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Macroscopic modeling of double emulsion systems

Thèse de doctorat de l'Université Paris-Saclay
préparée à CentraleSupélec

École doctorale n°579 : sciences mécaniques et énergétiques,
matériaux et géosciences (SMEMAG)
Spécialité de doctorat : Énergétique

Thèse présentée et soutenue à Gif-sur-Yvette, le 17 mai 2019, par

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Merci à ma grande famille et mes amis mexicains pour son soutien inconditionnel dans chaque étape de ma vie, à ma mère et ma grand-mère pour leur amitié inconditionnelle et à ma sœur pour m'avoir appris à être courageuse.

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Abstract

Liquid membrane separations as Double Emulsions (DE) have been extensively examined for potential application in fields such as metal recovery, gas separation, organic compound removal, pollutant removal, and bioseparations. The difficulties in the application of these processes did not consist in sophisticated equipment or installation but in a good understanding of the complex phenomena that occur inside these systems. Since its invention, efforts have been made for successful modeling of DE process separation; however, information about the diffusion and reaction phenomena inside the DE has not been included in the mathematical descriptions in detail yet. Therefore, the objective of this thesis is to describe the solute transport with chemical reaction through DE systems by means of rigorous modeling that can provide with valuable information from the micro-scale to be applied in the macro-scale.

To accomplish this, a DE system has been analyzed as a three-phase system characterized by more than one disparate length scales. The method of volume averaging has been used to derive rigorous averaged equations in the context of the *non-local mass equilibrium* (NLME). The structure of the DES has been studied from two different perspectives: 1) the DES as a single domain where concentration changes occur in the same length scale and 2) the DES consists in two homogeneous regions where concentration changes occur at two different length scales. As a result of these different standpoints of representing the system, two different averaged macroscopic models were obtained: the three-phase and the two-region models. Both models present effective coefficients that include information about the micro-scale. These latter are related to closure variables which are solutions of associated boundary-value problems. Finally an analysis of a DE-containing separation process in a stirred tank by applying both models was made.

Résumé

Les séparations à l'aide de membranes liquides sous forme d'émulsions doubles (DE) ont fait l'objet de nombreuses études compte tenu des applications potentielles notamment dans le domaine de la récupération des métaux, la séparation des gaz, l'élimination des composés organiques, l'élimination des polluants ou les bioséparations. Les difficultés de mise en œuvre de tels procédés ne relèvent pas de la complexité technique des installations mais avant tout dans la bonne compréhension des phénomènes couplés qui se produisent au sein de ces systèmes. Depuis leur invention, des progrès ont été réalisés dans la modélisation des procédés de séparation mais une description fine des mécanismes de diffusion-réaction au sein des émulsions doubles reste à établir.

L'objectif de cette thèse est précisément de décrire le transport d'un soluté avec réaction chimique au sein d'un système DE à l'aide d'une modélisation macroscopique par changement d'échelle permettant la prise en compte des mécanismes à l'échelle locale. La méthode de la prise de moyenne a été utilisée pour établir rigoureusement les équations moyennes dans le cas où l'équilibre massique local n'est pas satisfait (non-équilibre local massique, NLME).

L'émulsion double a été modélisée de deux manières différentes : un premier modèle consiste à considérer l'émulsion comme un système à un seul domaine composé de trois phases et défini à l'aide d'une seule échelle caractéristique. Le deuxième modèle distingue deux régions dont l'une résulte d'une homogénéisation de la phase interne. Les deux modélisations macroscopique font intervenir les propriétés effectives dont la détermination passe par la résolution des problèmes de fermeture associés.

Enfin, ces deux modèles sont comparés dans le cas d'un procédé de séparation par agitation d'une émulsion double au sein d'un réservoir.

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Part I

Double Emulsion Systems : Definition and analysis of its application in separation processes

Chapter 1

General description and definition of the Double Emulsion systems

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1.1 Double Emulsion Systems: Theory

1.1.1 Definition of a membrane and a membrane process

A membrane is a semipermeable barrier or an inter-phase between two phases and restrict the movement of molecules across it in a very particular manner (Ho and Sirkar 1992). If one component of a mixture moves through a membrane faster than another mixture component, a separation can be accomplished, see Figure 1.1. There are two important aspects to note considering this definition. First, a membrane is defined based on its function, not the material used to fabricate it. Secondly, a membrane separation is a rate process and the separation occurs due to a chemical potential gradient, not by equilibrium between phases. A gradient in chemical potential may be due to a concentration gradient or pressure gradient or both (Mulder 1996).

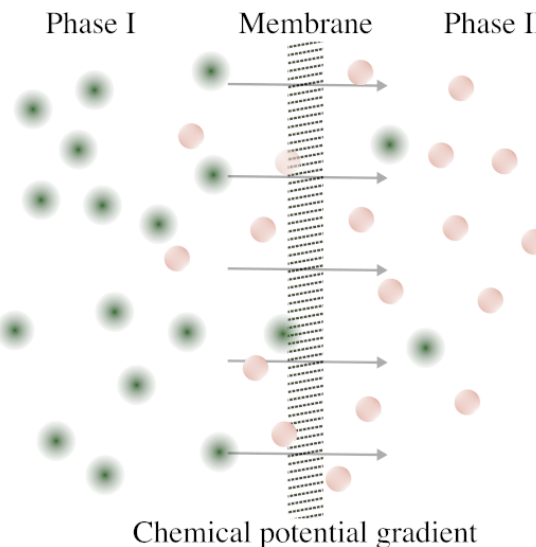


Figure 1.1: Diagram of a two phases system selectivity separate by a membrane

The first recorded study of membrane phenomena appears to be that of Abbe Nollet in 1748, demonstrating semi-permeability for the first time. In 1855, Fick published his phenomenological laws of diffusion, which we still use today as a description of diffusion through membranes. In the same year, Fick also prepared and studied some of the earliest artificial semipermeable membranes (Lonsdale 1982). From that mo-

ment to the present, membrane separation processes have evolved into an expanding and diverse field, process like dialysis (1861) and gas permeation (1866), micro-porous membranes (1907) and hemodialysis were observed and studied. In the last 50 years, membranes have developed from a research topic to a mature industrial separation technology. This increase in the use of membrane technology is driven by spectacular advances in membrane development, the wider acceptance of the technology in preference to conventional separation processes, increased environmental awareness and, most importantly, strict environmental regulations and legislation. Various membrane processes are currently applied in the chemical, petrochemical, pharmaceutical, and food and beverage industries. Particularly, strong development and growth of membrane technology can be observed in the purification of wastewater and the production of drinking water (Sastre et al. 2008)

1.1.2 Liquid Membranes

If membranes are viewed as semipermeable phase separators, then the traditional concept of membranes as polymer films can be extended to include liquids. Liquid membrane (LM) system involves a liquid which is an immiscible with the other two solutions and serves as a semipermeable barrier between these liquid phases (Noble 1987).

LM system can be developed in three different configurations: bulk liquid membrane (BLM), supported liquid membrane (SLM) and liquid membrane as double emulsions (ELM). (Bartsch and Way 1996). See Figure 1.2. BLM consists of a bulk aqueous external phase (phase I), and receiving aqueous phase (phase II) separated by a bulk organic, water - immiscible phase. Liquid impregnated (or immobilized) in the pores of a thin microporous solid support is defined as a SLM. And finally in ELM the receiving phase is emulsified in an immiscible liquid membrane and then the emulsion is dispersed in the external solution. The general properties of liquid membrane separation process have been a subject of extensive theoretical and experimental studies. Some general characteristics of LM processes are : Simple operation, high efficiency, larger interfacial area and very selective separations are possible. In particular, the ELM process are known to have great potential for separate mixtures of inorganic and organic substances, in recovering metal ions, mineral and biochemical components, also for separating acidic, basic and hydrocarbons wastewater substances. Following,

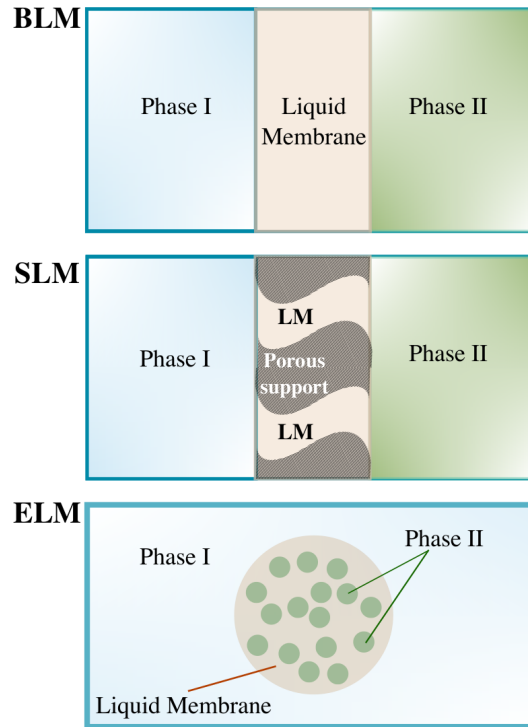


Figure 1.2: Three configurations of liquid membrane systems: bulk (BLM), supported (immobilized) (SLM or ILM), and emulsion (ELM). Phase I is the source or feed phase, LM is the liquid membrane, and Phase II is the receiving phase.

we will discuss in detail this ELM configuration, which is the study system of this thesis.

1.1.3 Double Emulsion Systems

The emulsion liquid membranes are also known as Double Emulsions (DE). A double emulsion system (DES) is a three-phase system where an external phase (γ -phase) contains dispersed drops called membrane phase (μ -phase), themselves containing small dispersed droplets of receiving phase (σ -phase). In general, the σ -phase globules have diameters around $1-10\mu m$ and emulsion drops (μ -phase + σ -phase) diameters between $0.1-2 mm$, i.e. there is a disparity in length scales that characterize each phase, see Figure 3.2. From now on to make it simpler, when we refer to the emulsion drops we will use the letter ω instead of μ -phase + σ -phase. The size of the emulsion drops, produce a very large mass transfer area adjacent to continuous phase ($\mathcal{A}_{\gamma\mu}$) and each emulsion drop contains many internal droplets (σ -phase). Thus, the internal

mass transfer surface area ($\mathcal{A}_{\mu\sigma}$), typically $10^6 \left(\frac{m^2}{\text{per unity of volume } m^3} \right)$, is even much larger than the external mass transfer surface area, $\mathcal{A}_{\gamma\mu}$. Therefore, a rapid mass transfer in DE separation process can occur from either the external phase to the internal phase or vice versa. Depending of the characteristics of his phases, DES may

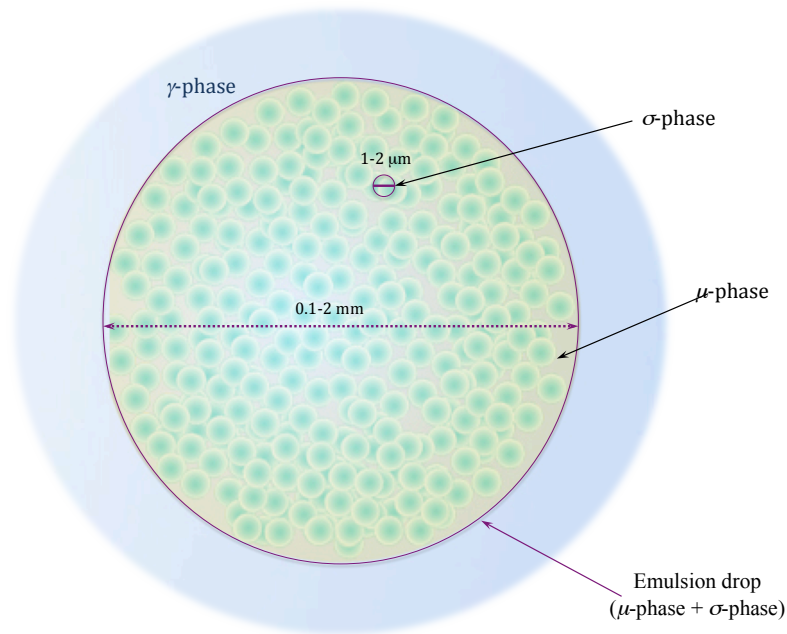


Figure 1.3: *Schema of Double Emulsion System*

be of two types, : water-in-oil emulsion dispersed in an external aqueous phase and oil-in-water emulsion dispersed in an outer organic phase. The μ -phase in the water-in-oil-in-water (W/O/W) type is the immiscible oil phase separating the aqueous phases, while in the O/W/O type the immiscible water phase separating the two organic phases acts as the membrane. Consequently, the μ -phase has two functions: permitting selective transfer of one or more components through it from γ -phase to σ -droplets and vice versa and preventing mixing of γ and σ phases. An example of double emulsions is shown in Figure 1.4.

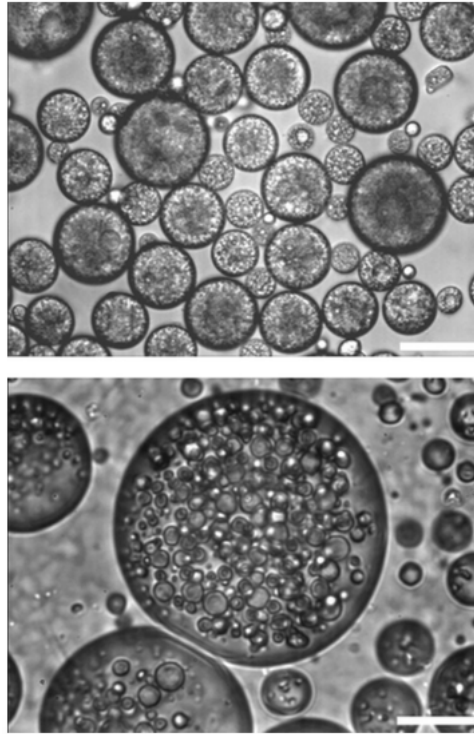


Figure 1.4: Microscopic images of double emulsions stabilized by two types of silica particles. (Top) W/O/W with triglyceride oil (scale bar = 50 μ m). (Bottom) O/W/O with toluene (scale bar = 20 μ m) *Aveyard et al. (2003)*

1.1.3.1 Transport mechanism in Double Emulsion Systems

The separation processes with DES involve the transport of a solute of interest, species A , from the γ -phase to the σ -phase through μ -phase. The widely accepted explanation used to describe this transport is the *solution-diffusion* model. The solute species dissolves in the liquid membrane and immediately after diffuses through the membrane due to an imposed concentration gradient (*Wijmans and Baker 1995*). Different solutes will have different solubilities and diffusion coefficients in a liquid. The product of these two terms is a measure of the permeability.

Furthermore, the efficiency and selectivity of transport across the LM may be markedly enhanced by the presence of a reversible or an irreversible chemical reaction in the liquid membrane or in phase II, thus increases the concentration gradient of solute A between phase I and phase II. This procedure is known as *facilitated transport process*. Hence, the various separation mechanisms are broadly classified into two

types : *simple* and *facilitated*.

1.1.3.2 Simple transport

If the solute A is soluble and has reasonable diffusivity through the μ -phase, then the transfer of solute A through the μ -phase will be due to solubility and diffusive transport of A from higher to lower concentration i.e. from the γ -phase to σ -phase. Hence, thermodynamic and transport phenomena that determine the essential operation of all DES processes are set in the simple mechanism. Double emulsion separations with simple transport mechanism were first used by Li (Li 1968) for separation of hydrocarbons.

1.1.3.3 Facilitated transport

The effectiveness of the transfer of solute A through the μ -phase is improved by maximizing the flux through the μ -phase and the capacity for the diffusing species in the σ -phase. This may be achieved by means of a chemical reaction in the μ -phase or σ -phase or both as follows:

Type I: In this case, the mass transfer rate through the μ -phase is increased by incorporating a membrane insoluble reactive (R) in the σ -phase which reacts irreversibly with the solute A yielding a product (P) which is insoluble in the μ -phase, according to the equation : $A + R \rightarrow P$. Examples of this system are extraction of weak acids or bases from wastewater such as phenol and benzene and their derivatives removal (Kargaria and Abbassiana 2015, Reis et al. 2011, Mohagheghi et al. 2008). In Figure 1.5, an example with phenol is illustrated. In this diagram, phenol from the continuous phase (γ -phase) solubilizes in the membrane oil phase (μ -phase) and then diffuses into the internal phase (σ -phase) where it reacts with the sodium hydroxide to form sodium phenolate. Being an ionic species, it is not soluble in the oil μ -phase and is effectively captured in the internal aqueous phase. The concentration of phenol in the internal phase is effectively zero.

Type II: This facilitation is also known as carrier facilitated transport, since a carrier compound, that is, an extractant or complexing agent, solubilized in the organic μ -phase is used to assist transfer across the membrane. In this process, a reactive component or carrier (C) is incorporated in the μ -phase, this carrier is soluble only

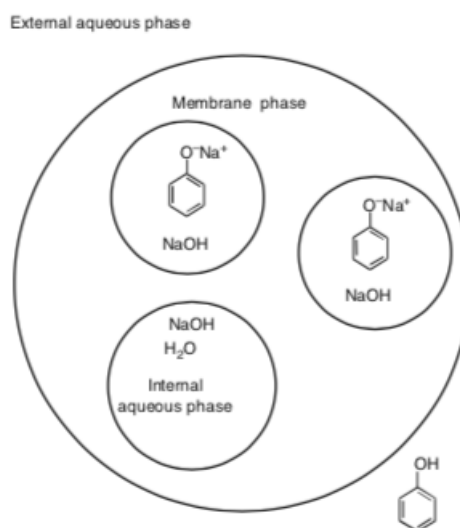


Figure 1.5: Schematic diagram of type I facilitation in a DES composed by: External aqueous phase containing phenol (γ -phase), oil membrane phase (μ -phase) and Internal aqueous phase containing NaOH (σ -phase), *Ho and Sirkar (1992)*

in this phase. At the $\gamma\mu$ -interface species C forms a membrane-soluble compound or carrier-solute complex (AB) by reversible reaction with species A to be transported, according to: $A + C \rightleftharpoons AB$. The reaction product, AB , diffuses through the membrane to the $\mu\sigma$ -interface and dissociates, discharging the solute A to the σ -phase. The unchanged carrier C then diffuses back to the $\gamma\mu$ -interface. In this way each carrier molecule is able to transport solute molecules as many times as necessary so that only a small amount of species C is required in the μ -phase even for achieving a high degree of separation. Examples of this system are removal of metal ions (*Hachemaoui et al. 2010, Gameiro et al. 2007*). A case of such a process is the removal of copper from wastewater by the extractant DEHPA (di-2-ethylhexyl phosphoric acid, represented as HL) as shown in Figure 1.6. In this case, the carrier also enhances the selectivity as most extractants are specifically designed to extract particular metal ions under given conditions. The metal ion, Cu^{2+} in the continuous γ -phase reacts with the DEHPA in the oil μ -phase to form the oil soluble complex, $\text{Cu}(\text{HL})_2$. Concentrated sulfuric acid in the internal aqueous phase strips the metal ion from the oil phase complex and transfers it into the internal phase, exchanging the metal ion for protons.

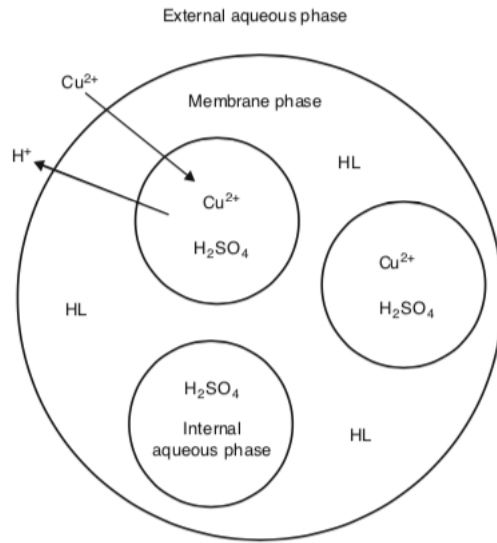


Figure 1.6: Schematic diagram of type II facilitation in a DES composed by: External aqueous phase containing Cu^{2+} (γ -phase), oil membrane phase (μ -phase) and carrier HL and Internal aqueous phase containing H_2SO_4 (σ -phase), *Ho and Sirkar (1992)*

In summary, the diffusive transfer of the solute of interest A from the γ -phase into the droplets of the σ -internal phase can be improved via two mechanisms, referred to as type I and type II facilitations by chemical reaction, either by an irreversible reaction in the σ -phase or a reversible reaction in the μ -phase or by both, see Figure 1.7.

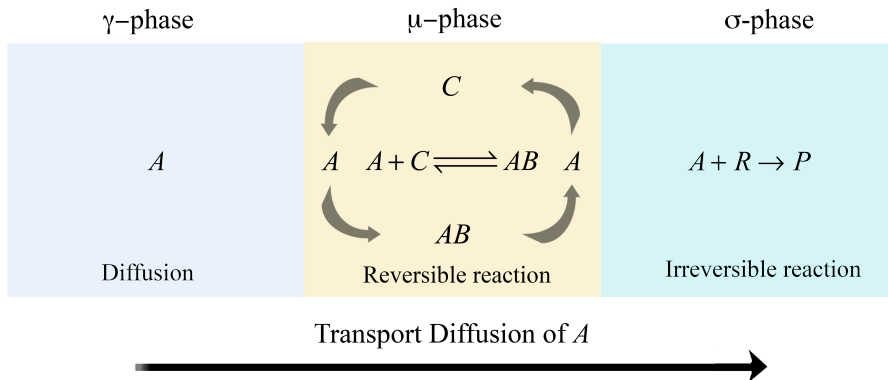


Figure 1.7: Diagram of Diffusion and Reaction in a Double Emulsion System

1.2 Design considerations in double emulsion separation process

The extraction capabilities of DES have been used successfully in many areas. Since the work of Li (1968), efforts have been made for successful industrial application of DE technology. Emphasis has been on facilitated transport. Emulsion liquid process can be divided in four stages i) emulsification, ii) Dispersion and extraction, iii) Settling, and iv) Demulsification, see Figure 1.8. The components of a DES normally

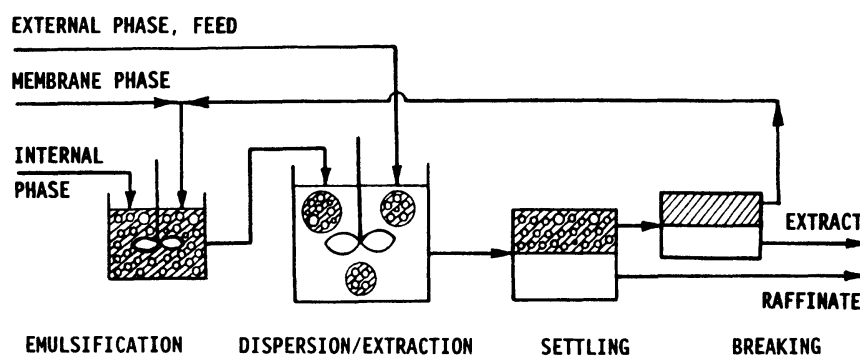


Figure 1.8: Schematic of a continuous double emulsion separation process, (Ho and Sirkar 1992)

used are surfactant, the diluent (part of the μ -phase), internal aqueous phase (σ -phase), continuous phase (γ -phase), and carrier in the case of type II facilitation (species C) and for the effective working of a DES all components must be carefully chosen and each composition is critical. Each stage and associated critical parameters are described in the following section.

1.2.1 Emulsification

Double emulsions can be *tailor-made* to meet the requirements of different separations, and thus they can offer versatile processes capable of separating a wide range of liquid mixtures. Emulsification is usually achieved by high speed or ultrasonic stirrers for batch operations and high-pressure static dispersion or colloid mills for continuous mode.(Ho and Sirkar 1992). The presence of a surfactant is necessary to ensure adequate stability of the emulsion during the extraction process. However, an ultra

stable emulsion is not desirable as it will lead to difficulties in the demulsification stage. The critical parameters for the emulsification stage are described below.

1.2.1.1 Surfactants

Surfactant is a fundamental component for the formation of a stable emulsion, and the size of the emulsion drops depends on its characteristics and concentration. Ideal surfactant properties, apart from being relatively cheap and nontoxic include (Perera et al. 2008) :

1. Virtually no water is carried during operation to prevent or reduce osmotic swelling
2. No reaction with the extractant in the membrane phase. Any possible reaction should enhance the extraction rather than cause decomposition of the extractant.
3. Low interfacial resistance to mass transfer
4. Inhibition to demulsification
5. Solubility in the membrane phase, but not in the internal and external phases.
6. Stability in the presence of acids, bases, and bacteria

1.2.1.2 Diluents

The diluent in which the extractant or C compound and surfactant are solubilized, is a major component of a DE system. It impacts on the membrane properties such as distribution coefficient and diffusion coefficient and on the effectiveness of the membrane system. Apart from being relatively cheap and readily available, the desired properties of the diluent include

1. Low solubility in the internal and external aqueous phases.
2. Compatibility with the extractant and surfactant and the inability to form new phases
3. Moderate viscosity (not too low as to compromise membrane stability)
4. Having a density that is sufficiently different to the aqueous phase
5. Low toxicity and high flash point

To date the most commonly used diluents for DE systems include kerosene, isoparaffin, cyclohexane, toluene, Shellsol T, heptane, decane, dodecane, nitrobenzene, S100N, and Escaid 110.

1.2.1.3 Carriers

Screening of the extractant agent system requires considerable chemical insight. Generally, his selection is based on the thermodynamic and kinetic considerations. The key criterion in selecting a carrier/extractant is that it and the complex formed must be soluble in the membrane phase, but not soluble in both the internal and continuous phases (Ho and Sirkar 1992). Further precipitation within the membrane or at the interfaces must be prevented. To ensure successful stripping, it is necessary to have a solute-complex of moderate stability so as to maximize the effectiveness of the stripping agent.

1.2.1.4 Internal Phase

Parameters relating to the internal phase such as volume fraction of the internal aqueous phase, pH, and volume ratio of membrane phase to internal aqueous phase impact on the working of a DE system. Its concentration and its chemical and physical properties have an important role in the extraction and settling stages.

1.2.2 Extraction

Following emulsification, the emulsion is dispersed by mechanical agitation into the external feed phase, γ -phase containing the solute A to be extracted. The efficiency of this extraction process is dependent on several parameters as stirring speed, time and temperature but also to the DES composition.

1.2.2.1 Surfactant, carrier and additives concentration

These different components have an impact on DE stability and mass transfer rates. Finding the ideal ratio between their concentrations has been the subject of many scientific works. Teramoto et al. (1983), Bart et al. (1992) and Li and Shi (1993) found that an increase in the surfactant concentration also increases the membrane phase viscosity making difficult the mobility of the carrier. Also mass transfer rates can be increased by increasing the carrier concentration, however increasing this concentration usually lowers the DE stability and increases swelling (Sastre et al. 2008, Ho and Sirkar 1992). Finally had been reported that the use of some additives can be modified the properties of the diluents increasing the stability of the DES,

reducing the amount of surfactant required for stabilization which, in turn, could lead to a reduction in swelling.

1.2.2.2 Internal Phase composition

As with the continuous phase, the internal phase properties also influence the properties of the DES. Ionic strength, pH, and the presence of organic species will impact on the DE stability. Emulsion liquid membranes work on the basis that the polar substances (usually high concentrations of acid or base) contained in the internal phase are impermeable to the membrane phase. However, the presence of the surfactant can cause the uptake of these compounds by the formation of reverse micelles (Bart et al. 1995). Care should be taken to ensure that the internal phase reagent concentration is sufficient to effect removal of the solute but not so high as to destabilize the system. Decreasing the volume fraction of the internal phase will lead to a more stable emulsion in terms of osmosis and leakage due to the increase in the membrane phase layer around the internal droplets (Ma and Shi 1987, Sastre et al. 2008). However, this leads to an increase in surfactant content in the emulsion and a consequent increase in the probability of entrapment (Sastre et al. 2008)

Finally has been observed that internal phase drop size increases with increasing volume (Teramoto et al. 1983). However, increasing the drop size will reduce the thickness of the membrane phase and lead to a lower mass transfer resistance. Optimization is a trade-off between interfacial area reduction and the increase in the mass transfer rate because of the reduced membrane thickness and thus small mass transfer resistance.

1.2.3 Settling

One of the disadvantages of DE systems is their tendency to undergo swelling. There are two types of emulsion swelling, namely, osmotic swelling and entrainment swelling. In the case of W/O/W type systems osmotic swelling occurs as a result of water transfer from the continuous phase into the internal phase due to the large difference in osmotic pressure between the internal and external aqueous phases (Wan and Zhang 2002). Entrainment swelling is caused by the entrainment of the external phase into the internal phase due to the repeated coalescence and redispersion of emulsion globules during the dispersion operation thus causing an increase in the volume of the

internal phase (Van et al. 1987, Wan and Zhang 2002). The disadvantages of swelling are dilution of the separated product in the internal phase, an increase in membrane rupture i. e. breakage, and an increase in agitation power required to disperse the emulsion (Itoh et al. 1990). Swelling is usually quantified in terms of the swelling ratio, which is defined as the ratio of the diameter of the W/O/W

1.2.4 Demulsification

The breaking of the loaded emulsion (μ -phase/ σ -phase) is one of the key steps in the double emulsion extraction process. After extraction, the membrane phase (μ -phase) must be recycled repeatedly, and the enriched internal phase (σ -phase) is usually recovered. Therefore, demulsification of the loaded emulsion is unavoidable for the use of this separation process.

The demulsification process can be divided into three stages (Hsu and Li 1985):

1. Droplet coalescence and growth
2. Droplet settling
3. Coalescence of the large water and oil droplets with their respective continuous phases in the coalescer

To date, chemical or physical treatment is the method used for demulsification

1.2.4.1 Chemical treatment

This treatment involves the addition of a demulsifier. For example acetone (Gadekar et al. 1992), n-butanol (Hsu and Li 1985, Larson et al. 1994), and 2-propanol have been found to be effective demulsifying agents for particular applications. However, the added demulsifier will change the properties of the membrane phase and thus prohibit its reuse. Therefore, chemical treatment is usually not suitable for breaking liquid membrane emulsions, although few examples of chemical demulsification have been reported for certain liquid membrane systems.

1.2.4.2 Physical treatments

Physical treatments include heating, centrifugation, high shear, ultrasonics, solvent dissolution, and the use of high-voltage electrostatic fields (Ho and Sirkar 1992). Other nonconventional methods, such as microwave demulsification (Chan and Chen 2002) and the use of porous glass membranes (Sun et al. 1998), have also been

investigated. A summary of the advantages and disadvantages of these physical treatments is presented in table 1.1.

Treatment	Advantages	Disadvantages	Publication
Heat treatment	Reduction in the density and viscosity of the oil and weakening of the interfacial film	Slow demulsification kinetics. It must be combined with some other technique that improves coalescence kinetics	Larson et al. (1994)
High shear	Fast and effectively demulsification	Requires the addition of solvent mixtures and centrifugation	Ho and Sirkar (1992)
High voltage electrostatic fields	Faster coalescence can be achieved and membrane phase can be recycled. Efficient and economic	Their mechanisms are not completely understood	Gang et al. (1997)

Table 1.1: *Physical treatments of Demulsification stage*

1.3 Applications

The extraction capabilities of double emulsion systems have been used successfully in many areas. As an emerging technology, liquid membrane separations as double emulsions have been extensively examined for potential application in many fields such as metal recovery, gas separation, organic compound removal, pollutant removal, and bioseparations. The difficulties in the application of these processes did not consist in sophisticated equipment or installation but in the adequate choice of reagent to allow the selective extraction of solute in required quantity. Since DES invented (Li 1968) efforts have been made for successful industrial application of double emulsion process separation technology. Some of the possible commercial applications are discussed below.

1.3.1 Separation of inorganic species

1.3.1.1 Metal ion extraction

The use of DE separation process for the hydrometallurgical recovery of heavy metals has drawn attention of many investigators. Kitagawa, Frankenfeld and Li (Kitagawa

et al. 1977), Martin and Davies (Martin and Davies 1977) were among the earliest investigators to report the extraction of metal ions. Then, in 1986, the method has been successfully commercialized to remove zinc from wastewater in the viscous fiber industry at Lenzing, AG, Austria (Kislik and Vladimir 2010). This process can treat up to $75 \text{ m}^3/\text{h}$ of zinc bearing wastewater with the zinc concentration ranging from 0.3 to 200 mg/l . Zinc can be removed with up to 99.5% efficiency (Ho and Sirkar 1992). Other three industrial plants for zinc removal are located at Glanzstoff, AG, Austria ($700 \text{ m}^3/\text{h}$ capacity), at CFK Schwarza, Germany ($200 \text{ m}^3/\text{h}$ capacity), and at AKZO Iede, Netherlands ($200 \text{ m}^3/\text{h}$ capacity) (Sastre et al. 2008). Studies have been made on the mechanism of separation, process kinetics, mass transfer modeling, and engineering evaluation with metals like copper, zinc, cadmium, cobalt, nickel, mercury, uranium, chromium, rhenium, arsenic, lead and several others, including noble metals like gold and silver, lanthanides and rare earths (Sastre et al. 2008, Kislik and Vladimir 2010). Table 1.2 presents some examples.

Solute	External phase	Membrane phase	Internal phase	Publication
Cooper	CuSO ₄ solution	Kerosene	Sulfuric acid solutions	Ma and Waters (2017)
Cu (II) from acidic mine drainage	Metal-containing solution from acidic cooper mine drainage	Kerosene	Sulfuric acid solutions	Valenzuela et al. (2009)
Cadmium	Hydrochloric acid solution	Corn oil	0.1 M aqueous ammonia solution	Ahmad et al. (2017)
Silver	Potographic waste solution	Kerosene, n-dodecane and toluene	Acidic thiourea solution	Othman et al. (2006)
Uranium (VI)	Sodium nitrate solution	Liquid paraffin with tri-n-butyl phosphate	Aqueous sodium carbonate	Kulkarni et al. (2018)
Gold (III)	Gold chloride solution	Liquid paraffin	Sodium sulfite with sodium hydroxide solution	Kargari et al. (2006)
Dysprosium	Acidic solutions	Kerosene	Hydrochloric acid solution	Raji et al. (2018)
Cobalt	Acidic leach solutions	Kerosene	Sulfuric acid solution	Kumbasar (2010)
Gadolinium(III)	Acidic solution containing Gadolinium(III)	Kerosene	Nitric acid solution	Davoodi-Nasab et al. (2018)
Bi(III)	Acidic solution containing Bi(III)	n-pentanol	Sulfuric acid solution	Mokhtari and Pourabdollah (2015)
Cr(VI)	Aqueous solution containing Cr(VI)	Rice bran oil	NaOH solution	Kumar et al. (2019b)

Table 1.2: Double Emulsion Systems (DES) for recovery metal ions

Ahmad et al. (2011) analyzed more than 65 different studies of heavy metal DE extraction. Metals like copper, zinc, nickel, chromium, silver, molybdenum, ruthenium, platinum, uranium, rare earth metals, gallium, cadmium were recovered using different emulsion compositions. Generally, the most widely used are Span 80 and kerosene for surfactant and diluent, respectively. While the use of extractant and internal phase depend on the kinds of metals to be extracted. For example, in case of copper removal, the use of LIX as an extractant and H_2SO_4 as an internal phase are more favorable than others. While in case of cadmium removal, the use of TOA and TIOA as an extractant and NaOH as an internal phase are the most used by researchers. From the same study, they found that DE separation is a promising method for industrial waste water recovery including heavy metals. They consider that the successful application is not only depend on the selection of suitable emulsification method but also the emulsion formulation in accordance with the solute which is to be recovered. For them, the great challenge in the application of the DE extraction at industrial scale is related to the emulsion stability.

1.3.1.2 Removal of weak acids/bases

Weak acids like phenol and cresol and weak bases like ammonium and amines have been successfully removed from wastewater (Sastre et al. 2008, Kislik and Vladimir 2010). Among them, the extraction of phenol and its derivatives like hydroquinone, nitrophenols, and chlorophenols, have been intensively investigated (Raza et al. 2019). Cahn and Li (1974) were among the first to report the separation of phenol from wastewater by DE separation technique. In most of these systems phenol extraction through the membranes was based on the solubility difference of phenol between the aqueous and organic phases. Phenol, being somewhat oil soluble, was transferred into the membrane phase and then diffused across the membrane into the internal aqueous caustic phase where it was immediately neutralized by the caustic and tied up as phenolate that is insoluble in oil and consequently could not diffuse back again. As a result, a high phenol concentration gradient was maintained across the liquid membrane and thus the phenol was readily removed from the external aqueous phase (Mortaheb et al. 2008, Ng et al. 2010, Reis et al. 2011)

The recovery of aniline, ethylaniline, nitrophenol, citric acid, acetic acid also have been studied. Table 1.3 presents recent studies.

Solute	External phase	Membrane phase	Internal phase	Publication
Phenol	Aqueous solution containing phenols	Iso-kerosene	NaOH solution	Abbassian and Kargari (2016)
Phenol	Industrial wastewater containing phenols	Soltrol 220	0.5N NaOH solution	Park et al. (2006)
Lactic acid	Aqueous solutions of lactic acid	Rice bran oil	NaOH solutions	Kumar et al. (2019a)
Succinic acid	Aqueous solution of succinic acid	Kerosene	NaOH solution, Na ₂ CO ₃ solution	Lee (2011)
Citric acid	Aqueous solution of citric and sulfuric acids and D-xylose	Kerosene	Na ₂ CO ₃ solution	Lee (2015)
Gibberellic acid	Aqueous solution containing GA ₃	n-Heptane	Aqueous solution of KCl	Berrios et al. (2010)

Table 1.3: Double Emulsion Systems (DES) for recovery of weak acids/bases

Lately new development in the existing double emulsion systems technique is the use of green solvents and ionic liquids to form a stable green emulsion ionic liquid membrane which will help in curbing the environmental problems caused by petroleum-based solvents (Othman et al. 2017, Ahmad et al. 2017, Kumar et al. 2018, Kumar et al. 2019a, Kumar et al. 2019b)

1.3.2 Biochemical and biomedical applications

DE separation process has promise in the fields of biotechnology and biomedicine and has found application in the separation of organic acids, extraction of fatty acids and amino acids, purification of antibiotics, enzyme catalyzed reactions, and detoxification of blood (Kislik and Vladimir 2010). The first application of DES to bioseparations was for drug delivery and drug overdose prevention systems (Thien and Hatton 1988). Thien et al. (1988) and Itoh et al. (1990) reported the separation and concentration of amino acids using DES. Stobbe et al. (1997) introduced a three step extraction mechanism, including solubilization, transportation, and release of the protein with

a DES. Table 1.4 presents some of the most recent studies in this field.

Solute	External phase	Membrane phase	Internal phase	Publication
Chlorpheniramine	Aqueous solution containing Chlorpheniramine	Dodecane and Parleam 4	HCl solution	Razo-Lazcano et al. (2018)
Tropane alkaloids	Aqueous solution containing Radix physochlainae	Chloroform	[C ₃ Tr][PF ₆] aqueous solution	Tang et al. (2019)
Ethylparaben	Aqueous solution containing Ethylparaben	n-Heptane	Na ₂ CO ₃ solution	Kohli et al. (2018)
Diclofenac	Aqueous solution containing diclofenac	Dichloromethane	NaOH solution	Seifollahi and Rahbar-Kelishami (2017)
Propylparaben	Aqueous solution containing propylparaben	n-Hexane	Na ₂ CO ₃ solution	Chaouchi and Hamdaoui (2015)

Table 1.4: *Double Emulsion Systems (DES) for the recovery of biomedical compounds*

1.3.3 Commercial Applications

Nearly 40 years since the initial reporting of the double emulsion system concept and the many potential applications discussed in the literature, very few commercial plants are operating successfully, see Table 1.5. This technology offers a number of distinct advantages including reduction in the volume of organic, the large interfacial area, hence transfer rates are compared with traditional solvent extraction. However, issues of osmotic swelling, the stabilization, and destabilization of the emulsion remain a problem. Also, the influence of surface active impurities on the stabilization process is an issue during reuse of these systems. These challenges to the industry implementation of this technology remain as barriers to more wide spread application. At present, however, the technology has found some application in the treatment of relatively low concentration waste streams where other technologies are not economical.

Hence experience in these applications will drive further development and confidence in this technology and so find its niche in the available separation technologies.

