometric simplifications can substantially affect the physical interpretation of solvent transport, particularly when diffusion parameters are identified by fitting simulation results to experimental data. In this respect, the study makes clear that the apparent agreement of a simplified model with measurements does not necessarily imply a physically reliable description, because fitted parameters may partly compensate for missing geometric information. The three-dimensional representation proved to provide the most realistic description of solvent transport, as it incorporates all relevant geometric features of the sample. By contrast, a reduction to lower-dimensional representations may lead to substantial distortion of this parameter, with deviations from the three-dimensional result of approximately 28% for the two-dimensional model and 29% for the one-dimensional model. The results indicate that the necessity of multidimensional modeling is not universal but depends strongly on the dominant diffusion regime. Diffusion-controlled flux is more sensitive to geometric effects, whereas transport controlled by polymer chain relaxation is less strongly affected, since viscoelastic contributions are primarily localized near the boundary. Consequently, the relevance of geometric extension increases whenever the transport process is governed by mechanisms that respond sensitively to spatial gradients and shape-dependent effects. From a methodological perspective, this means that lower-dimensional models may still be acceptable in specific benchmark situations or for reduced fitting purposes, especially when geometric effects remain small or when robust scaling relations between simplified and more realistic cases can be established. However, such use must be justified carefully and should not be generalized beyond the investigated conditions. For reliable predictive modeling, especially in application-oriented contexts involving complex component geometries, higher-dimensional approaches offer clear advantages because they enable a more realistic representation of the physical system and improve the interpretability of the identified diffusion parameters.

The developed framework was further extended to drying and to solvent transport under non-uniform temperature conditions in application-relevant systems. The results showed that drying cannot be transferred directly from swelling in a purely predictive manner without additional consideration of boundary effects, since the diffusion coefficients identified from swelling did not reproduce the drying behavior satisfactorily. Applying swelling-based coefficients to drying overestimated the drying rate by a factor of about 1.33 unless the diffusion coefficient was refitted. According to the discussion, this discrepancy is attributed primarily to neglected interfacial or surface-transport effects caused by the idealized Dirichlet boundary condition. This deviation arises because desorption is associated with a phase transition from the polymer phase to the gas phase, whereas swelling corresponds to mass transfer from the liquid phase into the polymer phase using the penetrating solvent. Therefore, the treatment of the phase boundary requires a more detailed description in the case of drying in order to capture

both phenomena consistently. In addition, the investigation of inhomogeneous temperature fields showed that thermal gradients have a pronounced influence on local equilibrium conditions and transport kinetics. Depending on the direction of transport, heat flux was found to retard swelling and accelerate drying, thereby affecting both the spatial and temporal evolution of solvent transport. The transfer of the framework to an encapsulated electronic component demonstrated that the combined treatment of heat and mass transport can be used to identify critical regions and characteristic exposure behavior under solvent exposure. Solvent accumulated rapidly at the corners of the device, while heat generation protected the sensitive inner regions through thermosmotic effects; nevertheless, a small amount of solvent penetrated critical areas along the edges where temperature gradients were weaker.

In summary, this work establishes a unified framework for the description of swelling and drying in highly cross-linked polymer systems that consistently links thermodynamic equilibrium, diffusion kinetics, viscoelastic effects, multidimensional geometry, and non-uniform temperature fields. In this way, the thesis answers the research questions posed in the introduction and demonstrates that a reliable representation of solvent transport in such systems requires the simultaneous consideration of material-specific, geometric, and thermal influences. The developed approach therefore contributes to a more comprehensive understanding of solvent transport in highly cross-linked polymers and provides a basis for the transfer of such models to technically relevant systems.

Future work could proceed in several directions based on the results of this study. Future studies could aim to measure the Soret and Dufour coefficients directly. This might be achieved by comparing drying rates on a heated surface with those at constant temperature, where the observed differences could be used to determine the values. Furthermore, the drying model should be extended to capture the phase transition, thereby reducing discrepancies between the diffusion coefficients derived from swelling and drying experiments. An approach based on a penetration model, coupled with a thermodynamic model at the sample surface, may be promising. Additional studies could also address the effect of solvent mixtures during swelling, since the present measurements were carried out only with pure solvents. Future studies could use special synthesized epoxy resins and phenolic resins, allowing PC-SAFT parameters to be determined without uncertainties arising from unknown crosslinker or filler contributions. Finally, establishing a correlation between crosslinking density and diffusion speed could provide a pathway for predicting diffusion coefficients.



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# Appendix

## Model Constants PC-SAFT

Table A - 1: Universal Model Constants for PC-SAFT EOS

| i | $a_{0i}$    | $a_{1i}$    | $a_{2i}$    | $b_{0i}$      | $b_{1i}$      | $b_{1i}$      |
|---|-------------|-------------|-------------|---------------|---------------|---------------|
| 0 | 0.91056314  | -0.30840169 | -0.09061484 | 0.7240946941  | -0.5755498075 | 0.0976883116  |
| 1 | 0.63612814  | 0.18605312  | 0.45278428  | 2.2382791861  | 0.6995095521  | -0.2557574982 |
| 2 | 2.68613479  | -2.50300473 | 0.59627007  | -4.0025849485 | 3.8925673390  | -9.1558561530 |
| 3 | -26.5473625 | 21.4197936  | -1.72418291 | -21.003576815 | -17.215471648 | 20.642075974  |
| 4 | 97.7592088  | -65.2558853 | -4.13021125 | 26.855641363  | 192.67226447  | -38.804430052 |
| 5 | -159.591541 | 83.3186805  | 13.7766319  | 206.55133841  | -161.82646165 | 93.626774077  |
| 6 | 91.2977741  | -33.7469229 | -8.67284704 | -355.60235612 | -165.20769346 | -29.666905585 |

Table A - 2: Model Constants of the Dipole Equation-of-State Contribution for PCP-SAFT EOS

| i | $a_{0i}$   | $a_{1i}$   | $a_{2i}$   | $b_{0i}$   | $b_{1i}$   | $b_{1i}$   |
|---|------------|------------|------------|------------|------------|------------|
| 0 | 0.3043504  | 0.9534641  | -1.1610080 | 0.2187939  | -0.5873164 | 3.4869576  |
| 1 | -0.1358588 | -1.8396383 | 4.5258607  | -1.1896431 | 1.2489132  | -14.915974 |
| 2 | 1.4493329  | 2.0131180  | 0.9751222  | 1.1626889  | -0.5085280 | 15.372022  |
| 3 | 0.3556977  | -7.3724958 | -12.281038 | 0          | 0          | 0          |
| 4 | -2.0653308 | 8.2374135  | 5.9397575  | 0          | 0          | 0          |

## Tabulated Experimental and Model Data

### Silicon

Table A - 3: Experimental and calculated values for silicone in toluene at 50 °C with sample thicknesses of 8.27 mm and 20.3 mm.

| time  | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|-------|----------------------------|----------------------------|-----------------------------|
| [h]   | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00  | 0.00                       | 0.00                       | 0.00                        |
| 1.42  | 489.80                     | 25.01                      | 392.25                      |
| 4.18  | 826.13                     | 27.01                      | 786.12                      |
| 5.17  | 885.33                     | 25.05                      | 884.92                      |
| 6.59  | 941.70                     | 21.36                      | 983.21                      |
| 8.28  | 997.95                     | 18.27                      | 1043.41                     |
| 9.75  | 1030.39                    | 17.45                      | 1065.35                     |
| 11.48 | 1053.43                    | 11.39                      | 1081.85                     |
| 12.97 | 1065.69                    | 7.87                       | 1103.84                     |
| 14.33 | 1076.42                    | 8.76                       | 1123.92                     |
| 15.67 | 1078.35                    | 5.76                       | 1143.60                     |

Table A - 4: Experimental and calculated values for silicone in toluene at 65 °C with sample thicknesses of 8.84 mm and 21.3 mm.