Application	Company	Plant Size	Efficiency	Publication
Revomal of cooper from mine solutions	Bureau of Mines, USA	Pilot plant : 90-159L/h	>90%	Wright et al. (1995)
Revomal of cooper from synthetic mine solutions	Davy McKee Company, United Kingdom	18L/h	95%	Frankenfeld et al. (1981)
Revomal of cadmium	Delf University of, United Kingdom	Pilot plant 90 L/h	95%	Breembroek et al. (2000)
Revomal of phenol	Nanchung Plastic, Factory Guangzhou, PR China	Pilot plant 200-250 L/h Commercial plant : 400-500 L/h	99.6%	Xiujuan et al. (1988)

Table 1.5: Commercial application of Double Emulsion Systems (*Sastre et al. (2008).*)

Chapter 2

State of the art of DE separation processes modeling

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2.1 The solution-diffusion model for membranes

The principal property of membranes used in separation applications is the ability to control the permeation of different species (Mulder 1996). The starting point for the mathematical description of permeation in all membranes is the proposition, solidly based in thermodynamics, that the driving forces of pressure, temperature, concentration, and electromotive force are interrelated and that the overall driving force producing movement of a permeant is the gradient in its chemical potential (Wijmans and Baker 1995, Mulder 1996). Following this idea, Wijmans and Baker (1995) suggested that the flux, J_i , of a component, i , is described by the simple equation:

$$J_i = -L_i \frac{d\mu_i}{dx} \quad (2.1)$$

where $\frac{d\mu_i}{dx}$ is the gradient in chemical potential of component i and L_i is a coefficient of proportionality (not necessarily constant) linking this chemical potential driving force with flux. All the common driving forces, such as gradients in concentration, pressure, temperature, and electromotive force, can be reduced to chemical potential gradients, and their effect on flux expressed by equation 2.1. Restricting ourselves to driving forces generated by concentration and pressure gradients, the chemical potential for incompressible phases, is written as

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i c_i) + v_i(p - p_{isat}) \quad (2.2)$$

where c_i is the molar concentration of component i , γ_i is the activity coefficient, p is the pressure, p_{isat} is the saturation vapor pressure and v_i is the molar volume of component i . Wijmans and Baker (1995) explain that a number of assumptions must be made to define any model of permeation and they assumed that the governing transport through membranes is that the fluids on either side of the membrane are in equilibrium with the membrane material at the interface. This assumption means that there is a continuous gradient in chemical potential from one side of the membrane to the other. It is implicit in this assumption that the rates of absorption and desorption at the membrane interface are much higher than the rate of diffusion through the membrane. This appears to be the case in almost all membrane processes, but the authors point up that may fail, for example, in transport processes involving chemical reactions, such as facilitated transport, or in diffusion of gases through metals, where

interracial absorption can be slow. The solution-diffusion model assumes that the pressure within a membrane is uniform and that the chemical potential gradient across the membrane is expressed only as a concentration gradient. Thus, combining equations 2.1 and 2.2 one can obtain:

$$J_i = -\frac{RTL_i}{c_i} \frac{dc_i}{dx} \quad (2.3)$$

This has the same form as Fick's law where the term RTL_i/c_i can be replaced by the diffusion coefficient D . Thus:

$$J_i = -D_i \frac{dc_i}{dx} \quad (2.4)$$

and integrating over the thickness of the membrane then gives:

$$J_i = \frac{D_i(c_i^{\gamma\mu} - c_i^{\mu\gamma})}{\delta} \quad (2.5)$$

where $c_i^{\gamma\mu}$ represents the concentration of component i in the external fluid (γ -phase) in contact with the membrane at the feed interface ($\gamma - \mu$), and $c_i^{\mu\gamma}$ is the concentration of component i in the membrane at the feed interface ($\mu - \gamma$).

Wijmans and Baker (1995) demonstrated that the solution-diffusion model is a good description for the transport through dialysis, reverse osmosis, gas separation, and pervaporation membranes. Since 1970 this model has been used in separation processes with liquid membranes and has been fundamental for the models of separation processes with double emulsions. This will be developed in the following sections.

2.2 Double emulsion separation processes modeling

A number of studies have been reported in the literature for the development and testing of mathematical descriptions for solute transport through liquid membranes as DES. Kislik and Vladimir (2010) classified the existing models into:

1. *Membrane film model* in which the entire resistance to mass transfer is assumed to be concentrated in a membrane film of constant thickness
2. *Distributed resistance model* which considers the mass transfer resistance to be distributed throughout the emulsion drop.

The development of these models over the years has been discussed extensively. Some of the development highlights are presented in the following sections.

2.2.1 Membrane film models for DE separation process

2.2.1.1 Uniform flat sheet model

Mathematical descriptions of membrane film models began with the pioneering work of [Cahn and Li \(1974\)](#), they proposed the uniform flat sheet model, which assumes the membrane to be a planar film. They suggested that the mass transfer rate through the film is directly related to the solute concentration difference (Δc), across the film of constant thickness (δ). The rate equation then becomes:

$$-\frac{dC_\gamma}{dt} = DA \frac{\Delta c}{\delta} \quad (2.6)$$

where C_γ is the solute concentration in the external continuous phase, D is the diffusivity of the solute through the membrane phase, and A is the mass transfer area per unit volume of feed solution. Since A and D are difficult to measure for a DES, the authors proposed that $\frac{DA}{\delta}$ can be replaced by:

$$D_{eff} \frac{V_\omega}{V_\gamma} \quad (2.7)$$

where D_{eff} is an effective diffusivity and $\frac{V_\omega}{V_\gamma}$ is the volume ratio of drop emulsion to external phase. In the case of Type I facilitated transport mechanism, where the solute is removed by irreversible reaction with reagent in σ -phase, the solute concentration in the internal phase can be considered to be zero and hence Equation 2.6 becomes:

$$\ln \frac{C_{\gamma 0}}{C_\gamma} = D_{eff} \frac{V_\omega}{V_\gamma} t \quad (2.8)$$

where $C_{\gamma 0}$ and C_γ are the initial and final concentrations of solute in the external γ -phase and t any given interval of time. The model assumed a constant mass transfer resistance with time and also neglected solute accumulation in the membrane as well as in the internal phase. [Cahn and Li \(1974\)](#) used Eq. 2.8 to analyze data from batch experiments of phenol removal from wastewater with NaOH as the internal reagent. These authors also applied this model for analysis of simple transport processes such as separation of hydrocarbons using an aqueous medium as the membrane phase separating the organic feed and receiving phases ([Cahn and Li 1976](#)). [Kremesec and Slattery \(1982\)](#) adapted with limited success the flat sheet model, they considered the overall mass transfer resistance as a sum of the resistance through continuous, membrane, and internal phases.

2.2.1.2 Spherical shell model

Matulevicius and Li (1975) attempted to improve upon the uniform flat sheet model by considering the unsteady state mass transfer of solute through the membrane with the mass transfer resistance through the membrane film as the controlling resistance. They considered all the droplets of σ -phase as an agglomerate of reactive drop inside the μ -phase drop, i.e., two concentric circles of radius R_σ and R_ω respectively. This is equivalent to a large membrane film of constant thickness δ . Thus, the solute diffuses from the surface (R_ω) of the membrane to R_σ , where it is removed by reaction with the internal reagent. The model equation is:

$$\frac{\partial C_\mu}{\partial t} = D \frac{1}{r^2} \frac{\partial C_\mu}{\partial r} \left(r^2 \frac{\partial C_\mu}{\partial r} \right) \quad (2.9)$$

with initial and boundary conditions:

$$C_\mu = 0 \quad \text{at} \quad t = 0 \quad (2.10)$$

$$C_\mu = \alpha C_\gamma \quad \text{at} \quad r = R_\omega (t > 0) \quad (2.11)$$

$$C_\mu = 0 \quad \text{at} \quad r = R_\sigma (t > 0) \quad (2.12)$$

where C_μ is the membrane phase solute concentration and C_γ is the continuous phase solute concentration and α a solubility of permeate in membrane phase. Matulevicius and Li (1975) obtained a good agreement between their experimental results and the model predictions.

2.2.2 Distributed resistance models for DE separation process

The distributed resistance models describe adequately the emulsion homogeneity resulting from the presence of the droplets of σ -phase dispersed in the membrane μ -phase. Two different approaches have been reported based on the nature of reaction with the internal reagent R :

1. When the irreversible reaction $A + R \longrightarrow P$, occurs instantaneously due to a high concentration of reagent R in the σ -phase and consequently the concentration of solute A is identically zero in σ -phase
2. When the reversible reaction $A + R \rightleftharpoons P$ is considered.

2.2.2.1 Advancing front model

The membrane film models, do not account for the effect of the rate at which the internal reagent (R) is consumed. [Kopp et al. \(1978\)](#) recognized this problem, and proposed that the process be described in terms of a boundary at which a reversible reaction occurs, and which moves in towards the globule center as the reagent is consumed. The model equations were:

$$\frac{\partial C_\mu}{\partial t} = D_{\text{eff}} \frac{1}{r^2} \frac{\partial C_\mu}{\partial r} \left(r^2 \frac{\partial C_\mu}{\partial r} \right) - \frac{\partial C_\sigma}{\partial t} \quad (2.13)$$

$$\frac{\partial C_R}{\partial t} = K_f C_\mu - K_b C_\sigma \quad (2.14)$$

where C_μ and C_σ are the solute concentrations in the membrane phase and σ droplets respectively, C_R is the internal reagent concentration, D_{eff} is an effective diffusivity, and K_f and K_b are the rate constants of the forward and backward reactions, respectively. This model was improved upon by [Ho et al. \(1982\)](#). They assumed local equilibrium between the dispersed and continuous phases of the emulsion, and describe the concentration field within the globule (drop emulsion) in terms of the average local concentration; i.e., they disregarded the composite nature of the emulsion, and treat it as though it were a continuum ($\omega = \mu + \sigma$). In summary, they modeled the DE system in terms of a monodisperse, non-coalescing collection of spherical globules having no internal circulation. The solute taken up from the external phase diffuses through the globule to a reaction front, where it is removed by an instantaneous and irreversible chemical reaction. The reaction front advances in towards the globule center as the internal reagent is consumed. The model equations were:

In drop emulsion :

$$\frac{\partial C}{\partial t} = D_{\text{eff}} \frac{1}{r^2} \frac{\partial C}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \quad (2.15)$$

$$(2.16)$$

with initial and boundary conditions:

$$C = 0 \quad \text{at} \quad t = 0 \quad (2.17)$$

$$C = \alpha C_\gamma \quad \text{at} \quad r = R_\omega(t > 0) \quad (2.18)$$

$$C = 0 \quad \text{at} \quad r = R_\sigma(t)(t > 0) \quad (2.19)$$

In external γ -phase :

$$-V_\gamma \frac{dC_\gamma}{dt} = D_{\text{eff}} \left(\frac{\partial C}{\partial t} \right)_{r=R_\omega} (n4\pi R_\omega^2) = \frac{3}{R} (V_\mu + V_\sigma) D_{\text{eff}} \left(\frac{\partial C}{\partial t} \right)_{r=R_\omega} \quad (2.20)$$

with initial condition:

$$C_\gamma = C_{\gamma 0} \quad \text{at } t = 0 \quad (2.21)$$

A material balance over the reaction front (R_σ):

$$-\left(\frac{V_\sigma}{V_\mu + V_\sigma} \right) C_{\sigma 0} \frac{dR_\sigma}{dt} = D_{\text{eff}} \left(\frac{\partial C}{\partial t} \right)_{r=R_\sigma(t)} \quad (2.22)$$

with initial condition:

$$R_\sigma = R_\omega \quad \text{at } t = 0 \quad (2.23)$$

where $C(r)$ is the solute concentration within the globule phase(drop emulsion), averaged over the membrane and internal reagent phases ($\mu + \sigma$ phases). The external γ -phase, membrane μ -phase and internal σ -phase volumes are $V_\gamma, V_\mu, V_\sigma$ respectively, and the position of the advancing reaction front is denoted by R_σ , α is an equilibrium distribution coefficient with the following form:

$$\alpha = \frac{V_\sigma + \alpha' V_\mu}{V_\mu + V_\sigma} \quad (2.24)$$

$$\alpha' = \frac{C_\mu}{C_\gamma} \quad (2.25)$$

Like their predecessors, the authors used some experiments on the batch extraction of phenol from wastewater using an aqueous NaOH solution as the internal phase, to test the utility of the mathematical analysis. [Kim et al. \(1983\)](#) and [Stroevé and Varanasi \(1984\)](#), formulate advancing front theories which include both spherical geometry and depletion of solute in the bulk phase. [Stroevé and Varanasi \(1984\)](#) included a mass transfer resistance in the continuous phase. They show that their model reduces to that of [Ho et al. \(1982\)](#) when the mass transfer resistance becomes negligible. The mass flux from the continuous γ -phase to the surface of the emulsion drop of radius R_ω is given by:

$$N = K_\gamma 4\pi R_\omega^2 (C'_\gamma - C'_s) \quad (2.26)$$

where K_γ is the continuous phase mass transfer coefficient, C'_γ is the solute concentration in external continuous phase, and C'_s is the solute concentration in the external continuous phase at the surface of the double emulsion drops.

The flux of solute arriving at the reaction front (R_σ) is given by:

$$D_{\text{eff}} \frac{dC}{dr} = \frac{N}{4\pi R_\omega^2} \quad (2.27)$$

where D_{eff} is the effective solute diffusivity in the double emulsion drops and C is the solute concentration in the reacted region of the double emulsions. The rate of consumption of the internal reagent is given by:

$$-\frac{d}{dt} \left(\frac{4\pi R_\sigma^2}{3} \frac{V_\sigma}{(V_\sigma + V_\mu)} C_{\sigma 0} \right) = N - \frac{d}{dt} \left(\int_{R_\sigma}^{R_\omega} C(4\pi r^2) dr \right) \quad (2.28)$$

where R_σ is the reaction front position, V_σ is the volume of internal reagent phase, V_μ is the total membrane phase volume, and $C_{\gamma 0}$ is the initial solute concentration in the external continuous phase. The second term in the right-hand side accounts for the accumulation of unreacted solute present in the region depleted of internal reagent that is a partial correction for ignoring the solute accumulation.

[Kislik and Vladimir \(2010\)](#) remarked that one shortcoming of the advancing reaction front approach is the assumption of reaction irreversibility, which when combined with instantaneous kinetics requires that the solute concentration be identically zero inside σ -phase. This condition is not satisfied with systems having lower distribution coefficients and low solute concentrations. This has led to the development of the reversible reaction model in which there are no separate reacted and unreacted regions. Thus, it is conceivable that the solute can reach the center of the σ -phase either without contacting the internal reagent R or undergoing a series of forward and reverse reactions.

2.2.2.2 Reversible reaction model

The reversible reaction model removes the restriction of irreversibility of the σ -phase reaction. The reaction reversibility precludes the reaction advancing front since there is no separate reacted and unreacted region. Solute diffusing into the emulsion drop reacts with the internal reagent R or distributes itself between the two phases (μ and σ phases). The product formed inside the encapsulated droplets P may give rise to

reverse reaction producing unreacted solute that can diffuse back into the membrane.

Bunge and Noble (1984) considered a solute A which diffuses through the emulsion drop reacting with reagent R to produce product P in the droplets of σ -phase by reversible reaction: $A + R \rightleftharpoons P$. The authors proposed an equilibrium constant, K :

$$K = \frac{C_P}{C_A C_R} \quad (2.29)$$

The material balance equations describing the solute concentration in the membrane phase, $C_{A\mu}$ and in the external phase, $C_{A\gamma}$ are as follows:

In emulsion drops (ω -region):

$$\frac{\partial C_{A\mu}}{\partial t} = \frac{D_{\text{eff}}}{r^2} \frac{\partial}{\partial r} \left(\frac{r^2 \partial C_{A\mu}}{\partial r} \right) - \left(\frac{1 - f_\mu}{f_\mu} \right) \left(\frac{\partial C_{A\sigma}}{\partial t} + \frac{\partial C_{P\sigma}}{\partial t} \right) \quad (2.30)$$

In external γ -phase:

$$\frac{\partial C_{A\gamma}}{\partial t} = - \frac{3D_{\text{eff}}}{R\phi_\gamma} (1 - \phi_\gamma) \phi_\mu \left(\frac{\partial C_{A\mu}}{\partial r} \right)_{r=R_\omega} \quad (2.31)$$

with initial and boundary conditions

$$t = 0 \quad C_{A\mu} = 0 \quad (R_\omega > r \geq 0) \quad (2.32)$$

$$r = R_\omega \quad C_{A\mu} = k_\mu C_{A\gamma} \quad (2.33)$$

$$r = 0 \quad \frac{\partial C_{A\mu}}{\partial r} \quad (2.34)$$

where $C_{A\sigma}$ and $C_{P\sigma}$ are the concentrations of unreacted solute and reaction product, respectively, in the internal σ -phase, R_ω is the mean drop emulsion radius, k_μ is the solute partition coefficient between external and membrane phases, ϕ_μ and ϕ_γ are the volume fractions of membrane and external phases, respectively, and D_{eff} is the mean effective diffusivity based on the membrane phase driving force, including diffusion of both the reacted and unreacted solutes through the internal σ -phase. Finally, the authors considered in the Equation. 2.35 the changes in both $C_{A\sigma}$ and $C_{P\sigma}$ establishing local phase and reaction equilibria between the internal phase and the membrane phase and related them to the membrane concentration $C_{A\mu}$.

$$\frac{\partial C_{A\sigma}}{\partial t} + \frac{\partial C_{P\sigma}}{\partial t} = \frac{1}{k_{\sigma\mu}} \left(1 + \frac{K C_{R\sigma}^0}{\left(1 + \frac{K C_{A\mu}}{k_{\sigma\mu}} \right)^2} \right) \frac{\partial C_{A\mu}}{\partial t} \quad (2.35)$$

where K is the equilibrium constant of the reversible reaction and $k_{\sigma\mu}$ is the solute partition coefficient between the internal and membrane phases and the initial concentration of reactive $C_{R\sigma}^0$ in σ -phase. After [Bunge and Noble \(1984\)](#) presented the reversible reaction model, [Baird et al. \(1987\)](#) extended it to include the effects of multicomponent mixtures on the extraction rates of the individual components. [Lin and Long \(1997\)](#) also developed a model for carrier-mediated batch extraction of nitric acid based on the reversible reaction model.

2.2.2.3 Immobilized emulsion globule drop model

[Chan and Lee \(1987\)](#) proposed an immobilized emulsion globule drop model which assumes transport of solute by diffusion and reversible reaction in internal σ -phase. They also considered the continuous mass transfer resistance due to turbulent boundary layer in external γ phase, the interfacial resistance due to surfactant layer in the $\gamma - \mu$ -interface and the leakage of solute due to membrane rupture.

They proposed the next assumptions:

1. Isothermal batch separation process
2. Local physical and chemical equilibrium holds between the internal and membrane phases, i.e. no internal interfacial resistance is considered since the interfacial area is very large.
3. Concentration within the internal droplets of σ -phase is independent of position.
4. The physical partition coefficient of solute A between external and membrane phases, α_γ and that between internal and membrane phases α_σ are constant:

$$\alpha_\gamma = \frac{C_{A\mu}}{C_{A\gamma}}; \quad \alpha_\sigma = \frac{C_{A\mu}}{C_{A\sigma}} \quad (2.36)$$

5. At a constant given stirring speed, the volumetric leakage rate is assumed to be a product of a leakage function and the volume of the internal phase. In this model they assumed that the leakage function to be as follows:

$$J_\psi = -\frac{dV_\sigma}{dt} = \psi(t)V_\sigma \quad (2.37)$$

For the the leakage function, $\psi(t)$, the authors founded it independently by measuring the leakage rate of tracer from the drop emulsion to the external phase

The mass transfer equations proposed in this model are as follows:

In emulsion drops:

$$(1 - \phi_\sigma) \frac{\partial C_{A\mu}}{\partial t} + \phi_\sigma \frac{dC_{A\sigma}}{dt} = \frac{D_{\text{eff}}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{A\mu}}{\partial r} \right) \quad (2.38)$$

with the initial and boundary conditions:

$$t = 0 \quad C_{A\mu} = 0 \quad (2.39)$$

$$r = 0 \quad \frac{\partial C_{A\mu}}{\partial r} = 0 \quad (2.40)$$

$$r = R_\omega \quad D_{\text{eff}} \left(\frac{C_{A\mu}}{\partial r} \right) = K_0 \left(C_{A\gamma} - \frac{C_{A\mu}}{\alpha_\gamma} \Big|_{R_\omega} \right) \quad (2.41)$$

In Equation 2.41 K_0 is defined as:

$$\frac{1}{K_0} = \frac{1}{k} + \frac{1}{k_L} \quad (2.42)$$

Where $\frac{1}{k}$ is the interfacial resistance across the surfactant layer, $\frac{1}{k_L}$ is the external continuous phase mass transfer resistance across the boundary layer and $1/K_0$, is the combined overall resistance of these two effects.

In external continuous γ -phase :

$$-V_\gamma \frac{dC_{A\gamma}}{dt} = \frac{3(V_\sigma + V_\mu)}{R_\omega} D_{\text{eff}} \frac{\partial C_{A\mu}}{\partial r} \Big|_{r_\omega} - (J_A + J_P) \quad (2.43)$$

with the initial conditions:

$$t = 0 \quad C_{R\sigma} = C_{R\sigma}^0, \quad C_{A\gamma} = C_{A\gamma}^0 \quad (2.44)$$

The model has been found to predict satisfactorily the experimental results of the extraction of weak acids and weak bases in a batch separation system. [Chan and Lee \(1987\)](#) they suggested that an optimum extraction time is the time when the leakage rate equals the permeation rate.

[Yan et al. \(1992\)](#) developed a diffusion and reaction controlled model for Type-I facilitated transport of acetic acid (solute A) through a DES with NaOH as the internal reagent (R). The mass transfer, both inside and outside the emulsion globules, as well as the reaction between the solute and the internal reagent were taken into consideration in their model. Since far excess reagent was used, pseudo-first-order reaction between the solute and the internal reagent was assumed ($-r_A = k_\sigma C_{A\omega}$). The assumptions for this model are:

1. The emulsion drops (ω - region = γ - phase + μ - phase) are uniform and have no internal circulation. The internal droplets are evenly distributed in the emulsion drops.
2. No coalescence and redispersion occur between all emulsion drops. The external phase is well-mixed
3. The distribution coefficient and the diffusivity are constant
4. Emulsion breakage and swelling are neglected

Therefore, as a result the mass transfer equations proposed in this model are as follows:

In emulsion drops:

$$\frac{D_{\text{eff}}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{A\omega}}{\partial r} \right) = \frac{\partial C_{A\omega}}{\partial t} + \frac{\phi_{\sigma} k_{\sigma} C_{A\omega}}{\alpha} \quad (2.45)$$

with the initial and boundary conditions:

$$t = 0 \quad C_{A\omega} = 0 \quad (2.46)$$

$$r = 0 \quad \frac{\partial C_{A\omega}}{\partial r} = 0 \quad (2.47)$$

$$r = R_{\omega} \quad D_{\text{eff}} \left(\frac{C_{A\omega}}{\partial r} \right) = k \left(C_{A\gamma} - \frac{C_{A\omega}}{\alpha} \right) \quad (2.48)$$

In external continuous γ -phase :

$$V_{\gamma} \frac{dC_{A\gamma}}{dt} = \frac{3(V_{\sigma} + V_{\mu})}{R_{\omega}} D_{\text{eff}} \frac{\partial C_{A\omega}}{\partial r} \Big|_{r_{\omega}} \quad (2.49)$$

with the initial conditions:

$$t = 0 \quad C_{A\gamma} = C_{A\gamma}^0 \quad (2.50)$$

Where k is the mass transfer coefficient of solute A in external γ -phase, α is the distribution coefficient for solute between external γ -phase and the emulsion drop ω -region at equilibrium, which has the form:

$$\alpha = \frac{V_{\sigma} + \alpha' V_{\mu}}{V_{\sigma} + V_{\mu}} \quad (2.51)$$

where α' represents the distribution coefficient for solute between external γ -phase and the membrane μ -phase. Finally the authors stated that the agreement between model predictions and experimental data is much better than that of the advancing front model.

Yan (1993) also proposed a diffusion and reaction controlled model for Type-II-facilitated transport in which the next assumption was included:

"The solute A diffuses from the external phase onto the interface of the emulsion drop where it reacts with carrier C to form a complex AB . Then complex AB diffuses onto the interface of the internal phase where it reacts with the internal reagent R to release solute A and carrier C . Thereby A is separated from the external phase. The reactions may be expressed as follows:



Since the carrier is consumed on the outer interface of the membrane phase and regenerated on the inner interface, the concentration of the carrier on the interface is constant. Therefore, a pseudo-first-order forward reaction is assumed: $(-r_A) = k_\mu C_{A\gamma}$.

To test the applicability of the model, experiments on batch extraction of gold from auric chloride using DES were conducted. In general, the model was adequate to describe the extraction process. The model predictions were in good agreement with the experimental data.

Reis et al. (2006) proposed a similar diffusion controlled model that allows to predict the extraction for both type I and type II facilitated transports. The model is based on the improved advancing front model and takes into account the internal reaction. The authors concluded that the effects of the volume ratio of external phase to internal phase and the concentration of internal reagent are relevant to the extraction rate. The agreement between experimental and calculated results for solute extraction was found satisfactory for the systems under investigation. Huang et al. (2009) presented a model for type II facilitation that produces a closed-form solution and addresses most of the key ingredients in DES, including (1) external phase mass transfer resistance from external phase to the $\gamma - \mu$ interface, (2) mass fluxes at the $\gamma - \mu$ interface, (3) chemical equilibrium of reaction on the $\gamma - \mu$ interface, (4) simultaneous diffusion of the complex AB inside the emulsion drop, (5) reaction of the complex at the $\mu - \sigma$ interface, and (6) chemical equilibrium of the internal reaction at the $\mu - \sigma$ interface. Experimental data of DE extraction of arsenic were compared with model prediction. It shows that the model with its analytical solutions predicts experiments well.

2.3 Generalized one-equation model

Most of the studies reported in the literature for the development and testing of mathematical descriptions for solute transport with chemical reaction through DE membranes are based on intuitive considerations that could lead to rough approximations and inaccurate interpretation of experimental results. In their large majority, membrane film models (Cahn and Li 1974, Matulevicius and Li 1975, Kremesec and Slattery 1982) and distributed resistance models (Kopp et al. 1978, Ho et al. 1982, Kim et al. 1983, Stroeve and Varanasi 1984, Bunge and Noble 1984, Chan and Lee 1987, Yan et al. 1992, Reis et al. 2006, Huang et al. 2009), implicitly consider average equations where macroscopic quantities are not explicitly related to local values and therefore prediction of the effective coefficients is not considered. Morales-Zárate et al. (2008) were the first to derive a rigorous macroscopic model of diffusion and reaction in DES and to derive the jump boundary condition at the dividing surface. They divided the three-phase system into two homogeneous regions, η -region (γ -phase) and ω -region (μ -phase + σ -phase). Equations in both homogeneous regions were deduced from a generalized one-equation model, based on the *local mass equilibrium*, which establishes that the mass transfer process can be characterized by a single equilibrium weighted average concentration with the next form:

$$\{C_A\} = \varepsilon_\mu(\mathbf{x})\langle C_{A_\mu} \rangle^\mu + \frac{\varepsilon_\sigma(\mathbf{x})}{K_{\text{eq}}^{\mu\sigma}} \langle C_{A_\sigma} \rangle^\sigma + \frac{\varepsilon_\gamma(\mathbf{x})}{K_{\text{eq}}^{\mu\gamma}} \langle C_{A_\gamma} \rangle^\gamma \quad (2.54)$$

Where $\varepsilon_\lambda(\mathbf{x})$ is the volume fraction of the λ -phase and $\langle C_{A_\lambda} \rangle^\lambda$ is the volume average concentration of solute A in each of the phases involved i.e. $\lambda = \gamma, \mu, \sigma$. Furthermore $K_{\mu\gamma}^{\text{eq}}$ and $K_{\mu\sigma}^{\text{eq}}$ are the equilibrium distribution coefficients for the solute A in each phase. The equations governing the separation of solute A in the three-phase system were derived using the volume averaging method (Whitaker 1999). First, a generalized one-equation model was derived in order to describe the solute mass transfer in both homogeneous regions and in the inter-region ($\mathcal{A}_{\eta\omega}$). The volume average concentration and effective parameters were precisely defined in terms of local quantities. Order of magnitude analyses were performed to determine the length scale constraints associated to the macroscopic model.

The authors assumed that solute A is transferred from the η -region to the ω -region. In this latter region an irreversible reaction $A + R \longrightarrow P$ takes place in the σ -phase

while a reversible reaction $A \leftrightarrow B$ occurs in the μ -phase. The formulation of the problem is restricted to dilute solutions where convective transport is neglected. The closed set of equations describing the macroscopic mass transport of solute A in this three-phase system, is given by:

In the η -region:

$$\frac{\partial \{C_A\}_\eta}{\partial t} = \nabla \cdot (\mathbf{D}_{A\eta} \nabla \{C_A\}_\eta) \quad (2.55)$$

In the ω -region:

$$\frac{\partial \{C_A\}_\omega}{\partial t} = \nabla \cdot (\mathbf{D}_{A\omega} \nabla \{C_A\}_\omega) - \langle R \rangle_\omega \quad (2.56)$$

$$\langle R \rangle_\omega(\mathbf{x}) = \varepsilon_\sigma k_\sigma K_{\text{eq}}^{\mu\sigma} \{C_A\} \langle C_{R\sigma} \rangle^\sigma + \varepsilon_\mu k_\mu \left(\{C_A\} - \frac{\langle C_{B\mu} \rangle^\mu}{K_\mu} \right) \quad (2.57)$$

where $\langle R \rangle_\omega$ is the effective reaction rate term, k_σ, k_μ are the reaction rate constants in σ and μ -phases respectively, K_μ is the equilibrium reaction constant in μ -phase. $\mathbf{D}_{A\eta}$ and $\mathbf{D}_{A\omega}$ are the effectivity tensor of species A in the homogeneous region η and ω . Equations 2.55, 2.56 have the next boundary conditions at the inter region $\mathcal{A}_{\eta\omega}$:

$$-\mathbf{n}_{\eta\omega} \cdot \mathbf{D}_{A\eta} \nabla \{C_A\}_\eta|_{\mathbf{x}} = -\mathbf{n}_{\eta\omega} \cdot \mathbf{D}_{A\omega} \nabla \{C_A\}_\omega|_{\mathbf{x}} \quad (2.58)$$

$$-\mathbf{n}_{\eta\omega} \cdot \mathbf{D}_{A\omega} \nabla \{C_A\}_\omega|_{\mathbf{x}} = P_{\text{eff}}^\eta (\{C_A\}_\eta|_{\mathbf{x}} - K_{\text{eff}}^{\eta\omega} \{C_A\}_\omega|_{\mathbf{x}}) \quad (2.59)$$

where $\mathbf{n}_{\eta\omega}$ is the unit normal vector directed from the η -region towards ω -region, $K_{\text{eff}}^{\eta\omega}$ is the effective equilibrium coefficient at the $\eta - \omega$ dividing surface and P_{eff}^η is the effective permeability in the η -region.

Objectives

As mentioned in the previous chapter, the potential of DE in new and innovative separation processes has brought the attention of several research groups. However, information about the diffusion and reaction phenomena inside the emulsion drops has not been included in the mathematical descriptions in detail yet. Therefore, the general objective of this thesis is:

- To describe the solute transport with chemical reaction through DES by means of rigorous modeling that can provide with valuable information from the micro-scale to be applied in the macro-scale.

To accomplish this, the *method of volume averaging* (Whitaker 1999) will be used because it allows to rigorously derive continuum equations for multiphase systems characterized by more than one disparate length scales. The assumption of *non-local mass equilibrium* (NLME) is assumed due to the complex physicochemical composition of DE. The structure of the DES will be studied from two different perspectives: 1) the DES as a single domain where concentration changes occur in the same length scale and 2) the DES consists in two homogeneous regions where concentration changes occur at two different length scales. In order to achieve the above, the following specific objectives are proposed:

- To develop the averaged equations for the three-phase and two-regions macroscopic models.
- To predict the effective coefficients involved in the averaged equations for both models
- To analysis of a DE-containing separation process in a stirred tank by applying both models.

Part II

Diffusion and reaction in Double Emulsion systems

Chapter 3

Double emulsions and the method of volume averaging

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3.1 Averaging volume philosophy

The method of volume averaging is a technique proposed by Whitaker (1999) that can be used to rigorously derive continuum equations for multiphase-systems. This means that equations which are valid within a particular phase can be spatially smoothed to produce equations that are valid everywhere.

Whitaker (1999) explain that most porous media of practical importance are hierarchical in nature, i.e., they are characterized by more than one length scale. When these length scales are disparate, the hierarchical structure can be analyzed by the method of volume averaging. For example, in process where one needs to know how one species is transported through the pores to the external surface where the species can be removed, the direct analysis of this process, in terms of transport equations that are valid within the pores, is essentially impossible because of the complex structure of the typical porous medium. Rather than attack this problem in terms of equations and boundary conditions that are valid in the pores, one can use the pore-scale information to derive local volume averaged equations that are valid everywhere. At each level of the method of volume averaging there are three principle objectives:

1. Development of the spatially smoothed equations and the identification of the constraints that must be satisfied in order for these equations to be valid.
2. Derivation of the closure problems that are necessary to predict the effective transport coefficients that appear in the spatially smoothed transport equations.
3. Comparison between theory and experiment

3.1.1 Length scales and averaging volumes for a double emulsion system

The Double Emulsion multiphase Systems (γ, μ, σ phases) are characterized by more than one length scale and these length scales are disparate, in Figure 3.1 we can see the macroscopic batch-stirred tank reactor, *Scale I*. The essential macroscopic characteristic of the tank is the change in the solute concentration that occurs from the external γ -phase to the inlet of droplets of σ -phase, and this change is determined by the diffusion rate and the chemical reactions that take place in the emulsion drops, *Scale II*. The efficient design of the tank reactor requires the information about

interface transfer resistances at $\gamma\mu$ surface and $\mu\sigma$ surface and the rate of reactions in μ and σ phases respectively, that occur in *Scale III*. From this analysis, we can

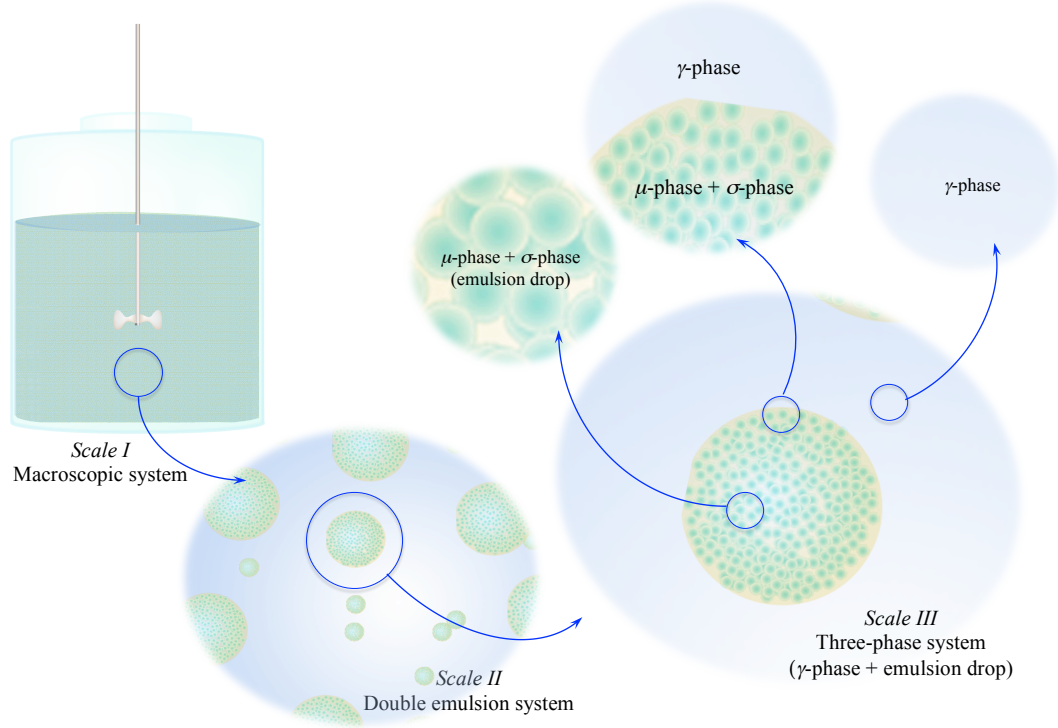


Figure 3.1: Length scales and averaging volumes for a Double Emulsion System

conclude that a DE separation process can be modeled with the volume average method since it is a hierarchical system with scale disparity. In this study our goal is to transport information from Scale III to Scale I.

3.1.2 Diffusion and reaction in porous media

Different systems in which diffusion and reaction phenomena occur have been studied with the method of volume averaging. For example, the process of bulk diffusion in a porous catalyst with heterogeneous reaction (Ochoa-Tapia et al. 1993), in biofilms (Wood and Whitaker 1998, Wood and Whitaker 2000) or the cell growth kinetics and substrate diffusion in a polymer scaffold (Galban and Locke 1999). A general procedure by which governing point equations and boundary conditions for diffusion and reaction can be spatially smoothed to produce continuum models for multiphase

systems is:

1. To illustrate the process of spatial smoothing which leads to the governing equation for the local volume averaged concentration, $\langle c_{A\gamma} \rangle$.
2. To develop the closure problem for the spatial deviation concentration $\tilde{c}_{A\gamma}$ that appears in the spatially smoothed equation for $\langle c_{A\gamma} \rangle$.
3. To solve the closure problem in order to predict values of the effective diffusivity tensor, \mathbf{D}_{eff} .

3.1.2.1 Non-local mass equilibrium

The concept of *local equilibrium* is strictly associated to multiphase systems. The *local mass and thermal equilibrium* have been introduced by Whitaker (1986), Whitaker (1999) to obtain a one-equation model in multiphase systems. When the principle of local mass equilibrium is valid a single transport equation can be used to describe the overall process of diffusion and reaction and it requires that certain time and length-scale constraints be valid. The dependent variable for this one-equation model is the equilibrium weighted average concentration.

In the case of diffusion and reaction in DES, Morales-Zárate et al. (2008) made use of the local mass equilibrium and proposed that the mass transfer process was characterized by the single equilibrium weighted average concentration (Eq. 6.1):

$$\{C_A\} = \varepsilon_\mu(\mathbf{x})\langle C_{A_\mu} \rangle^\mu + \frac{\varepsilon_\sigma(\mathbf{x})}{K_{\text{eq}}^{\mu\sigma}}\langle C_{A_\sigma} \rangle^\sigma + \frac{\varepsilon_\gamma(\mathbf{x})}{K_{\text{eq}}^{\mu\gamma}}\langle C_{A_\gamma} \rangle^\gamma \quad (3.1)$$

Nevertheless, Wood and Whitaker (1998) explain that if the constraints associated with local mass equilibrium are not valid, it will be necessary to propose a model that involves the transport equations for each phase in the system, i. e. a *Non-local equilibrium model*. In this respect Morales-Zárate et al. (2008) established that the assumption of local mass equilibrium was valid when:

1. The difference between the physicochemical coefficients of the σ -phase and the μ -phase is negligible
2. Either ε_μ or ε_σ is much less than the unity.

These two restrictions seem far from reality. First, as explained in previous chapters, the μ -phase and σ -phase are immiscible, which makes their physicochemical properties quite different between them, in addition their properties can vary greatly

depending on the surfactants and chemicals that are added to stabilize the system. Thus, to assume their physicochemical coefficients are similar can be very risky. And secondly because even though one knows that none of the volumetric fractions (ε_μ or ε_σ) can approach to unity, they are of the order of magnitude 10^{-1} . For example [Ahmad et al. \(2017\)](#) proposed for cadmium extraction from aqueous solution a volume ratio of internal:membrane phase equal to 1:3 i.e. $\varepsilon_\mu = 0.75$ and $\varepsilon_\sigma = 0.25$ and [Berrios et al. \(2010\)](#) reported a volume ration between 2:3 until 3:2. For all the above, one of the objectives of this thesis is to address the mass transport through DES from the perspective of *Non-local mass equilibrium*.

3.2 Governing equations and boundary conditions in a DES

Let us consider the three-phase DES illustrated in [Figure 3.2](#), thus *Scale III* in [Figure 3.1](#). In this three-phase system, it is assumed that species A is transferred from γ -phase to σ -phase. In this latter phase an irreversible reaction $A + R \rightarrow P$ takes place while a reversible reaction $A \rightleftharpoons B$ occurs in the μ -phase. The formulation of the problem is restricted to dilute solutions where convective transport is neglected. The local equations and the boundary conditions for the diffusive mass transfer with chemical reactions process in a DE have already proposed by [Morales-Zárata et al. \(2008\)](#) and for this work we base on them. Therefore the formulation of the problem is:

In γ -phase

$$\frac{\partial C_{A\gamma}}{\partial t} = \nabla \cdot (\mathcal{D}_{A\gamma} \nabla C_{A\gamma}) \quad (3.2)$$

In μ -phase

$$\frac{\partial C_{A\mu}}{\partial t} = \nabla \cdot (\mathcal{D}_{A\mu} \nabla C_{A\mu}) - R_\mu \quad (3.3)$$

$$\frac{\partial C_{B\mu}}{\partial t} = \nabla \cdot (\mathcal{D}_{B\mu} \nabla C_{B\mu}) + R_\mu \quad (3.4)$$

In σ -phase

$$\frac{\partial C_{A\sigma}}{\partial t} = \nabla \cdot (\mathcal{D}_{A\sigma} \nabla C_{A\sigma}) - R_\sigma \quad (3.5)$$

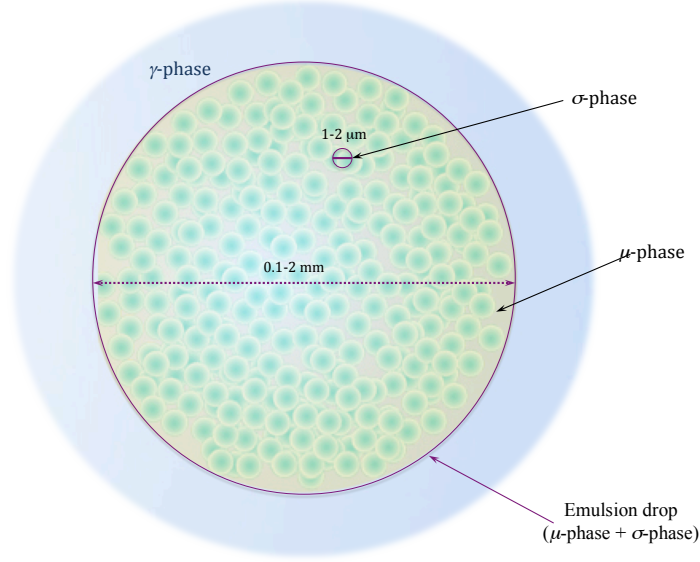


Figure 3.2: *Schema of Double Emulsion System*

The kinetics of the reversible and irreversible chemical reactions occurring in the μ and σ phases can be defined respectively as:

$$R_{\mu} = k_{\mu} \left(C_{A\mu} - \frac{C_{B\mu}}{K_{\mu}} \right) \quad (3.6)$$

$$R_{\sigma} = k_{\sigma} C_{A\sigma} \quad (3.7)$$

The first order rate of reaction in Eq. 3.7 is assumed that reactive R in σ -phase which reacts irreversibly with solute A is in excess thus one can consider that concentration of species R , C_R , is constant. Eqs. 3.2-3.5 are associated to the following interfacial boundary conditions:

At the interface between γ -phase and μ -phase ($\mathcal{A}_{\gamma\mu}$):

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla C_{A\mu} = -\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\gamma} \nabla C_{A\gamma} \quad (3.8)$$

$$-\mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla C_{A\gamma} = P_{\gamma\mu} (C_{A\gamma} - K_{\mu\gamma}^{eq} C_{A\mu}) \quad (3.9)$$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu} \nabla C_{B\mu} = 0 \quad (3.10)$$

At the interface between μ -phase and σ -phase ($\mathcal{A}_{\mu\sigma}$):

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla C_{A\mu} = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla C_{A\sigma} \quad (3.11)$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla C_{A\sigma} = P_{\sigma\mu} (C_{A\sigma} - K_{\mu\sigma}^{eq} C_{A\mu}) \quad (3.12)$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla C_{B\mu} = 0 \quad (3.13)$$

Here $C_{\beta\lambda}$ is the local concentration and $\mathcal{D}_{\beta\lambda}$ is the molecular diffusivity of species β in the λ -phase respectively. Where $\beta = A, B$ and $\lambda = \gamma, \mu, \sigma$. The boundary conditions Eqs. 3.8, 3.9, 3.11 and 3.12 have been derived following Wood and Whitaker (1998), who proposed a model for membrane transport based on a set of interfacial flux consecutive equations. Here, $\mathbf{n}_{\gamma\mu}$ and $\mathbf{n}_{\mu\sigma}$ are the unit normal vectors pointing from γ -phase to μ -phase ($\mathbf{n}_{\gamma\mu} = -\mathbf{n}_{\mu\gamma}$) and from μ -phase to σ -phase ($\mathbf{n}_{\mu\sigma} = -\mathbf{n}_{\sigma\mu}$) respectively. The permeabilities of the $\gamma\mu$ -interface and $\mu\sigma$ -interface are represented by $P_{\gamma\mu}$ and $P_{\mu\sigma}$. Furthermore $K_{\mu\gamma}^{eq}$ and $K_{\mu\sigma}^{eq}$ are the equilibrium distribution coefficients for the solute A in each phase, all the coefficients are functions of local equilibrium constants. Eqs. 3.10 and 3.13 indicate that species B is insoluble in γ and σ phases.