| time  | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|-------|----------------------------|----------------------------|-----------------------------|
| [h]   | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00  | 0.00                       | 0.00                       | 0.00                        |
| 1.30  | 536.81                     | 20.07                      | 403.50                      |
| 3.85  | 861.95                     | 25.69                      | 814.10                      |
| 4.82  | 925.26                     | 24.27                      | 918.08                      |
| 6.53  | 996.99                     | 19.07                      | 1026.66                     |
| 8.18  | 1037.93                    | 14.34                      | 1067.02                     |
| 9.47  | 1069.17                    | 9.75                       | 1078.46                     |
| 11.19 | 1075.01                    | 7.67                       | 1085.57                     |
| 12.67 | 1083.34                    | 1.60                       | 1091.98                     |
| 14.05 | 1085.16                    | 4.90                       | 1097.93                     |
| 15.58 | 1092.80                    | 1.19                       | 1104.55                     |

Table A - 5: Experimental and calculated values for silicone in toluene at 80 °C with sample thicknesses of 8.12 mm and 19.2 mm.

| time  | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|-------|----------------------------|----------------------------|-----------------------------|
| [h]   | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00  | 0.00                       | 0.00                       | 0.00                        |
| 0.93  | 489.82                     | 26.20                      | 388.15                      |
| 3.44  | 931.68                     | 24.08                      | 884.32                      |
| 4.57  | 982.49                     | 20.29                      | 998.00                      |
| 6.52  | 1046.17                    | 14.40                      | 1071.43                     |
| 8.18  | 1075.44                    | 5.30                       | 1085.41                     |
| 9.18  | 1078.88                    | 5.79                       | 1091.34                     |
| 10.97 | 1080.91                    | 5.07                       | 1101.93                     |
| 12.46 | 1084.69                    | 1.11                       | 1110.78                     |
| 13.82 | 1084.28                    | 2.29                       | 1118.86                     |
| 15.57 | 1087.02                    | 1.94                       | 1129.25                     |

Table A - 6: Experimental and calculated values for silicone in acetone at -10 °C with sample thicknesses of 8.91 mm and 20.7 mm.

| time   | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|--------|----------------------------|----------------------------|-----------------------------|
| [h]    | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00   | 0.00                       | 0.00                       | 0.00                        |
| 1.37   | 47.86                      | 1.01                       | 58.78                       |
| 2.76   | 72.05                      | 0.78                       | 80.26                       |
| 4.07   | 84.77                      | 1.02                       | 93.04                       |
| 5.79   | 96.38                      | 1.66                       | 104.03                      |
| 7.52   | 105.75                     | 1.19                       | 111.21                      |
| 8.69   | 112.97                     | 1.05                       | 114.70                      |
| 10.50  | 119.26                     | 0.72                       | 118.60                      |
| 11.99  | 123.69                     | 0.60                       | 120.87                      |
| 13.39  | 127.39                     | 0.54                       | 122.48                      |
| 14.89  | 128.35                     | 0.79                       | 123.77                      |
| 16.22  | 131.70                     | 0.74                       | 124.64                      |
| 27.76  | 139.40                     | 0.27                       | 127.36                      |
| 54.89  | 143.42                     | 1.19                       | 127.73                      |
| 77.96  | 142.47                     | 0.15                       | 127.74                      |
| 193.33 | 136.95                     | 0.33                       | 127.74                      |
| 209.77 | 133.62                     | 0.90                       | 127.74                      |

Table A - 7: Experimental and calculated values for silicone in acetone at 50 °C with sample thicknesses of 7.65 mm and 22.2 mm.

| time  | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|-------|----------------------------|----------------------------|-----------------------------|
| [h]   | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00  | 0.00                       | 0.00                       | 0.00                        |
| 1.15  | 159.37                     | 10.54                      | 159.85                      |
| 2.75  | 240.21                     | 12.14                      | 247.21                      |
| 3.98  | 292.82                     | 12.99                      | 288.10                      |
| 5.37  | 318.46                     | 12.26                      | 317.34                      |
| 7.07  | 337.92                     | 11.01                      | 338.04                      |
| 8.83  | 350.93                     | 11.03                      | 349.02                      |
| 9.94  | 359.21                     | 12.54                      | 352.87                      |
| 11.78 | 365.96                     | 12.62                      | 356.40                      |
| 13.27 | 373.84                     | 12.82                      | 357.83                      |
| 14.64 | 375.54                     | 13.42                      | 358.55                      |
| 16.20 | 373.20                     | 12.62                      | 358.99                      |
| 17.51 | 377.79                     | 12.57                      | 359.19                      |
| 29.30 | 377.69                     | 11.55                      | 359.46                      |
| 56.40 | 378.98                     | 12.37                      | 359.47                      |
| 79.25 | 377.69                     | 11.97                      | 359.47                      |
| 98.06 | 375.61                     | 12.04                      | 359.47                      |

Table A - 8: Experimental and calculated values for silicone in isopropanol at 50 °C with sample thicknesses of 8.5 mm 20.0 mm.

| time   | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|--------|----------------------------|----------------------------|-----------------------------|
| [h]    | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0      | 0                          | 0                          | 0                           |
| 0.82   | 54.47                      | 0.84                       | 44.65                       |
| 2.15   | 93.57                      | 1.74                       | 76.35                       |
| 3.05   | 110.07                     | 2.12                       | 92.16                       |
| 3.63   | 118.36                     | 2.18                       | 101.12                      |
| 4.25   | 126.16                     | 2.16                       | 109.91                      |
| 5.07   | 137.45                     | 2.80                       | 120.56                      |
| 5.97   | 148.11                     | 2.74                       | 131.24                      |
| 6.97   | 159.38                     | 2.98                       | 142.11                      |
| 7.77   | 166.90                     | 3.19                       | 150.18                      |
| 8.82   | 175.28                     | 2.87                       | 160.07                      |
| 9.80   | 180.23                     | 3.42                       | 168.67                      |
| 10.87  | 188.80                     | 3.21                       | 177.46                      |
| 12.38  | 197.02                     | 2.93                       | 188.91                      |
| 14.47  | 209.46                     | 2.87                       | 203.20                      |
| 16.62  | 220.92                     | 3.15                       | 216.28                      |
| 18.88  | 230.19                     | 2.70                       | 228.47                      |
| 21.07  | 237.82                     | 3.34                       | 238.96                      |
| 24.27  | 246.77                     | 2.95                       | 252.19                      |
| 25.13  | 251.62                     | 2.63                       | 255.35                      |
| 27.35  | 257.83                     | 2.45                       | 262.83                      |
| 28.92  | 263.48                     | 3.18                       | 267.55                      |
| 31.23  | 265.03                     | 2.52                       | 273.70                      |
| 105.30 | 306.50                     | 0.30                       | 306.69                      |
| 121.53 | 309.26                     | 0.83                       | 306.74                      |

Table A - 9: Experimental and calculated values for silicone in isopropanol at 65°C with sample thicknesses of 8.5 mm 20.0 mm.

| time   | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|--------|----------------------------|----------------------------|-----------------------------|
| [h]    | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0      | 0                          | 0                          | 0                           |
| 0.92   | 77.00                      | 2.23                       | 72.32                       |
| 2.27   | 137.19                     | 0.86                       | 119.09                      |
| 3.18   | 158.85                     | 0.71                       | 142.85                      |
| 3.77   | 171.66                     | 0.63                       | 156.46                      |
| 4.30   | 181.75                     | 1.15                       | 167.79                      |
| 5.22   | 199.65                     | 0.81                       | 185.84                      |
| 6.10   | 213.34                     | 0.89                       | 201.55                      |
| 7.08   | 226.26                     | 0.85                       | 217.57                      |
| 7.92   | 237.11                     | 1.50                       | 230.24                      |
| 8.98   | 250.09                     | 2.06                       | 245.01                      |
| 9.88   | 251.10                     | 3.35                       | 256.59                      |
| 11.00  | 266.94                     | 1.76                       | 269.87                      |
| 12.50  | 277.60                     | 1.94                       | 285.85                      |
| 14.60  | 294.32                     | 1.95                       | 305.08                      |
| 16.77  | 307.90                     | 2.87                       | 321.47                      |
| 18.98  | 318.27                     | 2.17                       | 334.94                      |
| 21.22  | 328.36                     | 2.66                       | 345.70                      |
| 23.75  | 340.93                     | 1.56                       | 354.94                      |
| 25.30  | 344.34                     | 2.22                       | 359.33                      |
| 27.50  | 352.42                     | 2.23                       | 364.24                      |
| 29.03  | 356.72                     | 2.07                       | 366.89                      |
| 31.35  | 358.34                     | 2.26                       | 370.00                      |
| 105.63 | 380.90                     | 2.17                       | 373.26                      |
| 121.92 | 380.46333                  | 1.2211                     | 373.25854                   |