The set of equations given by Eqs. 3.2 - 3.13 represents a reasonably simple model of mass transfer in a DE system, but it still retains the essential features of the separation process. However, the solution of this point problem is impractical, and may contain more information than is needed. We are interested in describing the system at the macroscopic scale (*Scale I* and *Scale II*), and to accomplish it, in the next chapters the spatially smoothed transport equations have been developed.

3.3 Averaging volumes in DES

The process of spatial smoothing begins by associating with every point in space an *averaging volume* (or representative elementary volume, REV) which is invariant with respect to time and space (Whitaker 1999). For the three-phase DES under consideration, we decided to express the averaging volume in two different ways:

- *Three-phase averaging volume*: when the averaging domain of volume is composed of γ, μ and σ phases

- *Two-regions averaging volumes*: when the system is view as a 2-region problem where two averaging volumes are established. The first one composed of μ and σ phases to form the ω -region and the second averaging volume composed of η (γ -phase) and ω regions.

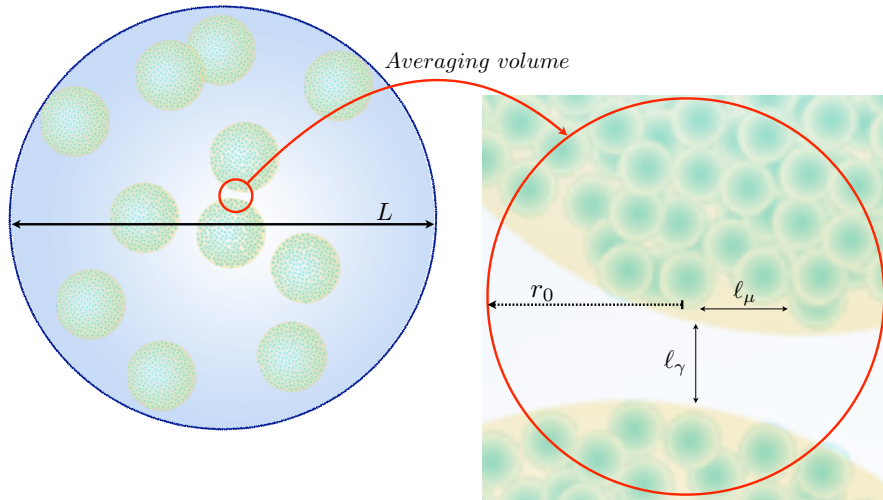
As a result of these ways of representing the problem, two different averaged macroscopic models were obtained. Each model presents important information about the *Scale III* in a different way. One of the interests of this thesis is to compare both assumptions.

3.3.1 Three-phase averaging volume

The three-phase averaging volume illustrated in Figure 3.3 includes a emulsion drop or parts of it and the γ -phase around it. This leads to expression:

$$\mathcal{V} = V_\gamma(\mathbf{x}) + V_\mu(\mathbf{x}) + V_\sigma(\mathbf{x}) \quad (3.14)$$

Here $V_\lambda(\mathbf{x})$ represents the volume of the λ -phase contained within the averaging



$$\mathcal{V} = V_\gamma + V_\mu + V_\sigma$$

Figure 3.3: Macroscopic region and three-phase averaging volume for the DES, $\mathcal{V} = V_\gamma(\mathbf{x}) + V_\mu(\mathbf{x}) + V_\sigma(\mathbf{x})$

volume. The assumption of the three-phase averaging volume and the non-local mass

equilibrium used in the modeling of DES, produce the Three-phase model which is composed of 3 coupled averaged equations, each one describing the mass transfer of species A in the corresponding phase. However the 3 coupled averaged equations are valid every where in the homogeneous averaged system. Detailed information about the structure of DE and the transport in the interfacial areas given by Eqs. 3.8 to 3.13 will be represented in effective coefficients and exchange terms respectively. To illustrate this, the simplified governing averaged equation of species A in γ -phase is presented:

$$\underbrace{\varepsilon_\gamma(\mathbf{x}) \frac{\partial \langle C_{A\gamma} \rangle^\gamma}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot [\mathbf{D}_{\gamma\gamma}(\mathbf{x}) \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{D}_{\gamma\mu}(\mathbf{x}) \cdot \nabla \langle C_{A\mu} \rangle^\mu]}_{\text{diffusion}} + \underbrace{a_{v_1} k_1^{\mu\gamma} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\gamma} \rangle^\gamma)}_{\text{exchange term}} + \underbrace{a_{v_1} k_1^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma)}_{\text{exchange term}} \quad (3.15)$$

Here it is highlighted that averaged concentration of A in γ -phase $\langle C_{A\gamma} \rangle^\gamma$ is coupled to averaged concentrations $\langle C_{A\mu} \rangle^\mu$ and $\langle C_{A\sigma} \rangle^\sigma$ by means of diffusion and exchange terms. Exchange terms have the function of providing information about mass exchange in the interfaces $\mathcal{A}_{\mu\gamma}$ and $\mathcal{A}_{\sigma\mu}$. $\mathbf{D}_{\gamma\gamma}$, $\mathbf{D}_{\gamma\mu}$, $a_{v_1} k_1^{\mu\gamma}$, $a_{v_1} k_1^{\mu\sigma}$ give information related to DE structure and molecular properties.

3.3.2 Two-regions averaging volumes

Another way to analyze the DE system at *Scale III* is to see the emulsion drop composed of μ -phase and σ -phase as a homogeneous region ω and the γ -phase as a homogeneous region η . This could be done by taking a first averaging volume as:

$$\mathcal{V} = V_\mu(\mathbf{x}) + V_\sigma(\mathbf{x}) \quad (3.16)$$

The assumption of the two-phase averaging volume, presented in Figure 3.4, and the non-local mass equilibrium produce 2 coupled averaged equations valid every where in the homogeneous region ω . Detailed information about the structure of an emulsion drop and the transport in the interfacial area gives by Eq. 5.7 will be represented in effective coefficients and the exchange term respectively. To illustrate the above,

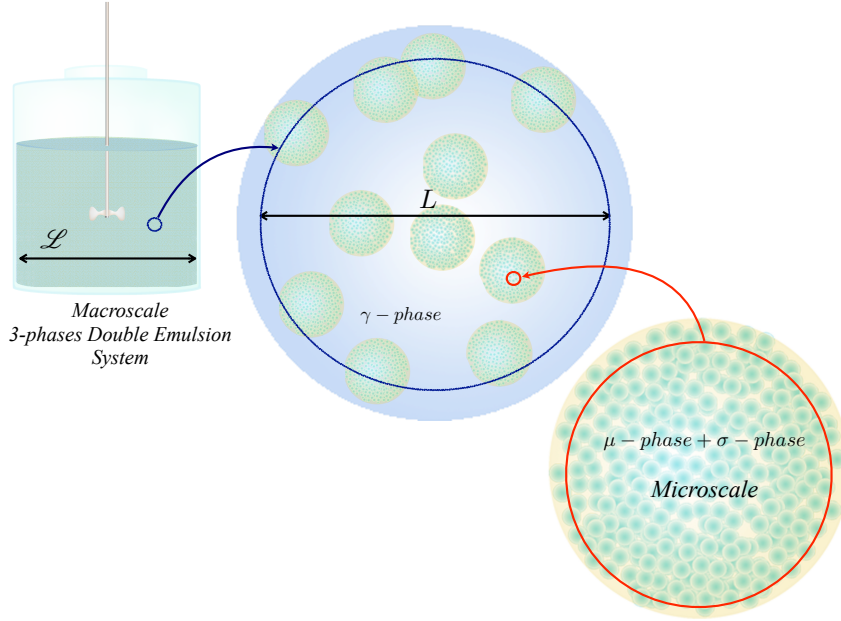


Figure 3.4: *Macroscopic region (\mathcal{L}) and averaging volume for the drop emulsion $\mu - \sigma$ -system*

the simplified governing averaged equation of species A in σ -phase is presented:

$$\underbrace{\varepsilon_{\sigma}(\mathbf{x}) \frac{\partial \langle C_{A\sigma} \rangle_{\omega}^{\sigma}}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot [\mathbf{D}_{\sigma\mu}(\mathbf{x}) \cdot \nabla \langle C_{A\mu} \rangle_{\omega}^{\mu} + \mathbf{D}_{\sigma\sigma}(\mathbf{x}) \cdot \nabla \langle C_{A\sigma} \rangle_{\omega}^{\sigma}]}_{\text{diffusion}} + \underbrace{(a_v k)_{\sigma} (\langle C_{A\sigma} \rangle_{\omega}^{\sigma} - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle_{\omega}^{\mu})}_{\text{exchange term}} - \underbrace{k_{\sigma} \varepsilon_{\sigma}(\mathbf{x}) \langle C_{A\sigma} \rangle_{\omega}^{\sigma}}_{\text{reaction}} \quad (3.17)$$

Just as in Eq. 3.15, one can observe that averaged concentration of A in σ -phase $\langle C_{A\sigma} \rangle_{\omega}^{\sigma}$ is coupled to averaged concentration $\langle C_{A\mu} \rangle_{\omega}^{\mu}$ by means of diffusion and exchange terms. $\mathbf{D}_{\sigma\mu}$, $\mathbf{D}_{\sigma\sigma}$, $(a_v k)_{\sigma}$ have information related to the emulsion drop structure.

Once the volume averaged equations for ω -region were derived, a new system by regions is defined as is shown in Figure 3.5 where homogeneous η -region, formed by γ -phase, contains drops of ω -region. Thus, it is convenient to establish the second volume averaging as:

$$\mathcal{V} = V_{\eta}(\mathbf{x}) + V_{\omega}(\mathbf{x}) \quad (3.18)$$

At this point, it is important to note that for this perspective two general length scales have been considered. One general length scale is associated with the droplets

of σ -phase disperse in the μ -phase, thus l_σ and l_μ lengths. A second general length scale is associated with emulsion drops of ω -region disperse in η -phase, l_ω and l_η which are larger than l_σ and l_μ .

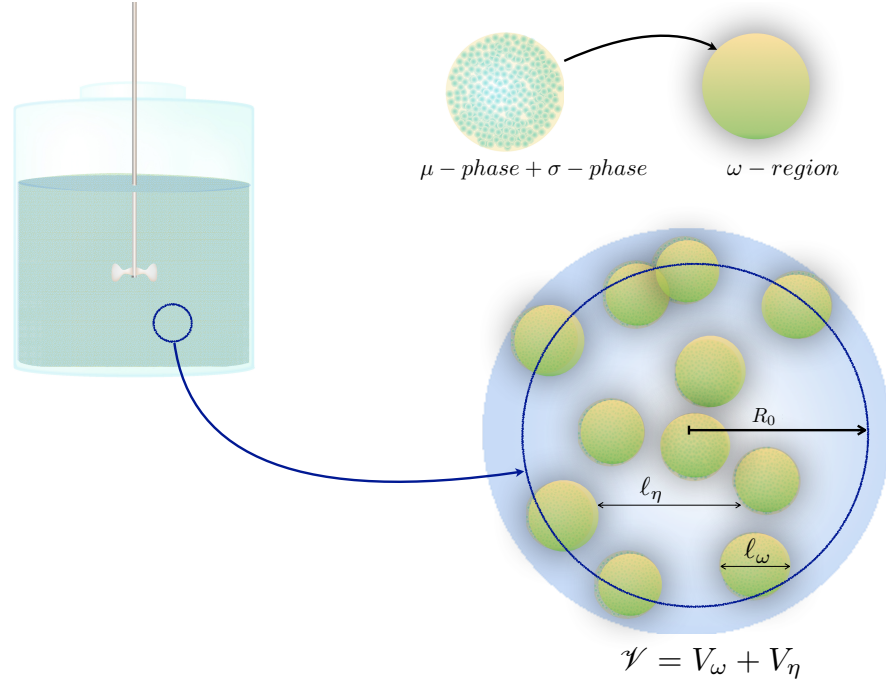


Figure 3.5: Macroscopic region and two-region averaging volume for the DES, $\mathcal{V} = V_\eta(\mathbf{x}) + V_\omega(\mathbf{x})$

This time, the use of the two-region averaging volume and the non-local mass equilibrium assumption in the smooth averaging has produced coupled regional averaged equations valid every where in the regional domain. Detailed information about the structure of the system and the transport in the interfacial area $\mathcal{A}_{\eta\omega}$ will be represented in effective coefficients and the exchange term respectively. To illustrate the above, the simplified governing averaged equation of species A in η -region is presented:

$$\begin{aligned}
 \underbrace{\varepsilon_\eta \frac{\partial \{C_{A\eta}\}^\eta}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot [\mathbf{D}_{\eta\gamma} \cdot \nabla \{C_{A\eta}\}^\eta + \mathbf{D}_{\eta\mu} \cdot \nabla \{\langle C_{A\mu} \rangle_\omega^\mu\} + \mathbf{D}_{\eta\sigma} \cdot \nabla \{\langle C_{A\sigma} \rangle_\omega^\sigma\}]}_{\text{diffusion}} \\
 &+ \underbrace{a_{v1} k_1^{\omega\eta} (K_{\mu\gamma}^{eq} \{\langle C_{A\mu} \rangle_\omega^\mu\} - \{C_{A\eta}\}^\eta)}_{\text{exchange term}}
 \end{aligned} \tag{3.19}$$

Chapter 4

Three-phase modeling approach of double emulsion system

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4.1 Spatial smoothing

The purpose of this section is to develop the volume averaged equations, base on the Eqs. 3.2 - 3.5 and associated with averaging volume \mathcal{V} (or representative elementary volume, REV) illustrated in Figure 3.3. The details of this averaging volume are presented in Figure 4.1 where we have used the position vector \mathbf{r}_γ to locate any point in the γ -phase. The position vector \mathbf{x} locates the centroid of the averaging volume which may lie in whether γ , μ or σ -phases. The relative position vector \mathbf{y}_γ is used to locate points in the γ -phase relative to the centroid of \mathcal{V}

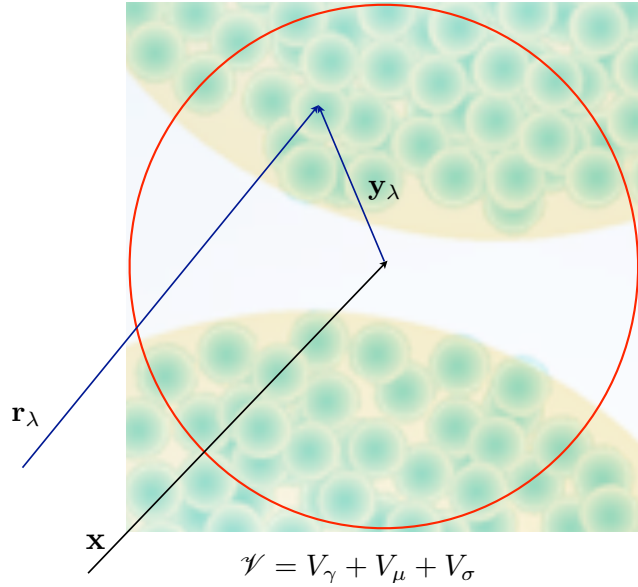


Figure 4.1: Three-phase averaging volume for the DES

In terms of the $\mathcal{V} = V_\gamma(\mathbf{x}) + V_\mu(\mathbf{x}) + V_\sigma(\mathbf{x})$, let us introduce the superficial averaging operator of a continuous property, ψ_λ ($\lambda = \gamma, \mu, \sigma$), as follows :

$$\langle \psi_\lambda \rangle |_{\mathbf{x}} = \frac{1}{\mathcal{V}} \int_{V_\lambda(\mathbf{x})} \psi_\lambda |_{\mathbf{x}+\mathbf{y}_\lambda} dV \quad (4.1)$$

where V_λ is the domain occupied by the λ -phase in the REV, and \mathbf{y}_λ is the vector that locates points of the λ -phase within the REV. The intrinsic averaging operator is defined as

$$\langle \psi_\lambda \rangle^\lambda |_{\mathbf{x}} = \frac{1}{V_\lambda} \int_{V_\lambda(\mathbf{x})} \psi_\lambda |_{\mathbf{x}+\mathbf{y}_\lambda} dV \quad (4.2)$$

Both averaging operators are related by

$$\langle \psi_\lambda \rangle = \varepsilon_\lambda(\mathbf{x}) \langle \psi_\lambda \rangle^\lambda \quad (4.3)$$

Where $\varepsilon_\lambda = V_\lambda(\mathbf{x})/\mathcal{V}$ is the volume fraction of the λ -phase within the averaging domain, therefore

$$\varepsilon_\gamma(\mathbf{x}) + \varepsilon_\mu(\mathbf{x}) + \varepsilon_\sigma(\mathbf{x}) = 1 \quad (4.4)$$

In the above expressions, we have explicitly indicated the spatial dependence of volume averaged quantities, this is convenient for the derivation of average macroscopic equations that are valid everywhere in the system.

4.1.1 Averaging model

The process of volume averaging is initiated by applying the superficial average operator to the governing equations Eqs. 3.2-3.5. As an example, upon averaging Eq. 3.2 one can obtain:

$$\left\langle \frac{\partial C_{A\gamma}}{\partial t} \right\rangle = \langle \nabla \cdot (\mathcal{D}_{A\gamma} \nabla C_{A\gamma}) \rangle \quad (4.5)$$

Since $V_\gamma(\mathbf{x})$ is not a function of the time, we can make use of the general transport theorem (Whitaker 1992) and interchange differentiation and integration in the left hand side (LHS) of Eq. 4.5, leading to

$$\frac{\partial \langle C_{A\gamma} \rangle}{\partial t} = \langle \nabla \cdot (\mathcal{D}_{A\gamma} \nabla C_{A\gamma}) \rangle \quad (4.6)$$

Applying the Spatial Averaging Theorem (Whitaker 1999), for some quantity ψ_γ associated with the γ -phase (Eq.4.7), and his vector form (Eq. 4.8):

$$\langle \nabla \psi_\gamma \rangle = \nabla \langle \psi_\gamma \rangle + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \psi_\gamma|_{\mathbf{x}+\mathbf{y}_\gamma} dA \quad (4.7)$$

$$\langle \nabla \cdot \mathbf{a}_\gamma \rangle = \nabla \cdot \langle \mathbf{a}_\gamma \rangle + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathbf{a}_\gamma|_{\mathbf{x}+\mathbf{y}_\gamma} dA \quad (4.8)$$

to the term of the right hand side (RHS) of Eq. 4.6 and assuming that $\mathcal{D}_{A\gamma}$ is constant within the averaging volume, it is possible to express in Eq. 4.6 the diffusive flux in

terms of $\langle C_{A\gamma} \rangle$ as:

$$\begin{aligned} \frac{\partial \langle C_{A\gamma} \rangle |_{\mathbf{x}}}{\partial t} = & \nabla \cdot \left[\mathcal{D}_{A\gamma} \left(\nabla \langle C_{A\gamma} \rangle |_{\mathbf{x}} + \frac{1}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} C_{A\gamma} |_{\mathbf{x}+\mathbf{y}_\lambda} dA \right) \right] \\ & + \frac{1}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla C_{A\gamma} |_{\mathbf{x}+\mathbf{y}_\lambda} dA \end{aligned} \quad (4.9)$$

In Eq. 4.9 all the terms associated with the area $\mathcal{A}_{\mu\sigma}$ are zero, since due to the nature of the system, the $C_{A\gamma}$ does not exist in this area. The same reasoning was used for the averaged equation in σ -phase, where all the terms associated with $\mathcal{A}_{\gamma\mu}$ are zero. Otherwise, Eq. 4.9 can be rewritten in terms of the intrinsic averaged quantities given by:

$$\begin{aligned} \varepsilon_\gamma(\mathbf{x}) \frac{\partial \langle C_{A\gamma} \rangle^\gamma |_{\mathbf{x}}}{\partial t} = & \nabla \cdot \mathcal{D}_{A\gamma} \left(\varepsilon_\gamma \nabla \langle C_{A\gamma} \rangle^\gamma |_{\mathbf{x}} + \langle C_{A\gamma} \rangle^\gamma |_{\mathbf{x}} \nabla \varepsilon_\gamma \right) \\ & + \nabla \cdot \mathcal{D}_{A\gamma} \left(\frac{1}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} C_{A\gamma} |_{\mathbf{x}+\mathbf{y}_\lambda} dA \right) \\ & + \frac{1}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla C_{A\gamma} |_{\mathbf{x}+\mathbf{y}_\lambda} dA \end{aligned} \quad (4.10)$$

Besides considering the diffusivity $\mathcal{D}_{A\gamma}$ as constant in the averaging volume, no additional assumptions were made. However it was use the following relation, deduced from the Spatial Averaging Theorem (SAT)

$$\frac{1}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} dA = -\nabla \varepsilon_\gamma, \quad (4.11)$$

in Eq. 4.10 leading to:

$$\begin{aligned} \varepsilon_\gamma(\mathbf{x}) \frac{\partial \langle C_{A\gamma} \rangle^\gamma |_{\mathbf{x}}}{\partial t} = & \nabla \cdot \mathcal{D}_{A\gamma} (\varepsilon_\gamma \nabla \langle C_{A\gamma} \rangle^\gamma |_{\mathbf{x}}) \\ & + \nabla \cdot \mathcal{D}_{A\gamma} \left(\frac{1}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} (C_{A\gamma} |_{\mathbf{x}+\mathbf{y}_\lambda} - \langle C_{A\gamma} \rangle^\gamma |_{\mathbf{x}}) dA \right) \\ & + \frac{1}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla C_{A\gamma} |_{\mathbf{x}+\mathbf{y}_\lambda} dA \end{aligned} \quad (4.12)$$

here we have the volume averaged concentration $\langle C_{A\gamma} \rangle$ and the local concentration $C_{A\gamma}|_{\mathbf{x}+\mathbf{y}_\lambda}$ (where $\mathbf{x} + \mathbf{y}_\lambda = \mathbf{r}_\lambda$), in order to remove the local concentration in Eq. 4.12, we make use of the spatial decomposition define by [Gray \(1975\)](#):

$$C_{i,\lambda}|_{\mathbf{r}_\lambda} = \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{r}_\lambda} + \tilde{C}_{i,\lambda}|_{\mathbf{r}_\lambda}, \quad \text{where } i = A, B \quad (4.13)$$

in which $\tilde{C}_{i,\lambda}$ is referred to as the *spatial deviation concentration*. In some respects [Whitaker \(1999\)](#) suggested that one could think of Eq. 4.13 as decomposing the point concentration into what we want and whatever else remains. Eq. 4.13 also represents a decomposition of length scales. Thus the average concentration undergoes significant changes only over the large length-scale L and the spatial deviation concentrations are dominated by the small length-scales ℓ_γ and ℓ_μ (See Figure 3.3)

When Eq. 4.13 is used in Eq. 4.12 we obtain the averaged equation:

$$\begin{aligned} \varepsilon_\gamma(\mathbf{x}) \frac{\partial \langle C_{A\gamma} \rangle^\gamma|_{\mathbf{x}}}{\partial t} &= \nabla \cdot \mathcal{D}_{A\gamma}(\varepsilon_\gamma \nabla \langle C_{A\gamma} \rangle^\gamma|_{\mathbf{x}}) \\ &+ \nabla \cdot \mathcal{D}_{A\gamma} \left(\frac{1}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} (\tilde{C}_{A\gamma}|_{\mathbf{x}+\mathbf{y}_\gamma} + \langle C_{A\gamma} \rangle^\gamma|_{\mathbf{x}+\mathbf{y}_\gamma}) dA \right) \\ &- \nabla \cdot \mathcal{D}_{A\gamma} \left(\frac{1}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \langle C_{A\gamma} \rangle^\gamma|_{\mathbf{x}} dA \right) \\ &+ \frac{1}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla (\langle C_{A\gamma} \rangle^\gamma|_{\mathbf{x}+\mathbf{y}_\gamma} + \tilde{C}_{A\gamma}|_{\mathbf{x}+\mathbf{y}_\gamma}) dA, \quad (4.14) \end{aligned}$$

here we have the non-closed averaged equation of A in γ -phase. It must be noted that besides the expected terms i.e., accumulation and diffusion, additional non-local terms are present. Eq. 4.14 is obviously more complicated than its point counterpart since no significant simplifications have been performed in the spatial smoothing process, this point will be discussed later. Continuing with the development of the averaged problem, an analogous averaging procedure has been applied to Eq. 3.3, using the

spatial averaging theorem for some quantity ψ_μ associated with the μ -phase,

$$\langle \nabla \psi_\mu \rangle = \nabla \langle \psi_\mu \rangle + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \psi_\mu|_{\mathbf{x}+\mathbf{y}_\mu} dA + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \psi_\mu|_{\mathbf{x}+\mathbf{y}_\mu} dA \quad (4.15)$$

$$\langle \nabla \cdot \mathbf{a}_\mu \rangle = \nabla \cdot \langle \mathbf{a}_\mu \rangle + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathbf{a}_\mu|_{\mathbf{x}+\mathbf{y}_\mu} dA + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathbf{a}_\mu|_{\mathbf{x}+\mathbf{y}_\mu} dA, \quad (4.16)$$

to obtain the non-closed averaged equation of species A in μ -phase which is given by:

$$\begin{aligned} \varepsilon_\mu(\mathbf{x}) \frac{\partial \langle C_{A\mu} \rangle^\mu|_{\mathbf{x}}}{\partial t} &= \nabla \cdot \mathcal{D}_{A\mu} (\varepsilon_\mu \nabla \langle C_{A\mu} \rangle^\mu|_{\mathbf{x}}) \\ &+ \nabla \cdot \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} (\tilde{C}_{A\mu}|_{\mathbf{x}+\mathbf{y}_\mu} + \langle C_{A\mu} \rangle^\mu|_{\mathbf{x}+\mathbf{y}_\mu}) dA \right) \\ &+ \nabla \cdot \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} (\tilde{C}_{A\mu}|_{\mathbf{x}+\mathbf{y}_\mu} + \langle C_{A\mu} \rangle^\mu|_{\mathbf{x}+\mathbf{y}_\mu}) dA \right) \\ &- \nabla \cdot \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \langle C_{A\mu} \rangle^\mu|_{\mathbf{x}} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \langle C_{A\mu} \rangle^\mu|_{\mathbf{x}} dA \right) \\ &+ \frac{1}{\mathcal{V}} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} (\nabla \langle C_{A\mu} \rangle^\mu|_{\mathbf{x}+\mathbf{y}_\mu} + \nabla \tilde{C}_{A\mu}|_{\mathbf{x}+\mathbf{y}_\mu}) dA \\ &+ \frac{1}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} (\nabla \langle C_{A\mu} \rangle^\mu|_{\mathbf{x}+\mathbf{y}_\mu} + \nabla \tilde{C}_{A\mu}|_{\mathbf{x}+\mathbf{y}_\mu}) dA \\ &- \varepsilon_\mu(\mathbf{x}) k_\mu \left(\langle C_{A\mu} \rangle^\mu|_{\mathbf{x}} - \frac{\langle C_{B\mu} \rangle^\mu|_{\mathbf{x}}}{K_\mu} \right), \end{aligned} \quad (4.17)$$

one can observe that Eq. 4.17 is composed of accumulation, diffusion and reversible reaction terms, and additional non-local terms as was observed in Eq. 4.14. However unlike the Eq. 4.14, it should be noted that in Eq. 4.17 both integrals on the interfacial areas $\mathcal{A}_{\mu\gamma}$ and $\mathcal{A}_{\mu\sigma}$ are presented, which indicates that the membrane μ -phase is adjacent to the other two phases and also mass exchange between them is presented.

In the case of the non-closed averaged equation of species B in μ -phase which has

the form :

$$\begin{aligned}
\varepsilon_\mu(\mathbf{x}) \frac{\partial \langle C_{B\mu} \rangle^\mu |_{\mathbf{x}}}{\partial t} &= \nabla \cdot \mathcal{D}_{B\mu} (\varepsilon_\mu \nabla \langle C_{B\mu} \rangle^\mu |_{\mathbf{x}}) \\
&+ \nabla \cdot \frac{\mathcal{D}_{B\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} (\tilde{C}_{B\mu} |_{\mathbf{x}+\mathbf{y}_\mu} + \langle C_{B\mu} \rangle^\mu |_{\mathbf{x}+\mathbf{y}_\mu}) dA \right) \\
&+ \nabla \cdot \frac{\mathcal{D}_{B\mu}}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} (\tilde{C}_{B\mu} |_{\mathbf{x}+\mathbf{y}_\mu} + \langle C_{B\mu} \rangle^\mu |_{\mathbf{x}+\mathbf{y}_\mu}) dA \\
&- \nabla \cdot \frac{\mathcal{D}_{B\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \langle C_{B\mu} \rangle^\mu |_{\mathbf{x}} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \langle C_{B\mu} \rangle^\mu |_{\mathbf{x}} dA \right) \\
&+ \varepsilon_\mu(\mathbf{x}) k_\mu \left(\langle C_{A\mu} \rangle^\mu |_{\mathbf{x}} - \frac{\langle C_{B\mu} \rangle^\mu |_{\mathbf{x}}}{K_\mu} \right) \tag{4.18}
\end{aligned}$$

one can remark that contrary to Eq. 4.17, the Eq. 4.18 does not contain the non local terms coming from:

$$\frac{1}{\mathcal{V}} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu} \nabla C_{B\mu} |_{\mathbf{x}+\mathbf{y}_\mu} dA + \frac{1}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla C_{B\mu} |_{\mathbf{x}+\mathbf{y}_\mu} dA \tag{4.19}$$

this can be shown by applying the averaging spatial theorem (Eq. 4.16) in the local equation (Eq. 3.4), and substituting impermeable boundary conditions (Eqs. 3.10 and 3.13). Finally, to obtain the non-closed averaged equation of species A in σ -phase, the averaging procedure has been repeated in local Eq. 3.5 and for this purpose the spatial averaging theorem for some quantity ψ_σ associated with the σ -phase has been used,

$$\langle \nabla \psi_\sigma \rangle = \nabla \langle \psi_\sigma \rangle + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \psi_\sigma |_{\mathbf{x}+\mathbf{y}_\sigma} dA \tag{4.20}$$

$$\langle \nabla \cdot \mathbf{a}_\sigma \rangle = \nabla \cdot \langle \mathbf{a}_\sigma \rangle + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathbf{a}_\sigma |_{\mathbf{x}+\mathbf{y}_\sigma} dA, \tag{4.21}$$

Therefore, the non-closed averaged equation of species A in σ -phase has the form

$$\begin{aligned}
\varepsilon_\sigma(\mathbf{x}) \frac{\partial \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}}}{\partial t} &= \nabla \cdot \mathcal{D}_{A\sigma} (\varepsilon_\sigma \nabla \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}}) \\
&+ \nabla \cdot \frac{\mathcal{D}_{A\sigma}}{\mathcal{V}} \left(\int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} (\tilde{C}_{A\sigma} |_{\mathbf{x}+\mathbf{y}_\sigma} + \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}+\mathbf{y}_\sigma}) dA \right) \\
&- \nabla \cdot \frac{\mathcal{D}_{A\sigma}}{\mathcal{V}} \left(\int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}} dA \right) \\
&+ \frac{1}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla (\langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}+\mathbf{y}_\sigma} + \tilde{C}_{A\sigma} |_{\mathbf{x}+\mathbf{y}_\sigma}) dA \\
&- k_\sigma \varepsilon_\sigma(\mathbf{x}) \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}}, \tag{4.22}
\end{aligned}$$

Eq. 4.22 contains the expected terms of accumulation, diffusion and irreversible reaction and, additional non-local terms. At this point it is important to stress that Eqs. 4.14 - 4.22 are non-local transport equations since the presence of the spatial deviation concentrations, $\tilde{C}_{i\lambda} |_{\mathbf{x}+\mathbf{y}_\lambda}$, and the volume average concentrations, $\langle C_{i\lambda} \rangle^\lambda |_{\mathbf{x}+\mathbf{y}_\lambda}$, evaluated at points other than the centroid \mathbf{x} . In order to express these equations only in terms of volume averaged quantities it is indispensable to 1) impose the following length-scale constraint (Whitaker 1999, Wood 2009),

$$\ell_\mu, \ell_\gamma \ll r_0 \ll L, \tag{4.23}$$

and 2) derive and solve the closure problems related to the spatial deviation concentrations, $\tilde{C}_{i\lambda}$. Therefore, in order to continue this analysis and simplify the averaged equations and obtain their closed form, a closure problem was developed which enables to predict the $\tilde{C}_{i,\lambda}$. The details of the derivation and formal solution of the closure problem are quite lengthy and are provided in Appendix A.

4.1.2 Closure variables

With the objective of obtaining a closed form for Eqs. 4.14 - 4.22, the formal solution of the spatial deviation concentrations is presented:

$$\begin{aligned}
\tilde{C}_{A\gamma} &= \mathbf{b}_{\gamma\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{b}_{\gamma\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{\gamma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{\gamma B} \cdot \nabla \langle C_{B\mu} \rangle^\mu \\
&- s_\gamma^{\mu\gamma} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\gamma} \rangle^\gamma) - s_\gamma^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma) \tag{4.24}
\end{aligned}$$

$$\begin{aligned}
\tilde{C}_{A\mu} &= \mathbf{b}_{\mu\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{b}_{\mu\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{\mu\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{\mu B} \cdot \nabla \langle C_{B\mu} \rangle^\mu \\
&+ s_\mu^{\mu\gamma} (\langle C_{A\gamma} \rangle^\gamma - K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu) + s_\mu^{\mu\sigma} (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu) \tag{4.25}
\end{aligned}$$

$$\begin{aligned}\tilde{C}_{B\mu} = & \mathbf{b}_{B\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{b}_{B\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{B\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{BB} \cdot \nabla \langle C_{B\mu} \rangle^\mu \\ & + s_B^{\mu\gamma} (\langle C_{A\gamma} \rangle^\gamma - K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu) + s_B^{\mu\sigma} (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu)\end{aligned}\quad (4.26)$$

$$\begin{aligned}\tilde{C}_{A\sigma} = & \mathbf{b}_{\sigma\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{b}_{\sigma\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{\sigma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{\sigma B} \cdot \nabla \langle C_{B\mu} \rangle^\mu \\ & - s_\sigma^{\mu\gamma} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\gamma} \rangle^\gamma) - s_\sigma^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma)\end{aligned}\quad (4.27)$$

Eqs. A.49 - A.52 have been proposed in terms of the sources of the boundary-value problems for $\tilde{C}_{i\lambda}$. As previously explained, the details of the development of these boundary-value problems are in Appendix A. In Eqs. A.49 - A.52, the variables \mathbf{b}_{ji} , $s_j^{\mu\gamma}$, $s_j^{\mu\sigma}$, where $j = \gamma, \mu, B, \sigma$ and $i = \gamma, \mu, \sigma, B$ are the closure variables, their derivation has been performed by considering the following length-scale constraints:

$$r_0 \ll L \quad (4.28)$$

$$r_0^2 \ll L^2 \quad (4.29)$$

$$\ell_\mu, \ell_\gamma \ll L \quad (4.30)$$

where it has been assumed that the characteristic lengths associated to the spatial variations of the volume averaged concentrations (and their gradients) can be represented by the system macroscopic length, L . In addition, the derivation of Eqs. A.49 - A.52, requires satisfying the following time-scale constraint:

$$\frac{\mathcal{D}_{A\lambda} t^*}{\ell_\lambda^2} \gg 1 \quad (4.31)$$

Substitution of A.49 - A.52 into 4.14 - 4.22 respectively, gives to the Three-phase averaged model considering NLME which is presented in the next section.

4.2 Closed averaged equations

In this section the Three-Phase Model is described. This averaged model is valid in the averaging volume formed by the homogeneous fluid (γ -phase) and emulsion drop ($\mu + \sigma$ phases). Since the *Non-local mass equilibrium* assumption has been used, the model is conformed of 3 averaged equations, each one describing the mass transfer of species A in the corresponding phase and the averaged equation of species B in μ -phase. Each equation contains terms of accumulation, diffusion, mass transfer exchange and convective-like transport. The latter terms are composed of effective

coefficients which provide information about one of the phases involved. For example, averaged equation of A in γ -phase, Eq. 4.77, has 3 effective diffusivity tensors with the form $\mathbf{D}_{\gamma j}$ where j can be γ, μ, σ , therefore when $j = \mu$, $\mathbf{D}_{\gamma\mu}$ contributes to Eq. 4.77 with information about the structure of the system related to μ -phase.

Governing averaged equation of species A in γ -phase:

$$\begin{aligned}
\underbrace{\varepsilon_\gamma \frac{\partial \langle C_{A\gamma} \rangle^\gamma}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot [\mathbf{D}_{\gamma\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{D}_{\gamma\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu]}_{\text{diffusion}} \\
&+ \underbrace{\nabla \cdot [\mathbf{D}_{\gamma B} \cdot \nabla \langle C_{B\mu} \rangle^\mu + \mathbf{D}_{\gamma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma]}_{\text{diffusion}} \\
&+ \underbrace{\nabla \cdot [\mathbf{u}_{\gamma\gamma} \langle C_{A\gamma} \rangle^\gamma + \mathbf{u}_{\gamma\mu} \langle C_{A\mu} \rangle^\mu + \mathbf{u}_{\gamma B} \langle C_{B\mu} \rangle^\mu + \mathbf{u}_{\gamma\sigma} \langle C_{A\sigma} \rangle^\sigma]}_{\text{convective-like transport term}} \\
&+ \underbrace{a_{v_1} k_1^{\mu\gamma} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\gamma} \rangle^\gamma)}_{\text{exchange term}} + \underbrace{a_{v_1} k_1^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma)}_{\text{exchange term}}
\end{aligned} \tag{4.32}$$

More in detail, in Eq. 4.32 one can see three types of effective transport coefficients: the effective diffusivity tensors $\mathbf{D}_{\gamma j}$, the effective velocity-like vectors $\mathbf{u}_{\gamma j}$ and the mass transfer coefficients $a_{v_1} k_1^{\mu j}$. All these coefficients can be computed from the fields of the closure variables (see Appendix A). For example the diffusivity tensor $\mathbf{D}_{\gamma\gamma}$ is defined as:

$$\mathbf{D}_{\gamma\gamma} = \mathcal{D}_{A\gamma} \left(\varepsilon_\gamma \mathbf{I} + \frac{1}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \mathbf{b}_{\gamma\gamma} dA \right) \tag{4.33}$$

in this case, the effective diffusivity tensor is function of the molecular diffusivity $\mathcal{D}_{A\gamma}$, the volumetric fraction ε_γ and the structure of the DES through the $\mathbf{b}_{\gamma\gamma}$ -field. In contrast the others effective diffusivity tensors, presented in Eq. 4.34 - 4.36, are functions of $\mathcal{D}_{A\gamma}$ and the $\mathbf{b}_{\gamma j}$ -field.

$$\mathbf{D}_{\gamma\mu} = \frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \mathbf{b}_{\gamma\mu} dA \tag{4.34}$$

$$\mathbf{D}_{\gamma B} = \frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \mathbf{b}_{\gamma B} dA \tag{4.35}$$

$$\mathbf{D}_{\gamma\sigma} = \frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \mathbf{b}_{\gamma\sigma} dA \tag{4.36}$$

In addition, the convective-like transport terms are generated by the mass exchange at the interfacial areas, and contain the effective velocity-like vectors which are defined by:

$$\mathbf{u}_{\gamma\gamma} = \frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \left(\int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \nabla \mathbf{b}_{\gamma\gamma} dA + \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} s_{\gamma}^{\mu\gamma} dA \right) \quad (4.37)$$

$$\mathbf{u}_{\gamma\mu} = \frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \left(\mathbf{n}_{\gamma\mu} \cdot \nabla \mathbf{b}_{\gamma\mu} - \mathbf{n}_{\gamma\mu} (K_{\mu\gamma}^{eq} s_{\gamma}^{\mu\gamma} + K_{\mu\sigma}^{eq} s_{\gamma}^{\mu\sigma}) \right) dA \quad (4.38)$$

$$\mathbf{u}_{\gamma B} = \frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \nabla \mathbf{b}_{\gamma B} dA \quad (4.39)$$

$$\mathbf{u}_{\gamma\sigma} = \frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \left(\int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \nabla \mathbf{b}_{\gamma\sigma} dA + \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} s_{\gamma}^{\mu\sigma} dA \right) \quad (4.40)$$

Whitaker (1999) has demonstrated that the convective-like transport term is negligible for the case of diffusion in porous catalysts and Paine et al. (1983) have shown that this contribution can be important when convection itself is important. In this sense in the next section it has been demonstrated that the effective velocity-like vectors presented here, are negligible for the case of mass transfer by diffusion and chemical reaction in DES. Lastly, the mass transfer coefficients of species A in Eq. 4.77 are defined as:

$$a_{v_1} k_1^{\mu\gamma} = -\frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \nabla s_{\gamma}^{\mu\gamma} dA \quad (4.41)$$

$$a_{v_1} k_1^{\mu\sigma} = -\frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \nabla s_{\gamma}^{\mu\sigma} dA, \quad (4.42)$$

in which a_{v_1} , is the interfacial area $\mathcal{A}_{\gamma\mu}$ per unit volume and $k_1^{\mu\gamma}$ is the film mass transfer coefficient in $\mathcal{A}_{\gamma\mu}$ the term $k_1^{\mu\sigma}$ is a cross coefficient.