Table A - 10: Experimental and calculated values for silicone in isopropanol at 80 °C with sample thicknesses of 8.5 mm 20.0 mm.

| time  | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|-------|----------------------------|----------------------------|-----------------------------|
| [h]   | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0     | 0                          | 0                          | 0                           |
| 0.98  | 114.62                     | 2.14                       | 102.53                      |
| 2.35  | 194.15                     | 2.20                       | 166.33                      |
| 3.22  | 224.80                     | 2.43                       | 197.42                      |
| 3.87  | 242.91                     | 1.84                       | 217.99                      |
| 4.40  | 255.00                     | 1.93                       | 233.47                      |
| 5.32  | 278.87                     | 2.56                       | 258.08                      |
| 6.18  | 295.17                     | 2.04                       | 278.87                      |
| 7.13  | 311.67                     | 2.08                       | 299.67                      |
| 8.02  | 327.40                     | 2.82                       | 317.27                      |
| 9.05  | 339.46                     | 1.90                       | 335.56                      |
| 9.95  | 342.67                     | 3.78                       | 349.79                      |
| 11.05 | 351.96                     | 6.97                       | 365.11                      |
| 12.58 | 371.72                     | 2.68                       | 382.90                      |
| 14.65 | 390.34                     | 1.55                       | 401.22                      |
| 16.85 | 404.93                     | 1.99                       | 414.78                      |
| 19.05 | 415.21                     | 1.59                       | 423.77                      |
| 21.32 | 420.86                     | 1.96                       | 429.72                      |
| 23.85 | 433.70                     | 1.30                       | 433.75                      |
| 25.38 | 434.97                     | 1.61                       | 435.31                      |
| 27.58 | 442.20                     | 1.41                       | 436.80                      |
| 29.10 | 439.35                     | 1.86                       | 437.48                      |
| 31.43 | 439.22                     | 1.17                       | 438.17                      |

Table A - 11: Experimental and calculated values for silicone in heptane at 50 °C with sample thicknesses of 8.5 mm 20.0 mm.

| time   | Exp. Solvent Absorption | Exp. Standard Deviation | Calc. Solvent Absorption |
|--------|-------------------------|-------------------------|--------------------------|
| [h]    | [mg/g]                  | [mg/g]                  | [mg/g]                   |
| 0.00   | 0.00                    | 0.00                    | 0.00                     |
| 0.22   | 222.76                  | 11.03                   | 165.67                   |
| 0.47   | 323.19                  | 11.93                   | 261.35                   |
| 0.73   | 400.58                  | 14.83                   | 341.74                   |
| 0.97   | 464.89                  | 15.35                   | 407.37                   |
| 1.20   | 509.16                  | 16.65                   | 464.48                   |
| 1.76   | 624.42                  | 13.12                   | 591.61                   |
| 2.20   | 692.01                  | 18.67                   | 676.45                   |
| 2.60   | 734.60                  | 21.86                   | 741.83                   |
| 16.23  | 839.26                  | 13.05                   | 910.22                   |
| 62.90  | 905.17                  | 8.84                    | 910.22                   |
| 203.62 | 900.33                  | 3.33                    | 910.22                   |
| 377.12 | 902.12                  | 5.70                    | 910.22                   |

Table A - 12: Experimental and calculated values for silicone in heptane at 65 °C with sample thicknesses of 8.5 mm 20.0 mm.

| time   | Exp. Solvent Absorption | Exp. Standard Deviation | Calc. Solvent Absorption |
|--------|-------------------------|-------------------------|--------------------------|
| [h]    | [mg/g]                  | [mg/g]                  | [mg/g]                   |
| 0.00   | 0.00                    | 0.00                    | 0.00                     |
| 0.22   | 227.44                  | 20.72                   | 168.88                   |
| 0.47   | 326.14                  | 19.43                   | 270.74                   |
| 0.70   | 402.63                  | 22.29                   | 343.71                   |
| 0.96   | 470.29                  | 23.48                   | 416.80                   |
| 1.21   | 524.94                  | 26.47                   | 481.63                   |
| 1.69   | 626.25                  | 10.59                   | 592.69                   |
| 2.21   | 702.38                  | 19.90                   | 693.70                   |
| 2.71   | 753.14                  | 21.97                   | 765.89                   |
| 3.97   | 839.94                  | 13.67                   | 854.75                   |
| 5.10   | 868.17                  | 1.65                    | 873.94                   |
| 6.13   | 869.39                  | 1.38                    | 877.79                   |
| 6.20   | 869.53                  | --                      | 877.91                   |
| 24.92  | 881.28                  | 10.47                   | 878.92                   |
| 73.62  | 889.05                  | 3.77                    | 878.92                   |
| 214.36 | 868.61                  | 5.31                    | 878.92                   |
| 387.84 | 878.41                  | 3.19                    | 878.92                   |

Table A - 13: Experimental and calculated values for silicone in heptane at 80 °C with sample thicknesses of 8.5 mm 20.0 mm.

| time   | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|--------|----------------------------|----------------------------|-----------------------------|
| [h]    | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00   | 0.00                       | 0.00                       | 0.00                        |
| 0.23   | 242.17                     | 20.06                      | 181.13                      |
| 0.46   | 331.37                     | 21.86                      | 278.39                      |
| 0.71   | 408.16                     | 13.35                      | 361.87                      |
| 0.97   | 471.26                     | 5.67                       | 437.13                      |
| 1.21   | 522.39                     | 17.95                      | 501.91                      |
| 1.73   | 630.45                     | 32.10                      | 620.73                      |
| 2.24   | 695.02                     | 15.25                      | 711.97                      |
| 2.87   | 764.47                     | 24.34                      | 785.27                      |
| 4.03   | 810.70                     | 10.04                      | 836.57                      |
| 4.83   | 831.54                     | 12.40                      | 845.03                      |
| 6.14   | 852.25                     | 4.85                       | 848.09                      |
| 25.67  | 847.70                     | 17.91                      | 848.52                      |
| 46.72  | 842.69                     | 6.38                       | 848.52                      |
| 95.58  | 852.64                     | 5.52                       | 848.52                      |
| 171.04 | 852.25                     | 4.85                       | 848.52                      |
| 214.84 | 842.93                     | 6.18                       | 848.52                      |
| 262.48 | 855.00                     | 5.61                       | 848.52                      |
| 337.58 | 866.30                     | 3.04                       | 848.52                      |

### Polyurethane

Table A - 14: Experimental and calculated values for polyurethane in toluene at 50 °C with sample thicknesses of 2.95 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 44.37   | 9.04                       | 0.17                       | 9.70                        |
| 117.77  | 15.93                      | 0.43                       | 16.34                       |
| 215.55  | 21.92                      | 0.51                       | 22.68                       |
| 337.35  | 27.92                      | 0.59                       | 29.04                       |
| 476.47  | 33.67                      | 0.60                       | 35.01                       |
| 644.87  | 39.26                      | 0.60                       | 40.84                       |
| 812.98  | 44.02                      | 0.67                       | 45.47                       |
| 982.22  | 47.64                      | 0.71                       | 49.23                       |
| 1149.20 | 50.59                      | 0.73                       | 52.29                       |
| 1317.13 | 53.54                      | 0.78                       | 54.90                       |

|         |       |      |       |
|---------|-------|------|-------|
| 1488.72 | 56.04 | 0.79 | 57.21 |
| 1656.35 | 58.23 | 0.87 | 59.23 |
| 1993.05 | 62.35 | 0.86 | 62.83 |
| 2325.52 | 65.84 | 0.87 | 66.03 |
| 2493.37 | 67.43 | 0.87 | 67.57 |
| 2711.90 | 69.46 | 0.95 | 69.52 |
| 2854.33 | 71.24 | 1.16 | 70.77 |
| 3025.37 | 72.41 | 1.00 | 72.25 |
| 3384.48 | 75.38 | 0.97 | 75.31 |
| 3505.25 | 76.79 | 1.16 | 76.32 |
| 3986.02 | 80.65 | 1.04 | 80.29 |
| 4675.53 | 86.20 | 1.19 | 85.86 |

Table A - 15: Experimental and calculated values for polyurethane in toluene at 65 °C with sample thicknesses of 3.2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 44.28   | 23.69                      | 0.63                       | 16.70                       |
| 117.68  | 37.83                      | 0.92                       | 29.98                       |
| 215.52  | 49.14                      | 1.14                       | 43.15                       |
| 337.45  | 60.46                      | 1.37                       | 55.88                       |
| 476.40  | 69.23                      | 1.55                       | 66.77                       |
| 644.80  | 77.32                      | 1.84                       | 76.52                       |
| 812.92  | 83.68                      | 1.98                       | 83.99                       |
| 982.13  | 89.15                      | 2.08                       | 90.26                       |
| 1149.13 | 93.90                      | 2.24                       | 95.79                       |
| 1317.07 | 98.78                      | 2.38                       | 100.98                      |
| 1488.65 | 103.14                     | 2.59                       | 106.07                      |
| 1656.30 | 107.51                     | 2.71                       | 110.91                      |
| 1992.98 | 116.13                     | 3.06                       | 120.38                      |
| 2325.47 | 124.28                     | 3.42                       | 129.52                      |
| 2493.30 | 128.61                     | 3.87                       | 134.08                      |
| 2711.83 | 133.40                     | 3.97                       | 139.98                      |
| 2854.27 | 136.60                     | 4.14                       | 143.80                      |
| 3025.28 | 140.55                     | 4.29                       | 148.31                      |
| 3384.42 | 147.23                     | 4.14                       | 151.74                      |
| 3505.18 | 149.07                     | 3.80                       | 152.03                      |
| 3981.20 | 155.75                     | 2.01                       | 152.35                      |
| 4675.82 | 159.94                     | 0.41                       | 152.38                      |

Table A - 16: Experimental and calculated values for polyurethane in toluene at 80 °C with sample thicknesses of 3.19 mm

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 44.23   | 41.11                      | 0.64                       | 37.11                       |
| 117.63  | 66.99                      | 0.82                       | 65.24                       |
| 215.50  | 87.67                      | 0.71                       | 89.75                       |
| 337.57  | 108.35                     | 0.75                       | 108.77                      |
| 476.35  | 130.85                     | 0.90                       | 124.26                      |
| 644.75  | 147.75                     | 1.50                       | 140.59                      |
| 812.85  | 157.32                     | 0.96                       | 156.31                      |
| 982.10  | 160.77                     | 0.63                       | 166.52                      |
| 1149.08 | 160.63                     | 0.31                       | 167.91                      |
| 1317.03 | 160.97                     | 0.29                       | 168.08                      |
| 1488.60 | 161.98                     | 0.27                       | 168.10                      |
| 1656.23 | 162.85                     | 0.22                       | 168.10                      |
| 1992.93 | 165.72                     | 0.24                       | 168.10                      |
| 2325.42 | 163.71                     | 0.93                       | 168.10                      |
| 2493.25 | 160.99                     | 1.11                       | 168.10                      |
| 2711.78 | 156.29                     | 1.50                       | 168.10                      |

Table A - 17: Experimental and calculated values for polyurethane in acetone at 50 °C with sample thicknesses of 2.82 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 42.51   | 74.18                      | 0.81                       | 71.60                       |
| 114.54  | 125.15                     | 0.96                       | 126.47                      |
| 190.64  | 163.04                     | 1.17                       | 169.06                      |
| 284.39  | 199.49                     | 1.56                       | 205.84                      |
| 355.26  | 223.17                     | 3.14                       | 223.28                      |
| 452.46  | 243.93                     | 1.70                       | 236.41                      |
| 525.66  | 249.65                     | 0.17                       | 241.17                      |
| 815.06  | 248.07                     | 0.62                       | 245.65                      |
| 981.56  | 247.11                     | 0.49                       | 245.87                      |
| 1151.11 | 246.45                     | 0.53                       | 245.91                      |
| 1411.59 | 242.70                     | 0.02                       | 245.92                      |
| 1650.73 | 244.44                     | 0.45                       | 245.92                      |
| 1871.73 | 243.85                     | 0.45                       | 245.92                      |
| 2326.21 | 242.91                     | 0.51                       | 245.92                      |

Table A - 18: Experimental and calculated values for polyurethane in methanol at 50 °C with sample thicknesses of 3.79 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 77.50   | 69.14                      | 4.22                       | 66.28                       |
| 148.90  | 94.58                      | 5.88                       | 95.13                       |
| 246.05  | 121.92                     | 9.23                       | 122.63                      |
| 262.97  | 125.68                     | 9.54                       | 126.16                      |
| 338.93  | 138.06                     | 8.08                       | 137.95                      |
| 430.77  | 146.37                     | 4.21                       | 145.54                      |
| 502.16  | 149.45                     | 1.81                       | 148.45                      |
| 647.90  | 151.15                     | 0.25                       | 150.77                      |
| 791.41  | 151.65                     | 0.06                       | 151.35                      |
| 962.28  | 151.79                     | 0.08                       | 151.51                      |
| 1269.98 | 152.11                     | 0.05                       | 151.55                      |
| 1324.56 | 151.86                     | 0.11                       | 151.55                      |

Table A - 19: Experimental and calculated values for polyurethane in isopropanol at 50 °C with sample thicknesses of 3.60 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 46.35   | 5.59                       | 0.71                       | 4.57                        |
| 144.48  | 9.28                       | 0.95                       | 8.47                        |
| 238.98  | 11.92                      | 1.20                       | 11.19                       |
| 311.10  | 13.34                      | 1.34                       | 12.93                       |
| 530.70  | 17.58                      | 1.60                       | 17.20                       |
| 670.78  | 19.49                      | 1.78                       | 19.36                       |
| 1008.58 | 23.15                      | 2.16                       | 23.52                       |
| 1175.45 | 25.03                      | 2.40                       | 25.24                       |
| 1345.57 | 26.72                      | 2.61                       | 26.85                       |
| 1513.67 | 28.16                      | 2.73                       | 28.34                       |
| 1848.93 | 31.03                      | 2.97                       | 31.11                       |
| 2015.50 | 32.32                      | 3.01                       | 32.42                       |
| 2187.32 | 33.58                      | 3.19                       | 33.74                       |
| 2857.08 | 39.30                      | 3.76                       | 38.67                       |
| 3024.27 | 39.69                      | 3.74                       | 39.86                       |
| 3242.27 | 41.33                      | 3.84                       | 41.39                       |
| 3386.97 | 42.34                      | 3.97                       | 42.40                       |
| 3556.10 | 43.73                      | 4.10                       | 43.57                       |
| 3916.40 | 46.25                      | 4.29                       | 46.01                       |
| 4035.65 | 47.42                      | 4.40                       | 46.81                       |
| 4515.28 | 51.12                      | 4.69                       | 49.98                       |
| 5195.72 | 56.51                      | 5.09                       | 54.34                       |

Table A - 20: Experimental and calculated values for polyurethane in isopropanol at 65 °C with sample thicknesses of 3.20 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 46.20   | 18.26                      | 1.40                       | 18.07                       |
| 143.92  | 30.76                      | 2.07                       | 33.94                       |
| 238.92  | 39.04                      | 2.69                       | 45.05                       |
| 310.90  | 44.23                      | 3.00                       | 51.90                       |
| 530.60  | 57.48                      | 3.91                       | 67.48                       |
| 670.72  | 64.66                      | 4.41                       | 74.75                       |
| 1008.50 | 79.69                      | 5.55                       | 88.24                       |
| 1175.55 | 86.16                      | 5.92                       | 93.90                       |
| 1345.47 | 92.72                      | 6.50                       | 99.33                       |
| 1513.58 | 97.53                      | 6.80                       | 104.53                      |
| 1848.85 | 108.72                     | 7.63                       | 114.59                      |
| 2015.42 | 114.13                     | 8.03                       | 119.50                      |
| 2187.25 | 119.16                     | 8.54                       | 124.52                      |
| 2857.00 | 141.25                     | 12.26                      | 143.94                      |
| 3024.20 | 147.17                     | 12.72                      | 148.79                      |
| 3242.18 | 151.27                     | 12.47                      | 155.14                      |
| 3386.87 | 153.33                     | 11.75                      | 158.63                      |
| 3556.00 | 154.99                     | 10.77                      | 160.04                      |
| 3916.33 | 157.55                     | 8.61                       | 160.58                      |
| 4035.57 | 158.90                     | 7.85                       | 160.61                      |
| 4510.25 | 163.09                     | 4.44                       | 160.62                      |
| 5195.67 | 163.09                     | 1.27                       | 160.62                      |