Continuing with this description, the governing averaged equation of species A in

μ -phase is presented:

$$\begin{aligned}
\underbrace{\varepsilon_\mu \frac{\partial \langle C_{A\mu} \rangle^\mu}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot [\mathbf{D}_{\mu\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{D}_{\mu\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu]}_{\text{diffusion}} \\
&+ \underbrace{\nabla \cdot [\mathbf{D}_{\mu B} \cdot \nabla \langle C_{B\mu} \rangle^\mu + \mathbf{D}_{\mu\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma]}_{\text{diffusion}} \\
&+ \underbrace{\nabla \cdot [\mathbf{u}_{\mu\gamma} \langle C_{A\gamma} \rangle^\gamma + \mathbf{u}_{\mu\mu} \langle C_{A\mu} \rangle^\mu + \mathbf{u}_{\mu B} \langle C_{B\mu} \rangle^\mu + \mathbf{u}_{\mu\sigma} \langle C_{A\sigma} \rangle^\sigma]}_{\text{convective-like transport term}} \\
&+ \underbrace{[a_{v_1} k_1^{\mu\gamma} + a_{v_2} k_2^{\mu\gamma}] (\langle C_{A\gamma} \rangle^\gamma - K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu)}_{\text{exchange term}} \\
&+ \underbrace{[a_{v_1} k_1^{\mu\sigma} + a_{v_2} k_2^{\mu\sigma}] (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu)}_{\text{exchange term}} \\
&- \underbrace{\varepsilon_\mu k_\mu \left(\langle C_{A\mu} \rangle^\mu - \frac{\langle C_{B\mu} \rangle^\mu}{K_\mu} \right)}_{\text{reaction}}
\end{aligned} \tag{4.43}$$

As Eq. 4.32, Eq. 4.43 contains effective diffusivity tensors, such as $\mathbf{D}_{\mu\mu}$:

$$\mathbf{D}_{\mu\mu} = \mathcal{D}_{A\mu} \left(\varepsilon_\mu \mathbf{1} + \frac{1}{\gamma} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \mathbf{b}_{\mu\mu} + \frac{1}{\sigma} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{\mu\mu} dA \right), \tag{4.44}$$

here the effective diffusivity tensor is function of the molecular diffusivity $\mathcal{D}_{A\mu}$, the volumetric fraction ε_μ and the structure of the DES through the $\mathbf{b}_{\mu\mu}$ -field. It should be remarked that due to μ -phase is bounded by γ and σ phases all the effective coefficients presented in Eq. 4.43 are defined by both integrals, the first over $\mathcal{A}_{\gamma\mu}$ and the second over $\mathcal{A}_{\mu\sigma}$, as seen in the following tensors:

$$\mathbf{D}_{\mu\gamma} = \frac{\mathcal{D}_{A\mu}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \mathbf{b}_{\mu\gamma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{\mu\gamma} dA \right) \tag{4.45}$$

$$\mathbf{D}_{\mu B} = \frac{\mathcal{D}_{A\mu}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \mathbf{b}_{\mu B} dA + \int_{A_{\mu\sigma}} \mathbf{n}_{\mu\sigma} \mathbf{b}_{\mu B} dA \right) \tag{4.46}$$

$$\mathbf{D}_{\mu\sigma} = \frac{\mathcal{D}_{A\mu}}{\sigma} \left(\int_{A_{\mu\gamma}} \mathbf{n}_{\mu\gamma} \mathbf{b}_{\mu\sigma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{\mu\sigma} dA \right) \tag{4.47}$$

the effective velocity-like vectors of species A in the μ -phase are defined by:

$$\mathbf{u}_{\mu\gamma} = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} (\mathbf{n}_{\mu\gamma} \cdot \nabla \mathbf{b}_{\mu\gamma} + \mathbf{n}_{\mu\gamma} s_{\mu}^{\mu\gamma}) dA + \int_{A_{\mu\sigma}(\mathbf{x})} (\mathbf{n}_{\mu\sigma} \cdot \nabla \mathbf{b}_{\mu\gamma} + \mathbf{n}_{\mu\sigma} s_{\mu}^{\mu\sigma}) dA \right) \quad (4.48)$$

$$\begin{aligned} \mathbf{u}_{\mu\mu} = & \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left[\int_{A_{\mu\gamma}(\mathbf{x})} \left(\mathbf{n}_{\mu\gamma} \cdot \nabla \mathbf{b}_{\mu\gamma} - \mathbf{n}_{\mu\gamma} (K_{\mu\gamma}^{eq} \mathbf{n}_{\mu\gamma} s_{\mu}^{\mu\gamma} + K_{\mu\sigma}^{eq} s_{\mu}^{\mu\sigma}) \right) dA \right. \\ & \left. + \int_{A_{\mu\sigma}(\mathbf{x})} \left(\mathbf{n}_{\mu\sigma} \cdot \nabla \mathbf{b}_{\mu\gamma} dA - \mathbf{n}_{\mu\sigma} (K_{\mu\gamma}^{eq} s_{\mu}^{\mu\gamma} + K_{\mu\sigma}^{eq} s_{\mu}^{\mu\sigma}) \right) dA \right] \end{aligned} \quad (4.49)$$

$$\mathbf{u}_{\mu B} = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \nabla \mathbf{b}_{\mu B} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \nabla \mathbf{b}_{\mu B} dA \right) \quad (4.50)$$

$$\mathbf{u}_{\mu\sigma} = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} (\mathbf{n}_{\mu\gamma} \cdot \nabla \mathbf{b}_{\mu\sigma} + \mathbf{n}_{\mu\gamma} s_{\mu}^{\mu\sigma}) dA + \int_{A_{\mu\sigma}(\mathbf{x})} (\mathbf{n}_{\mu\sigma} \cdot \nabla \mathbf{b}_{\mu\sigma} + \mathbf{n}_{\mu\sigma} s_{\mu}^{\mu\sigma}) dA \right) \quad (4.51)$$

As mentioned, has been demonstrated that the effective velocity-like vectors, are negligible for the case of mass transfer by diffusion and chemical reaction in DES. The mass transfer coefficients of species A in the μ -phase are defined by:

$$(a_{v_1} k_1^{\mu\gamma} + a_{v_2} k_2^{\mu\gamma}) = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \nabla s_{\mu}^{\mu\gamma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \nabla s_{\mu}^{\mu\gamma} dA \right) \quad (4.52)$$

$$(a_{v_1} k_1^{\mu\sigma} + a_{v_2} k_2^{\mu\sigma}) = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \nabla s_{\mu}^{\mu\sigma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \nabla s_{\mu}^{\mu\sigma} dA \right) \quad (4.53)$$

here, one can observed that Eq. 4.52 - 4.53 are conformed of two transfer coefficients, $a_{v_1} k_1^{\mu i}$ and $a_{v_2} k_2^{\mu i}$, where a_{v_1} , is the interfacial area $\mathcal{A}_{\gamma\mu}$ per unit volume and a_{v_2} , is the interfacial area $\mathcal{A}_{\mu\sigma}$ per unit volume; $k_1^{\mu\gamma}$ is the film mass transfer coefficient in $\mathcal{A}_{\gamma\mu}$ and $k_1^{\mu\sigma}$ is a cross coefficient. In the same way $k_2^{\mu\sigma}$ is the film mass transfer coefficient in $\mathcal{A}_{\mu\sigma}$ and $k_2^{\mu\gamma}$ is a cross coefficient.

The governing averaged equation of species B in μ -phase presents the same form as 4.43 excluding the exchange terms; as discussed above, species B is restricted to

μ -phase, and this leads to

$$\begin{aligned}
\underbrace{\varepsilon_\mu \frac{\partial \langle C_{B\mu} \rangle^\mu}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot [\mathbf{D}_{B\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{D}_{B\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu]}_{\text{diffusion}} \\
&+ \underbrace{\nabla \cdot [\mathbf{D}_{BB} \cdot \nabla \langle C_{B\mu} \rangle^\mu + \mathbf{D}_{B\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma]}_{\text{diffusion}} \\
&+ \underbrace{\nabla \cdot [\mathbf{u}_{B\gamma} \langle C_{A\gamma} \rangle^\gamma + \mathbf{u}_{B\mu} \langle C_{A\mu} \rangle^\mu + \mathbf{u}_{B\sigma} \langle C_{A\sigma} \rangle^\sigma]}_{\text{convective-like transport term}} \\
&+ \underbrace{\varepsilon_\mu k_\mu \left(\langle C_{A\mu} \rangle^\mu - \frac{\langle C_{B\mu} \rangle^\mu}{K_\mu} \right)}_{\text{reaction}}
\end{aligned} \tag{4.54}$$

where effective diffusivity tensors of species are defined by:

$$\mathbf{D}_{B\gamma} = \frac{\mathcal{D}_{B\mu}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \mathbf{b}_{B\gamma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{B\gamma} dA \right) \tag{4.55}$$

$$\mathbf{D}_{B\mu} = \frac{\mathcal{D}_{B\mu}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \mathbf{b}_{B\mu} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{B\mu} dA \right) \tag{4.56}$$

$$\mathbf{D}_{BB} = \mathcal{D}_{B\mu} \left(\varepsilon_\mu(\mathbf{x}) \mathbf{1} + \frac{1}{\gamma} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \mathbf{b}_{BB} + \frac{1}{\gamma} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{BB} dA \right) \tag{4.57}$$

$$\mathbf{D}_{B\sigma} = \frac{\mathcal{D}_{B\mu}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \mathbf{b}_{B\sigma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{B\sigma} dA \right) \tag{4.58}$$

$$\tag{4.59}$$

and the velocity-like vectors of species B in the μ -phase are defined by:

$$\mathbf{u}_{B\gamma} = \frac{\mathcal{D}_{B\mu}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} s_{B\gamma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} s_{B\gamma} dA \right) \tag{4.60}$$

$$\begin{aligned}
\mathbf{u}_{B\mu} &= -\frac{\mathcal{D}_{A\mu}}{\gamma} \left(K_{\mu\gamma}^{eq} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} s_{B\gamma} dA + K_{\mu\sigma}^{eq} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} s_{B\sigma} dA \right. \\
&\quad \left. + K_{\mu\gamma}^{eq} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} s_{B\gamma} dA + K_{\mu\sigma}^{eq} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} s_{B\sigma} dA \right)
\end{aligned} \tag{4.61}$$

$$\mathbf{u}_{B\sigma} = \frac{\mathcal{D}_{B\mu}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} s_{B\sigma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} s_{B\sigma} dA \right) \tag{4.62}$$

Finally, the governing averaged equation of species A in σ -phase is introduced:

$$\begin{aligned}
\underbrace{\varepsilon_\sigma \frac{\partial \langle C_{A\sigma} \rangle^\sigma}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot [\mathbf{D}_{\sigma\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{D}_{\sigma\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu]}_{\text{diffusion}} \\
&+ \underbrace{\nabla \cdot [\mathbf{D}_{\sigma B} \cdot \nabla \langle C_{B\mu} \rangle^\mu + \mathbf{D}_{\sigma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma]}_{\text{diffusion}} \\
&+ \underbrace{\nabla \cdot [\mathbf{u}_{\sigma\gamma} \langle C_{A\gamma} \rangle^\gamma + \mathbf{u}_{\sigma\mu} \langle C_{A\mu} \rangle^\mu + \mathbf{u}_{\sigma B} \langle C_{B\mu} \rangle^\mu + \mathbf{u}_{\sigma\sigma} \langle C_{A\sigma} \rangle^\sigma]}_{\text{convective-like transport term}} \\
&+ \underbrace{a_{v_2} k_2^{\mu\gamma} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\gamma} \rangle^\gamma)}_{\text{exchange term}} + \underbrace{a_{v_2} k_2^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma)}_{\text{exchange term}} \\
&- \underbrace{k_\sigma \varepsilon_\sigma \langle C_{A\sigma} \rangle^\sigma}_{\text{reaction}} \tag{4.63}
\end{aligned}$$

one can see, as in previous cases, the three types of effective transport coefficients: the effective diffusivity tensors $\mathbf{D}_{\sigma j}$, the effective velocity-like vectors $\mathbf{u}_{\sigma j}$ and the mass transfer coefficients $a_{v_2} k_2^{\mu j}$. The diffusivity tensor $\mathbf{D}_{\sigma\sigma}$ is defined by:

$$\mathbf{D}_{\sigma\sigma} = \mathcal{D}_{A\sigma} \left(\varepsilon_\sigma \mathbf{1} + \frac{1}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \mathbf{b}_{\sigma\sigma} dA \right), \tag{4.64}$$

it is function of the molecular diffusivity $\mathcal{D}_{A\sigma}$, the volumetric fraction ε_σ and the structure of the DES through the $\mathbf{b}_{\sigma\sigma}$ -field. The others tensor are defined by:

$$\mathbf{D}_{\sigma\gamma} = \frac{\mathcal{D}_{A\sigma}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \mathbf{b}_{\sigma\gamma} dA \tag{4.65}$$

$$\mathbf{D}_{\sigma\mu} = \frac{\mathcal{D}_{A\sigma}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \mathbf{b}_{\sigma\mu} dA \tag{4.66}$$

$$\mathbf{D}_{\sigma B} = \frac{\mathcal{D}_{A\sigma}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \mathbf{b}_{\sigma B} dA \tag{4.67}$$

the effective velocity-like vectors of species A in the σ -phase have the form:

$$\mathbf{u}_{\sigma\gamma} = \frac{\mathcal{D}_{A\sigma}}{\gamma} \left(\int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla \mathbf{b}_{\sigma\gamma} dA + \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} s_{\sigma}^{\mu\gamma} dA \right) \quad (4.68)$$

$$\mathbf{u}_{\sigma\mu} = \frac{\mathcal{D}_{A\sigma}}{\gamma} \left(\int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla \mathbf{b}_{\sigma\mu} dA - K_{\mu\gamma}^{eq} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} s_{\sigma}^{\mu\gamma} dA - K_{\mu\sigma}^{eq} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} s_{\sigma}^{\mu\sigma} dA \right) \quad (4.69)$$

$$\mathbf{u}_{\sigma B} = \frac{\mathcal{D}_{A\sigma}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla \mathbf{b}_{\sigma B} dA \quad (4.70)$$

$$\mathbf{u}_{\sigma\sigma} = \frac{\mathcal{D}_{A\sigma}}{\gamma} \left(\int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla \mathbf{b}_{\sigma\sigma} dA + \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} s_{\sigma}^{\mu\sigma} dA \right) \quad (4.71)$$

The cross mass transfer coefficient of species A in the σ -phase is defined by:

$$a_{v_2} k_2^{\mu\gamma} = -\frac{\mathcal{D}_{A\sigma}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla s_{\sigma}^{\mu\gamma} dA, \quad (4.72)$$

while the mass transfer coefficient related with the internal flux in $\mathcal{A}_{\mu\sigma}$ has the form:

$$a_{v_2} k_2^{\mu\sigma} = -\frac{\mathcal{D}_{A\sigma}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla s_{\sigma}^{\mu\sigma} dA \quad (4.73)$$

All the effective transport coefficients presented in this section, have been determined by solving the six local boundary-value problems for unit cells representative of the DES under consideration. In the following section the determination of these coefficients is presented while the derivation of the closure problem is illustrated in Appendix A.

4.3 Determination of the effective coefficients

In the preceding section, the *closed* averaged governing equations for $\langle C_{A\lambda} \rangle^\lambda$ ($\lambda = \gamma, \mu, \sigma$) have been developed, consequently, in this section the predictions of the geometrically dependent effective coefficients are presented. For this purpose, the six closure boundary-value problems for $\tilde{C}_{A\lambda}$ which compose the closure problem, are solved in 2D unit cells that take into account the geometric structure of a double emulsion drop dispersed in the γ -phase. Figure 4.2 shows a microscopic image of

double emulsions (left) and a theoretical representation of a DE (right) where the unit cell is located.

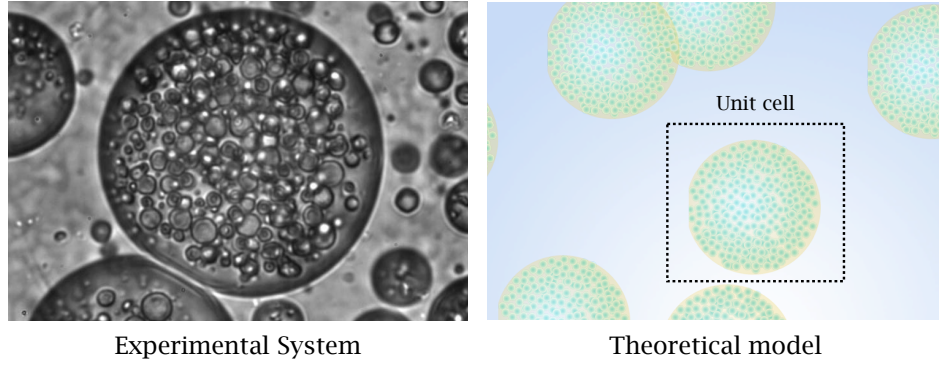


Figure 4.2: Microscopic image of double emulsions (Aveyard et al. 2003) and his theoretical representation

For practical purposes, a simpler system of this uni cell is proposed in Figure 4.3 which is composed of three domains, the first one (domain A) illustrated as a blue square with side l_{cell} , represents the γ -phase; the second domain, that symbolized the μ -phase (domain B), is characterized by a yellow concentric circle with a constant radius r_{ω} . Inside of domain B one green circle or an array of non-touching green circles depict σ -phase and consequently the third domain (domain C). This supposes that DES is a homogeneous system.

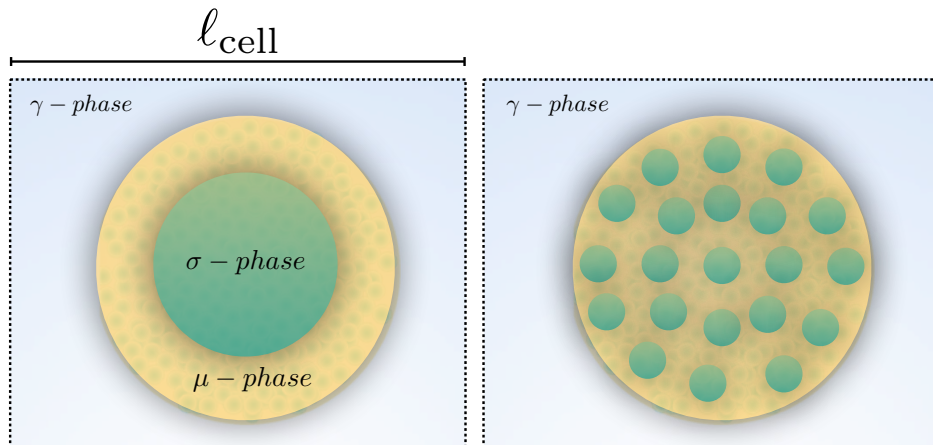


Figure 4.3: Unit cell representative of a emulsion drop dispersed in γ -phase

Therefore the behavior of the effective coefficients has been analyzed as function of the volumetric fractions of the three phases ($\varepsilon_\gamma + \varepsilon_\mu + \varepsilon_\sigma$) and the geometric structure of the 2D unit cells. It should be noted that, surface of $\mu\sigma$ -phases ($\mathcal{A}_{\mu\sigma}$ for 3D cases) depends directly on the number of circles of domain C (σ -phase) inside domain B (μ -phase). To illustrate this situation, one can imagine a double emulsion system with $\varepsilon_\gamma = 0.3$ and $\varepsilon_\omega = 0.7$, where the domain ω is composed of σ and μ -phases, thus $\varepsilon_\omega = \varepsilon_\mu + \varepsilon_\sigma$. The proportion between both volumetric fractions, δ , can vary from 1, i.e. the limit case when $\varepsilon_\mu = \varepsilon_\sigma$ (geometrically there can not be more σ -phase than μ -phase in the 2D unit cells), up to a very large number in such a way σ -phase tends to disappear, $\varepsilon_\mu = \delta\varepsilon_\sigma$. In this study, δ was varied from 1 to 10. Additionally, the number of circles (nd) of constant radius, r_σ , that will conform the domain C must be established. This relation can be written as follows:

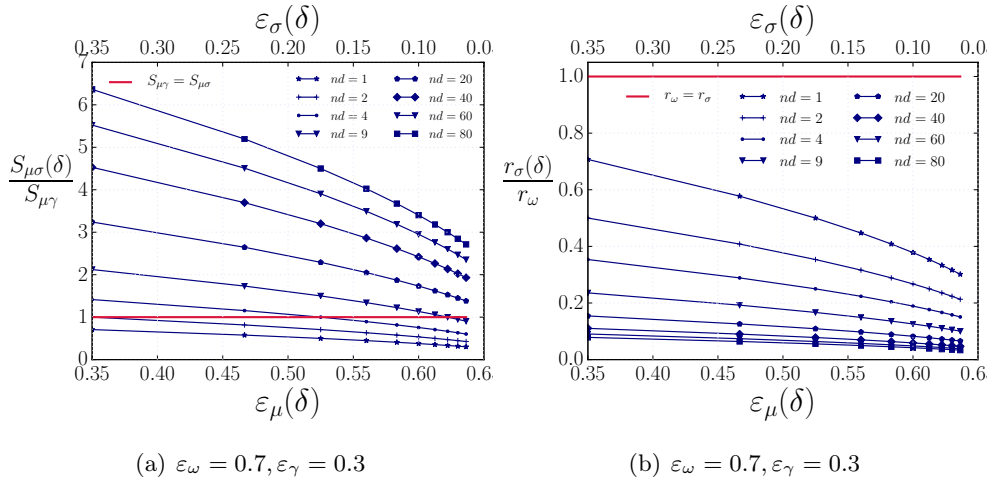


Figure 4.4: Interfacial surface as a function of the unit cell's geometry

$$r_\sigma = \sqrt{\frac{\varepsilon_\sigma}{nd\pi}} = \sqrt{\frac{\varepsilon_\omega}{\delta+1}} \quad (4.74)$$

Finally, one can calculate the interfacial surfaces for the 2D unit cell with $\varepsilon_\gamma = 0.3$ and $\varepsilon_\omega = 0.7$, according to the following expressions:

$$S_{\mu\gamma} = \sqrt{\frac{\varepsilon_\omega}{\pi}}, \quad S_{\mu\sigma} = \sqrt{\frac{\varepsilon_\sigma(\delta)}{nd\pi}} \quad (4.75)$$

A plot of the ratio between both interfacial surfaces is shown in Figure 4.4, here one can see that in **one-circle- σ -phase** case, the interfacial surface $S_{\mu\sigma}$, is always smaller than $S_{\mu\gamma}$ for any value of δ . In the opposite way, all occasions that σ -phase is constituted by more than 9 circles, $S_{\mu\sigma}$ is larger than the $S_{\mu\gamma}$ for any value of δ . Nevertheless, in the cases that the σ -phase is structured from 2 to 9 circles, the $S_{\mu\sigma}$ can be larger or smaller than or equal to $S_{\mu\gamma}$ depending on the value of δ . Following this idea and if it is also consider that the effective coefficients are directly related to the area integrals, $\int_{A_{\gamma\mu}} (\cdot) dA$ and $\int_{A_{\sigma\mu}} (\cdot) dA$, it is natural to ask, how the difference between the sizes of the interfacial surfaces can affect the effective coefficients?. In this chapter we continue this discussion by presenting a study of the behavior of the effective coefficients as a function of the geometry. The computation of the closure problem, in the 2D unit cells has been carried out using the commercial finite element solver Comsol Multiphysics 4.3b. The numerical procedure consists of solving the equations of closure boundary-value problems I - VI, Eq. A.53 - A.122, to determine the fields of the closure variables and then substitute these values in the equations of the effective coefficients to predict them.

The study of the behavior of the effective coefficients is presented for two different volumetric fractions of the external phase:

- *Test 1*: when $\varepsilon_\gamma = 0.3$
- *Test 2*: when $\varepsilon_\gamma = 0.7$.

and considering the ratios of molecular diffusivities as $\alpha_{\gamma\mu} = \mathcal{D}_{A\gamma}/\mathcal{D}_{A\mu}$, $\alpha_{\sigma\mu} = \mathcal{D}_{A\sigma}/\mathcal{D}_{A\mu}$ and the ratios, $\Omega_{\gamma\mu} = \frac{P_{\gamma\mu}}{\mathcal{D}_{A\gamma}}$ and $\Omega_{\sigma\mu} = \frac{P_{\sigma\mu}}{\mathcal{D}_{A\sigma}}$. In both tests, it has been considered that the solute A diffuses 10 times faster in the external phase than in the membrane phase, $\alpha_{\gamma\mu} = 10$, and at the same rate in the membrane phase and globular phase, $\alpha_{\sigma\mu} = 1$. Moreover, is supposed that the permeability of A in $\gamma\mu$ -interface is 10 times larger than his molecular diffusivity in the γ -phase, $\Omega_{\gamma\mu} = 10$. And in the opposite way, is established the molecular diffusivity of A in the μ -phase 10 times larger than the permeability in $\sigma\mu$ -interface, $\Omega_{\sigma\mu} = 0.1$. The equilibrium distribution coefficients, $K_{\mu\gamma}^{eq}$ and $K_{\mu\sigma}^{eq}$ are set equal to 2 and 0.1 respectively.

4.3.1 Geometry-dependent effective diffusivity tensors

As mentioned, diffusion terms in the closed averaged equations contain the geometry-dependent effective diffusivity tensors \mathbf{D}_{ij} . One must not forget that the first sub-

script refers to the phase where the averaged equation is valid and the second the influence of one of the phases.

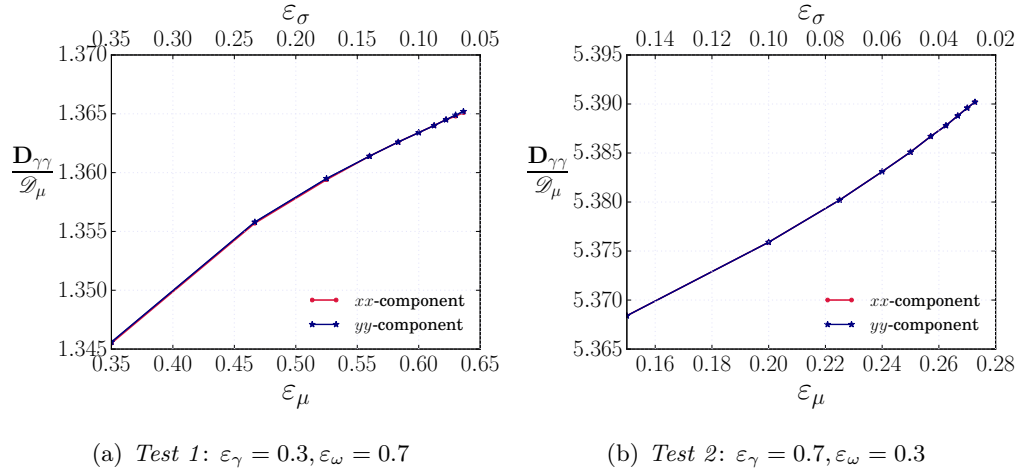


Figure 4.5: Spatial dependence of $\frac{\mathbf{D}_{\gamma\gamma}}{\mathcal{D}_{A\mu}}$ for two different values of ε_ω , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

Analyzing the diffusivity tensors present in the closed averaged equation for γ -phase (Eq. 4.32), in Figure 4.5, it is shown the normalized $\mathbf{D}_{\gamma\gamma}$ tensor with the molecular diffusivity $\mathcal{D}_{A\mu}$ in terms of the variable $\varepsilon_\mu = \delta\varepsilon_\sigma$, for a 2D unit cell with **one-circle- σ** -phase geometry, i.e., when $S_{\mu\gamma} > S_{\mu\sigma}$; in this figure one can see two types of behavior: 1) the diffusivity tensor increases directly with the volumetric fraction ε_γ , as would be expected according to

$$\frac{\mathbf{D}_{\gamma\gamma}}{\mathcal{D}_{A\mu}} = \alpha_{\gamma\mu} \left(\varepsilon_\gamma \mathbf{1} + \frac{1}{V} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \mathbf{b}_{\gamma\gamma} dA \right);$$

and 2) the tensor increases directly with ε_γ , however, this influence can increase in importance if the number of circles of domain C (np) increases, ($S_{\mu\gamma} \leq S_{\mu\sigma}$), as is shown in Figure 4.6 where the diffusivity tensor decreases with values of np less than 4.

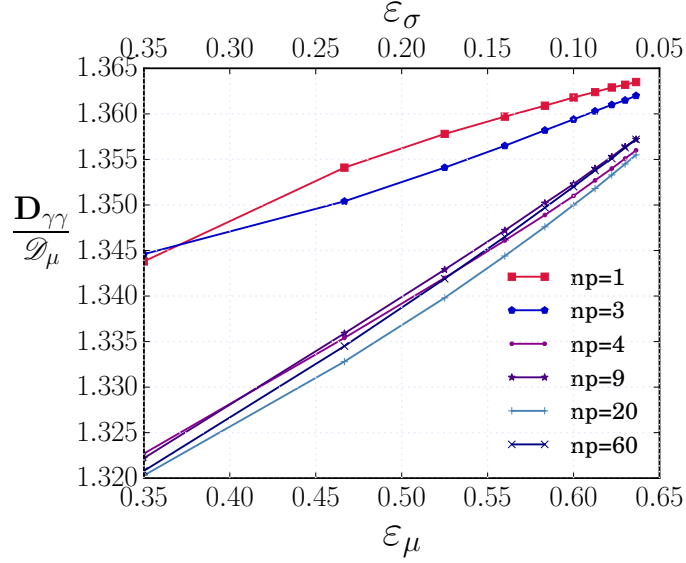


Figure 4.6: Spatial dependence of $\frac{\mathbf{D}_{\gamma\gamma}}{\mathcal{D}_\mu}$ for different values of np , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

It is worthwhile to note that the system in consideration is homogeneous and isotropic and the 2D unit cell is symmetric, thus for all the diffusivity tensors \mathbf{D}_{ij} has been obtained that:

$$(D_{ij})_{xx} = (D_{ij})_{yy}, \quad (D_{ij})_{xy} = (D_{ij})_{yx} = 0 \quad (4.76)$$

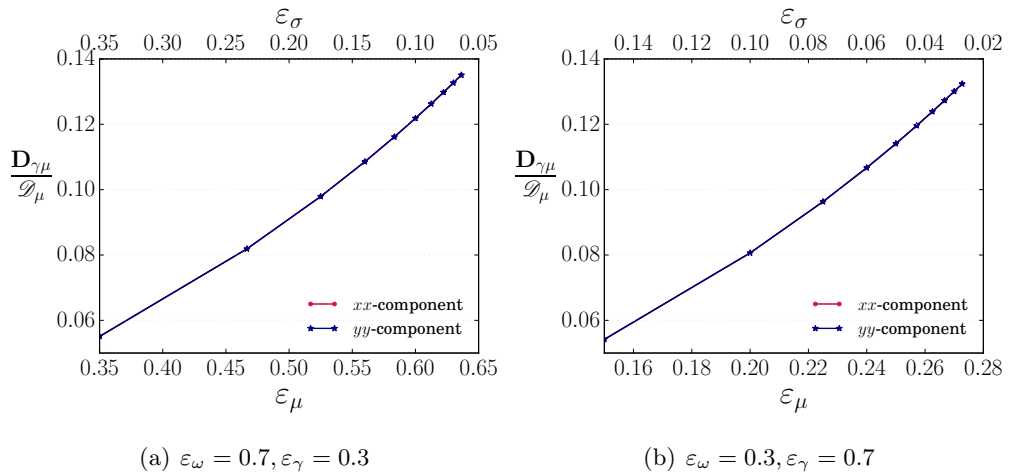


Figure 4.7: Spatial dependence of $\frac{\mathbf{D}_{\gamma\mu}}{\mathcal{D}_\mu}$ for two different values of ϵ_μ , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

The behavior of the cross tensors $\mathbf{D}_{\gamma\mu}$ and $\mathbf{D}_{\gamma\sigma}$, also normalized with the molecular diffusivity $\mathcal{D}_{A\mu}$, are presented for both tests in the Figures 4.7 and 4.8, these coefficients are on the order of the smallest of $\frac{\mathbf{D}_{\gamma\gamma}}{\mathcal{D}_{A\mu}}$ or even orders of magnitude smaller, almost null. In the case of $\frac{\mathbf{D}_{\gamma\mu}}{\mathcal{D}_{A\mu}}$ (Fig. 4.7), the variations between both tests are insignificant. In contrast to $\frac{\mathbf{D}_{\gamma\mu}}{\mathcal{D}_{A\mu}}$, $\frac{\mathbf{D}_{\gamma\sigma}}{\mathcal{D}_{A\mu}}$ tensor changes with respect ε_μ but the orders of magnitude are the smallest (Fig. 4.8).

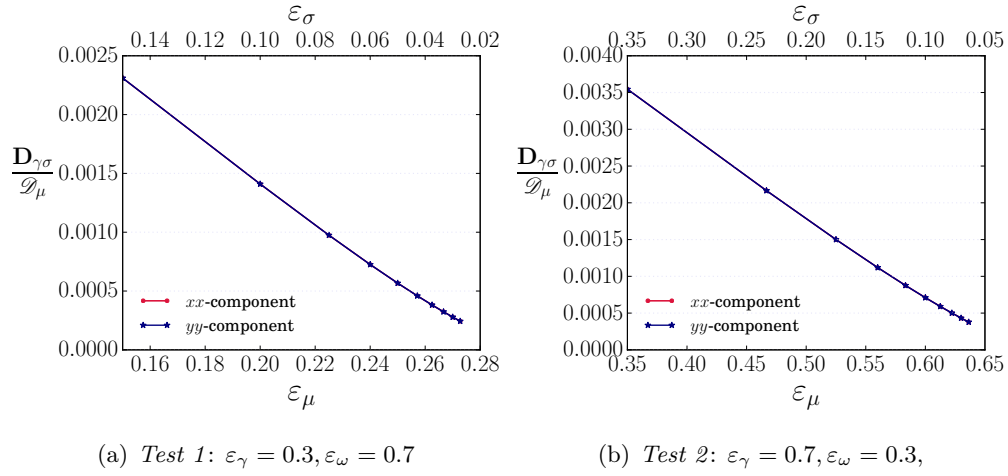


Figure 4.8: Spatial dependence of $\frac{\mathbf{D}_{\gamma\sigma}}{\mathcal{D}_{A\mu}}$ for two different values of ε_μ , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

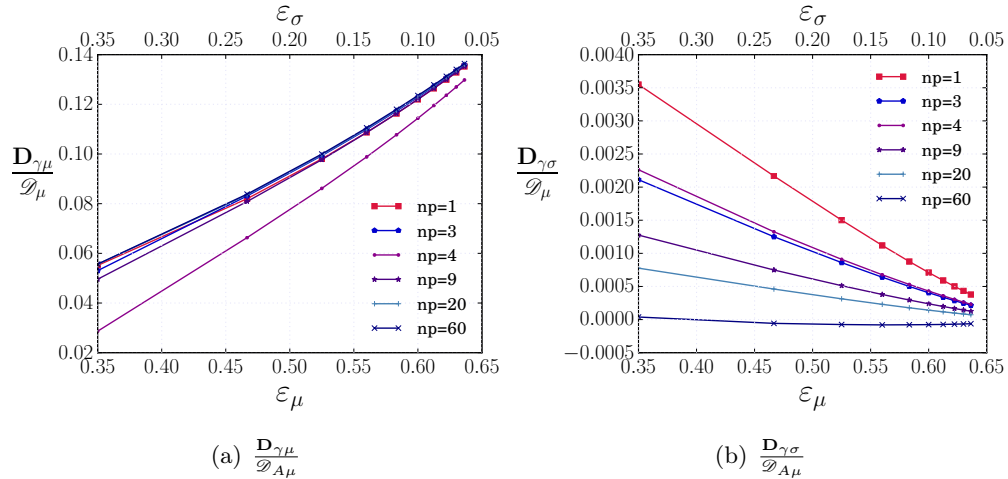


Figure 4.9: Spatial dependence of $\frac{\mathbf{D}_{\gamma\mu}}{\mathcal{D}_{A\mu}}$ and $\frac{\mathbf{D}_{\gamma\sigma}}{\mathcal{D}_{A\mu}}$ for different values of np taking $\varepsilon_\omega = 0.7, \alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

The influence that the $S_{\mu\sigma}$ can have on both cross-tensors ($\frac{\mathbf{D}_{\gamma\mu}}{\mathcal{D}_{A\mu}}$ and $\frac{\mathbf{D}_{\gamma\sigma}}{\mathcal{D}_{A\mu}}$) are shown in Figure 4.9; as mentioned $\frac{\mathbf{D}_{\gamma\mu}}{\mathcal{D}_{A\mu}}$ is not a function of the number of np , since $S_{\gamma\mu}$ is constant; on the other hand, $\frac{\mathbf{D}_{\gamma\sigma}}{\mathcal{D}_{A\mu}}$ approaches to zero for large values of np , i.e. for large values of $S_{\mu\sigma}$.