Table A - 21: Experimental and calculated values for polyurethane in isopropanol at 80 °C with sample thicknesses of 2.92 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 46.08   | 43.71                      | 1.59                       | 42.84                       |
| 143.80  | 79.75                      | 3.39                       | 84.57                       |
| 238.78  | 105.51                     | 5.47                       | 113.89                      |
| 310.60  | 123.57                     | 6.96                       | 131.11                      |
| 507.88  | 161.82                     | 6.08                       | 166.41                      |
| 670.60  | 173.68                     | 1.39                       | 175.43                      |
| 1008.38 | 178.01                     | 0.59                       | 176.60                      |
| 1175.42 | 179.31                     | 0.57                       | 176.61                      |
| 1345.37 | 180.64                     | 0.60                       | 176.61                      |
| 1513.47 | 180.95                     | 0.55                       | 176.61                      |

Table A - 22: Experimental and calculated values for phenoplast in water at 55 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 17.97   | 2.39                       | 0.02                       | 2.46                        |
| 39.53   | 3.47                       | 0.11                       | 3.79                        |
| 63.85   | 4.49                       | 0.10                       | 4.90                        |
| 87.72   | 5.30                       | 0.10                       | 5.80                        |
| 117.75  | 6.15                       | 0.09                       | 6.77                        |
| 158.48  | 7.17                       | 0.08                       | 7.90                        |
| 186.03  | 7.79                       | 0.08                       | 8.58                        |
| 238.45  | 8.89                       | 0.02                       | 9.71                        |
| 284.20  | 9.62                       | 0.04                       | 10.56                       |
| 326.15  | 10.39                      | 0.04                       | 11.25                       |
| 374.75  | 11.21                      | 0.03                       | 11.97                       |
| 422.96  | 11.82                      | 0.02                       | 12.60                       |
| 493.68  | 12.71                      | 0.01                       | 13.39                       |
| 546.56  | 13.44                      | 0.01                       | 13.91                       |
| 594.10  | 13.91                      | 0.01                       | 14.32                       |
| 661.18  | 14.50                      | 0.01                       | 14.83                       |
| 737.78  | 15.17                      | 0.02                       | 15.33                       |
| 834.61  | 15.68                      | 0.21                       | 15.85                       |
| 1167.13 | 17.48                      | 0.22                       | 17.00                       |
| 1216.23 | 17.67                      | 0.21                       | 17.12                       |
| 1378.50 | 18.36                      | 0.23                       | 17.42                       |
| 1562.68 | 18.69                      | 0.24                       | 17.65                       |
| 1662.68 | 18.69                      | 0.23                       | 17.75                       |
| 1762.21 | 18.69                      | 0.23                       | 17.83                       |

Table A - 23: Experimental and calculated values for phenoplast in water at 70 °C with sample thicknesses of 2 mm

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 17.62   | 3.67                       | 0.01                       | 3.66                        |
| 39.90   | 5.45                       | 0.01                       | 5.68                        |
| 64.28   | 6.92                       | 0.02                       | 7.31                        |
| 88.09   | 8.09                       | 0.02                       | 8.61                        |
| 118.11  | 9.37                       | 0.04                       | 9.98                        |
| 158.84  | 10.84                      | 0.07                       | 11.51                       |
| 186.36  | 11.74                      | 0.08                       | 12.37                       |
| 206.34  | 12.37                      | 0.09                       | 12.94                       |
| 236.86  | 13.15                      | 0.11                       | 13.70                       |
| 283.53  | 14.14                      | 0.13                       | 14.68                       |
| 325.01  | 14.99                      | 0.14                       | 15.40                       |
| 373.21  | 15.74                      | 0.14                       | 16.10                       |
| 421.01  | 16.38                      | 0.17                       | 16.66                       |
| 491.68  | 17.04                      | 0.17                       | 17.33                       |
| 544.99  | 17.55                      | 0.11                       | 17.72                       |
| 736.70  | 18.73                      | --                         | 18.62                       |
| 830.52  | 18.83                      | --                         | 18.88                       |
| 1165.63 | 18.92                      | 0.04                       | 19.33                       |
| 1214.19 | 19.04                      | 0.04                       | 19.36                       |
| 1309.58 | 19.06                      | 0.05                       | 19.40                       |

Table A - 24: Experimental and calculated values for phenoplast in water at 85 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 15.37   | 5.06                       | 0.00                       | 4.53                        |
| 39.77   | 8.05                       | 0.03                       | 7.52                        |
| 63.58   | 10.16                      | 0.05                       | 9.59                        |
| 93.58   | 12.16                      | 0.05                       | 11.61                       |
| 134.47  | 14.35                      | 0.06                       | 13.70                       |
| 161.48  | 15.44                      | 0.05                       | 14.77                       |
| 181.05  | 16.22                      | 0.07                       | 15.44                       |
| 211.63  | 17.01                      | 0.07                       | 16.33                       |
| 259.32  | 17.74                      | 0.07                       | 17.41                       |
| 300.30  | 18.26                      | 0.07                       | 18.12                       |
| 348.50  | 18.66                      | 0.07                       | 18.76                       |
| 396.30  | 18.94                      | 0.07                       | 19.24                       |
| 466.97  | 19.18                      | 0.10                       | 19.76                       |
| 634.33  | 19.58                      | 0.12                       | 20.41                       |
| 712.05  | 19.80                      | 0.14                       | 20.57                       |
| 805.87  | 19.94                      | 0.09                       | 20.68                       |
| 1140.57 | 20.54                      | 0.17                       | 20.83                       |
| 1189.48 | 20.54                      | 0.06                       | 20.83                       |
| 1309.58 | 20.52                      | 0.10                       | 20.83                       |

Table A - 25: Experimental and calculated values for phenoplast in heptane at 50 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 24.32   | 0.16                       | 0.01                       | 0.36                        |
| 46.60   | 0.26                       | 0.00                       | 0.51                        |
| 73.43   | 0.36                       | 0.01                       | 0.66                        |
| 91.95   | 0.45                       | 0.01                       | 0.75                        |
| 196.03  | 0.68                       | 0.01                       | 1.12                        |
| 212.13  | 0.74                       | 0.02                       | 1.17                        |
| 239.35  | 0.80                       | 0.01                       | 1.24                        |
| 337.72  | 0.96                       | 0.02                       | 1.50                        |
| 358.05  | 1.01                       | 0.02                       | 1.54                        |
| 384.32  | 1.07                       | 0.02                       | 1.60                        |
| 432.63  | 1.17                       | 0.02                       | 1.71                        |
| 502.97  | 1.32                       | 0.02                       | 1.86                        |
| 552.12  | 1.42                       | 0.03                       | 1.95                        |
| 597.43  | 1.52                       | 0.03                       | 2.04                        |
| 671.70  | 1.67                       | 0.03                       | 2.17                        |
| 723.25  | 1.80                       | 0.04                       | 2.26                        |
| 766.35  | 1.91                       | 0.04                       | 2.34                        |
| 890.80  | 2.10                       | 0.06                       | 2.54                        |
| 1006.43 | 2.27                       | 0.04                       | 2.72                        |
| 1077.62 | 2.40                       | 0.05                       | 2.83                        |
| 1221.80 | 2.62                       | 0.06                       | 3.04                        |
| 1397.23 | 2.90                       | 0.07                       | 3.28                        |
| 1677.25 | 3.26                       | 0.03                       | 3.63                        |
| 1775.13 | 3.37                       | 0.04                       | 3.75                        |
| 1943.65 | 3.60                       | 0.05                       | 3.94                        |
| 2237.58 | 3.90                       | 0.06                       | 4.26                        |
| 2759.20 | 4.72                       | 0.07                       | 4.77                        |
| 3261.53 | 5.24                       | 0.09                       | 5.21                        |
| 3696.67 | 5.53                       | 0.07                       | 5.55                        |
| 4080.82 | 5.82                       | 0.08                       | 5.84                        |
| 4530.75 | 6.08                       | 0.07                       | 6.15                        |
| 5395.77 | 6.58                       | 0.03                       | 6.70                        |
| 5802.48 | 6.80                       | 0.06                       | 6.94                        |
| 6215.95 | 6.98                       | 0.06                       | 7.17                        |
| 6454.93 | 7.11                       | 0.06                       | 7.30                        |
| 6813.98 | 7.28                       | 0.08                       | 7.50                        |
| 7128.28 | 7.44                       | 0.07                       | 7.67                        |
| 7652.83 | 7.71                       | 0.06                       | 7.94                        |

|          |      |      |      |
|----------|------|------|------|
| 7989.48  | 7.79 | 0.07 | 8.09 |
| 8324.58  | 7.92 | 0.06 | 8.22 |
| 8661.33  | 8.05 | 0.06 | 8.33 |
| 8998.40  | 8.19 | 0.07 | 8.42 |
| 9335.00  | 8.35 | 0.07 | 8.50 |
| 9670.02  | 8.54 | 0.07 | 8.58 |
| 10003.42 | 8.72 | 0.07 | 8.64 |
| 10340.17 | 8.86 | 0.07 | 8.70 |
| 10676.10 | 8.99 | 0.08 | 8.75 |
| 10928.05 | 9.15 | 0.07 | 8.78 |
| 11349.22 | 9.08 | 0.07 | 8.83 |
| 11665.10 | 9.14 | 0.08 | 8.86 |

Table A - 26: Experimental and calculated values for phenoplast in heptane at 65 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 24.65   | 0.14                       | 0.01                       | 0.46                        |
| 46.62   | 0.28                       | 0.01                       | 0.65                        |
| 73.42   | 0.45                       | 0.01                       | 0.84                        |
| 91.98   | 0.57                       | 0.02                       | 0.95                        |
| 195.98  | 0.93                       | 0.02                       | 1.42                        |
| 211.00  | 1.00                       | 0.02                       | 1.47                        |
| 240.47  | 1.08                       | 0.02                       | 1.58                        |
| 337.92  | 1.32                       | 0.01                       | 1.89                        |
| 357.88  | 1.39                       | 0.01                       | 1.95                        |
| 384.28  | 1.46                       | 0.01                       | 2.03                        |
| 432.60  | 1.60                       | 0.01                       | 2.16                        |
| 502.92  | 1.79                       | 0.02                       | 2.34                        |
| 551.65  | 1.88                       | 0.02                       | 2.46                        |
| 597.90  | 2.03                       | 0.02                       | 2.57                        |
| 671.62  | 2.20                       | 0.02                       | 2.74                        |
| 723.25  | 2.32                       | 0.02                       | 2.85                        |
| 766.33  | 2.44                       | 0.02                       | 2.95                        |
| 892.67  | 2.66                       | 0.03                       | 3.20                        |
| 1003.72 | 2.85                       | 0.03                       | 3.42                        |
| 1078.50 | 2.98                       | 0.02                       | 3.55                        |
| 1221.80 | 3.22                       | 0.02                       | 3.80                        |
| 1397.25 | 3.55                       | 0.01                       | 4.09                        |
| 1677.25 | 4.06                       | 0.04                       | 4.50                        |

---

|          |       |      |      |
|----------|-------|------|------|
| 1775.13  | 4.16  | 0.03 | 4.64 |
| 1943.63  | 4.45  | 0.03 | 4.86 |
| 2237.17  | 4.82  | 0.05 | 5.21 |
| 2757.57  | 5.59  | 0.03 | 5.76 |
| 3262.80  | 6.15  | 0.01 | 6.22 |
| 3696.67  | 6.46  | 0.04 | 6.57 |
| 4080.45  | 6.76  | 0.07 | 6.86 |
| 4531.60  | 7.06  | 0.08 | 7.17 |
| 5396.18  | 7.92  | 0.09 | 7.72 |
| 5802.75  | 8.13  | 0.09 | 7.96 |
| 6216.22  | 8.22  | 0.08 | 8.20 |
| 6455.23  | 8.27  | 0.06 | 8.33 |
| 6812.15  | 8.45  | 0.05 | 8.53 |
| 7126.47  | 8.55  | 0.05 | 8.70 |
| 7651.02  | 8.78  | 0.04 | 8.97 |
| 7987.67  | 8.86  | 0.07 | 9.14 |
| 8659.58  | 9.35  | 0.04 | 9.38 |
| 8996.67  | 9.51  | 0.07 | 9.47 |
| 9333.25  | 9.57  | 0.08 | 9.54 |
| 9668.27  | 9.64  | 0.06 | 9.61 |
| 10001.60 | 9.71  | 0.05 | 9.66 |
| 10338.43 | 9.69  | 0.05 | 9.71 |
| 10674.35 | 9.80  | 0.07 | 9.75 |
| 10926.30 | 9.95  | 0.05 | 9.78 |
| 11347.42 | 10.10 | 0.05 | 9.81 |
| 11663.35 | 9.90  | 0.02 | 9.84 |

Table A - 27: Experimental and calculated values for phenoplast in toluene at 50 °C with sample thicknesses of 1 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 46.48   | 0.26                       | 0.10                       | 0.49                        |
| 91.72   | 0.40                       | 0.12                       | 0.72                        |
| 167.28  | 0.67                       | 0.16                       | 1.00                        |
| 240.30  | 0.85                       | 0.20                       | 1.23                        |
| 337.22  | 1.11                       | 0.21                       | 1.50                        |
| 404.35  | 1.27                       | 0.20                       | 1.67                        |
| 524.47  | 1.49                       | 0.24                       | 1.96                        |
| 693.15  | 1.95                       | 0.30                       | 2.34                        |
| 864.68  | 2.42                       | 0.30                       | 2.70                        |
| 1030.30 | 2.68                       | 0.27                       | 3.04                        |
| 1197.83 | 3.10                       | 0.28                       | 3.36                        |
| 1389.97 | 3.57                       | 0.31                       | 3.72                        |
| 1536.55 | 3.92                       | 0.30                       | 3.98                        |
| 1705.15 | 4.26                       | 0.31                       | 4.27                        |
| 1872.40 | 4.49                       | 0.34                       | 4.55                        |
| 2061.77 | 4.74                       | 0.37                       | 4.86                        |
| 2205.55 | 4.87                       | 0.35                       | 5.09                        |
| 2545.82 | 5.30                       | 0.33                       | 5.61                        |
| 2712.15 | 5.48                       | 0.33                       | 5.86                        |
| 2878.72 | 5.74                       | 0.32                       | 6.10                        |
| 3025.57 | 5.86                       | 0.32                       | 6.32                        |
| 3216.73 | 6.19                       | 0.32                       | 6.59                        |
| 3357.45 | 6.38                       | 0.35                       | 6.79                        |
| 3599.93 | 6.61                       | 0.32                       | 7.12                        |
| 3716.12 | 6.75                       | 0.32                       | 7.28                        |
| 3884.42 | 7.05                       | 0.49                       | 7.51                        |
| 4052.58 | 7.10                       | 0.35                       | 7.73                        |
| 4221.90 | 7.40                       | 0.33                       | 7.96                        |
| 4388.82 | 7.97                       | 0.39                       | 8.18                        |
| 4556.80 | 8.24                       | 0.32                       | 8.40                        |
| 4728.13 | 8.48                       | 0.33                       | 8.62                        |
| 4895.83 | 8.77                       | 0.32                       | 8.83                        |
| 5232.60 | 9.15                       | 0.31                       | 9.26                        |
| 5565.22 | 9.50                       | 0.30                       | 9.62                        |
| 5732.53 | 9.58                       | 0.30                       | 9.76                        |
| 5950.38 | 9.77                       | 0.29                       | 9.92                        |
| 6093.88 | 9.94                       | 0.29                       | 10.01                       |
| 6264.88 | 10.01                      | 0.29                       | 10.10                       |

|         |       |      |       |
|---------|-------|------|-------|
| 6623.95 | 10.47 | 0.29 | 10.27 |
| 6744.92 | 10.52 | 0.29 | 10.32 |
| 7273.17 | 10.75 | 0.24 | 10.48 |
| 7500.00 | 10.75 | 0.24 | 10.54 |