Next, the theoretical results for the diffusivity tensors present in the averaged equation for μ -phase are analyzed. First the $\mathbf{D}_{\mu\mu}$ tensor which has the normal form,

$$\frac{\mathbf{D}_{\mu\mu}}{\mathcal{D}_{A\mu}} = \left(\varepsilon_\mu \mathbf{1} + \frac{1}{\mathcal{V}} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \mathbf{b}_{\mu\mu} + \frac{1}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{\mu\mu} dA \right),$$

increases directly with the volumetric fraction ε_μ as one can see in Figure 4.10. Comparing *Test 1* between *Test 2*, in the same figure, it can also be seen that the tensor decrease for small values of ε_γ

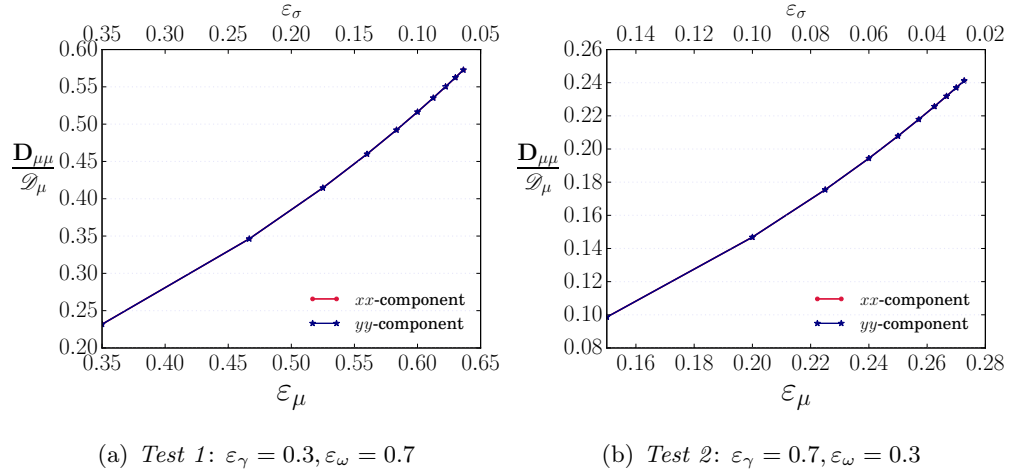


Figure 4.10: Spatial dependence of $\mathbf{D}_{\mu\mu}$ for two different values of ε_μ , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

Nevertheless in Figure 4.11 is shown that this tensor does not change with the surface $S_{\mu\sigma}$. Additionally, the cross-tensor $\frac{\mathbf{D}_{\mu\gamma}}{\mathcal{D}_{A\mu}}$ is on the order of magnitude smaller than $\frac{\mathbf{D}_{\mu\mu}}{\mathcal{D}_{A\mu}}$; the changes of this tensor with respect to ε_γ and ε_ω is insignificant as one can see in Figure 4.12

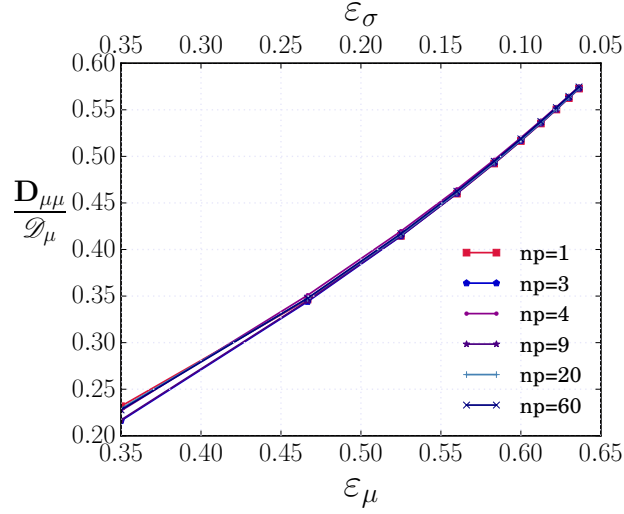


Figure 4.11: Spatial dependence of $\frac{\mathbf{D}_{\mu\mu}}{\mathcal{D}_\mu}$ for different values of np , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

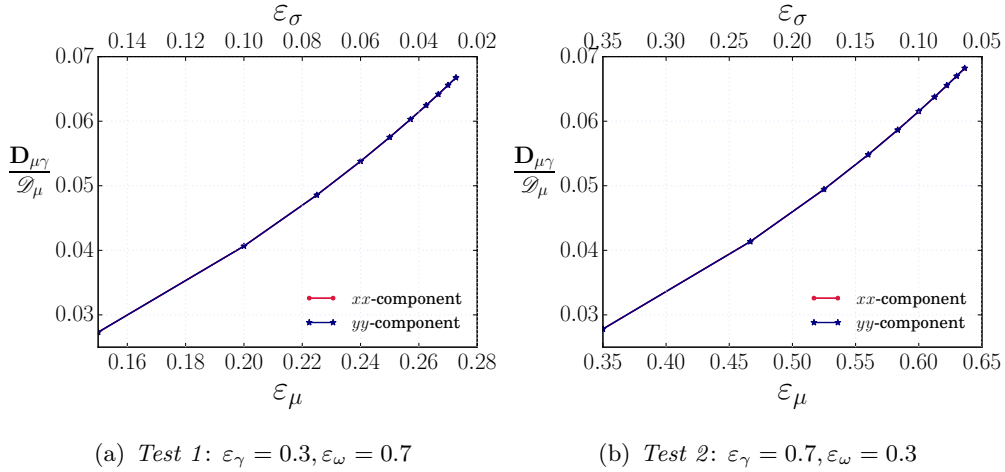


Figure 4.12: Spatial dependence of $\frac{\mathbf{D}_{\mu\gamma}}{\mathcal{D}_\mu}$ for two different values of ϵ_μ , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

On the other hand, the cross-tensor $\frac{\mathbf{D}_{\mu\sigma}}{\mathcal{D}_{A\mu}}$ presents the smallest orders of magnitude, and decreases directly with ϵ_σ , as shown in Figure 4.13

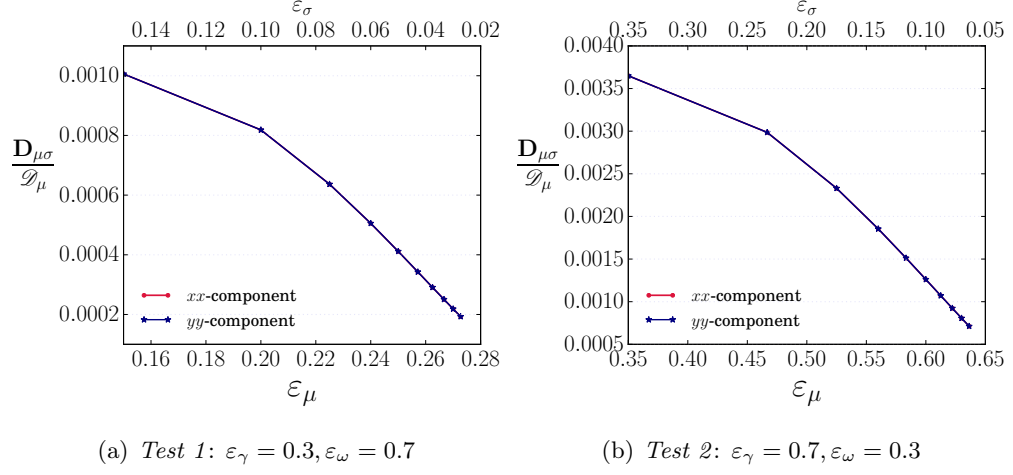


Figure 4.13: Spatial dependence of $\frac{\mathbf{D}_{\mu\sigma}}{\mathcal{D}_\mu}$ for two different values of ε_μ , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

The influence that the $S_{\mu\sigma}$ can have on both cross-tensors ($\frac{\mathbf{D}_{\mu\gamma}}{\mathcal{D}_{A\mu}}$ and $\frac{\mathbf{D}_{\mu\sigma}}{\mathcal{D}_{A\mu}}$) are shown in Figure 4.14. In this case, $\frac{\mathbf{D}_{\mu\gamma}}{\mathcal{D}_{A\mu}}$ is not a function of the number of np , since $S_{\gamma\mu}$ is constant; on the other hand, $\frac{\mathbf{D}_{\mu\sigma}}{\mathcal{D}_{A\mu}}$ approaches to zero for large values of np , i.e. for large values of $S_{\mu\sigma}$.

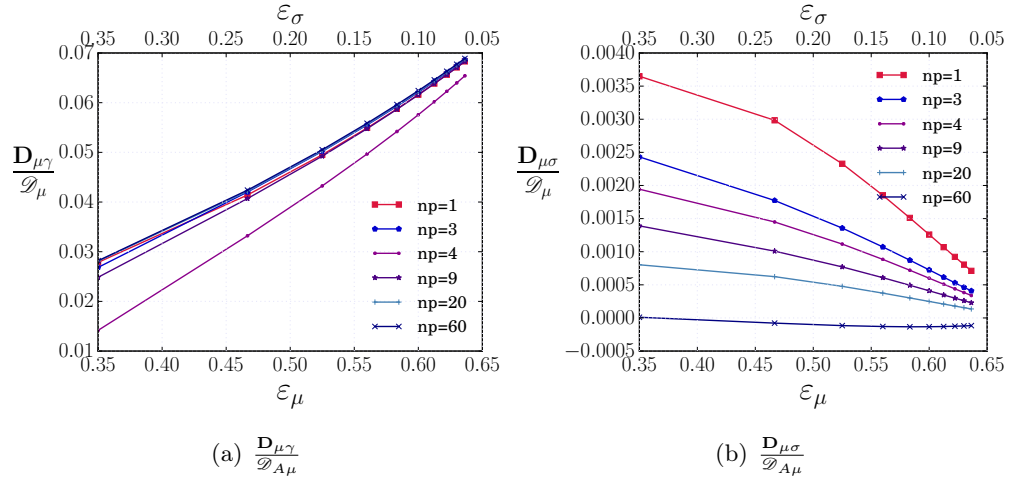


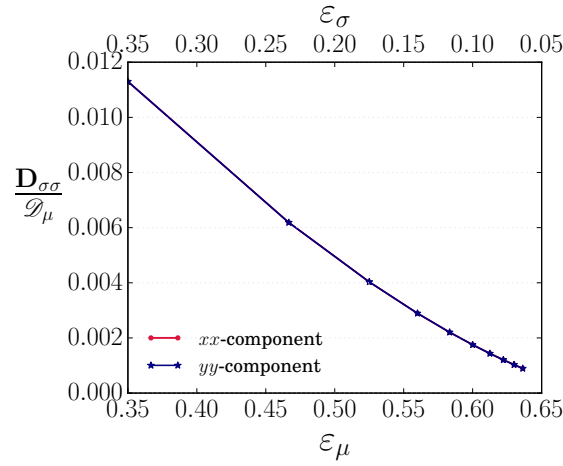
Figure 4.14: Spatial dependence of $\frac{\mathbf{D}_{\mu\gamma}}{\mathcal{D}_{A\mu}}$ and $\frac{\mathbf{D}_{\mu\sigma}}{\mathcal{D}_{A\mu}}$ for different values of np taking $\varepsilon_\omega = 07, \alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

Finally, the results for the diffusivity tensors present in the averaged equation for

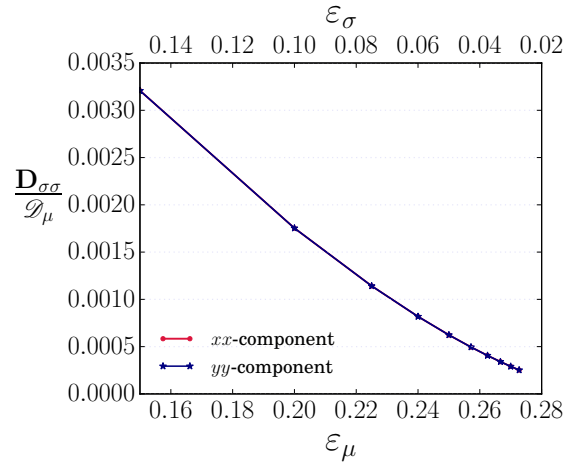
σ -phase are analyzed. First the $\mathbf{D}_{\sigma\sigma}$ tensor which has the normal form,

$$\mathbf{D}_{\sigma\sigma} = \mathcal{D}_{A\sigma} \left(\varepsilon_\sigma \mathbf{1} + \frac{1}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \mathbf{b}_{\sigma\sigma} dA \right),$$

increases directly with the volumetric fraction ε_σ as one can see in Figure 4.15. Comparing *Test 1* between *Test 2*, in the same figure, it can also be seen that the tensor decrease for small values of ε_γ



(a) *Test 1*: $\varepsilon_\gamma = 0.3, \varepsilon_\omega = 0.7$



(b) *Test 2*: $\varepsilon_\gamma = 0.7, \varepsilon_\omega = 0.3$

Figure 4.15: Spatial dependence of $\mathbf{D}_{\sigma\sigma}$ for two different values of ε_μ , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

Nevertheless in Figure 4.16 is shown that this tensor decreases with large values of surface $S_{\mu\sigma}$. Additionally, the cross-tensor $\frac{D_{\sigma\gamma}}{\mathcal{D}_{A\mu}}$ is on the order of magnitude smaller than $\frac{D_{\sigma\sigma}}{\mathcal{D}_{A\mu}}$; the changes of this tensor with respect to ε_γ and ε_ω is insignificant how one can see in Figure 4.17.

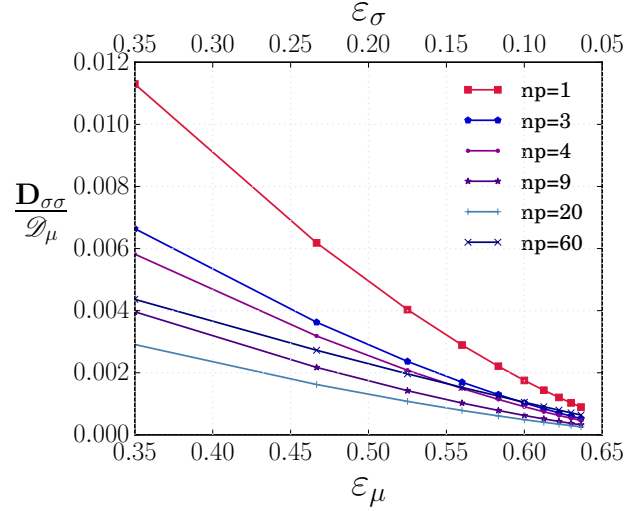
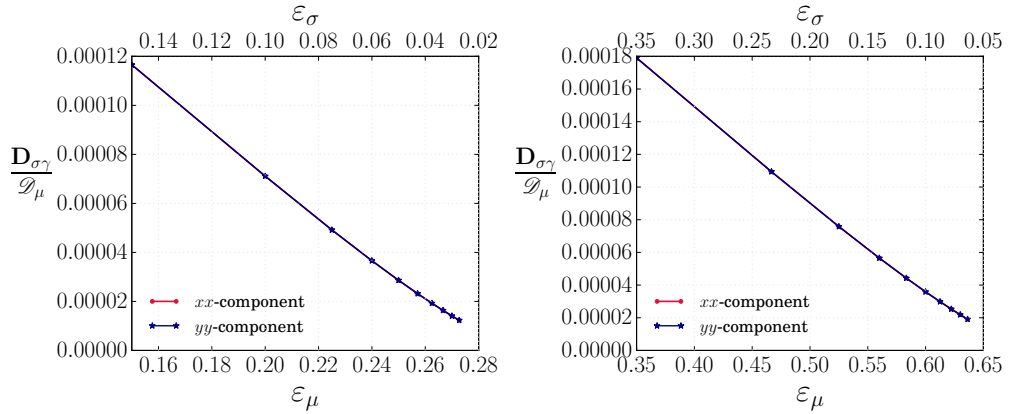


Figure 4.16: Spatial dependence of $\frac{D_{\mu\mu}}{\mathcal{D}_{A\mu}}$ for different values of np , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$



(a) Test 1: $\varepsilon_\gamma = 0.3, \varepsilon_\omega = 0.7$

(b) Test 2: $\varepsilon_\gamma = 0.7, \varepsilon_\omega = 0.3$

Figure 4.17: Spatial dependence of $\frac{D_{\sigma\gamma}}{\mathcal{D}_{A\mu}}$ for two different values of ε_μ , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

On the other hand, the cross-tensor $\frac{D_{\sigma\mu}}{\mathcal{D}_{A\mu}}$ presents the smallest orders of magnitude,

and decreases directly with ε_σ , as shown in Figure 4.13

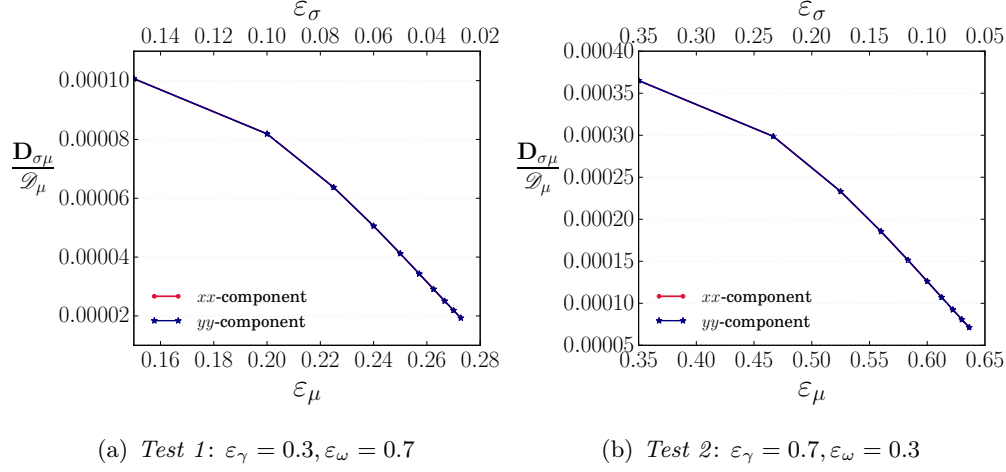


Figure 4.18: Spatial dependence of $\frac{D_{\sigma\mu}}{\mathcal{D}_{A\mu}}$ for two different values of ε_μ , taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

The influence, that the $S_{\mu\sigma}$ can have on both cross-tensors ($\frac{D_{\sigma\gamma}}{\mathcal{D}_{A\mu}}$ and $\frac{D_{\sigma\mu}}{\mathcal{D}_{A\mu}}$) are shown in Figure 4.19. In both cases, the cross-tensor are a function of the number of np , these approach to zero for large values of np , i.e. for large values of $S_{\mu\sigma}$.

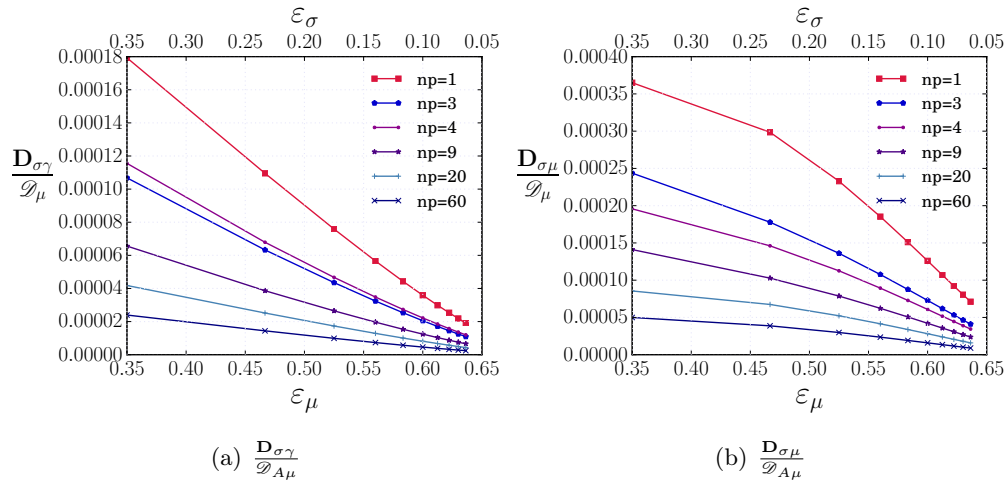
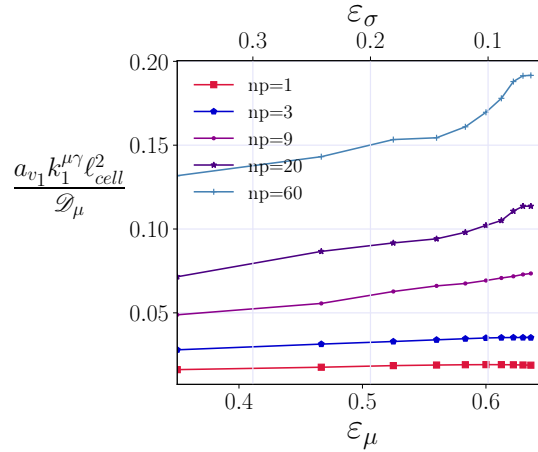


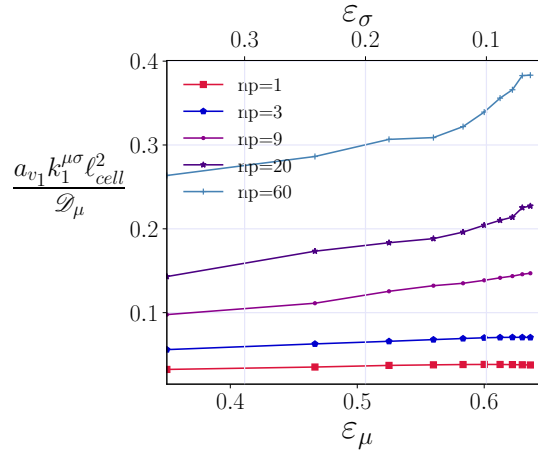
Figure 4.19: Spatial dependence of $\frac{D_{\sigma\gamma}}{\mathcal{D}_{A\mu}}$ and $\frac{D_{\sigma\mu}}{\mathcal{D}_{A\mu}}$ for different values of np taking $\varepsilon_\omega = 0.7, \alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

4.3.2 Geometry-dependent mass transfer coefficients

Regarding the behavior of the 4 mass transfer coefficients which have been normalized with $\frac{\ell_{cell}^2}{\mathcal{D}_{A\mu}}$, here the results for *Test 1* are presented. First in Figure 4.20 one can observe the mass transfer coefficients related with the averaged equations for γ and μ -phases. Both coefficients increase with ε_μ and also are a function of the np variable.



(a) *Test 1*: $\varepsilon_\gamma = 0.3, \varepsilon_\omega = 0.7$

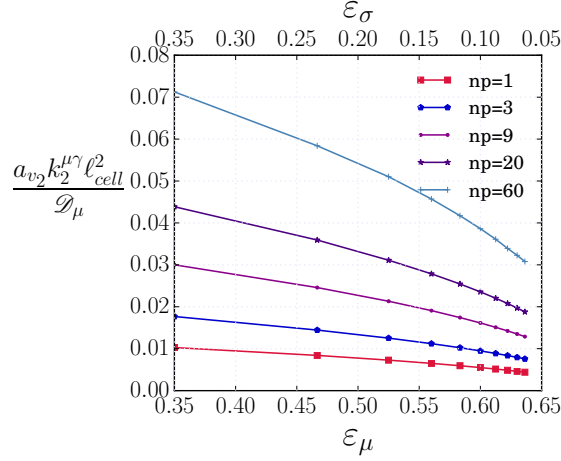


(b) *Test 1*: $\varepsilon_\gamma = 0.3, \varepsilon_\omega = 0.7$

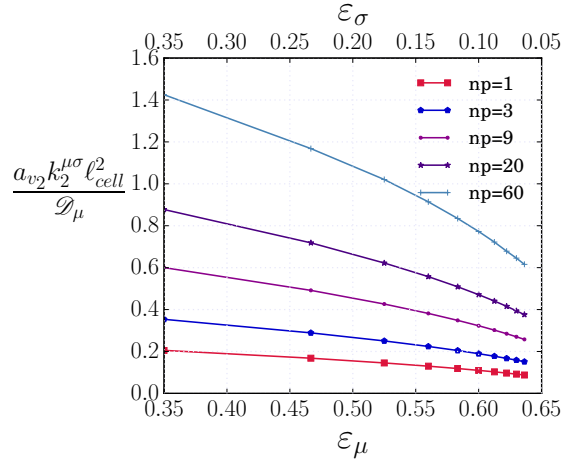
Figure 4.20: Spatial dependence of: $\frac{a_{v1} k_1^{\mu\gamma} \ell_{cell}^2}{\mathcal{D}_{A\mu}}$ and $\frac{a_{v1} k_1^{\mu\sigma} \ell_{cell}^2}{\mathcal{D}_{A\mu}}$, taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

In contrast with Figure 4.20, Figure 4.21 present the mass transfer coefficients related

with the averaged equations for μ and σ -phases. Both coefficients decrease with ε_σ and also are a function of the np variable.



(a) Test 1: $\varepsilon_\gamma = 0.3, \varepsilon_\omega = 0.7$



(b) Test 1: $\varepsilon_\gamma = 0.3, \varepsilon_\omega = 0.7$

Figure 4.21: Spatial dependence of: $\frac{a_{v_2} k_2^{\mu\gamma} \ell_{cell}^2}{\mathcal{D}_{A\mu}}$ and $\frac{a_{v_2} k_2^{\mu\sigma} \ell_{cell}^2}{\mathcal{D}_{A\mu}}$, taking $\alpha_{\gamma\mu} = 10, \alpha_{\sigma\mu} = 0.1, \Omega_{\gamma\mu} = 10, \Omega_{\sigma\mu} = 0.1$

4.3.3 Effective velocity-like vectors

The effective velocity-like vectors have been also determined; since, all of them for both test have very small values, of orders of magnitude of 10^{-10} , their contribution in the averaged equations has been considered negligible. Due to the above stated,

the corresponding figures are not presented.

4.4 Three-phase simplified model

Finally, after determination and analysis of the different effective coefficients presented in the closed set of averaged equations describing the macroscopic mass transport of species A in this three-phase system, it was possible to simplify the problem obtaining:

Governing averaged equation of species A in γ -phase:

$$\underbrace{\varepsilon_\gamma \frac{\partial \langle C_{A\gamma} \rangle^\gamma}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot [\mathbf{D}_{\gamma\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{D}_{\gamma\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu]}_{\text{diffusion}} + \underbrace{a_{v_1} k_1^{\mu\gamma} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\gamma} \rangle^\gamma)}_{\text{exchange term}} + \underbrace{a_{v_1} k_1^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma)}_{\text{exchange term}} \quad (4.77)$$

Governing averaged equation of species A in μ -phase:

$$\underbrace{\varepsilon_\mu \frac{\partial \langle C_{A\mu} \rangle^\mu}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot [\mathbf{D}_{\mu\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{D}_{\mu\mu}(\mathbf{x}) \cdot \nabla \langle C_{A\mu} \rangle^\mu]}_{\text{diffusion}} + \underbrace{[a_{v_1} k_1^{\mu\gamma} + a_{v_2} k_2^{\mu\gamma}](\langle C_{A\gamma} \rangle^\gamma - K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu)}_{\text{exchange term}} + \underbrace{[a_{v_1} k_1^{\mu\sigma} + a_{v_2} k_2^{\mu\sigma}](\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu)}_{\text{exchange term}} - \underbrace{\varepsilon_\mu k_\mu \left(\langle C_{A\mu} \rangle^\mu - \frac{\langle C_{B\mu} \rangle^\mu}{K_\mu} \right)}_{\text{reaction}} \quad (4.78)$$

Governing averaged equation of species B in μ -phase:

$$\underbrace{\varepsilon_\mu(\mathbf{x}) \frac{\partial \langle C_{B\mu} \rangle^\mu}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot [\mathbf{D}_{BB}(\mathbf{x}) \cdot \nabla \langle C_{B\mu} \rangle^\mu]}_{\text{diffusion}} + \underbrace{\varepsilon_\mu(\mathbf{x}) k_\mu \left(\langle C_{A\mu} \rangle^\mu - \frac{\langle C_{B\mu} \rangle^\mu}{K_\mu} \right)}_{\text{reaction}} \quad (4.79)$$

Governing averaged equation of species A in σ -phase:

$$\underbrace{\varepsilon_\sigma \frac{\partial \langle C_{A\sigma} \rangle^\sigma}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot [\mathbf{D}_{\sigma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma]}_{\text{diffusion}} - \underbrace{k_\sigma \varepsilon_\sigma \langle C_{A\sigma} \rangle^\sigma}_{\text{reaction}} + \underbrace{a_{v_2} k_2^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma)}_{\text{exchange term}} \quad (4.80)$$

In summary, the *Three-phase model* under *non-local mass equilibrium* conditions is composed of 3 coupled averaged equations, each one describing the mass transfer of species A in the corresponding phase by the accumulation, diffusion and mass transfer exchange terms. Eqs. (4.77)-(4.80) are valid everywhere in the homogeneous averaged system. Detailed information about the structure and transfer phenomena in the DE drops by chemical reaction and permeation in the microscale, *Scale III*, is represented in the effective coefficients.

Chapter 5

Hierarchical modeling approach (2-region)

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5.1 Spatial smoothing (ω -region)

The purpose of this chapter is to develop the volume averaged equations that describe the transport of species A in the homogeneous ω -region, this can be done considering the governing equations in the μ and σ phases. Therefore the system under consideration is illustrated in Figure 5.1 and the governing equations and boundary conditions are given by:

In μ -phase

$$\frac{\partial C_{A\mu}}{\partial t} = \nabla \cdot (\mathcal{D}_{A\mu} \nabla C_{A\mu}) - R_\mu \quad (5.1)$$

$$\frac{\partial C_{B\mu}}{\partial t} = \nabla \cdot (\mathcal{D}_{B\mu} \nabla C_{B\mu}) + R_\mu \quad (5.2)$$

In σ -phase

$$\frac{\partial C_{A\sigma}}{\partial t} = \nabla \cdot (\mathcal{D}_{A\sigma} \nabla C_{A\sigma}) - R_\sigma \quad (5.3)$$

The kinetics of the reversible and irreversible chemical reactions are:

$$R_\mu = k_\mu \left(C_{A\mu} - \frac{C_{B\mu}}{K_\mu} \right) \quad (5.4)$$

$$R_\sigma = k_\sigma C_{A\sigma} \quad (5.5)$$

Eqs. 5.1-5.3 are associated to the interfacial boundary conditions at $\mathcal{A}_{\mu\sigma}$:

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla C_{A\mu} = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla C_{A\sigma} \quad (5.6)$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla C_{A\sigma} = P_{\sigma\mu} (C_{A\sigma} - K_{\mu\sigma}^{eq} C_{A\mu}) \quad (5.7)$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla C_{B\mu} = 0 \quad (5.8)$$

The local equations 5.1 - 5.3 are associated with averaging volume \mathcal{V} illustrated in Figure 3.4 and detailed in Figure 5.1, where ℓ_μ and ℓ_σ represent the characteristic lengths for the μ and σ phases respectively. The averaging volume is defined as:

$$\mathcal{V} = V_\mu(\mathbf{x}) + V_\sigma(\mathbf{x}) \quad (5.9)$$

In the same way as was done in previous sections, for purposes of spatial smoothing, a position vector \mathbf{r}_λ located in λ -phase, a position vector \mathbf{x} located in the centroid

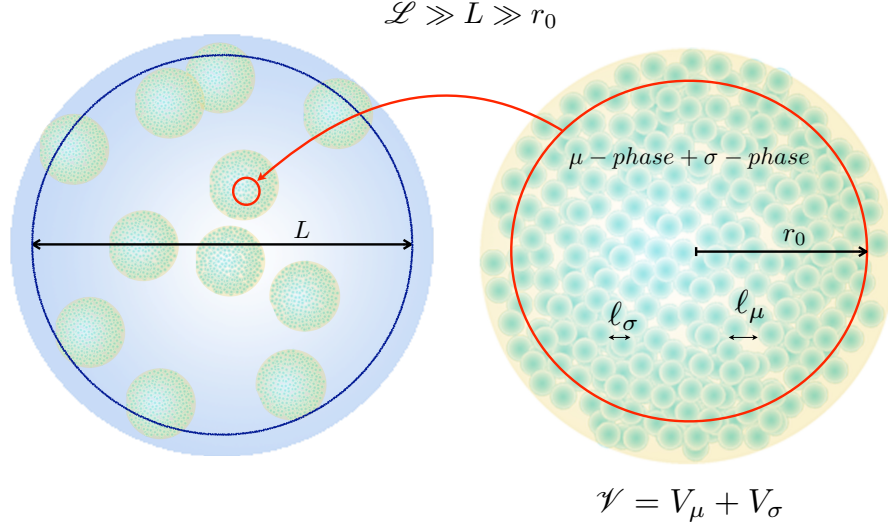


Figure 5.1: Averaging volume for the drop emulsion (μ - σ -system, ω -region)

of the averaging volume and the relative position vector \mathbf{y}_λ used to locate points in the λ -phase ($\lambda = \mu, \sigma$) relative to the centroid of \mathcal{V} were defined. Consequently, the superficial averaging operator of a continuous property, ψ_λ has the form:

$$\langle \psi_\lambda \rangle |_{\mathbf{x}} = \frac{1}{\mathcal{V}} \int_{V_\lambda(\mathbf{x})} \psi_\lambda |_{\mathbf{x}+\mathbf{y}_\lambda} dV \quad (5.10)$$

The intrinsic averaging operator is defined as

$$\langle \psi_\lambda \rangle^\lambda |_{\mathbf{x}} = \frac{1}{V_\lambda} \int_{V_\lambda(\mathbf{x})} \psi_\lambda |_{\mathbf{x}+\mathbf{y}_\lambda} dV \quad (5.11)$$

and both averaging operators are related by

$$\langle \psi_\lambda \rangle = \varepsilon_\lambda(\mathbf{x}) \langle \psi_\lambda \rangle^\lambda \quad (5.12)$$

Where $\varepsilon_\lambda = V_\lambda(\mathbf{x})/\mathcal{V}$ is the volume fraction of the λ -phase within the averaging domain, and therefore

$$\varepsilon_\mu(\mathbf{x}) + \varepsilon_\sigma(\mathbf{x}) = 1 \quad (5.13)$$

In the above expressions, we have explicitly indicated the spatial dependence of volume averaged quantities, this is convenient for the derivation of average equations that are valid everywhere in ω -region.

5.1.1 Averaged equations

As in the previous chapter, the process of volume averaging is initiated by applying the superficial averaged operator, Eq. 5.10, to the governing equations Eqs. 5.1-5.3; then, the Spatial Averaging Theorem for the μ - σ system, Eq. 5.14 :

$$\langle \nabla \cdot \mathbf{a}_\lambda \rangle = \nabla \cdot \langle \mathbf{a}_\lambda \rangle + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathbf{a}_\lambda|_{\mathbf{x}+\mathbf{y}_\lambda} dA, \quad (5.14)$$

has been used to interchange differentiation and integration and to express the diffusive flux in terms of averaged concentrations, considering that $\mathcal{D}_{A\mu}$ and $\mathcal{D}_{B\mu}$ are constants in the averaging volume; and in this way, obtaining the averaged equations as function of the volume averaged and local concentrations. Finally, as stated before, for developing the non-closed averaged equations of A in μ and σ phases the local concentrations were decomposed according to Gray (1975) as:

$$C_{i,\lambda} = \langle C_{i,\lambda} \rangle^\lambda + \tilde{C}_{i,\lambda}, \quad \text{where } i = A, B; \quad (5.15)$$

here the average concentration undergoes significant changes only over the large length-scale L and the spatial deviation concentrations are dominated by the small length-scales ℓ_μ and ℓ_σ (See Figure 5.1). As a result of the averaging procedure, one obtains, in Eq. 5.16 - Eq. 5.18, the non-closed averaged equations of species i in μ and σ phases. It should be noted that at this point no significant simplifications have been performed in the spatial smoothing process thus, the non-closed averaged equations are more complicated than their point counterparts. For example, the non-closed averaged equation of A in μ -phase, Eq. 5.16, has the expected terms i.e.,

accumulation, diffusion and reversible reaction, and additional non-local terms:

$$\begin{aligned}
\varepsilon_\mu(\mathbf{x}) \frac{\partial \langle C_{A\mu} \rangle^\mu |_{\mathbf{x}}}{\partial t} &= \nabla \cdot \left[\mathcal{D}_{A\mu} \left(\varepsilon_\mu \nabla \langle C_{A\mu} \rangle^\mu |_{\mathbf{x}} \right) \right] \\
&+ \nabla \cdot \left[\mathcal{D}_{A\mu} \left(\frac{1}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} (\tilde{C}_{A\mu} |_{\mathbf{x}+\mathbf{y}_\lambda} + \langle C_{A\mu} \rangle^\mu |_{\mathbf{x}+\mathbf{y}_\lambda} - \langle C_{A\mu} \rangle^\mu |_{\mathbf{x}}) dA \right) \right] \\
&+ \frac{1}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} (\nabla \langle C_{A\mu} \rangle^\mu |_{\mathbf{x}+\mathbf{y}_\lambda} + \nabla \tilde{C}_{A\mu} |_{\mathbf{x}+\mathbf{y}_\lambda}) dA \\
&- \varepsilon_\mu(\mathbf{x}) k_\mu \left(\langle C_{A\mu} \rangle^\mu |_{\mathbf{x}} - \frac{\langle C_{B\mu} \rangle^\mu |_{\mathbf{x}}}{K_\mu} \right)
\end{aligned} \tag{5.16}$$

Moreover, as in the previous case, the non-closed averaged equation of B in μ -phase does not contain the non local terms coming from the internal flux, since species B is insoluble in γ and σ phases, therefore this equation can be written as:

$$\begin{aligned}
\varepsilon_\mu(\mathbf{x}) \frac{\partial \langle C_{B\mu} \rangle^\mu |_{\mathbf{x}}}{\partial t} &= \nabla \cdot \left[\mathcal{D}_{B\mu} (\varepsilon_\mu \nabla \langle C_{B\mu} \rangle^\mu |_{\mathbf{x}}) \right] \\
&+ \nabla \cdot \left[\mathcal{D}_{B\mu} \left(\frac{1}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} (\tilde{C}_{B\mu} |_{\mathbf{x}+\mathbf{y}_\lambda} + \langle C_{B\mu} \rangle^\mu |_{\mathbf{x}+\mathbf{y}_\lambda} - \langle C_{B\mu} \rangle^\mu |_{\mathbf{x}}) dA \right) \right] \\
&+ \varepsilon_\mu(\mathbf{x}) k_\mu \left(\langle C_{A\mu} \rangle^\mu |_{\mathbf{x}} - \frac{\langle C_{B\mu} \rangle^\mu |_{\mathbf{x}}}{K_\mu} \right),
\end{aligned} \tag{5.17}$$

nevertheless, Eq. 5.17 has the accumulation, diffusion and reversible reaction terms, and additional non-local terms. Finally the non-closed averaged equation of species A in σ -phase is presented:

$$\begin{aligned}
\varepsilon_\sigma(\mathbf{x}) \frac{\partial \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}}}{\partial t} &= \nabla \cdot \left[\mathcal{D}_{A\sigma} \left(\varepsilon_\sigma \nabla \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}} \right) \right] \\
&+ \nabla \cdot \left[\mathcal{D}_{A\sigma} \left(\frac{1}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} (\tilde{C}_{A\sigma} |_{\mathbf{x}+\mathbf{y}_\lambda} + \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}+\mathbf{y}_\lambda} - \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}}) dA \right) \right] \\
&+ \frac{1}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla (\langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}+\mathbf{y}_\lambda} + \tilde{C}_{A\sigma} |_{\mathbf{x}+\mathbf{y}_\lambda}) dA \\
&- k_\sigma \varepsilon_\sigma(\mathbf{x}) \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{x}}
\end{aligned} \tag{5.18}$$

Eq. 5.18 contains the expected terms of accumulation, diffusion and irreversible reaction and, additional non-local terms. As discussed in the previous chapter, Eqs. 5.16 - 5.18 are non-local transport equations since the presence of the spatial deviation concentrations, $\tilde{C}_{i\lambda} |_{\mathbf{x}+\mathbf{y}_\lambda}$, and the volume average concentrations, $\langle C_{i\lambda} \rangle^\lambda |_{\mathbf{x}+\mathbf{y}_\lambda}$, evaluated at points other than the centroid \mathbf{x} . In order to express these equations only

in terms of volume averaged quantities it is indispensable to 1) impose the following length-scale constraint,

$$\ell_\mu, \ell_\sigma \ll r_0 \ll L, \quad (5.19)$$

and 2) derive and solve the closure problems related to the spatial deviation concentrations, $\tilde{C}_{i\lambda}$. Therefore, in order to continue this analysis and simplify the averaged equations and obtain their closed form, a closure problem was developed which enables to predict the $\tilde{C}_{i\lambda}$. The details of the derivation and formal solution of the closure problem are quite lengthy and are provided in Appendix B

5.1.2 Closure variables

With the purpose of obtaining a closed form for Eqs. 5.16 - 5.18, the formal solution of the spatial deviation concentrations is presented:

$$\begin{aligned} \tilde{C}_{A\mu} = & \mathbf{b}_{\mu\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{\mu\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{\mu B} \cdot \nabla \langle C_{B\mu} \rangle^\mu \\ & + s_\mu (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu) \end{aligned} \quad (5.20)$$

$$\begin{aligned} \tilde{C}_{B\mu} = & \mathbf{b}_{B\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{B\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{BB} \cdot \nabla \langle C_{B\mu} \rangle^\mu \\ & + s_B (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu) \end{aligned} \quad (5.21)$$

$$\begin{aligned} \tilde{C}_{A\sigma} = & \mathbf{b}_{\sigma\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{\sigma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{\sigma B} \cdot \nabla \langle C_{B\mu} \rangle^\mu \\ & - s_\sigma (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma) \end{aligned} \quad (5.22)$$

These expressions, have been proposed in terms of the sources of the boundary-value problems for $\tilde{C}_{i\lambda}$. As previously explained, the details of the development of these boundary-value problems are in Appendix B. The variables \mathbf{b}_{ji} , s_j , where $j = \mu, B, \sigma$ and $i = \mu, \sigma, B$ are the closure variables, their derivation has been performed by considering the following length-scale constraints:

$$r_0 \ll L \quad (5.23)$$

$$r_0^2 \ll L^2 \quad (5.24)$$

$$\ell_\sigma, \ell_\mu \ll L \quad (5.25)$$

where it has been assumed that the characteristic lengths associated to the spatial variations of the volume averaged concentrations and their gradients, can be represented by the macroscopic length, L . In addition, the derivation of , $\tilde{C}_{i\lambda}$, requires

satisfying the following time-scale constraint:

$$\frac{\mathcal{D}_{A\lambda} t^*}{\ell_\lambda^2} \gg 1 \quad (5.26)$$

5.1.3 Closed averaged equations in ω -region

In this section the averaged equations valid in the homogeneous ω -region are presented. As mentioned, the *non-local mass equilibrium* assumption has been imposed, resulting in a local volume averaged equations system formed by coupled equations, each one describing the mass transfer of species i in the corresponding phase. Each equation contains terms of accumulation, diffusion, reaction, mass transfer exchange and convective-like transport. The latter terms are composed of effective coefficients which provide information about one of the phases. For example, governing averaged equation of species A in μ -phase, Eq. 5.27, has 3 effective diffusivity tensors with the form $\mathbf{D}_{\mu j}$ where j can be μ, σ, B , therefore when $j = \sigma$, $\mathbf{D}_{\mu\sigma}$ contributes with information about the structure of the emulsion drop related to σ -phase.

$$\begin{aligned} \underbrace{\varepsilon_\mu \frac{\partial \langle C_{A\mu} \rangle^\mu}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot [\mathbf{D}_{\mu\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{D}_{\mu B} \cdot \nabla \langle C_{B\mu} \rangle^\mu + \mathbf{D}_{\mu\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma]}_{\text{diffusion}} \\ &+ \underbrace{\nabla \cdot [\mathbf{u}_{\mu\mu} \langle C_{A\mu} \rangle^\mu + \mathbf{u}_{\mu B} \langle C_{B\mu} \rangle^\mu + \mathbf{u}_{\mu\sigma} \langle C_{A\sigma} \rangle^\sigma]}_{\text{convective-like transport term}} \\ &+ \underbrace{(a_v k) (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu)}_{\text{exchange term}} - \varepsilon_\mu(\mathbf{x}) k_\mu \underbrace{\left(\langle C_{A\mu} \rangle^\mu - \frac{\langle C_{B\mu} \rangle^\mu}{K_\mu} \right)}_{\text{reaction}}, \end{aligned} \quad (5.27)$$

it should be noted that the interfacial boundary conditions 5.6 and 5.7 have influenced the volume averaged equation 5.27 since the interfacial flux is incorporated directly into it by means of the exchange term. In the case of diffusion term, diffusivity tensor $\mathbf{D}_{\mu\mu}$ is defined as:

$$\mathbf{D}_{\mu\mu} = \mathcal{D}_{A\mu} \left(\varepsilon_\mu \mathbf{1} + \frac{1}{\gamma} \int_{A_{\mu\sigma}} \mathbf{n}_{\mu\sigma} \mathbf{b}_{\mu\mu} dA \right) \quad (5.28)$$

one can observe that this tensor is function of the molecular diffusivity $\mathcal{D}_{A\mu}$, the volumetric fraction ε_μ and the structure of the emulsion drop through the $\mathbf{b}_{\mu\mu}$ -field.

The others difussivity tensors have the form:

$$\mathbf{D}_{\mu B} = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{\mu B} dA \quad (5.29)$$

$$\mathbf{D}_{\mu\sigma} = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{\mu\sigma} dA \quad (5.30)$$

The position-dependent effective velocity-like vectors of species A in the μ -phase are represented as:

$$\mathbf{u}_{\mu\mu} = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \nabla \mathbf{b}_{\mu\mu} dA - K_{\mu\sigma}^{eq} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} s_{\mu} dA \right) \quad (5.31)$$

$$\mathbf{u}_{\mu B} = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \nabla \mathbf{b}_{\mu B} dA \right) \quad (5.32)$$

$$\mathbf{u}_{\mu\sigma} = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \nabla \mathbf{b}_{\mu\sigma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\sigma\mu} s_{\mu} dA \right) \quad (5.33)$$

it will be demonstrated that the effective velocity-like vectors presented here, are negligible for the case of mass transfer by diffusion and chemical reaction in DES, being consistent with the exposed by [Whitaker \(1999\)](#) and [Paine et al. \(1983\)](#). Lastly, the mass transfer coefficient of species A in the μ -phase is presented in Eq. 5.34,

$$a_v k = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \nabla s_{\mu} dA \quad (5.34)$$

here a_v is the interfacial area $\mathcal{A}_{\mu\sigma}$ per unit volume and k is the film mass transfer coefficient in $\mathcal{A}_{\mu\sigma}$. Continuing with this analysis, the governing averaged equation of species B in μ -phase is presented:

$$\begin{aligned} \underbrace{\varepsilon_{\mu} \frac{\partial \langle C_{B\mu} \rangle^{\mu}}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot [\mathbf{D}_{B\mu} \cdot \nabla \langle C_{A\mu} \rangle^{\mu} + \mathbf{D}_{BB} \cdot \nabla \langle C_{B\mu} \rangle^{\mu} + \mathbf{D}_{B\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^{\sigma}]}_{\text{diffusion}} \\ &+ \underbrace{\nabla \cdot [\mathbf{u}_{B\mu} \langle C_{A\mu} \rangle^{\mu} + \mathbf{u}_{BB} \langle C_{B\mu} \rangle^{\mu} + \mathbf{u}_{B\sigma} \langle C_{A\sigma} \rangle^{\sigma}]}_{\text{convective-like transport term}} \\ &+ \underbrace{\varepsilon_{\mu} k_{\mu} \left(\langle C_{A\mu} \rangle^{\mu} - \frac{\langle C_{B\mu} \rangle^{\mu}}{K_{\mu}} \right)}_{\text{reaction}} \end{aligned} \quad (5.35)$$

it is also important to highlight that in the governing averaged equation of species B in μ -phase, Eq. 5.35 there is no mass exchange term since species B is restricted

to the membrane μ -phase. In Eq. 5.35, the position-dependent effective diffusivity tensors of species B in the μ -phase are defined by:

$$\mathbf{D}_{B\mu} = \frac{\mathcal{D}_{B\mu}}{\gamma} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{B\mu} dA \quad (5.36)$$

$$\mathbf{D}_{BB} = \mathcal{D}_{B\mu} \left(\varepsilon_{\mu}(\mathbf{x}) \mathbf{1} + \frac{1}{\gamma} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{BB} dA \right) \quad (5.37)$$

$$\mathbf{D}_{B\sigma} = \frac{\mathcal{D}_{B\mu}}{\gamma} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{B\sigma} dA, \quad (5.38)$$

and the position-dependent effective velocity-like vectors have the form:

$$\begin{aligned} \mathbf{u}_{B\mu} &= -\frac{\mathcal{D}_{A\mu}}{\gamma} \left(K_{\mu\sigma}^{eq} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} s_B dA \right) \\ \mathbf{u}_{B\sigma} &= \frac{\mathcal{D}_{B\mu}}{\gamma} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} s_{B\sigma} dA \right) \end{aligned} \quad (5.39)$$

Lastly, the averaged equations system valid in ω -region contains the governing averaged equation of species A in σ -phase which is defined by:

$$\begin{aligned} \underbrace{\varepsilon_{\sigma} \frac{\partial \langle C_{A\sigma} \rangle^{\sigma}}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot [\mathbf{D}_{\sigma\mu} \cdot \nabla \langle C_{A\mu} \rangle^{\mu} + \mathbf{D}_{\sigma B} \cdot \nabla \langle C_{B\mu} \rangle^{\mu} + \mathbf{D}_{\sigma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^{\sigma}]}_{\text{diffusion}} \\ &+ \underbrace{\nabla \cdot [\mathbf{u}_{\sigma\mu} \langle C_{A\mu} \rangle^{\mu} + \mathbf{u}_{\sigma B} \langle C_{B\mu} \rangle^{\mu} + \mathbf{u}_{\sigma\sigma} \langle C_{A\sigma} \rangle^{\sigma}]}_{\text{convective-like transport term}} \\ &+ \underbrace{(a_v k) (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^{\mu} - \langle C_{A\sigma} \rangle^{\sigma})}_{\text{exchange term}} - \underbrace{k_{\sigma} \varepsilon_{\sigma}(\mathbf{x}) \langle C_{A\sigma} \rangle^{\sigma}}_{\text{reaction}} \end{aligned} \quad (5.40)$$

As expected, Eq. 5.40 presents accumulation, diffusion, reaction, mass transfer exchange and convective-like transport terms. The position-dependent effective diffusivity tensors are defined by:

$$\mathbf{D}_{\sigma\mu} = \frac{\mathcal{D}_{A\sigma}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \mathbf{b}_{\sigma\mu} dA \quad (5.41)$$

$$\mathbf{D}_{\sigma B} = \frac{\mathcal{D}_{A\sigma}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \mathbf{b}_{\sigma B} dA \quad (5.42)$$

$$\mathbf{D}_{\sigma\sigma} = \mathcal{D}_{A\sigma} \left(\varepsilon_{\sigma} \mathbf{1} + \frac{1}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \mathbf{b}_{\sigma\sigma} dA \right) \quad (5.43)$$

and the position-dependent effective velocity-like vectors of species A in the σ -phase have the form:

$$\mathbf{u}_{\sigma\mu} = \frac{\mathcal{D}_{A\sigma}}{\gamma} \left(\int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla \mathbf{b}_{\sigma\mu} dA - K_{\mu\sigma}^{eq} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} s_{\sigma} dA \right) \quad (5.44)$$

$$\mathbf{u}_{\sigma B} = \frac{\mathcal{D}_{A\sigma}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla \mathbf{b}_{\sigma B} dA \quad (5.45)$$

$$\mathbf{u}_{\sigma\sigma} = \frac{\mathcal{D}_{A\sigma}}{\gamma} \left(\int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla \mathbf{b}_{\sigma\sigma} dA + \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} s_{\sigma} dA \right) \quad (5.46)$$

The mass transfer coefficient (Eq. 5.34) can be also represented by:

$$(a_v k) = -\frac{\mathcal{D}_{A\sigma}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla s_{\sigma} dA, \quad (5.47)$$

since $a_v k = a_v k_{\mu} = a_v k_{\sigma}$. Once the volume averaged equations representing the mass transport by diffusion and reaction in the ω -region were obtained, the second level of averaging between ω and η regions can be developed.

5.2 Determination of the effective coefficients

The *closed* averaged governing equations for $\langle C_{A\lambda} \rangle^{\lambda}$ ($\lambda = \mu, \sigma$) have been developed, consequently, in this section the predictions of the geometrically dependent effective coefficients are presented. For this purpose, the four closure boundary-value problems for $\tilde{C}_{A\lambda}$ which compose the closure problem, are solved in 2D unit cells that take into account the geometric structure of an emulsion drop. Figure 5.2 shows a microscopic image of emulsion drop (left) and a theoretical representation of a emulsion drop (right) where the unit cell is located.

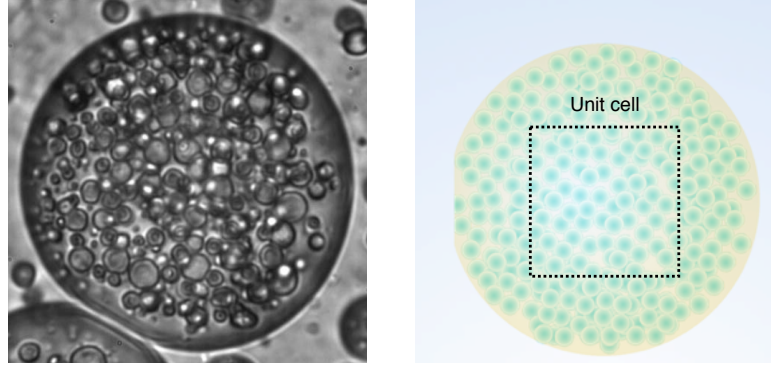


Figure 5.2: Microscopic image of an emulsion drop (Aveyard et al. 2003) and his theoretical representation

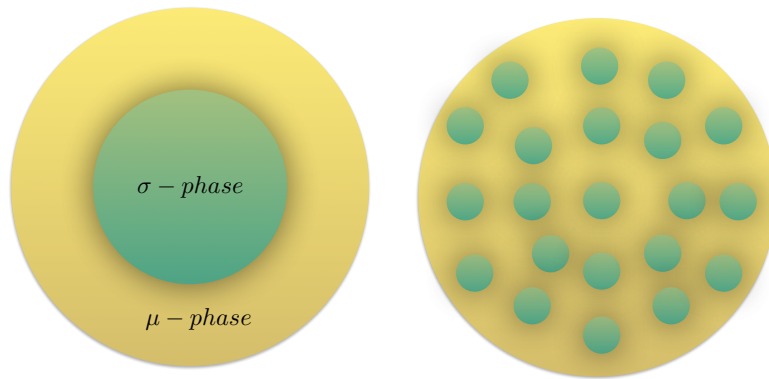


Figure 5.3: Chang's-like unit cell, representative of an emulsion emulsion drop ($\mu+\sigma$ -phases)

For practical purposes, a simpler system of this uni cell is proposed in Figure 5.3 which is composed of two domains, the first one (domain A) illustrated as a yellow circle with radius r_μ , represents the μ -phase. Inside of domain A one green circle or an array of non-touching green circles depict σ -phase and consequently the second domain (domain B). This supposes that emulsion drop is a homogeneous system. Therefore the behavior of the effective coefficients has been analyzed as function of the volumetric fractions of the two phases ($\varepsilon_\mu + \varepsilon_\sigma$) and the geometric structure of the 2D unit cells. It should be noted that, surface of $\mu\sigma$ -phases ($\mathcal{A}_{\mu\sigma}$ for 3D cases) depends directly on the number of circles of domain B (σ -phase). The proportion between both volumetric fractions, δ , can vary from 1, i.e. the limit case when $\varepsilon_\mu = \varepsilon_\sigma$

(geometrically there can not be more σ -phase than μ -phase in the 2D unit cells), up to a very large number in such a way σ -phase tends to disappear, $\varepsilon_\mu = \delta\varepsilon_\sigma$. In this study, δ has been varied from 1 to 10. Additionally, the number of circles (nd) of constant radius, r_σ , that will conform the domain B must be established. The study of the behavior of the effective coefficients is presented considering the ratio of molecular diffusivities as, $\alpha_{\sigma\mu} = \mathcal{D}_{A\sigma}/\mathcal{D}_{A\mu}$ and the ratio, $\Omega_{\sigma\mu} = \frac{P_{\sigma\mu}}{\mathcal{D}_{A\sigma}}$.

It has been considered that the solute A diffuses 10 times faster in the μ -phase than in the internal phase, $\alpha_{\sigma\mu} = 0.1$. The molecular diffusivity of A in the μ -phase 10 times larger than the permeability in $\sigma\mu$ -interface, $\Omega_{\sigma\mu} = 0.1$. The equilibrium distribution coefficient $K_{\mu\sigma}^{eq}$ is set equal to 2.

5.2.1 Geometry-dependent effective diffusivity tensors

As mentioned in previous section, diffusion terms in the closed averaged equations contain the geometry-dependent effective diffusivity tensors \mathbf{D}_{ij} . One must not forget that the first subscript refers to the phase where the averaged equation is valid and the second the influence of one of the phases.

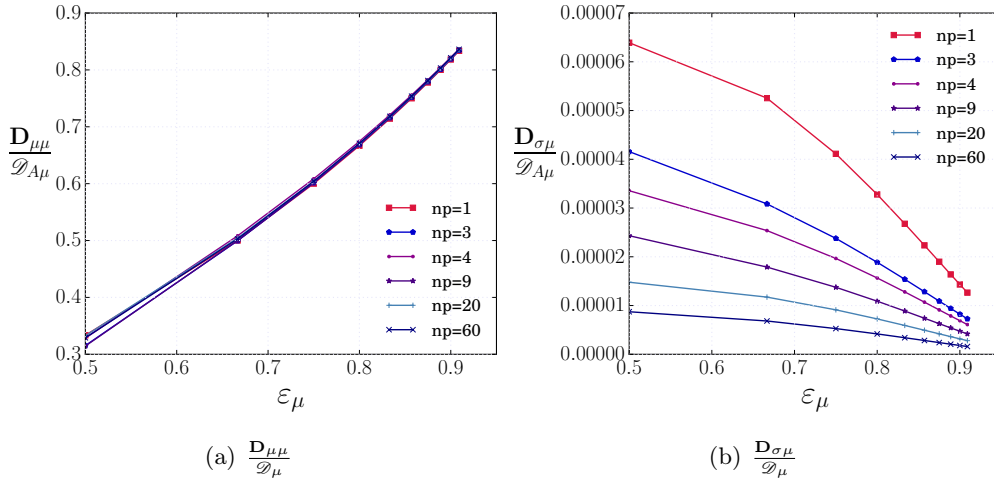


Figure 5.4: $\frac{\mathbf{D}_{\mu\mu}}{\mathcal{D}_{A\mu}}$ and $\frac{\mathbf{D}_{\sigma\mu}}{\mathcal{D}_{A\mu}}$ taking $\alpha_{\sigma\mu} = 0.1$, $\Omega_{\sigma\mu} = 0.1$

Analyzing the diffusivity tensors present in the closed averaged equation for μ -phase (Eq. 5.27), in Figure 5.4 (a), it is shown the normalized $\mathbf{D}_{\mu\mu}$ tensor with the molecular diffusivity $\mathcal{D}_{A\mu}$ in terms of the variable $\varepsilon_\mu = \delta\varepsilon_\sigma$, for a Chang's-type unit cell (Figure 5.3); in this figure one can see that the diffusivity tensor increases directly

with the volumetric fraction ε_μ , as would be expected according to

$$\frac{\mathbf{D}^{\mu\mu}}{\mathcal{D}_\mu} = \left(\varepsilon_\mu \mathbf{1} + \frac{1}{\gamma} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \mathbf{b}_{\mu\mu} dA \right),$$

however the tensor is not affected by the number of circles of σ -phase, i.e. is not a function of the $S_{\mu\sigma}$. On the contrary, the cross-tensor $\mathbf{D}_{\sigma\mu}$ decrease with ε_μ and is affected by the surface $S_{\mu\sigma}$. The $\frac{\mathbf{D}^{\sigma\mu}}{\mathcal{D}_\mu}$ is smallest compare to $\frac{\mathbf{D}^{\mu\mu}}{\mathcal{D}_\mu}$ as one can see in Figure 5.4 (b). Concerning with the diffusivity tensors present in the closed averaged equation for σ -phase, Eq. 5.40, one can observe in Figure 5.5 (a) that the diffusivity tensor increases directly with the volumetric fraction ε_σ , as would be expected according to

$$\frac{\mathbf{D}_{\sigma\sigma}}{\mathcal{D}_\mu} = \alpha_{\sigma\mu} \left(\varepsilon_\sigma \mathbf{1} + \frac{1}{\gamma} \int_{A_{\sigma\mu}} \mathbf{n}_{\sigma\mu} \mathbf{b}_{\sigma\sigma} dA \right),$$

moreover, the tensor is affected by the number of circles of σ -phase, which decrease with large values of $S_{\mu\sigma}$. The cross-tensor $\mathbf{D}_{\mu\sigma}$ is smallest compare to $\mathbf{D}_{\sigma\sigma}$ and is equal to $\mathbf{D}_{\sigma\mu}$ as is shown in Figure 5.5 (b). This behavior has already been found in the teoretical studies of [Quintard and Whitaker \(1993\)](#) and [Aguilar-Madera et al. \(2011\)](#) for heat conduction between a porous medium and a fluid.

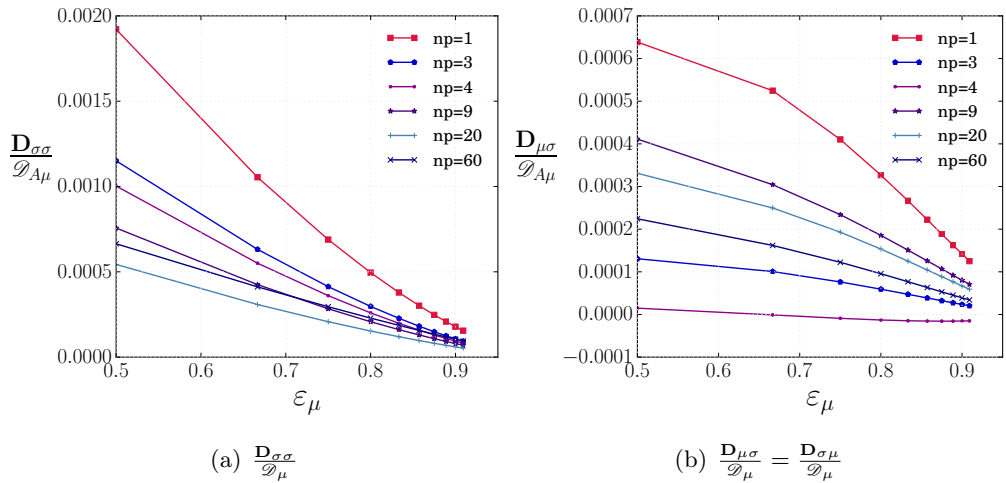


Figure 5.5: $\frac{\mathbf{D}^{\sigma\sigma}}{\mathcal{D}_\mu}$ and $\frac{\mathbf{D}^{\sigma\mu}}{\mathcal{D}_\mu}$ taking $\alpha_{\sigma\mu} = 0.1$, $\Omega_{\sigma\mu} = 0.1$

5.2.2 Geometry-dependent mass transfer coefficients

Regarding the behavior of the mass transfer coefficient which have been normalized with $\frac{\ell_{cell}^2}{\mathcal{D}_{A\mu}}$, here the results are presented. In Figure 5.6 one can observe the mass transfer coefficient increase with ε_σ and also are a function of the np variable.

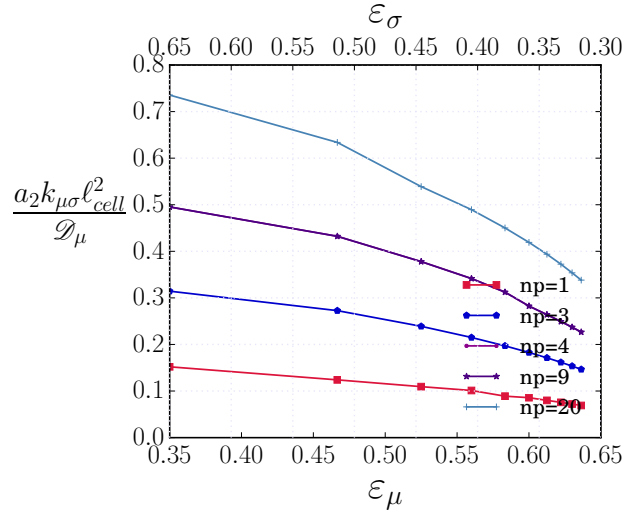


Figure 5.6: Spatial dependence of $\frac{a_{v1} k_1 \gamma^\sigma \ell_{cell}^2}{\mathcal{D}_{A\mu}}$, taking $\alpha_{\sigma\mu} = 0.1, \Omega_{\sigma\mu} = 0.1$

5.2.3 Effective velocity-like vectors

As in the three-phase model, the effective velocity-like for this case has been also determined; since, all of them have very small values, of orders of magnitude of 10^{-10} , their contribution in the averaged equations has been considered negligible. Due to the above stated, the corresponding figures are not presented.

5.3 Large-scale averaging (2-region averaging volume)

Once the μ and σ phases are modeled as continua and the governing equations at the emulsion drops (*Scale III*) are derived, a new system by regions is defined as is shown in Figure 5.7 where homogeneous η -region, formed by γ -phase, contain drops of ω -region. Thus the description of the transport of species A by diffusion and reaction in the ω - η system is:

In η -region

$$\frac{\partial \langle C_{A\gamma} \rangle_\gamma^\eta}{\partial t} = \nabla \cdot (\mathcal{D}_{A\eta} \nabla \langle C_{A\gamma} \rangle_\gamma^\eta) \quad (5.48)$$

In ω -region

In μ -phase

$$\begin{aligned} \underbrace{\varepsilon_\mu \frac{\partial \langle C_{A\mu} \rangle_\omega^\mu}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot [\mathbf{D}_{\mu\mu} \cdot \nabla \langle C_{A\mu} \rangle_\omega^\mu]}_{\text{diffusion}} + \underbrace{(a_v k) (\langle C_{A\sigma} \rangle_\omega^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle_\omega^\mu)}_{\text{exchange term}} \\ &\quad - \underbrace{\varepsilon_\mu k_\mu \left(\langle C_{A\mu} \rangle_\omega^\mu - \frac{\langle C_{B\mu} \rangle_\omega^\mu}{K_\mu} \right)}_{\text{reaction}} \end{aligned} \quad (5.49)$$

$$\underbrace{\varepsilon_\mu \frac{\partial \langle C_{B\mu} \rangle_\omega^\mu}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot [\mathbf{D}_{BB} \cdot \nabla \langle C_{B\mu} \rangle_\omega^\mu]}_{\text{diffusion}} + \underbrace{\varepsilon_\mu k_\mu \left(\langle C_{A\mu} \rangle_\omega^\mu - \frac{\langle C_{B\mu} \rangle_\omega^\mu}{K_\mu} \right)}_{\text{reaction}} \quad (5.50)$$

In σ -phase

$$\begin{aligned} \underbrace{\varepsilon_\sigma \frac{\partial \langle C_{A\sigma} \rangle_\omega^\sigma}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot [\mathbf{D}_{\sigma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle_\omega^\sigma]}_{\text{diffusion}} + \underbrace{(a_v k) (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle_\omega^\mu - \langle C_{A\sigma} \rangle_\omega^\sigma)}_{\text{exchange term}} \\ &\quad - \underbrace{k_\sigma \varepsilon_\sigma(\mathbf{x}) \langle C_{A\sigma} \rangle_\omega^\sigma}_{\text{reaction}} \end{aligned} \quad (5.51)$$

The boundary condition at the inter-region $\eta\omega$ i.e. at $\mathcal{A}_{\eta\omega}$, was based on the rough assumption that spatial deviation of the concentrations in η and ω regions ($\tilde{C}_{A,\gamma}, \tilde{C}_{A,\mu}$) are negligible, thus one can express the local concentrations in terms of local averaged concentrations as:

$$C_{A\gamma} \approx \langle C_{A\gamma} \rangle_\gamma^\eta \quad (5.52)$$

$$C_{A\mu} \approx \langle C_{A\mu} \rangle_\omega^\mu \quad (5.53)$$

Following this idea, and observing the diffusion term in Eq. 5.49, one can substitute Eqs. 5.52 - 5.53 into the local boundary conditions, Eqs. 3.8 - 3.9, and use the diffusion term to define the regional boundary conditions as:

$$-\mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \langle C_{A\mu} \rangle_\omega^\mu) = -\mathbf{n}_{\omega\eta} \cdot \mathcal{D}_{A\eta} \nabla \langle C_{A\gamma} \rangle_\gamma^\eta \quad (5.54)$$

$$-\mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \langle C_{A\gamma} \rangle_\gamma^\eta = P_{\eta\omega} (\langle C_{A\gamma} \rangle_\gamma^\eta - K_{\eta\omega}^{eq} \langle C_{A\mu} \rangle_\omega^\mu) \quad (5.55)$$

A similar analysis was done for the regional boundary condition for species B , obtaining:

$$-\mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{BB}(\mathbf{x}) \cdot \nabla \langle C_{B\mu} \rangle_{\omega}^{\mu}) = 0 \quad (5.56)$$

Here, $\mathbf{n}_{\eta\omega}$ is the unit normal vector pointing from η -region to ω -region ($\mathbf{n}_{\eta\omega} = -\mathbf{n}_{\omega\eta}$). The permeability of the $\eta\omega$ -region is represented by $P_{\eta\omega}$ and $K_{\omega\eta}^{eq}$ is the equilibrium distribution coefficient for the solute A ; both coefficients are functions of local equilibrium constants. The diffusivities tensor, $\mathbf{D}_{\mu\mu}$, \mathbf{D}_{BB} , $\mathbf{D}_{\sigma\sigma}$, are also constant. It should be noted that for the η -region, since it is a homogeneous region formed by γ -phase only, we know that $\mathbf{D}_{\eta\eta} \rightarrow \mathcal{D}_{A\eta}$ and this diffusivity is also constant.

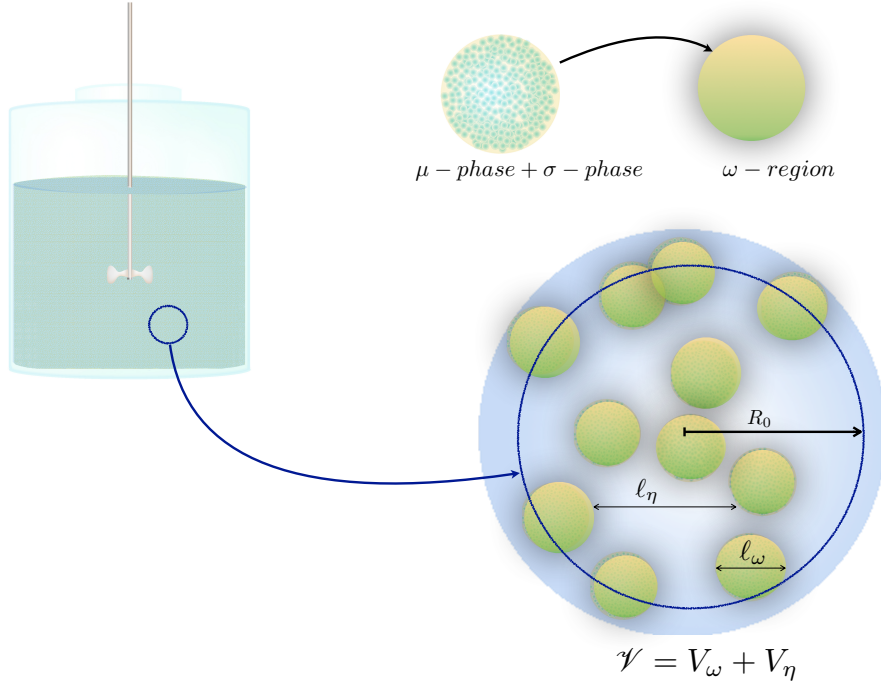


Figure 5.7: Macroscopic \mathcal{L} and averaging volume for η - ω regions

Once the problem of regions is established, in the same way as was done in the previous problems to spatially smooth the local averaged equations, an regional averaging domain of volume \mathcal{V} is defined:

$$\mathcal{V} = V_{\eta}(\mathbf{x}) + V_{\omega}(\mathbf{x}) \quad (5.57)$$

In the method of large-scale averaging, one will make use of both superficial averages

and intrinsic averages. Thus, the definition of the superficial regional averaging operator of a continuous property in a region, $\langle \psi_\beta \rangle_\lambda^\beta$ ($\beta = \mu, \sigma$ and $\lambda = \omega, \eta$), is defined as:

$$\{\langle \psi_\beta \rangle_\lambda^\beta\} | \mathbf{x} = \frac{1}{\mathcal{V}} \int_{V_\lambda(\mathbf{x})} \langle \psi_\beta \rangle_\lambda^\beta | \mathbf{x} + \mathbf{y}_\lambda dV \quad (5.58)$$

where V_λ is the domain occupied by the λ -region in the averaging volume, \mathbf{x} is the position vector locating the centroid of \mathcal{V} and \mathbf{y}_λ is the vector that locates points of the λ -region within the \mathcal{V} . The intrinsic regional averaging operator is defined as

$$\{\langle \psi_\beta \rangle_\lambda^\beta\}^\lambda | \mathbf{x} = \frac{1}{V_\lambda} \int_{V_\lambda(\mathbf{x})} \langle \psi_\beta \rangle_\lambda^\beta | \mathbf{x} + \mathbf{y}_\lambda dV \quad (5.59)$$

Both averaging operators are related by

$$\{\langle \psi_\beta \rangle_\lambda^\beta\} = \varepsilon_\lambda(\mathbf{x}) \{\langle \psi_\beta \rangle_\lambda^\beta\}^\lambda \quad (5.60)$$

Where $\varepsilon_\lambda = V_\lambda(\mathbf{x})/\mathcal{V}$ is the volume fraction of the λ -region within the averaging domain, therefore:

$$\varepsilon_\eta(\mathbf{x}) + \varepsilon_\omega(\mathbf{x}) = 1 \quad (5.61)$$

The averaging theorem for a two-region model, (Howes and Whitaker 1985), can be expressed as

$$\{\nabla \langle \psi_\beta \rangle_\lambda^\beta\} = \nabla \{\langle \psi_\beta \rangle_\lambda^\beta\} + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \langle \psi_\beta \rangle_\lambda^\beta | \mathbf{x} + \mathbf{y}_\lambda dA \quad (5.62)$$

In the nomenclature illustrated in Eqs. 5.58 - 5.62 the subscripts always identify phases or regions while the presence of a superscript always indicates an intrinsic average. Even though the process under investigation is mathematically analogous to the previous process, the physics of the regional system is considerably more complex and it is best to retain the complex nomenclature as a reminder of physics of the emulsion drop, i.e. in ω -region.

5.3.1 Averaged model

The process of volume averaging is initiated by applying the superficial averaged operator, Eq. 5.58, to the governing equations Eqs. 5.48 - 5.51. In this respect Eq.

5.48 is written as:

$$\begin{aligned} \frac{\partial \{C_{A\eta}\} |_{\mathbf{x}}}{\partial t} = & \nabla \cdot \left[\mathcal{D}_{A\eta} \left(\nabla \{C_{A\eta}\} |_{\mathbf{x}} + \frac{1}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} C_{A\eta} |_{\mathbf{x}+\mathbf{y}_\lambda} dA \right) \right] \\ & + \frac{1}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla C_{A\eta} |_{\mathbf{x}+\mathbf{y}_\lambda} dA, \end{aligned} \quad (5.63)$$

up here, it should be pointed out that, since the homogeneous η -region is just formed by γ -phase and in sake of simplify the nomenclature, the local intrinsic averaged concentration of species A in η -region, $\langle C_{A\gamma} \rangle_\eta^\gamma$, has been substituted by $C_{A\eta}$. As in the previous spatial smoothing procedure, the desired dependent variable is an intrinsic averaged quantity, thus making use of the relation in Eq. 5.60, Eq. 5.63 can be rewritten under the form:

$$\begin{aligned} \varepsilon_\eta(\mathbf{x}) \frac{\partial \{C_{A\eta}\}^\eta |_{\mathbf{x}}}{\partial t} = & \nabla \cdot \left[\mathcal{D}_{A\eta} \left(\varepsilon_\eta \nabla \{C_{A\eta}\}^\eta |_{\mathbf{x}} \right) \right] \\ & + \nabla \cdot \left[\mathcal{D}_{A\eta} \left(\frac{1}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} (C_{A\eta} |_{\mathbf{x}+\mathbf{y}_\lambda} - \{C_{A\eta}\}^\eta |_{\mathbf{x}}) dA \right) \right] \\ & + \frac{1}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla C_{A\eta} |_{\mathbf{x}+\mathbf{y}_\lambda} dA \end{aligned} \quad (5.64)$$

To obtain the final form of the non-closed averaged equation in η -region the following relation, deduced from the Spatial Averaging Theorem (SAT)

$$\frac{1}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} dA = -\nabla \varepsilon_\eta, \quad (5.65)$$

has been used in Eq. 5.64. Also in order to remove the local concentration $C_{A\eta} |_{\mathbf{x}+\mathbf{y}}$, the spatial decomposition define by:

$$C_{A,\eta} |_{\mathbf{x}+\mathbf{y}_\eta} = \{C_{A,\eta}\}^\eta |_{\mathbf{x}+\mathbf{y}_\eta} + \tilde{C}_{A,\eta} |_{\mathbf{x}+\mathbf{y}_\eta} \quad (5.66)$$

has been applied, thus Eq. 5.64 can be written as:

$$\begin{aligned} \varepsilon_\eta(\mathbf{x}) \frac{\partial \{C_{A\eta}\}^\eta |_{\mathbf{x}}}{\partial t} = & \nabla \cdot \left[\mathcal{D}_{A\eta} \left(\varepsilon_\eta \nabla \{C_{A\eta}\}^\eta |_{\mathbf{x}} \right) \right] \\ & + \nabla \cdot \left[\mathcal{D}_{A\eta} \left(\frac{1}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} (\tilde{C}_{A\eta} |_{\mathbf{x}+\mathbf{y}_\eta} + \{C_{A\eta}\}^\eta |_{\mathbf{x}+\mathbf{y}_\eta} - \{C_{A\eta}\}^\eta |_{\mathbf{x}}) dA \right) \right] \\ & + \frac{1}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla (\{C_{A\eta}\}^\eta |_{\mathbf{x}+\mathbf{y}_\eta} + \tilde{C}_{A\eta} |_{\mathbf{x}+\mathbf{y}_\eta}) dA \end{aligned} \quad (5.67)$$

Eq. 5.67 is the non-closed averaged equation of A in η -region which contains terms of accumulation, diffusion and additional non-local terms. Eq. 5.67 is obviously more complicated than its point counterpart since no significant simplifications have been performed in the spatial smoothing process, this point will be discussed later. It is worth emphasized that the last term of the left hand side of this equation is related to the interfacial flux at $\mathcal{A}_{\eta\omega}$ and connects the η -region transport equation to the ω -region transport equations. To continue with the spatial smoothing of Eq. 5.49 - Eq. 5.51 it is necessary to establish the following regional spatial decomposition of a local averaged concentration :

$$\langle C_{j\beta} \rangle_{\omega}^{\beta} |_{\mathbf{x}+\mathbf{y}_{\eta}} = \{ \langle C_{j\beta} \rangle_{\omega}^{\beta} \}^{\omega} |_{\mathbf{x}+\mathbf{y}_{\omega}} + \tilde{C}_{j\beta\omega} |_{\mathbf{x}+\mathbf{y}_{\omega}}, \quad j = A, B; \beta = \mu, \sigma, \quad (5.68)$$

It should be noted that, Eqs. 5.66 and 5.68 also represents a decomposition of length scales. Thus the average concentration undergoes significant changes only over the large length-scale \mathcal{L} and the spatial deviation concentrations are dominated by the small length-scales ℓ_{η} and ℓ_{ω} (See Figure 5.7).

Repeating the averaging procedure in Eq. 5.49 - Eq. 5.51, the non-local form of the regional averaged equations are derived; for example the non-local regional averaged equation of species A in ω -region is defined as:

$$\begin{aligned} \varepsilon_{\omega} \varepsilon_{\mu} \frac{\partial \{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega}}{\partial t} &= \nabla \cdot [\mathbf{D}_{\mu\mu} \cdot \varepsilon_{\omega} \nabla \{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega}] \\ &+ \nabla \cdot \left[\frac{1}{\gamma} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{\mu\mu} (\{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega} |_{\mathbf{x}+\mathbf{y}_{\eta}} - \{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega}) dA \right] \\ &+ \nabla \cdot \left[\frac{1}{\gamma} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{\mu\mu} (\tilde{C}_{A\mu\omega} |_{\mathbf{x}+\mathbf{y}_{\eta}}) dA \right] \\ &+ \frac{1}{\gamma} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{\mu\mu} \cdot (\nabla \{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega} |_{\mathbf{x}+\mathbf{y}_{\omega}} + \nabla \tilde{C}_{A\mu\omega} |_{\mathbf{x}+\mathbf{y}_{\omega}}) dA \\ &+ \varepsilon_{\omega} (a_v k) (\{ \langle C_{A\sigma} \rangle_{\omega}^{\sigma} \}^{\omega} - K_{\mu\sigma}^{eq} \{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega}) \\ &- \varepsilon_{\omega} \varepsilon_{\mu} k_{\mu} \left(\{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega} - \frac{ \{ \langle C_{B\mu} \rangle_{\omega}^{\mu} \}^{\omega} }{ K_{\mu} } \right), \end{aligned} \quad (5.69)$$

which contains terms of accumulation, diffusion, mass exchange and, reversible reaction, and additional non-local terms. In Eq. 5.69 it should be stressed that the mass exchange term is related to the interfacial mass flux at $\mathcal{A}_{\mu\sigma}$. In contrast with

this equation the non-local regional averaged equation for species B contains: accumulation, diffusion, reversible reaction, and additional non-local terms as one can see in the following expression: As mention before, the impermeable nature of species B , in this regional case in η -region, leads to Eq. ?? without mass exchange term. Finally the non-local regional averaged equation for species A in ω -region is defined by 5.70 which contains the expected terms of accumulation, diffusion, mass exchange and irreversible reaction and, additional non-local terms as following:

$$\begin{aligned}
\varepsilon_\omega \varepsilon_\sigma \frac{\partial \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega}{\partial t} &= \nabla \cdot [\mathbf{D}_{\sigma\sigma} \cdot \varepsilon_\omega \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega] \\
&+ \nabla \cdot \left[\frac{1}{\mathcal{V}} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{\sigma\sigma} (\{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega |_{\mathbf{x}+\mathbf{y}_\omega} - \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega) dA \right] \\
&+ \nabla \cdot \left[\frac{1}{\mathcal{V}} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{\sigma\sigma} (\tilde{C}_{A\sigma\omega} |_{\mathbf{x}+\mathbf{y}_\omega}) dA \right] \\
&+ \frac{1}{\mathcal{V}} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{\sigma\sigma} \cdot (\nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega |_{\mathbf{x}+\mathbf{y}_\omega} + \nabla \tilde{C}_{A\sigma\omega} |_{\mathbf{x}+\mathbf{y}_\omega}) dA \\
&+ \varepsilon_\omega (a_v k) (K_{\mu\sigma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega - \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega) \\
&- \varepsilon_\omega \varepsilon_\sigma k_\sigma \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega
\end{aligned} \tag{5.70}$$

At this point it is important to stress that Eqs. 5.67 - 5.70 are non-local regional averaged transport equations since the presence of the regional spatial deviation concentrations, and the regional volume average concentrations, $\{ \langle C_{i\beta} \rangle_\lambda^\beta \}^\lambda$, evaluated at points other than the centroid \mathbf{x} . In order to express these equations only in terms of regional volume averaged quantities it is indispensable to 1) impose the following length-scale constraint (Whitaker 1999, Wood 2009),

$$\ell_\eta, \ell_\omega \ll R_0 \ll \mathcal{L}, \tag{5.71}$$

and 2) derive and solve the closure problems related to the regional spatial deviation concentrations, $\tilde{C}_{i\lambda}$. Therefore, in order to continue this analysis and simplify the averaged equations and obtain their closed form, a closure problem was developed which enables to predict the $\tilde{C}_{i\lambda}$. The details of the derivation and formal solution of the closure problem are quite lengthy and are provided in Appendix B along with the closure problem for the ω -region.