Table A - 28: Experimental and calculated values for phenoplast in toluene at 80 °C with sample thicknesses of 1 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 164.93  | 0.52                       | 0.08                       | 1.40                        |
| 235.98  | 0.93                       | 0.07                       | 1.78                        |
| 331.60  | 1.81                       | 0.10                       | 2.27                        |
| 499.57  | 2.61                       | 0.27                       | 3.14                        |
| 671.65  | 3.85                       | 0.24                       | 4.02                        |
| 838.77  | 4.92                       | 0.32                       | 4.88                        |
| 1175.62 | 6.48                       | 0.45                       | 6.59                        |
| 1508.18 | 7.52                       | 0.57                       | 8.25                        |
| 1676.27 | 8.38                       | 0.63                       | 9.03                        |
| 1893.42 | 8.42                       | 0.66                       | 9.77                        |
| 2036.77 | 8.80                       | 0.66                       | 10.16                       |
| 2207.83 | 9.23                       | 0.64                       | 10.55                       |
| 2566.90 | 11.37                      | 0.68                       | 11.16                       |
| 2687.87 | 11.12                      | 0.66                       | 11.32                       |
| 3162.83 | 11.64                      | 0.78                       | 11.78                       |

*Epoxy resin*

Table A - 29: Experimental and calculated values for epoxy resin in water at 50 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 17.25   | 2.20                       | 0.04                       | 1.99                        |
| 39.47   | 3.30                       | 0.05                       | 3.05                        |
| 63.78   | 4.10                       | 0.04                       | 3.86                        |
| 87.65   | 4.67                       | 0.04                       | 4.45                        |
| 117.68  | 5.16                       | 0.05                       | 4.99                        |
| 158.42  | 5.63                       | 0.05                       | 5.48                        |
| 185.73  | 5.86                       | 0.05                       | 5.71                        |
| 238.15  | 6.18                       | 0.05                       | 5.99                        |
| 283.90  | 6.36                       | 0.05                       | 6.14                        |
| 325.85  | 6.55                       | 0.05                       | 6.24                        |
| 374.45  | 6.67                       | 0.05                       | 6.33                        |
| 422.67  | 6.79                       | 0.05                       | 6.41                        |
| 493.38  | 6.93                       | 0.06                       | 6.51                        |
| 737.95  | 7.33                       | 0.06                       | 6.82                        |
| 834.78  | 7.35                       | 0.06                       | 6.95                        |
| 1167.35 | 7.65                       | 0.05                       | 7.25                        |
| 1216.47 | 7.68                       | 0.06                       | 7.25                        |
| 1359.08 | 7.73                       | 0.05                       | 7.26                        |
| 1522.73 | 7.80                       | 0.06                       | 7.26                        |
| 1906.45 | 7.88                       | 0.07                       | 7.26                        |

Table A - 30: Experimental and calculated values for epoxy resin in water at 65 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 17.42   | 3.07                       | 0.02                       | 2.84                        |
| 39.93   | 4.51                       | 0.02                       | 4.30                        |
| 64.25   | 5.30                       | 0.02                       | 5.31                        |
| 88.07   | 5.80                       | 0.02                       | 5.95                        |
| 118.08  | 6.18                       | 0.03                       | 6.45                        |
| 158.82  | 6.52                       | 0.03                       | 6.81                        |
| 206.98  | 6.78                       | 0.03                       | 7.02                        |
| 237.50  | 6.88                       | 0.03                       | 7.10                        |
| 284.17  | 7.03                       | 0.04                       | 7.19                        |
| 333.07  | 7.17                       | 0.07                       | 7.27                        |
| 374.93  | 7.33                       | 0.04                       | 7.33                        |
| 422.03  | 7.45                       | 0.04                       | 7.39                        |
| 492.72  | 7.56                       | 0.05                       | 7.49                        |
| 737.13  | 7.69                       | 0.06                       | 7.82                        |
| 833.90  | 7.93                       | 0.05                       | 7.95                        |
| 1165.87 | 8.18                       | 0.06                       | 8.29                        |
| 1214.95 | 8.23                       | 0.07                       | 8.29                        |
| 1358.15 | 8.19                       | 0.07                       | 8.30                        |
| 1497.47 | 8.17                       | 0.08                       | 8.30                        |

Table A - 31: Experimental and calculated values for epoxy resin in water at 80 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 15.37   | 4.33                       | 0.07                       | 3.66                        |
| 39.77   | 6.09                       | 0.06                       | 5.77                        |
| 63.58   | 6.82                       | 0.08                       | 6.84                        |
| 93.58   | 7.29                       | 0.10                       | 7.49                        |
| 134.47  | 7.64                       | 0.12                       | 7.84                        |
| 181.32  | 7.92                       | 0.14                       | 8.00                        |
| 211.90  | 8.00                       | 0.17                       | 8.06                        |
| 259.58  | 8.11                       | 0.18                       | 8.14                        |
| 307.98  | 8.29                       | 0.20                       | 8.21                        |
| 349.85  | 8.37                       | 0.21                       | 8.27                        |
| 396.95  | 8.43                       | 0.25                       | 8.34                        |
| 467.63  | 8.54                       | 0.29                       | 8.44                        |
| 712.35  | 8.87                       | 0.30                       | 8.79                        |
| 809.12  | 8.88                       | 0.31                       | 8.93                        |
| 1140.73 | 9.30                       | 0.33                       | 9.41                        |
| 1189.80 | 9.41                       | 0.31                       | 9.45                        |
| 1333.52 | 9.31                       | 0.34                       | 9.46                        |

Table A - 32: Experimental and calculated values for epoxy resin in acetone at 50 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 22.60   | 2.34                       | 0.21                       | 2.08                        |
| 46.90   | 3.25                       | 0.45                       | 3.21                        |
| 71.08   | 4.27                       | 0.45                       | 4.08                        |
| 95.03   | 4.82                       | 0.61                       | 4.81                        |
| 170.05  | 5.64                       | 0.78                       | 6.75                        |
| 362.07  | 10.46                      | 1.44                       | 10.74                       |
| 529.55  | 14.22                      | 1.86                       | 13.95                       |
| 696.95  | 17.47                      | 2.07                       | 17.30                       |
| 866.42  | 20.81                      | 2.25                       | 21.10                       |
| 1056.75 | 24.34                      | 2.55                       | 26.46                       |
| 1201.45 | 27.10                      | 2.78                       | 30.83                       |
| 1369.48 | 30.79                      | 3.26                       | 34.91                       |
| 1541.00 | 36.41                      | 4.86                       | 38.71                       |
| 1706.95 | 41.82                      | 5.35                       | 42.21                       |
| 1872.72 | 45.20                      | 4.29                       | 45.34                       |
| 2066.70 | 47.97                      | 3.38                       | 48.25                       |
| 2211.17 | 49.66                      | 2.43                       | 49.77                       |
| 2380.47 | 50.75                      | 1.39                       | 50.93                       |
| 2548.80 | 51.42                      | 1.08                       | 51.60                       |
| 2736.73 | 51.78                      | 0.94                       | 51.99                       |
| 2881.42 | 51.99                      | 0.99                       | 52.15                       |
| 3239.62 | 52.30                      | 0.91                       | 52.30                       |
| 3388.53 | 52.40                      | 1.06                       | 52.32                       |

Table A - 33: Experimental and calculated values for epoxy resin in heptane at 50 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 23.45   | 0.11                       | 0.02                       | 0.19                        |
| 46.78   | 0.17                       | 0.03                       | 0.27                        |
| 73.32   | 0.27                       | 0.03                       | 0.35                        |
| 92.33   | 0.37                       | 0.03                       | 0.40                        |
| 195.75  | 0.56                       | 0.03                       | 0.65                        |
| 213.00  | 0.63                       | 0.03                       | 0.68                        |
| 238.82  | 0.69                       | 0.02                       | 0.74                        |
| 335.28  | 0.94                       | 0.03                       | 0.93                        |
| 360.43  | 1.02                       | 0.04                       | 0.98                        |
| 384.32  | 1.09                       | 0.03                       | 1.02                        |
| 432.55  | 1.15                       | 0.03                       | 1.11                        |
| 502.95  | 1.26                       | 0.03                       | 1.23                        |
| 551.98  | 1.32                       | 0.03                       | 1.32                        |
| 600.58  | 1.42                       | 0.04                       | 1.40                        |
| 669.05  | 1.53                       | 0.04                       | 1.51                        |
| 723.73  | 1.60                       | 0.04                       | 1.60                        |
| 766.22  | 1.75                       | 0.05                       | 1.66                        |
| 891.52  | 1.83                       | 0.02                       | 1.83                        |
| 1011.40 | 1.94                       | 0.02                       | 1.93                        |
| 1077.13 | 2.00                       | 0.03                       | 1.97                        |

Table A - 34: Experimental and calculated values for epoxy resin in heptane at 80 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 23.87   | 0.08                       | 0.01                       | 0.47                        |
| 48.68   | 0.29                       | 0.02                       | 0.68                        |
| 95.72   | 0.61                       | 0.05                       | 0.97                        |
| 144.86  | 1.11                       | 0.05                       | 1.22                        |
| 263.72  | 1.69                       | 0.06                       | 1.68                        |
| 407.98  | 2.11                       | 0.06                       | 2.08                        |
| 671.86  | 2.35                       | 0.08                       | 2.58                        |
| 839.94  | 2.68                       | 0.10                       | 2.82                        |
| 1008.11 | 3.00                       | 0.13                       | 3.02                        |
| 1175.97 | 3.16                       | 0.13                       | 3.20                        |
| 1368.00 | 3.26                       | 0.10                       | 3.39                        |
| 1511.97 | 3.44                       | 0.14                       | 3.54                        |
| 1679.91 | 3.70                       | 0.13                       | 3.70                        |
| 1848.11 | 3.82                       | 0.12                       | 3.86                        |
| 2015.87 | 3.83                       | 0.14                       | 4.01                        |
| 2351.93 | 4.15                       | 0.18                       | 4.16                        |
| 2495.97 | 4.12                       | 0.17                       | 4.18                        |
| 2880.02 | 5.21                       | 0.26                       | 4.21                        |
| 3024.00 | 7.11                       | 0.42                       | 4.22                        |
| 3192.17 | 8.19                       | 0.38                       | 4.22                        |
| 3359.80 | 8.79                       | 0.36                       | 4.22                        |
| 3408.04 | 8.78                       | 0.35                       | 4.22                        |
| 3527.94 | 9.15                       | 0.39                       | 4.22                        |
| 3600.01 | 9.35                       | 0.38                       | 4.22                        |
| 3864.00 | 10.08                      | 0.46                       | 4.22                        |
| 4032.00 | 9.94                       | 0.48                       | 4.22                        |
| 4224.00 | 9.91                       | 0.44                       | 4.22                        |
| 4391.96 | 9.34                       | 0.44                       | 4.22                        |
| 4536.06 | 8.63                       | 0.43                       | 4.22                        |
| 4703.97 | 8.36                       | 0.42                       | 4.22                        |

Table A - 35: Experimental and calculated values for epoxy resin in methanol at 25 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 27.42   | 1.96                       | 0.10                       | 0.81                        |
| 70.30   | 3.32                       | 0.18                       | 2.79                        |
| 145.90  | 5.19                       | 0.28                       | 5.16                        |
| 189.28  | 6.03                       | 0.34                       | 6.31                        |
| 235.68  | 6.87                       | 0.37                       | 7.35                        |
| 311.43  | 7.86                       | 0.37                       | 8.90                        |
| 406.87  | 9.53                       | 0.50                       | 10.59                       |
| 478.07  | 10.50                      | 0.50                       | 11.75                       |
| 572.65  | 11.72                      | 0.61                       | 13.15                       |
| 645.67  | 12.46                      | 0.61                       | 14.17                       |
| 741.65  | 13.64                      | 0.61                       | 15.43                       |
| 910.19  | 15.39                      | 0.77                       | 17.49                       |
| 1057.58 | 17.48                      | 0.34                       | 19.15                       |
| 1249.92 | 19.02                      | 0.91                       | 21.19                       |
| 1417.35 | 20.23                      | 1.14                       | 22.86                       |
| 1549.03 | 22.54                      | 1.16                       | 24.14                       |
| 1681.08 | 24.29                      | 1.33                       | 25.39                       |
| 1749.29 | 25.95                      | 1.57                       | 26.03                       |
| 1917.25 | 29.12                      | 1.90                       | 27.60                       |
| 2060.72 | 31.35                      | 1.84                       | 28.92                       |
| 2232.57 | 33.46                      | 1.39                       | 30.46                       |
| 2352.63 | 34.50                      | 1.11                       | 31.48                       |
| 2520.93 | 35.35                      | 0.81                       | 32.80                       |
| 2688.50 | 35.76                      | 0.68                       | 33.98                       |
| 2882.82 | 36.31                      | 0.59                       | 35.09                       |
| 3026.50 | 36.70                      | 0.58                       | 35.76                       |
| 3192.90 | 36.72                      | 0.48                       | 36.37                       |
| 3362.68 | 37.02                      | 0.48                       | 36.85                       |
| 3527.64 | 36.87                      | 0.65                       | 37.20                       |
| 3863.88 | 37.47                      | 0.43                       | 37.66                       |

Table A - 36: Experimental and calculated values for epoxy resin in methanol at 50 °C with sample thicknesses of 2 mm.

| time    | Exp. Solvent<br>Absorption | Exp. Standard<br>Deviation | Calc. Solvent<br>Absorption |
|---------|----------------------------|----------------------------|-----------------------------|
| [h]     | [mg/g]                     | [mg/g]                     | [mg/g]                      |
| 0.00    | 0.00                       | 0.00                       | 0.00                        |
| 27.25   | 8.63                       | 0.52                       | 10.66                       |
| 71.05   | 14.81                      | 0.84                       | 17.95                       |
| 146.12  | 23.40                      | 1.28                       | 27.17                       |
| 189.43  | 30.07                      | 1.68                       | 31.98                       |
| 235.87  | 35.12                      | 0.61                       | 35.62                       |
| 311.03  | 36.56                      | 0.13                       | 37.84                       |
| 407.17  | 37.78                      | 0.45                       | 38.01                       |
| 478.47  | 37.90                      | 0.40                       | 38.08                       |
| 572.82  | 38.08                      | 0.31                       | 38.17                       |
| 646.00  | 38.50                      | 0.32                       | 38.10                       |
| 741.90  | 38.86                      | 0.33                       | 38.07                       |
| 910.42  | 39.23                      | 0.37                       | 38.08                       |
| 1078.42 | 39.22                      | 0.38                       | 38.09                       |
| 1222.42 | 39.23                      | 0.37                       | 38.09                       |



# Curriculum Vitae

## Personal Information

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## Education

|           |                                                                                                                  |
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| 2016–2019 | Bachelor of Science in Chemistry<br>University of Technology and University of Graz (NAWI<br>Graz Cooperation)   |
| 2019–2021 | Master of Science in Chemistry<br>University of Technology and University of Graz (NAWI<br>Graz Cooperation)     |
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## First-author publications

S. Wagner, R. Nagl, A. Weissensteiner, J. Strunčnik, L. Schönbacher, M. Gschwandl, M. Fischlschweiger and T. Zeiner, "**Solvent Diffusion Modeling in Silicone**" J. Chem. Eng. Data, vol. 69, no. 2, p. 472–481, 2024.

S. Wagner, J. Strunčnik, L. Schönbacher, M. Gschwandl, M. Fischlschweiger and T. Zeiner, "**Swelling and solvent uptake kinetic in electronic polymer encapsulations – Coupling PC-SAFT with Maxwell-Stefan approach**" Fluid Phase Equilib., vol. 594, p. 114393, 2025.