5.3.2 Closure variables

With the purpose of obtaining a closed form for Eqs. 5.67 - 5.70, the formal solution of the spatial deviation concentrations is presented:

$$\begin{aligned}\tilde{C}_{A\eta} = & \mathbf{b}_{\eta\eta} \cdot \nabla \{C_{A\eta}\}^\eta + \mathbf{b}_{\eta\omega} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega + \mathbf{b}_{\eta\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\sigma \\ & + \mathbf{b}_{\eta B} \cdot \nabla \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega - s_\eta (\{C_{A\eta}\}^\eta - K_{\eta\omega}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega)\end{aligned}\quad (5.72)$$

$$\begin{aligned}\tilde{C}_{A\mu\omega} = & \mathbf{b}_{\mu\eta} \cdot \nabla \{C_{A\eta}\}^\eta + \mathbf{b}_{\mu\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega + \mathbf{b}_{\mu\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\sigma \\ & + \mathbf{b}_{\mu B} \cdot \nabla \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega + s_\omega (K_{\eta\omega}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega - \{C_{A\eta}\}^\eta)\end{aligned}\quad (5.73)$$

$$\begin{aligned}\tilde{C}_{B\mu\omega} = & \mathbf{b}_{B\eta} \cdot \nabla \{C_{A\eta}\}^\eta + \mathbf{b}_{B\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega + \mathbf{b}_{B\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\sigma \\ & + \mathbf{b}_{BB} \cdot \nabla \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega + s_B (K_{\eta\omega}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega - \{C_{A\eta}\}^\eta)\end{aligned}\quad (5.74)$$

$$\begin{aligned}\tilde{C}_{A\sigma\omega} = & \mathbf{b}_{\sigma\eta} \cdot \nabla \{C_{A\eta}\}^\eta + \mathbf{b}_{\sigma\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega + \mathbf{b}_{\sigma\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\sigma \\ & + \mathbf{b}_{\sigma B} \cdot \nabla \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega + s_\sigma (K_{\eta\omega}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega - \{C_{A\eta}\}^\eta)\end{aligned}\quad (5.75)$$

These expressions, have been proposed in terms of the sources of the boundary-value problems for $\tilde{C}_{i\lambda}$. As previously explained, the details of the development of these boundary-value problems are in Appendix B. The variables \mathbf{b}_{ji} , s_j , where $j = \eta, \mu, B, \sigma$ and $i = \eta, \mu, B, \sigma$ are the closure variables, their derivation has been performed by considering the following length-scale constraints:

$$R_0 \ll \mathcal{L} \quad (5.76)$$

$$R_0^2 \ll \mathcal{L}^2 \quad (5.77)$$

$$\ell_\eta, \ell_\omega \ll \mathcal{L} \quad (5.78)$$

where it has been assumed that the characteristic lengths associated to the regional spatial variations of the volume averaged concentrations and their gradients, can be represented by the system macroscopic length, L . In addition, the derivation of , $\tilde{C}_{i,\lambda}$, requires satisfying the following time-scale constraint:

$$\frac{\mathcal{D}_{A\eta} t^*}{\ell_\eta^2} \gg 1 \quad (5.79)$$

$$\frac{\mathbf{D}_{ii} t^*}{\ell_\omega^2} \gg \mathbf{1}; \quad i = \mu, \sigma \quad (5.80)$$

5.3.3 Closed averaged model

In this section the large-scale averaged equations valid in the regional averaged domain are presented. Since the non-local mass equilibrium assumption is used, the large-scale volume averaged equation system is formed by coupled equations, each one describing the mass transfer of species i in the corresponding region. As has been shown in the two previous cases, each equation contains terms of accumulation, diffusion, reaction, mass transfer exchange and convective-like transport. The latter terms are composed of large-scale effective coefficients which provide information about one of the regions. To begin this analysis, the large-scale averaged equation of species A in η -region, Eq. 5.81, is described:

$$\begin{aligned}
 \underbrace{\varepsilon_\eta \frac{\partial \{C_{A\eta}\}^\eta}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot [\mathbf{D}_{\eta\gamma} \cdot \nabla \{C_{A\eta}\}^\eta + \mathbf{D}_{\eta\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega]}_{\text{diffusion}} \\
 &+ \underbrace{\nabla \cdot [\mathbf{D}_{\eta\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega]}_{\text{diffusion}} \\
 &+ \underbrace{\nabla \cdot [\mathbf{u}_{\eta\gamma} \langle C_{A\gamma} \rangle^\gamma + \mathbf{u}_{\eta\mu} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega + \mathbf{u}_{\eta B} \langle C_{B\mu} \rangle^\mu + \mathbf{u}_{\eta\sigma} \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega]}_{\text{convective-like transport term}} \\
 &+ \underbrace{a_v k_{\eta\omega} (K_{\mu\gamma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega - \{C_{A\eta}\}^\eta)}_{\text{exchange term}} \tag{5.81}
 \end{aligned}$$

Eq. 5.81 has 3 large-scale effective diffusivity tensors with the form $\mathbf{D}_{\eta j}$ where j can be γ, μ, σ , therefore when $j = \mu$, $\mathbf{D}_{\eta\mu}$ contributes with information about the structure of the emulsion drop related to ω -region but also implicitly with the μ -phase. The exchange term contains the large-scale mass transfer coefficient which has the information related with regional mass flux. The convective-like transport and the large-scale vector-like coefficient are negligible as has been discussed throughout this thesis. More in detail, in Eq. 5.81 one can see three types of effective transport coefficients: the effective diffusivity tensors $\mathbf{D}_{\eta j}$, the effective velocity-like vectors $\mathbf{u}_{\eta j}$ and the mass transfer coefficient $a_v k_{\eta\omega}$. All these coefficients can be computed from the fields of the closure variables (see Appendix B). For example the diffusivity tensor $\mathbf{D}_{\eta\gamma}$ is defined as:

$$\mathbf{D}_{\eta\gamma} = \mathcal{D}_{A\eta} \left(\varepsilon_\eta \mathbf{1} + \frac{1}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \mathbf{b}_{\eta\eta} dA \right) \tag{5.82}$$

in this case, the effective diffusivity tensor is function of the diffusivity $\mathcal{D}_{A\eta}$, the volumetric fraction ε_η and the structure of the DES through the $\mathbf{b}_{\eta\gamma}$ -field. In contrast the others effective diffusivity tensors, presented in Eq. 5.83 - 5.85, are not directly functions of the ε_η .

$$\mathbf{D}_{\eta\mu} = \frac{\mathcal{D}_{A\eta}}{\gamma} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \mathbf{b}_{\eta\mu} dA \quad (5.83)$$

$$\mathbf{D}_{\eta B} = \frac{\mathcal{D}_{A\eta}}{\gamma} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \mathbf{b}_{\eta B} dA \quad (5.84)$$

$$\mathbf{D}_{\eta\sigma} = \frac{\mathcal{D}_{A\eta}}{\gamma} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \mathbf{b}_{\eta\sigma} dA \quad (5.85)$$

In addition, the convective-like transport terms are generated by the mass exchange at the interfacial area, and contain the effective velocity-like vectors which are defined by:

$$\mathbf{u}_{\eta\gamma} = \frac{\mathcal{D}_{A\eta}}{\gamma} \left(\int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \nabla \mathbf{b}_{\eta\gamma} dA + \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} s_\eta dA \right) \quad (5.86)$$

$$\mathbf{u}_{\eta\mu} = \frac{\mathcal{D}_{A\eta}}{\gamma} \int_{A_{\eta\omega}(\mathbf{x})} \left(\mathbf{n}_{\eta\omega} \cdot \nabla \mathbf{b}_{\eta\mu} - \mathbf{n}_{\eta\omega} K_{\mu\sigma}^{eq} s_\eta \right) dA \quad (5.87)$$

$$\mathbf{u}_{\eta B} = \frac{\mathcal{D}_{A\eta}}{\gamma} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \nabla \mathbf{b}_{\eta B} dA \quad (5.88)$$

$$\mathbf{u}_{\eta\sigma} = \frac{\mathcal{D}_{A\eta}}{\gamma} \left(\int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \nabla \mathbf{b}_{\eta\sigma} dA + \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} s_\eta dA \right) \quad (5.89)$$

As mentioned in the others cases, [Whitaker \(1999\)](#) has demonstrated that the convective-like transport term is negligible for the case of diffusion in porous catalysts and [Paine et al. \(1983\)](#) have shown that this contribution can be important when convection itself is important. In this senses, has been demonstrated that the effective velocity-like vectors presented here, are negligible for the case of mass transfer by diffusion and chemical reaction in DES. Lastly, the mass transfer coefficients of species A in Eq. 5.81 is defined as:

$$a_v k_{\eta\omega} = -\frac{\mathcal{D}_{A\eta}}{\gamma} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \nabla s_\eta dA \quad (5.90)$$

$$(5.91)$$

in which $a_v k_{\eta\omega}$, is the interfacial area $\mathcal{A}_{\eta\omega}$ per unit volume. Continuing with this description, the large-scale averaged equation of species A in ω -region is presented:

In μ -phase

$$\begin{aligned}
\varepsilon_\omega \varepsilon_\mu \frac{\partial \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega}{\partial t} = & \underbrace{\nabla \cdot [\mathbf{D}_{\omega(\mu)\eta} \cdot \nabla \{ C_{A\eta} \}^\eta + \mathbf{D}_{\omega(\mu)\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega]}_{\text{diffusion}} \\
& + \underbrace{\nabla \cdot [\mathbf{D}_{\omega(\mu)\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega]}_{\text{diffusion}} \\
& + \underbrace{\nabla \cdot [\mathbf{u}_{\omega(\mu)\eta} \{ C_{A\eta} \}^\eta + \mathbf{u}_{\omega(\mu)\mu} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega]}_{\text{convective-like transport term}} \\
& + \underbrace{\nabla \cdot [\mathbf{u}_{\omega(\mu)B} \langle C_{B\mu} \rangle^\mu + \mathbf{u}_{\omega(\mu)\sigma} \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega]}_{\text{convective-like transport term}} \\
& + \underbrace{a_v k_{\eta\omega} (K_{\mu\gamma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega - \{ C_{A\eta} \}^\eta)}_{\text{exchange term}} \\
& + \varepsilon_\omega (a_v k)_\mu (\{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega - K_{\mu\sigma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega) \\
& - \varepsilon_\omega \varepsilon_\mu k_\mu \left(\{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega - \frac{ \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega }{ K_\mu } \right)
\end{aligned} \tag{5.92}$$

As Eq. 5.81, Eq. 5.92 contains effective diffusivity tensors, such as $\mathbf{D}_{\omega(\mu)\mu}$:

$$\mathbf{D}_{\omega(\mu)\mu} = \mathbf{D}_{\mu\mu} : \mathbf{l} \left(\varepsilon_\omega \mathbf{l} + \frac{1}{\gamma} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \mathbf{b}_{\mu\mu} dA \right), \tag{5.93}$$

here the effective diffusivity tensor is function of the effective diffusivity $\mathbf{D}_{\mu\mu}$, the volumetric fraction ε_ω and the structure of the DES through the $\mathbf{b}_{\mu\mu}$ -field. The cross-diffusivity tensor are defined as

$$\mathbf{D}_{\omega(\mu)\eta} = \frac{\mathbf{D}_{\mu\mu} : \mathbf{l}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \mathbf{b}_{\mu\eta} dA \right) \tag{5.94}$$

$$\mathbf{D}_{\omega(\mu)B} = \frac{\mathbf{D}_{\mu\mu} : \mathbf{l}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \mathbf{b}_{\mu B} dA \right) \tag{5.95}$$

$$\mathbf{D}_{\omega(\mu)\sigma} = \frac{\mathbf{D}_{\mu\mu} : \mathbf{l}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \mathbf{b}_{\mu\sigma} dA \right) \tag{5.96}$$

Finally, the governing averaged equation of species A related to σ -phase is introduced:

In σ -phase

$$\begin{aligned}
\varepsilon_\omega \varepsilon_\sigma \frac{\partial \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega}{\partial t} &= \underbrace{\nabla \cdot [\mathbf{D}_{\omega(\sigma)\eta} \cdot \nabla \{ C_{A\eta} \}^\eta + \mathbf{D}_{\omega(\sigma)\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega]}_{\text{diffusion}} \\
&+ \underbrace{\nabla \cdot [\mathbf{D}_{\omega(\sigma)\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega]}_{\text{diffusion}} \\
&+ \underbrace{\nabla \cdot [\mathbf{u}_{\omega(\sigma)\eta} \{ C_{A\eta} \}^\eta + \mathbf{u}_{\omega(\sigma)\mu} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega]}_{\text{convective-like transport term}} \\
&+ \underbrace{\nabla \cdot [\mathbf{u}_{\omega(\sigma)B} \langle C_{B\mu} \rangle^\mu + \mathbf{u}_{\omega(\sigma)\sigma} \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega]}_{\text{convective-like transport term}} \\
&+ \underbrace{a_v k_{\eta\omega} (K_{\mu\gamma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega - \{ C_{A\eta} \}^\eta)}_{\text{exchange term}} \\
&+ \varepsilon_\omega (a_v k) (\{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega - K_{\mu\sigma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega) \\
&- \varepsilon_\omega \varepsilon_\sigma k_\sigma \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega
\end{aligned} \tag{5.97}$$

Repeating the procedure, as Eq.5.92, Eq. 5.97 contains effective diffusivity tensors, such as $\mathbf{D}_{\omega(\sigma)\sigma}$:

$$\mathbf{D}_{\omega(\sigma)\sigma} = \mathbf{D}_{\sigma\sigma} : \mathbf{l} \left(\varepsilon_\omega \mathbf{l} + \frac{1}{\gamma} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \mathbf{b}_{\sigma\sigma} dA \right), \tag{5.98}$$

here the effective diffusivity tensor is function of the effective diffusivity $\mathbf{D}_{\mu\mu}$, the volumetric fraction ε_ω and the structure of the DES through the $\mathbf{b}_{\mu\mu}$ -field. The cross-diffusivity tensors are defined as

$$\mathbf{D}_{\omega(\sigma)\eta} = \frac{\mathbf{D}_{\sigma\sigma} : \mathbf{l}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \mathbf{b}_{\mu\eta} dA \right) \tag{5.99}$$

$$\mathbf{D}_{\omega(\sigma)B} = \frac{\mathbf{D}_{\sigma\sigma} : \mathbf{l}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \mathbf{b}_{\mu B} dA \right) \tag{5.100}$$

$$\mathbf{D}_{\omega(\sigma)\sigma} = \frac{\mathbf{D}_{\sigma\sigma} : \mathbf{l}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \mathbf{b}_{\mu\sigma} dA \right) \tag{5.101}$$

As in the previous model, the effective velocity-like for this case has been also determined; since, all of them have very small values, of orders of magnitude of 10^{-10} , their contribution in the regional averaged equations has been considered negligible.

Finally the mass transfer coefficient related with the internal flux in $\mathcal{A}_{\eta\omega}$ has the form:

$$a_v k_{\eta\omega} = -\frac{\mathcal{D}_{A\eta}}{\gamma} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \nabla s_{\eta} dA \quad (5.102)$$

5.4 2-region simplified model

Finally, after determination of the effective coefficients the closed set of equations describing the macroscopic mass transport of species A in this two-region system, is given by:

$$\underbrace{\varepsilon_{\eta} \frac{\partial \{C_{A\eta}\}^{\eta}}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot [\mathbf{D}_{\eta\gamma} \cdot \nabla \{C_{A\eta}\}^{\eta} + \mathbf{D}_{\eta\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega}]}_{\text{diffusion}} + \underbrace{a_v k_{\eta\omega} (K_{\mu\gamma}^{eq} \{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega} - \{C_{A\eta}\}^{\eta})}_{\text{exchange term}} \quad (5.103)$$

$$\begin{aligned} \varepsilon_{\omega} \varepsilon_{\mu} \frac{\partial \{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega}}{\partial t} &= \underbrace{\nabla \cdot [\mathbf{D}_{\omega(\mu)\eta} \cdot \nabla \{C_{A\eta}\}^{\eta} + \mathbf{D}_{\omega(\mu)\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega}]}_{\text{diffusion}} \\ &+ \underbrace{\nabla \cdot [\mathbf{D}_{\omega(\mu)\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_{\omega}^{\sigma} \}^{\omega}]}_{\text{diffusion}} \\ &+ \underbrace{a_v k_{\eta\omega} (K_{\mu\gamma}^{eq} \{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega} - \{C_{A\eta}\}^{\eta})}_{\text{exchange term}} \\ &+ \varepsilon_{\omega} (a_v k)_{\mu} (\{ \langle C_{A\sigma} \rangle_{\omega}^{\sigma} \}^{\omega} - K_{\mu\sigma}^{eq} \{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega}) \\ &- \varepsilon_{\omega} \varepsilon_{\mu} k_{\mu} \left(\{ \langle C_{A\mu} \rangle_{\omega}^{\mu} \}^{\omega} - \frac{\{ \langle C_{B\mu} \rangle_{\omega}^{\mu} \}^{\omega}}{K_{\mu}} \right) \end{aligned} \quad (5.104)$$

$$\begin{aligned}
\varepsilon_\omega \varepsilon_\sigma \frac{\partial \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega}{\partial t} &= \underbrace{\nabla \cdot [\mathbf{D}_{\omega(\sigma)\eta} \cdot \nabla \{ C_{A\eta} \}^\eta + \mathbf{D}_{\omega(\sigma)\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega]}_{\text{diffusion}} \\
&+ \underbrace{\nabla \cdot [\mathbf{D}_{\omega(\sigma)\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega]}_{\text{diffusion}} \\
&+ \underbrace{a_v k_{\eta\omega} (K_{\mu\gamma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega - \{ C_{A\eta} \}^\eta)}_{\text{exchange term}} \\
&+ \varepsilon_\omega (a_v k) (\{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega - K_{\mu\sigma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega) \\
&- \varepsilon_\omega \varepsilon_\sigma k_\sigma \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega
\end{aligned} \tag{5.105}$$

In summary, the *Two-region model* under *non-local mass equilibrium* conditions is composed of 3 coupled averaged equations, each one describing the mass transfer of species A in the corresponding region by the accumulation, diffusion and mass transfer exchange terms. Eqs. (5.103)-(5.105) are valid everywhere in the homogeneous averaged system. Detailed information about the structure and transfer phenomena in the DE drops by chemical reaction and permeation in the microscale, *Scale III*, is represented in the effective coefficients.

Part III

Application of macroscopic models to double emulsion separation processes

Chapter 6

Design of a separation process in a batch-stirred tank

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6.1 Batch-stirred tank design equation

This chapter is dedicated to the deduction of a design equation for a batch-stirred tank, where the separation of the solute A in an DE system occurs. The essential macroscopic characteristic of the tank is the change in the solute concentration that occurs from the external γ -phase to the inlet of droplets of σ -phase, and this change is determined by the diffusion rate and the chemical reactions that take place in the drop emulsion. Thus, the separation process is analyzed in *Scale I*, the macroscopic level (see Figure 6.1)

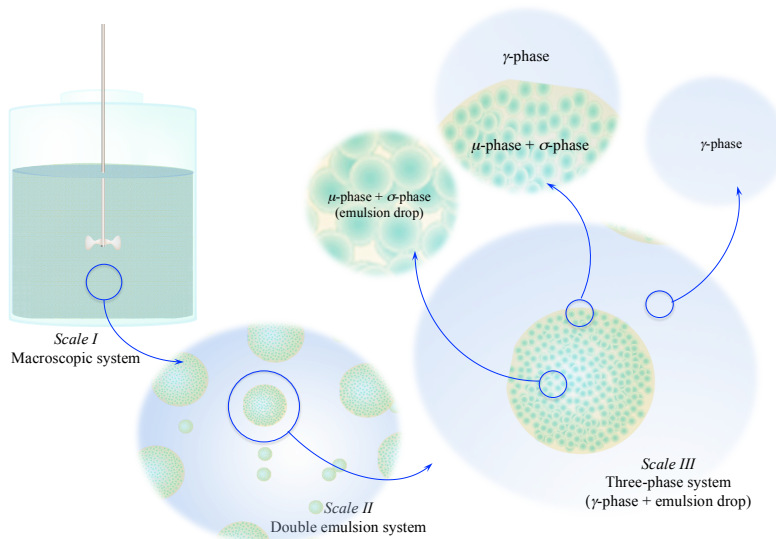


Figure 6.1: Length scales and averaging volumes for a Double Emulsion System

The deduction of the batch-stirred tank model, implies the following general assumptions:

- Very well mixed fluid
- Hypothesis of the continuum
- Newtonian and incompressible fluid
- The γ -phase is a diluted solution of species A
- The reactive B and the AB complex are restricted to the membrane phase
- The reactive R in σ -phase which reacts irreversibly with solute is in excess,

Since, one of the objectives of this thesis is to compare the accuracy and the applicability of the averaged model deduced in this work, three macroscopic model are

presented, each one based on a different averaged model. First the generalized one-equation model proposed by [Morales-Zárate et al. \(2008\)](#) is used to obtain a design equation that is based on the *local-mass equilibrium*. Finally, the design equations for the same tank based on the **Three-phase model** and the **Two-region model** are deduced.

6.1.1 Generalized one-equation model

As previously mentioned, [Morales-Zárate et al. \(2008\)](#) derived a rigorous macroscopic model of diffusion and reaction in DES and derived the jump boundary condition at the dividing surface. They divided the three-phase system into two homogeneous regions, η -region (γ -phase) and ω -region (μ -phase + σ -phase). Equations in both homogeneous regions were deduced from a generalized one-equation model, based on the *local mass equilibrium*, which establishes that the mass transfer process can be characterized by a single equilibrium weighted average concentration with the next form:

$$\{C_A\} = \varepsilon_\mu(\mathbf{x})\langle C_{A_\mu} \rangle^\mu + \frac{\varepsilon_\sigma(\mathbf{x})}{K_{\text{eq}}^{\mu\sigma}}\langle C_{A_\sigma} \rangle^\sigma + \frac{\varepsilon_\gamma(\mathbf{x})}{K_{\text{eq}}^{\mu\gamma}}\langle C_{A_\gamma} \rangle^\gamma \quad (6.1)$$

Additionally, it has been assumed that,

- The emulsion drops and the droplets are considered rigid and spherical
- Uniformity in the size of rigid emulsion drops and droplets
- The transport of solute A in the emulsion drop is considered only in the radial direction.

thus the Eqs. 2.55 can be rewritten as

$$\underbrace{\frac{\partial \{C_A\}_\eta}{\partial t}}_{\text{accumulation}} + \underbrace{\nabla \cdot (\{C_A\}_\eta \mathbf{v}_\eta)}_{\text{convection}} = \underbrace{\nabla \cdot (\mathcal{D}_{A\eta} \nabla \{C_A\}_\eta)}_{\text{diffusion}} \quad (6.2)$$

since the batch-tank is stirred, it has been added the convective term, the velocity vector of the η -region is defined as, \mathbf{v}_η . Additionally, the boundary condition at the inter-region $\mathcal{A}_{\eta\omega}$ is defined as

$$-\mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \{C_A\}_\eta = P_{\text{eff}}^\eta (\{C_A\}_\eta - K_{\text{eff}}^{\eta\omega} \{C_A\}_\omega) \quad (6.3)$$

and the equations for ω -region can be rewritten as

$$\begin{aligned} (\varepsilon_\mu + \varepsilon_\sigma K_{\text{eq}}^{\mu\sigma}) \frac{\partial \{C_A\}_\omega}{\partial t} &= D_{A\omega} \left(\frac{1}{\partial r} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \{C_A\}_\omega}{\partial r} \right) \right) \\ &\quad - \varepsilon_\sigma k_\mu \left(\{C_A\}_\omega - \frac{\langle C_B \rangle_\omega}{K_\mu} \right) - k_\sigma \{C_A\}_\omega \\ \varepsilon_\mu \frac{\partial \langle C_B \rangle_\omega}{\partial t} &= D_{B\omega} \left(\frac{1}{\partial r} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{A\omega}}{\partial r} \right) \right) + \varepsilon_\sigma k_\mu \left(\{C_A\}_\omega - \frac{\langle C_B \rangle_\omega}{K_\mu} \right) \end{aligned} \quad (6.4)$$

Continuing with this modeling, the volume of the batch-stirred tank is defined as

$$\mathcal{V}_T = \mathcal{V}_\eta + \mathcal{V}_\omega \quad (6.5)$$

The total volume of the homogeneous ω -region, \mathcal{V}_ω , is described by the ratio between the total number of emulsion drops, N , and the radius of the emulsion drops R_p ; in the same way the inter-region $\mathcal{A}_{\eta\omega}$ is defined as a function of N and R_p variables, illustrated in Eqs. 6.6 and 6.7,

$$\mathcal{V}_\omega = \sum_{n=1}^N \mathcal{V}_{\omega,i} = \frac{4}{3} \pi N R_p^3 \quad (6.6)$$

$$\mathcal{A}_{\eta\omega} = \sum_{n=1}^N A_{\eta\omega,i} = 4N\pi R_p^2 \quad (6.7)$$

To deduced the design equation of the tank, an average concentration in η -region presented in the volume of the tank, \mathcal{V}_T , is proposed

$$\langle C_A \rangle^f = \frac{1}{\mathcal{V}_\eta} \int_{\mathcal{V}_\eta} \{C_A\}_\eta dV \quad (6.8)$$

Applying Eq. 6.8 to Eq. 6.2 and since \mathcal{V}_η is not a function of the time, the general transport theorem has been used to express Eq. 6.2 as

$$\frac{\partial \langle C_A \rangle^f}{\partial t} + \frac{1}{\mathcal{V}_\eta} \int_{\mathcal{A}_\eta} \mathbf{n} \cdot \{C_A\}_\eta (\mathbf{v}_\eta - \mathbf{w}) dA = \frac{1}{\mathcal{V}_\eta} \int_{\mathcal{A}_\eta} \mathbf{n} \cdot (\mathcal{D}_{A\eta} \nabla \{C_A\}_\eta) dA \quad (6.9)$$

it should be noted that the divergence theorem has been used to represent this expression in terms of area integrals. The velocity vector \mathbf{w} represents the speed of displacement of the surface that defines the volume of η -region. Because the assumption of fluid well mixed, it has been established that

$$\mathbf{w} = \mathbf{v}_\eta \quad (6.10)$$

thus, the second term in Eq. 6.9 is null. Analyzing the area of η -region one can imagine that this area is delimited by the walls of the tank and surface of the inter-region $\eta\omega$, thus one can establish that

$$\mathcal{A}_\eta = \mathcal{A}_{\text{tank walls}} + \mathcal{A}_{\eta\omega} \quad (6.11)$$

this area has been substituted in the third term of the Eq. 6.9, one can obtain

$$\frac{1}{\mathcal{V}_\eta} \int_{\mathcal{A}_\eta} \mathbf{n} \cdot (\mathcal{D}_{A\eta} \nabla \{C_A\}_\eta) dA + \frac{1}{\mathcal{V}_\eta} \int_{\mathcal{A}_{\text{tank walls}}} \mathbf{n} \cdot (\mathcal{D}_{A\eta} \nabla \{C_A\}_\eta) dA \quad (6.12)$$

due to species A is impermeable to the walls of the tank and making use of the boundary condition illustrated in Eq. 6.3, the Eq. 6.9 can be rewritten as

$$\frac{\partial \langle C_A \rangle^f}{\partial t} = \frac{\mathcal{A}_{\eta\omega} P_{\text{eff}}^\eta}{\mathcal{V}_\eta} \left(K_{\text{eff}}^{\eta\omega} \{C_A\}_\omega|_{r=R_p} - \langle C_A \rangle^f|_{r=R_p} \right) \quad (6.13)$$

Finally, if one suppose that the $\langle C_A \rangle^f$ is the same in all the volume of the tank since it is well mixed, then the assumption,

$$\langle C_A \rangle^f = \langle C_A \rangle^f|_{r=R_p} \quad (6.14)$$

can be accepted, thus the Eq. 6.13 take his finally form

$$\frac{\partial \langle C_A \rangle^f}{\partial t} = \frac{\mathcal{A}_{\eta\omega} P_{\text{eff}}^\eta}{\mathcal{V}_\eta} \left(K_{\text{eff}}^{\eta\omega} \{C_A\}_\omega|_{r=R_p} - \langle C_A \rangle^f \right) \quad (6.15)$$

Eq. 6.15 is the equation for a batch-stirred tank base on the generalized one-domain equation model assuming local mass equilibrium.

6.1.2 Three-phase model

The design equation for a batch-stirred tank base on the simplified three-phase model is developed. For this modeling, as mentioned it has been assumed:

- Very well mixed fluid
- Hypothesis of the continuum
- Newtonian and incompressible fluid
- The γ -phase is a diluted solution of species A
- The reactive B and the AB complex are restricted to the membrane phase
- The reactive R in σ -phase which reacts irreversibly with solute is in excess,

It should be remembered that the governing equations for this system represented one domain assuming the non-local mass equilibrium, therefore the model is formed by the following coupled averaged equation:

Governing averaged equation of species A in γ -phase contained in the tank:

$$\underbrace{\varepsilon_\gamma \frac{\partial \langle C_{A\gamma} \rangle^\gamma}{\partial t}}_{\text{accumulation}} + \underbrace{\nabla \cdot (\langle C_{A\gamma} \rangle^\gamma \mathbf{v}_\gamma)}_{\text{convection}} = \underbrace{\nabla \cdot [\mathbf{D}_{\gamma\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma]}_{\text{diffusion}} + \underbrace{a_{v_1} k_1^{\mu\gamma} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\gamma} \rangle^\gamma)}_{\text{exchange term}} + \underbrace{a_{v_1} k_1^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma)}_{\text{exchange term}} \quad (6.16)$$

Governing averaged equation of species A in μ -phase contained in the tank:

$$\underbrace{\varepsilon_\mu \frac{\partial \langle C_{A\mu} \rangle^\mu}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot [\mathbf{D}_{\mu\mu}(\mathbf{x}) \cdot \nabla \langle C_{A\mu} \rangle^\mu]}_{\text{diffusion}} + \underbrace{[a_{v_1} k_1^{\mu\gamma} + a_{v_2} k_2^{\mu\gamma}](\langle C_{A\gamma} \rangle^\gamma - K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu)}_{\text{exchange term}} + \underbrace{[a_{v_1} k_1^{\mu\sigma} + a_{v_2} k_2^{\mu\sigma}](\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu)}_{\text{exchange term}} - \underbrace{\varepsilon_\mu k_\mu \left(\langle C_{A\mu} \rangle^\mu - \frac{\langle C_{B\mu} \rangle^\mu}{K_\mu} \right)}_{\text{reaction}} \quad (6.17)$$

Governing averaged equation of species B in μ -phase contained in the tank:

$$\underbrace{\varepsilon_\mu \frac{\partial \langle C_{B\mu} \rangle^\mu}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot [\mathbf{D}_{BB} \cdot \nabla \langle C_{B\mu} \rangle^\mu]}_{\text{diffusion}} + \underbrace{\varepsilon_\mu k_\mu \left(\langle C_{A\mu} \rangle^\mu - \frac{\langle C_{B\mu} \rangle^\mu}{K_\mu} \right)}_{\text{reaction}} \quad (6.18)$$

Governing averaged equation of species A in σ -phase contained in the tank:

$$\underbrace{\varepsilon_\sigma \frac{\partial \langle C_{A\sigma} \rangle^\sigma}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot [\mathbf{D}_{\sigma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma]}_{\text{diffusion}} - \underbrace{k_\sigma \varepsilon_\sigma \langle C_{A\sigma} \rangle^\sigma}_{\text{reaction}} + \underbrace{a_{v_2} k_2^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma)}_{\text{exchange term}} \quad (6.19)$$

To continue, the volume of the batch-stirred tank is defined as

$$\mathcal{V}_T = \mathcal{V}_\gamma + \mathcal{V}_\mu + \mathcal{V}_\sigma \quad (6.20)$$

and to deduced the design equation of the tank, an average concentration for each phase that is presented in the volume of the tank, \mathcal{V}_T , is proposed

$$\langle C_{A\lambda} \rangle^f = \frac{1}{\mathcal{V}_T} \int_{\mathcal{V}_\lambda} \langle C_{A\lambda} \rangle^\lambda dV \quad (6.21)$$

where $\lambda = \gamma, \mu, \sigma$. The next step for this modeling is to use Eq. 6.21 in Eqs. 6.16, then apply the general transport theorem as it has been done in the previous section, to obtain

$$\underbrace{\varepsilon_\gamma \frac{\langle C_A \rangle^\gamma}{\partial t}}_{\text{accumulation}} = - \frac{1}{\mathcal{V}_\gamma} \int_{\mathcal{A}_\gamma} \mathbf{n} \cdot \langle C_{A\gamma} \rangle^\gamma (\mathbf{v}_\eta - \mathbf{w}) dA + \frac{1}{\mathcal{V}_\gamma} \int_{\mathcal{A}_\gamma} \mathbf{n} \cdot (\mathcal{D}_{\gamma\gamma} \nabla \langle C_{A\gamma} \rangle^\gamma) dA$$

$$+ \underbrace{a_{v_1} k_1^{\mu\gamma} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^{f,\mu} - \langle C_{A\gamma} \rangle^{f,\gamma})}_{\text{exchange term}} + \underbrace{a_{v_1} k_1^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^{f,\mu} - \langle C_A \rangle^{f,\sigma})}_{\text{exchange term}}$$

(6.22)

here, the velocity vector \mathbf{w} represents the speed of displacement of the surface that defines the volume of γ -phase. Because the assumption of fluid well mixed, it has been established that

$$\mathbf{w} = \mathbf{v}_\gamma \tag{6.23}$$

as consequence, the second term in Eq. 6.22 is null. Since the surface that defined γ -phase is delimited by the walls of the tank and the species A is impermeable to them, the third term of Eq. 6.22, which is associated to the diffusion term, is null. Finally Eq. 6.22 take his finally form

$$\underbrace{\varepsilon_\gamma \frac{\langle C_{A\gamma} \rangle^{f,\gamma}}{\partial t}}_{\text{accumulation}} = \underbrace{a_{v_1} k_1^{\mu\gamma} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^{f,\mu} - \langle C_{A\gamma} \rangle^{f,\gamma})}_{\text{exchange term}} + \underbrace{a_{v_1} k_1^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^{f,\mu} - \langle C_{A\sigma} \rangle^{f,\sigma})}_{\text{exchange term}}$$

(6.24)

Repeating this procedure, one can use Eq. 6.21 in Eqs. 6.17 - 6.19 to obtained the equation of $\langle C_{A\mu} \rangle^{f,\mu}$ and $\langle C_{A\sigma} \rangle^{f,\mu}$ associated to Eq. 6.24, thus the final expressions are:

$$\underbrace{\varepsilon_\mu \frac{\partial \langle C_{A\mu} \rangle^{f,\mu}}{\partial t}}_{\text{accumulation}} = \underbrace{[a_{v_1} k_1^{\mu\gamma} + a_{v_2} k_2^{\mu\gamma}] (\langle C_{A\gamma} \rangle^{f,\gamma} - K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^{f,\mu})}_{\text{exchange term}}$$

$$+ \underbrace{[a_{v_1} k_1^{\mu\sigma} + a_{v_2} k_2^{\mu\sigma}] (\langle C_{A\sigma} \rangle^{f,\sigma} - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^{f,\mu})}_{\text{exchange term}}$$

$$- \underbrace{\varepsilon_\mu k_\mu \left(\langle C_{A\mu} \rangle^{f,\mu} - \frac{\langle C_{B\mu} \rangle^{f,\mu}}{K_\mu} \right)}_{\text{reaction}}$$

(6.25)

$$\underbrace{\varepsilon_\mu \frac{\partial \langle C_{B\mu} \rangle^{f,\mu}}{\partial t}}_{\text{accumulation}} = \underbrace{\varepsilon_\mu(\mathbf{x}) k_\mu \left(\langle C_{A\mu} \rangle^{f,\mu} - \frac{\langle C_{B\mu} \rangle^{f,\mu}}{K_\mu} \right)}_{\text{reaction}} \quad (6.26)$$

$$\underbrace{\varepsilon_\sigma \frac{\partial \langle C_{A\sigma} \rangle^{f,\sigma}}{\partial t}}_{\text{accumulation}} = \underbrace{k_\sigma \varepsilon_\sigma \langle C_{A\sigma} \rangle^{f,\sigma}}_{\text{reaction}} + \underbrace{a_{v_2} k_2^{\mu\sigma} (K_\mu^{eq} \langle C_{A\mu} \rangle^{f,\mu} - \langle C_{A\sigma} \rangle^{f,\sigma})}_{\text{exchange term}} \quad (6.27)$$

6.1.3 Two-region model

The design equation for a batch-stirred tank base on the simplified two-region model is developed. Since the philosophy for this modeling is the same that in the three-phase model case and to avoid the repetition, only the main steps are presenting in this section.

For this model the following assumption are made

- Very well mixed fluid
- Hypothesis of the continuum
- Newtonian and incompressible fluid
- The γ -phase is a diluted solution of species A
- The reactive B and the AB complex are restricted to the membrane phase
- The reactive R in σ -phase which reacts irreversibly with solute is in excess
- The volume of the batch-stirred tank is defined as, $\mathcal{V}_T = \mathcal{V}_\eta + \mathcal{V}_\omega$

The governing equations for this system represented one domain assuming the non-local mass equilibrium, therefore the model is formed by the following coupled regional averaged equation:

$$\underbrace{\varepsilon_\eta \frac{\partial \{C_{A\eta}\}^\eta}{\partial t}}_{\text{accumulation}} + \underbrace{\nabla \cdot (\{C_{A\eta}\}^\eta \mathbf{v}_\eta)}_{\text{convection}} = \underbrace{\nabla \cdot [\mathbf{D}_{\eta\gamma} \cdot \nabla \{C_{A\eta}\}^\eta]}_{\text{diffusion}} + \underbrace{a_v k_{\eta\omega} (K_{\mu\gamma}^{eq} \{C_{A\mu}\}^\omega - \{C_{A\eta}\}^\eta)}_{\text{exchange term}} \quad (6.28)$$

$$\begin{aligned}
 \varepsilon_\omega \varepsilon_\mu \frac{\partial \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega}{\partial t} &= \underbrace{\nabla \cdot [\mathbf{D}_{\omega(\mu)\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega]}_{\text{diffusion}} + \underbrace{a_v k_{\eta\omega} \{ \langle C_{A\eta} \rangle^\eta \} - K_{\mu\gamma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega}_{\text{exchange term}} \\
 &+ \underbrace{\varepsilon_\omega (a_v k)_\mu \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega - K_{\mu\sigma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega}_{\text{exchange term}} \\
 &- \underbrace{\varepsilon_\omega \varepsilon_\mu k_\mu \left(\{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega - \frac{ \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega }{ K_\mu } \right)}_{\text{reaction}} \quad (6.29)
 \end{aligned}$$

$$\begin{aligned}
 \varepsilon_\omega \varepsilon_\mu \frac{\partial \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega}{\partial t} &= \underbrace{\nabla \cdot [\mathbf{D}_{\omega(B)\mu} \cdot \nabla \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega]}_{\text{diffusion}} + \underbrace{\varepsilon_\omega \varepsilon_\mu k_\mu \left(\{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega - \frac{ \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega }{ K_\mu } \right)}_{\text{reaction}} \quad (6.30)
 \end{aligned}$$

$$\begin{aligned}
 \varepsilon_\omega \varepsilon_\sigma \frac{\partial \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega}{\partial t} &= \underbrace{\nabla \cdot [\mathbf{D}_{\omega(\sigma)\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega]}_{\text{diffusion}} \\
 &+ \underbrace{a_v k_{\eta\omega} \{ \langle C_{A\eta} \rangle^\eta \} - K_{\mu\gamma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega}_{\text{exchange term}} \\
 &+ \underbrace{\varepsilon_\omega (a_v k) (K_{\mu\sigma}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}) - \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}}_{\text{exchange term}} \\
 &- \underbrace{\varepsilon_\omega \varepsilon_\sigma k_\sigma \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega}_{\text{reaction}} \quad (6.31)
 \end{aligned}$$

Then, once the system is established, the average concentrations for each region that is presented in the volume of the tank, \mathcal{V}_T , is proposed

$$\langle C_{A\eta} \rangle^f = \frac{1}{\mathcal{V}_T} \int_{\mathcal{V}_\eta} \{ C_{A\eta} \}^\eta dV \quad (6.32)$$

$$\langle C_{A\beta} \rangle^{\omega,f} = \frac{1}{\mathcal{V}_T} \int_{\mathcal{V}_\omega} \{ \langle C_{A\beta} \rangle_\omega^\beta \}^\omega; \quad \beta = \mu, \sigma \quad (6.33)$$

Finally averaging the tank we obtain as final result the following equations

$$\underbrace{\varepsilon_\eta \frac{\partial \langle C_{A\eta} \rangle^f}{\partial t}}_{\text{accumulation}} = \underbrace{a_v k_{\eta\omega} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^{\omega,f} - \langle C_{A\eta} \rangle^f)}_{\text{exchange term}} \quad (6.34)$$

$$\begin{aligned}
\varepsilon_\omega \varepsilon_\mu \frac{\partial \langle C_{A\mu} \rangle^{\omega,f}}{\partial t} &= \underbrace{a_v k_{\eta\omega} (\langle C_{A\eta} \rangle^f - K_{\mu\gamma}^{eq} \{ \langle C_{A\mu} \rangle^{\omega,f} \})}_{\text{exchange term}} \\
&+ \varepsilon_\omega (a_v k)_\mu (\langle C_{A\sigma} \rangle^{\omega,f} - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^{\omega,f}) \\
&- \varepsilon_\omega \varepsilon_\mu k_\mu \left(\langle C_{A\mu} \rangle^{\omega,f} - \frac{\{ \langle C_{B\mu} \rangle^{\omega,f} \}}{K_\mu} \right)
\end{aligned} \tag{6.35}$$

$$\varepsilon_\omega \varepsilon_\mu \frac{\partial \langle C_{B\mu} \rangle^{\omega,f}}{\partial t} = \varepsilon_\omega \varepsilon_\mu k_\mu \left(\langle C_{A\mu} \rangle^{\omega,f} - \frac{\{ \langle C_{B\mu} \rangle^{\omega,f} \}}{K_\mu} \right) \tag{6.36}$$

$$\begin{aligned}
\varepsilon_\omega \varepsilon_\sigma \frac{\partial \langle C_{A\sigma} \rangle^{\omega,f}}{\partial t} &= \underbrace{a_v k_{\eta\omega} (\{ \langle C_{A\eta} \rangle^\eta - K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^{\omega,f})}_{\text{exchange term}} \\
&+ \varepsilon_\omega (a_v k) (\langle C_{A\sigma} \rangle^{\omega,f} - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^{\omega,f}) \\
&- \varepsilon_\omega \varepsilon_\sigma k_\sigma \langle C_{A\sigma} \rangle^{\omega,f}
\end{aligned} \tag{6.37}$$

6.2 Comparison between the macroscopic models

Once the different macroscopic design equations for a batch-stirred tank are developed, it is possible to analyze the information that each of the macroscopic models provides. It should be noted that in a general form the three averaged equations for the continuous phase or region (γ -phase or η -region), contained in the tank, are formed by an accumulation term and one or several mass exchange terms, i.e. the change of the concentration is a function of the time and a difference of concentrations weighted by effective terms which contain information related to the molecular properties of the DES as well as the geometrical structure of the emulsion drops. For example the Eq. 6.38 is the design equation based on the *Generalized one-domain model* stand on the local mass equilibrium,

$$\underbrace{\frac{\partial \langle C_A \rangle^f}{\partial t}}_{\text{accumulation}} = \frac{\mathcal{A}_{\eta\omega} P_{\text{eff}}^\eta}{\mathcal{V}_\eta} \underbrace{\left(K_{\text{eff}}^{\eta\omega} \{ C_A \}_\omega |_{r=R_p} - \langle C_A \rangle^f \right)}_{\text{exchange term}} \tag{6.38}$$

in this equation it has been assumed that the ω -region is defined by N rigid spheres and one has to know the values of the ω -region concentration at radius $r = R_p, \{ C_A \}_\omega |_{r=R_p}$,

i.e in the inter-region between η and ω -regions. It should be remarked that the $\{C_A\}_\omega$ is defined as

$$\{C_A\}_\omega = \varepsilon_\mu \langle C_{A_\mu} \rangle^\mu + \frac{\varepsilon_\sigma}{K_{\text{eq}}^{\mu\sigma}} \langle C_{A_\sigma} \rangle^\sigma \quad (6.39)$$

thus, Eq. 6.38 contained information about the proportions of the systems and information about their molecular properties. To obtain the values of $\{C_A\}_\omega|_{r=R_p}$, it is necessary to resolve the Eqs. 6.4.

In contrast with Eq. 6.38, Eq. 6.40 which has the form,

$$\underbrace{\varepsilon_\gamma \frac{\partial \langle C_{A_\gamma} \rangle^{f,\gamma}}{\partial t}}_{\text{accumulation}} = \underbrace{a_{v_1} k_1^{\mu\gamma} (K_{\mu\gamma}^{\text{eq}} \langle C_{A_\mu} \rangle^{f,\mu} - \langle C_{A_\gamma} \rangle^{f,\gamma})}_{\text{exchange term}} + \underbrace{a_{v_1} k_1^{\mu\sigma} (K_{\mu\sigma}^{\text{eq}} \langle C_{A_\mu} \rangle^{f,\mu} - \langle C_{A_\sigma} \rangle^{f,\sigma})}_{\text{exchange term}}, \quad (6.40)$$

is based on the *Three-phase model* that consider the system as a one-domain assuming non-local mass equilibrium. In Eq. 6.40 one can see two different mass transfer terms related to $\langle C_{A_\mu} \rangle^{f,\mu}$ and $\langle C_{A_\sigma} \rangle^{f,\mu}$ and two different effective mass transfer coefficients which are related to, and have information about the system in the microscale, *Scale III*. Eq. 6.40 is coupled with Eqs. 6.25 to 6.27 which are also composed by mass transfer terms. This system of equation provide the information about all the interchange that occurs in a DES by chemical reaction and permeation. Thus to know the changes in the $\langle C_{A_\gamma} \rangle^{f,\gamma}$ with time, it is necessary resolve the coupled equation system Eq. 6.40, 6.25 - 6.27.

Finally, the design equation base on the *Two-regions model* (Eq. 6.41) is analyzed,

$$\underbrace{\varepsilon_\eta \frac{\partial \langle C_{A_\eta} \rangle^f}{\partial t}}_{\text{accumulation}} = \underbrace{a_v k_{\eta\omega} (K_{\mu\gamma}^{\text{eq}} \langle C_{A_\mu} \rangle^{\omega,f} - \langle C_{A_\eta} \rangle^f)}_{\text{exchange term}} \quad (6.41)$$

here as the previous case, one-domain assuming non-local mass equilibrium has been considered. In Eq. 6.41 one can observed the mass transfer related to $\langle C_{A_\mu} \rangle^{\omega,f}$ and an effective mass transfer coefficient which is associated to, and has information about the system in the η and ω -regions, *Scale II*. Eq. 6.41 is coupled with Eqs. 6.35 to 6.37 which are also composed by mass transfer terms. In contrast to Eq.6.40, this mass transfer coefficients provide information associated a two different length of scale. This system of equation provide the information about all the interchange that

occurs in a DES by chemical reaction and permeation. Thus to know the changes in the $\langle C_{A\eta} \rangle^f$ with time, it is necessary resolve the coupled equation system Eq. 6.41, 6.35 - 6.37.

These three design equations are capable to described the process of transfer of solute A from the continuous fluid to the inner of the droplets of the DES; the difference between these equations is the degree of detail in the information that each one can be provide. To study their relevance and accuracy the latter equation systems must be resolve.

Conclusion

This thesis has been devoted to modeling the solute transport of species A with chemical reaction through a DES. This system has been analyzed as a three-phase system characterized by more than one disparate length scales. The method of volume averaging has been used to derive rigorous averaged equations in the context of the *non-local mass equilibrium* (NLME). This modeling consist of two averaged models :

1. The *three-phase model* which describe the solute mass transfer in a homogeneous domain formed by three-phases, where concentration changes occur in the same length scale.
2. The *two-region model* which describe the same transport problem, but in a homogeneous domain formed by two-regions, where concentration changes occur at two different length scales.

The averaged concentration and effective parameters for both models have been defined and order of magnitude analyses have been performed to determine the length scale constraints associated to these macroscopic models. Associated closure problems for the determination of the effective coefficients were obtained and resolved.

Both models present three types of effective coefficients: the effective diffusivity tensors \mathbf{D}_{ij} , the effective velocity-like vectors \mathbf{u}_{ij} and the mass transfer coefficients $a_v k^{ij}$. In this work has been demonstrated that the effective velocity-like vectors are negligible for diffusion transport. Finally an analysis of a DE-containing separation process in a batch-stirred tank by applying the simplified version of both models has been made and have been compared with the design equation for the batch-stirred tank stand on the generalized one-domain model which assumes local mass equilibrium. Moreover, the three design macroscopic equations deduced the last chapter of this thesis, are capable to described the process of transfer of solute A from the continuous fluid to the inner of the droplets of the DES; the difference between these equations

is the degree of detail in the information that each one can provide. It has been proved, that for the macroscopic extraction process the mass exchange between the inter phases is the dominant phenomena.

6.2.1 Perspectives

Throughout this thesis, rigorous models for the study of the solute transport of species A with chemical reaction through a DES were presented; providing valuable information in the macroscopic modeling of separation processes with DES. However to complete this study and to know the relevance and accuracy of each model presented, it must be necessary to resolve all the macroscopic models. The solution of this models can be provided information about the pertinence of the non local mass equilibrium assumption in systems which involved chemical reactions.

This study allows a better understanding of DE separation processes lays more realistic modeling, however, to include convective effects in the continuous phase in a local scale, will be necessary to improve the modeling and get closer to reality.

Appendix A

Closed problem for the three phase modeling approach

A.1 The Closure Problem

This section is devoted to obtain a *closed form* of the averaged equations presented in the chapter 4, Eqs. 4.14 - 4.22, and this means that a representation for the spatial deviation concentrations has to be developed. To achieve it, Eq. 4.13 can be rewritten as:

$$\tilde{C}_{i\lambda}|_{\mathbf{r}_\lambda} = C_{i\lambda}|_{\mathbf{r}_\lambda} - \langle C_{i\lambda} \rangle^\lambda|_{\mathbf{r}_\lambda}, \quad (\text{A.1})$$

where $\mathbf{r}_\lambda = \mathbf{x} + \mathbf{y}_\lambda$, is the position vector of locating points of the λ -phase ($\lambda = \gamma, \mu, \sigma$) within the domain averaging, with respect to an external reference frame. Base on Eq. A.1 one can obtain the governing equations for spatial deviation concentrations by subtracting the average equation when $\mathbf{x} \rightarrow \mathbf{r}_\lambda$, which are presented below:

In γ -phase:

$$\begin{aligned} \frac{\partial \langle C_{A\gamma} \rangle^\gamma|_{\mathbf{r}_\gamma}}{\partial t} &= \nabla \cdot (\mathcal{D}_{A\gamma} \nabla \langle C_{A\gamma} \rangle^\gamma|_{\mathbf{r}_\gamma}) + \varepsilon_\gamma^{-1} \nabla \varepsilon_\gamma \cdot \mathcal{D}_{A\gamma} \nabla \langle C_{A\gamma} \rangle^\gamma|_{\mathbf{r}_\gamma} \\ &+ \varepsilon_\gamma^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \tilde{C}_{A\gamma}|_{\mathbf{r}_\gamma} dA \right] \\ &+ \frac{\varepsilon_\gamma^{-1}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla (\langle C_{A\gamma} \rangle^\gamma|_{\mathbf{r}_\gamma} + \tilde{C}_{A\gamma}|_{\mathbf{r}_\gamma}) dA \end{aligned} \quad (\text{A.2})$$

$$(\text{A.3})$$

In μ -phase: Species A:

$$\begin{aligned}
\frac{\partial \langle C_{A\mu} \rangle^\mu |_{\mathbf{r}_\mu}}{\partial t} &= \nabla \cdot (\mathcal{D}_{A\mu} \nabla \langle C_{A\mu} \rangle^\mu |_{\mathbf{r}_\mu}) + \varepsilon_\mu^{-1} \nabla \varepsilon_\mu \cdot \mathcal{D}_{A\mu} \nabla \langle C_{A\mu} \rangle^\mu |_{\mathbf{r}_\mu} \\
&\quad \varepsilon_\mu^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \tilde{C}_{A\mu} |_{\mathbf{r}_\mu} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{A\mu} |_{\mathbf{r}_\mu} dA \right) \right] \\
&\quad + \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} (\nabla \langle C_{A\mu} \rangle^\mu |_{\mathbf{r}_\mu} + \nabla \tilde{C}_{A\mu} |_{\mathbf{r}_\mu}) dA \\
&\quad + \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} (\nabla \langle C_{A\mu} \rangle^\mu |_{\mathbf{r}_\mu} + \nabla \tilde{C}_{A\mu} |_{\mathbf{r}_\mu}) dA \\
&\quad - k_\mu \left(\langle C_{A\mu} \rangle^\mu |_{\mathbf{r}_\mu} - \frac{\langle C_{B\mu} \rangle^\mu |_{\mathbf{r}_\mu}}{K_\mu} \right)
\end{aligned} \tag{A.4}$$

Species B:

$$\begin{aligned}
\frac{\partial \langle C_{B\mu} \rangle^\mu |_{\mathbf{r}_\mu}}{\partial t} &= \nabla \cdot (\mathcal{D}_{B\mu} \nabla \langle C_{B\mu} \rangle^\mu |_{\mathbf{r}_\mu}) + \varepsilon_\mu^{-1} \nabla \varepsilon_\mu \cdot \mathcal{D}_{B\mu} \nabla \langle C_{B\mu} \rangle^\mu |_{\mathbf{r}_\mu} \\
&\quad + k_\mu \left(\langle C_{A\mu} \rangle^\mu |_{\mathbf{r}_\mu} - \frac{\langle C_{B\mu} \rangle^\mu |_{\mathbf{r}_\mu}}{K_\mu} \right) \\
&\quad + \varepsilon_\mu^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{B\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \tilde{C}_{B\mu} |_{\mathbf{r}_\mu} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{B\mu} |_{\mathbf{r}_\mu} dA \right) \right]
\end{aligned} \tag{A.5}$$

In σ -phase:

$$\begin{aligned}
\frac{\partial \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{r}_\sigma}}{\partial t} &= \nabla \cdot (\mathcal{D}_{A\sigma} \nabla \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{r}_\sigma}) + \varepsilon_\sigma^{-1} \nabla \varepsilon_\sigma \cdot \mathcal{D}_{A\sigma} \nabla \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{r}_\sigma} \\
&\quad + \varepsilon_\sigma^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{A\sigma}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \tilde{C}_{A\sigma} |_{\mathbf{r}_\sigma} dA \right] \\
&\quad + \frac{\varepsilon_\sigma^{-1}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla (\langle C_{A\sigma} \rangle^\sigma |_{\mathbf{r}_\sigma} + \tilde{C}_{A\sigma} |_{\mathbf{r}_\sigma}) dA - k_\sigma \langle C_{A\sigma} \rangle^\sigma |_{\mathbf{r}_\sigma},
\end{aligned} \tag{A.6}$$

to the local equations (also evaluated in \mathbf{r}_λ), which have the form:

In γ -phase:

$$\frac{\partial C_{A\gamma} |_{\mathbf{r}_\gamma}}{\partial t} = \nabla \cdot (\mathcal{D}_{A\gamma} \nabla C_{A\gamma} |_{\mathbf{r}_\gamma}) \tag{A.7}$$

In μ -phase: Species A:

$$\frac{\partial C_{A\mu}|_{\mathbf{r}_\mu}}{\partial t} = \nabla \cdot (\mathcal{D}_{A\mu} \nabla C_{A\mu}|_{\mathbf{r}_\mu}) - k_\mu \left(C_{A\mu}|_{\mathbf{r}_\mu} - \frac{C_{B\mu}|_{\mathbf{r}_\mu}}{K_\mu} \right) \quad (\text{A.8})$$

Species B:

$$\frac{\partial C_{B\mu}|_{\mathbf{r}_\mu}}{\partial t} = \nabla \cdot (\mathcal{D}_{B\mu} \nabla C_{B\mu}|_{\mathbf{r}_\mu}) + k_\mu \left(C_{A\mu}|_{\mathbf{r}_\mu} - \frac{C_{B\mu}|_{\mathbf{r}_\mu}}{K_\mu} \right) \quad (\text{A.9})$$

In σ -phase:

$$\frac{\partial C_{A\sigma}|_{\mathbf{r}_\sigma}}{\partial t} = \nabla \cdot (\mathcal{D}_{A\sigma} \nabla C_{A\sigma}|_{\mathbf{r}_\sigma}) - k_\sigma C_{A\sigma}|_{\mathbf{r}_\sigma} \quad (\text{A.10})$$

Finally the result, the transport equations for the spatial deviation concentrations can be expressed as:

In γ -phase:

$$\begin{aligned} \frac{\partial \tilde{C}_{A\gamma}}{\partial t} = & \nabla \cdot (\mathcal{D}_{A\gamma} \nabla \tilde{C}_{A\gamma}) - \varepsilon_\gamma^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \tilde{C}_{A\gamma} dA \right) \\ & - \frac{\varepsilon_\gamma^{-1}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla \tilde{C}_{A\gamma} dA \\ & - \frac{\varepsilon_\gamma^{-1}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla \langle C_{A\gamma} \rangle^\gamma dA - \varepsilon_\gamma^{-1} \nabla \varepsilon_\gamma \cdot \mathcal{D}_{A\gamma} \langle C_{A\gamma} \rangle^\gamma \end{aligned} \quad (\text{A.11})$$

In μ -phase: Species A:

$$\begin{aligned} \frac{\partial \tilde{C}_{A\mu}}{\partial t} = & \nabla \cdot (\mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu}) - \varepsilon_\mu^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \tilde{C}_{A\mu} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{A\mu} dA \right) \right] \\ & - k_\mu \left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu} \right) \\ & - \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} dA \right) \\ & - \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \langle C_{A\mu} \rangle^\mu dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \langle C_{A\mu} \rangle^\mu dA \right) \\ & - \varepsilon_\mu^{-1} \nabla \varepsilon_\mu \cdot \mathcal{D}_{A\mu} \nabla \langle C_{A\mu} \rangle^\mu \end{aligned} \quad (\text{A.12})$$

Species B :

$$\begin{aligned}
\frac{\partial \tilde{C}_{B\mu}}{\partial t} = & \nabla \cdot (\mathcal{D}_{B\mu} \nabla \tilde{C}_{B\mu}) + \varepsilon_\mu^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{B\mu}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \tilde{C}_{B\mu} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{B\mu} dA \right) \right] \\
& + k_\mu \left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu} \right) \\
& - \frac{\varepsilon_\mu^{-1}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{B\mu} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \tilde{C}_{B\mu} dA \right) \\
& - \frac{\varepsilon_\mu^{-1}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu} \nabla \langle C_{B\mu} \rangle^\mu dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \langle C_{B\mu} \rangle^\mu dA \right) \\
& - \varepsilon_\mu^{-1} \nabla \varepsilon_\mu \cdot \mathcal{D}_{B\mu} \nabla \langle C_{B\mu} \rangle^\mu \tag{A.13}
\end{aligned}$$

In σ -phase:

$$\begin{aligned}
\frac{\partial \tilde{C}_{A\sigma}}{\partial t} = & \nabla \cdot (\mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma}) - k_\sigma \tilde{C}_{A\sigma} - \varepsilon_\sigma^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{A\sigma}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \tilde{C}_{A\sigma} dA \right] \\
& - \frac{\varepsilon_\sigma^{-1}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma} dA \\
& - \frac{\varepsilon_\sigma^{-1}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \langle C_{A\sigma} \rangle^\sigma dA + \varepsilon_\sigma^{-1} \nabla \varepsilon_\sigma \cdot \mathcal{D}_{A\sigma} \nabla \langle C_{A\sigma} \rangle^\sigma \tag{A.14}
\end{aligned}$$

Eqs. A.11 - A.14 contain averaged local and non-local sources, in the same way as the non-closed averaged equations, Eqs. 4.14 - 4.22. In order to remove these averaged concentrations from the area integrals, the following expansions in Taylor series about the centroid of the averaging volume (\mathbf{x}), are proposed for the averaged concentrations $\langle C_{i\lambda} \rangle^\lambda$:

$$\langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{r}_\lambda} = \underbrace{\langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}}}_{\mathcal{O}(\langle C_{i,\lambda} \rangle^\lambda)} + \underbrace{\mathbf{y}_\lambda \cdot \nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}}}_{\mathcal{O}(\frac{r_0}{L} \langle C_{i,\lambda} \rangle^\lambda)} + \underbrace{\frac{1}{2} \mathbf{y}_\lambda \mathbf{y}_\lambda : \nabla \nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}}}_{\mathcal{O}(\frac{r_0^2}{L^2} \langle C_{i,\lambda} \rangle^\lambda)} + \dots \tag{A.15}$$

$$\nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{r}_\lambda} = \underbrace{\nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}}}_{\mathcal{O}(\nabla \langle C_{i,\lambda} \rangle^\lambda)} + \underbrace{\mathbf{y}_\lambda \cdot \nabla \nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}}}_{\mathcal{O}(\frac{r_0}{L} \nabla \langle C_{i,\lambda} \rangle^\lambda)} + \dots \tag{A.16}$$

In Eqs. A.15 and A.16 the estimates of order of magnitude of the first terms of the series have been included, one can observe that it has been assumed that the characteristic length associated with spatial variations of $\langle C_{i,\lambda} \rangle^\lambda$ and $\nabla \langle C_{i,\lambda} \rangle^\lambda$ are of

the same order of magnitude which is the large length-scale L . In order to solve the closure problem, the following length-scale constraints are imposed.

$$r_0 \ll L \quad (\text{A.17})$$

$$r_0^2 \ll L^2 \quad (\text{A.18})$$

Therefore, Eqs. A.15 and A.16 lead to the following:

$$\mathbf{O}\left(\langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{r}_\lambda} - \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}}\right) \ll 1 \quad (\text{A.19})$$

$$\mathbf{O}\left(\nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{r}_\lambda} - \nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}}\right) \ll 1 \quad (\text{A.20})$$

Under these conditions, one can remove the averaged quantities from the area integrals in Eqs. A.11 - A.14 and obtain:

In γ -phase:

$$\begin{aligned} \underbrace{\frac{\partial \tilde{C}_{A\gamma}}{\partial t}}_{\mathbf{O}(\tilde{C}_{A\gamma}/t^*)} &= \underbrace{\nabla \cdot (\mathcal{D}_{A\gamma} \nabla \tilde{C}_{A\gamma})}_{\mathbf{O}(\mathcal{D}_{A\gamma} \tilde{C}_{A\gamma}/\ell_\gamma^2)} - \underbrace{\varepsilon_\gamma^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \tilde{C}_{A\gamma} dA \right)}_{\mathbf{O}(\mathcal{D}_{A\gamma} \tilde{C}_{A\gamma}/(L\ell_\gamma\varepsilon_\gamma))} \\ &\quad - \underbrace{\frac{1}{V_\gamma} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla \tilde{C}_{A\gamma} dA}_{\mathbf{O}(\mathcal{D}_{A\gamma} \tilde{C}_{A\gamma}/\ell_\gamma^2)} \end{aligned} \quad (\text{A.21})$$

In μ -phase:

Species A :

$$\begin{aligned} \underbrace{\frac{\partial \tilde{C}_{A\mu}}{\partial t}}_{\mathbf{O}(\tilde{C}_{A\mu}/t^*)} &= \underbrace{\nabla \cdot (\mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu})}_{\mathbf{O}(\mathcal{D}_{A\mu} \tilde{C}_{A\mu}/\ell_\mu^2)} - \underbrace{k_\mu \left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu} \right)}_{\mathbf{O}(k_\mu \tilde{C}_{B\mu} \tilde{C}_{A\mu}/K_\mu)} \\ &\quad - \underbrace{\varepsilon_\mu^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \tilde{C}_{A\mu} dA \right) \right]}_{\mathbf{O}(\mathcal{D}_{A\mu} \tilde{C}_{A\mu}/(L\ell_\mu\varepsilon_\mu))} - \underbrace{\varepsilon_\mu^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{A\mu} dA \right) \right]}_{\mathbf{O}(\mathcal{D}_{A\mu} \tilde{C}_{A\mu}/(L\ell_\mu\varepsilon_\mu))} \\ &\quad - \underbrace{\frac{1}{V_\mu} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} dA \right)}_{\mathbf{O}(\mathcal{D}_{A\mu} \tilde{C}_{A\mu}/\ell_\mu^2)} - \underbrace{\frac{1}{V_\mu} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} dA \right)}_{\mathbf{O}(\mathcal{D}_{A\mu} \tilde{C}_{A\mu}/\ell_\mu^2)} \end{aligned} \quad (\text{A.22})$$

In μ -phase:

Species B :

$$\begin{aligned}
\underbrace{\frac{\partial \tilde{C}_{B\mu}}{\partial t}}_{\mathcal{O}(\tilde{C}_{B\mu}/t^*)} &= \underbrace{\nabla \cdot (\mathcal{D}_{B\mu} \nabla \tilde{C}_{B\mu})}_{\mathcal{O}(\mathcal{D}_{B\mu} \tilde{C}_{B\mu}/\ell_\mu^2)} + \underbrace{k_\mu \left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu} \right)}_{\mathcal{O}(k_\mu \tilde{C}_{B\mu} \tilde{C}_{A\mu}/K_\mu)} \\
&\quad - \underbrace{\varepsilon_\mu^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{B\mu}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \tilde{C}_{B\mu} dA \right) \right]}_{\mathcal{O}(\mathcal{D}_{B\mu} \tilde{C}_{B\mu}/(L\ell_\gamma \varepsilon_\mu))} \underbrace{\varepsilon_\mu^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{B\mu}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{B\mu} dA \right) \right]}_{\mathcal{O}(\mathcal{D}_{B\mu} \tilde{C}_{B\mu}/(L\ell_\mu \varepsilon_\mu))} \\
&\quad - \underbrace{\frac{1}{V_\mu} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu} \nabla \tilde{C}_{B\mu} dA \right)}_{\mathcal{O}(\mathcal{D}_{B\mu} \tilde{C}_{B\mu}/\ell_\gamma^2)} - \underbrace{\frac{1}{V_\mu} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \tilde{C}_{B\mu} dA \right)}_{\mathcal{O}(\mathcal{D}_{A\mu} \tilde{C}_{B\mu}/\ell_\mu^2)}
\end{aligned} \tag{A.23}$$

In σ -phase:

$$\begin{aligned}
\underbrace{\frac{\partial \tilde{C}_{A\sigma}}{\partial t}}_{\mathcal{O}(\tilde{C}_{A\sigma}/t^*)} &= \underbrace{\nabla \cdot (\mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma})}_{\mathcal{O}(\mathcal{D}_{A\sigma} \tilde{C}_{A\sigma}/\ell_\mu^2)} - \underbrace{k_\sigma \tilde{C}_{A\sigma}}_{\mathcal{O}(k_\sigma \tilde{C}_{A\sigma})} \\
&\quad - \underbrace{\varepsilon_\sigma^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{A\sigma}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \tilde{C}_{A\sigma} dA \right]}_{\mathcal{O}(\mathcal{D}_{A\sigma} \tilde{C}_{A\sigma}/(L\ell_\mu \varepsilon_\sigma))} - \underbrace{\frac{1}{V_\sigma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma} dA}_{\mathcal{O}(\mathcal{D}_{A\sigma} \tilde{C}_{A\sigma}/\ell_\mu^2)}
\end{aligned} \tag{A.24}$$

To simplify Eqs. A.21 - A.24, it should be provided the order of magnitude estimates of some terms and one can notice that, on the basis of the length scale constraint,

$$\ell_\mu \ll \ell_\gamma \ll L, \tag{A.25}$$

the following inequality is satisfied for Eq. A.21,

$$\underbrace{\varepsilon_\gamma^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{A\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \tilde{C}_{A\gamma} dA \right)}_{\text{non-local diffusion}} \ll \underbrace{\mathcal{D}_{A\gamma} \nabla^2 \tilde{C}_{A\gamma}}_{\text{diffusion}} \tag{A.26}$$

since $\ell_\gamma \ll L$. In a similar manner, for Eq. A.22 the inequalities given by,

$$\varepsilon_\mu^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \tilde{C}_{A\mu} dA \right) \ll \mathcal{D}_{A\mu} \nabla^2 \tilde{C}_{A\mu} \quad (\text{A.27})$$

$$\varepsilon_\mu^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{A\mu} dA \right) \ll \mathcal{D}_{A\mu} \nabla^2 \tilde{C}_{A\mu}, \quad (\text{A.28})$$

are satisfied, i. e. the non-local diffusion term is smaller than diffusion term since $\ell_\mu \ll L$. And exactly for Eq. A.23 as one can see in the next expressions:

$$\varepsilon_\mu^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{B\mu}}{\mathcal{V}} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \tilde{C}_{B\mu} dA \right) \ll \mathcal{D}_{B\mu} \nabla^2 \tilde{C}_{B\mu} \quad (\text{A.29})$$

$$\varepsilon_\mu^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{B\mu}}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{B\mu} dA \right) \ll \mathcal{D}_{B\mu} \nabla^2 \tilde{C}_{B\mu} \quad (\text{A.30})$$

The inequality related to Eq. A.24 is given by:

$$\varepsilon_\sigma^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{A\sigma}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \tilde{C}_{A\sigma} dA \right) \ll \mathcal{D}_{A\sigma} \nabla^2 \tilde{C}_{A\sigma} \quad (\text{A.31})$$

In addition, as a final simplification, we limit the closure problem as quasi-steady. The constraint associated to this simplification is:

$$\frac{\mathcal{D}_{A\lambda} t^*}{\ell_\lambda^2} \gg 1 \quad (\text{A.32})$$

In this way, Eqs. A.21 - A.24 take the form of the closure problem:

In γ -phase:

$$0 = \underbrace{\mathcal{D}_{A\gamma} \nabla^2 \tilde{C}_{A\gamma}}_{\text{diffusion}} - \underbrace{\frac{\varepsilon_\gamma^{-1}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla \tilde{C}_{A\gamma} dA}_{\text{non-local flux}} \quad (\text{A.33})$$

In μ -phase

Species A:

$$0 = \underbrace{\mathcal{D}_{A\mu} \nabla^2 \tilde{C}_{A\mu}}_{\text{diffusion}} - \underbrace{k_\mu \left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu} \right)}_{\text{reaction}} - \underbrace{\frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} dA \right)}_{\text{non-local flux}} \quad (\text{A.34})$$

Species B :

$$0 = \underbrace{\mathcal{D}_{B\mu} \nabla^2 \tilde{C}_{B\mu}}_{\text{diffusion}} + \underbrace{k_\mu \left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu} \right)}_{\text{reaction}} \quad (\text{A.35})$$

In σ -phase:

$$0 = \underbrace{\mathcal{D}_{A\sigma} \nabla^2 \tilde{C}_{A\sigma}}_{\text{diffusion}} - \underbrace{k_\sigma \tilde{C}_{A\sigma}}_{\text{reaction}} - \underbrace{\frac{\varepsilon_\sigma^{-1}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma} dA}_{\text{non local flux}} \quad (\text{A.36})$$

It should be remarked that the closure problem has in Eqs. A.34, A.35 and A.36 reaction terms. In this respect Wood and Whitaker (1998), suggest that reaction can be neglected in the closure problem even when the reaction is a domain effect at the macroscopic level and following this idea, an additional simplification is made. Imposing that the reaction terms are negligible compared with the diffusion terms one can obtain the constraints given by:

$$\frac{\ell_\mu^2 k_\mu}{\mathcal{D}_{A\mu}} \left(1 - \frac{\tilde{C}_{B\mu}}{\tilde{C}_{A\mu} K_\mu} \right) \ll 1 \quad (\text{A.37})$$

$$\frac{\ell_\sigma^2 k_\sigma}{\mathcal{D}_{A\sigma}} \ll 1 \quad (\text{A.38})$$

After this last simplification, the closure problem takes the final form:

In γ -phase:

$$0 = \underbrace{\mathcal{D}_{A\gamma} \nabla^2 \tilde{C}_{A\gamma}}_{\text{diffusion}} - \underbrace{\frac{\varepsilon_\gamma^{-1}}{\gamma} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla \tilde{C}_{A\gamma} dA}_{\text{non-local flux}} \quad (\text{A.39})$$

In μ -phase

Species A :

$$0 = \underbrace{\mathcal{D}_{A\mu} \nabla^2 \tilde{C}_{A\mu}}_{\text{diffusion}} - \underbrace{\frac{\varepsilon_\mu^{-1}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} dA \right)}_{\text{non-local flux}} \quad (\text{A.40})$$

Species B :

$$0 = \underbrace{\mathcal{D}_{B\mu} \nabla^2 \tilde{C}_{B\mu}}_{\text{diffusion}} \quad (\text{A.41})$$

In σ -phase:

$$0 = \underbrace{\mathcal{D}_{A\sigma} \nabla^2 \tilde{C}_{A\sigma}}_{\text{diffusion}} - \underbrace{\frac{\varepsilon_\sigma^{-1}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma} dA}_{\text{non local flux}} \quad (\text{A.42})$$

From Eqs. 3.8 - 3.13 and the decomposition represented by Eq. A.1 we obtain the interfacial boundary conditions for the closure problem, which can be express as:

At the interfacial area $\mathcal{A}_{\gamma\mu}$:

$$\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\gamma} \nabla \tilde{C}_{A\gamma} - \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} = \underbrace{\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \langle C_{A\mu} \rangle^\mu - \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\gamma} \nabla \langle C_{A\gamma} \rangle^\gamma}_{\text{surface diffusive source}} \quad (\text{A.43})$$

$$\begin{aligned} -\mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla \tilde{C}_{A\gamma} - P_{\gamma\mu} (\tilde{C}_{A\gamma} - K_{\mu\gamma}^{eq} \tilde{C}_{A\mu}) &= \underbrace{P_{\gamma\mu} (\langle C_{A\gamma} \rangle^\gamma - K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu)}_{\text{surface exchange source}} \\ &+ \underbrace{\mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla \langle C_{A\gamma} \rangle^\gamma}_{\text{surface diffusive source}} \end{aligned} \quad (\text{A.44})$$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu} \nabla \tilde{C}_{B\mu} = \underbrace{\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu} \nabla \langle C_{B\mu} \rangle^\mu}_{\text{surface diffusive source}} \quad (\text{A.45})$$

At the interfacial area $\mathcal{A}_{\mu\sigma}$:

$$\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma} - \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} = \underbrace{\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \langle C_{A\mu} \rangle^\mu - \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla \langle C_{A\sigma} \rangle^\sigma}_{\text{surface diffusive source}} \quad (\text{A.46})$$

$$\begin{aligned} -\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma} - P_{\sigma\mu} (\tilde{C}_{A\sigma} - K_{\mu\sigma}^{eq} \tilde{C}_{A\mu}) &= \underbrace{P_{\sigma\mu} (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu)}_{\text{surface exchange source}} \\ &+ \underbrace{\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \langle C_{A\sigma} \rangle^\sigma}_{\text{surface diffusive source}} \end{aligned} \quad (\text{A.47})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \tilde{C}_{B\mu} = \underbrace{\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \langle C_{B\mu} \rangle^\mu}_{\text{surface diffusive source}} \quad (\text{A.48})$$

Eqs. A.33 - A.48 represent the closure problem, however we have no intention of solving it over the entire macroscopic region illustrated. Instead, one can to solve for

$\tilde{C}_{i\lambda}$ in some representative region and use the computed results in Eqs. 4.14, 4.17, 4.18 and 4.22 to affect the closure.

A.1.1 Closure Variables

Given the nature of the boundary-value problem for $\tilde{C}_{i\lambda}$, we propose a solution in terms of the sources, see Eqs. A.43-A.48 which can be express as:

$$\begin{aligned} \tilde{C}_{A\gamma} = & \mathbf{b}_{\gamma\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{b}_{\gamma\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{\gamma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{\gamma B} \cdot \nabla \langle C_{B\mu} \rangle^\mu \\ & - s_\gamma^{\mu\gamma} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\gamma} \rangle^\gamma) - s_\gamma^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma) \end{aligned} \quad (\text{A.49})$$

$$\begin{aligned} \tilde{C}_{A\mu} = & \mathbf{b}_{\mu\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{b}_{\mu\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{\mu\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{\mu B} \cdot \nabla \langle C_{B\mu} \rangle^\mu \\ & + s_\mu^{\mu\gamma} (\langle C_{A\gamma} \rangle^\gamma - K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu) + s_\mu^{\mu\sigma} (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu) \end{aligned} \quad (\text{A.50})$$

$$\begin{aligned} \tilde{C}_{B\mu} = & \mathbf{b}_{B\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{b}_{B\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{B\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{BB} \cdot \nabla \langle C_{B\mu} \rangle^\mu \\ & + s_B^{\mu\gamma} (\langle C_{A\gamma} \rangle^\gamma - K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu) + s_B^{\mu\sigma} (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu) \end{aligned} \quad (\text{A.51})$$

$$\begin{aligned} \tilde{C}_{A\sigma} = & \mathbf{b}_{\sigma\gamma} \cdot \nabla \langle C_{A\gamma} \rangle^\gamma + \mathbf{b}_{\sigma\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{\sigma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{\sigma B} \cdot \nabla \langle C_{B\mu} \rangle^\mu \\ & - s_\sigma^{\mu\gamma} (K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\gamma} \rangle^\gamma) - s_\sigma^{\mu\sigma} (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma) \end{aligned} \quad (\text{A.52})$$

In Eqs. A.49 - A.52, the variables \mathbf{b}_{ji} , $s_{j\gamma}$, $s_{j\sigma}$, where $j = \gamma, \mu, B, \sigma$ and $i = \gamma, \mu, \sigma, B$ are the closure variables. The closure variables are determined by solving the corresponding boundary-value problems that result from substituting Eqs. A.49 - A.52 into Eqs. A.33 - A.36.

Problem I (source $\nabla\langle C_{A\gamma}\rangle^\gamma$):

In γ -phase

$$0 = \mathcal{D}_{A\gamma} \nabla^2 \mathbf{b}_{\gamma\gamma} - \frac{\varepsilon_\gamma^{-1}}{\gamma} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla \mathbf{b}_{\gamma\gamma} dA \quad (\text{A.53})$$

In μ -phase,

$$0 = \mathcal{D}_{A\mu} \nabla^2 \mathbf{b}_{\mu\gamma} - \frac{\varepsilon_\mu^{-1}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \mathbf{b}_{\mu\gamma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \mathbf{b}_{\mu\gamma} dA \right) \quad (\text{A.54})$$

$$0 = \mathcal{D}_{B\mu} \nabla^2 \mathbf{b}_{B\gamma} \quad (\text{A.55})$$

In σ -phase:

$$0 = \mathcal{D}_{A\sigma} \nabla^2 \mathbf{b}_{\sigma\gamma} - \frac{\varepsilon_\sigma^{-1}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma\gamma} dA \quad (\text{A.56})$$

At $\mathcal{A}_{\gamma\mu}$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \mathbf{b}_{\mu\gamma} = -\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\gamma} \nabla \mathbf{b}_{\gamma\gamma} - \mathcal{D}_{A\gamma} \mathbf{n}_{\mu\gamma} \quad (\text{A.57})$$

$$-\mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla \mathbf{b}_{\gamma\gamma} = \mathbf{n}_{\gamma\mu} \mathcal{D}_{A\gamma} + P_{\gamma\mu} (\mathbf{b}_{\gamma\gamma} - K_{\mu\gamma}^{eq} \mathbf{b}_{\mu\gamma}) \quad (\text{A.58})$$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu} \nabla \mathbf{b}_{B\gamma} = 0 \quad (\text{A.59})$$

At $\mathcal{A}_{\mu\sigma}$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \mathbf{b}_{\mu\gamma} = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma\gamma} \quad (\text{A.60})$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma\gamma} = P_{\sigma\mu} (\mathbf{b}_{\sigma\gamma} - K_{\mu\gamma}^{eq} \mathbf{b}_{\mu\gamma}) \quad (\text{A.61})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \mathbf{b}_{B\gamma} = 0 \quad (\text{A.62})$$

Periodicity and restriction:

$$\mathbf{b}_{j\gamma}(\mathbf{r} + \mathbf{l}_k) = \mathbf{b}_{j\gamma}(\mathbf{r}), \quad k = 1, 2; \quad j = \gamma, \mu, \sigma, B \quad (\text{A.63})$$

$$\langle \mathbf{b}_{j\gamma} \rangle^j = 0, \quad j = \gamma, \mu, \sigma, B \quad (\text{A.64})$$

Problem II (source $\nabla\langle C_{A\mu}\rangle^\mu$):

In γ -phase

$$0 = \mathcal{D}_{A\gamma}\nabla^2\mathbf{b}_{\gamma\mu} - \frac{\varepsilon_\gamma^{-1}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma}\nabla\mathbf{b}_{\gamma\mu} dA \quad (\text{A.65})$$

In μ -phase,

$$0 = \mathcal{D}_{A\mu}\nabla^2\mathbf{b}_{\mu\mu} - \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu\mu} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu\mu} dA \right) \quad (\text{A.66})$$

$$0 = \mathcal{D}_{B\mu}\nabla^2\mathbf{b}_{B\mu} \quad (\text{A.67})$$

In σ -phase:

$$0 = \mathcal{D}_{A\sigma}\nabla^2\mathbf{b}_{\sigma\mu} - \frac{\varepsilon_\sigma^{-1}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma}\nabla\mathbf{b}_{\sigma\mu} dA \quad (\text{A.68})$$

At $\mathcal{A}_{\gamma\mu}$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu\mu} = -\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\gamma}\nabla\mathbf{b}_{\gamma\mu} + \mathcal{D}_{A\mu}\mathbf{n}_{\mu\gamma} \quad (\text{A.69})$$

$$-\mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma}\nabla\mathbf{b}_{\gamma\mu} = P_{\gamma\mu}(\mathbf{b}_{\gamma\mu} - K_{\mu\gamma}^{eq}\mathbf{b}_{\mu\mu}) \quad (\text{A.70})$$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu}\nabla\mathbf{b}_{B\mu} = 0 \quad (\text{A.71})$$

At $\mathcal{A}_{\mu\sigma}$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu\mu} = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma}\nabla\mathbf{b}_{\sigma\mu} + \mathbf{n}_{\mu\sigma}\mathcal{D}_{A\mu} \quad (\text{A.72})$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma}\nabla\mathbf{b}_{\sigma\mu} = P_{\sigma\mu}(\mathbf{b}_{\sigma\mu} - K_{\mu\gamma}^{eq}\mathbf{b}_{\mu\mu}) \quad (\text{A.73})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu}\nabla\mathbf{b}_{B\mu} = 0 \quad (\text{A.74})$$

Periodicity and restriction:

$$\mathbf{b}_{j\mu}(\mathbf{r} + \mathbf{l}_k) = \mathbf{b}_{j\mu}(\mathbf{r}), \quad k = 1, 2; \quad j = \gamma, \mu, \sigma, B \quad (\text{A.75})$$

$$\langle \mathbf{b}_{j\mu} \rangle^j = 0, \quad j = \gamma, \mu, \sigma, B \quad (\text{A.76})$$

Problem III (source $\nabla\langle C_{A\sigma}\rangle^\sigma$):

In γ -phase

$$0 = \mathcal{D}_{A\gamma}\nabla^2\mathbf{b}_{\gamma\sigma} - \frac{\varepsilon_\gamma^{-1}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma}\nabla\mathbf{b}_{\gamma\sigma} dA \quad (\text{A.77})$$

In μ -phase,

$$0 = \mathcal{D}_{A\mu}\nabla^2\mathbf{b}_{\mu\sigma} - \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu\sigma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu\sigma} dA \right) \quad (\text{A.78})$$

$$0 = \mathcal{D}_{B\mu}\nabla^2\mathbf{b}_{B\sigma} \quad (\text{A.79})$$

In σ -phase:

$$0 = \mathcal{D}_{A\sigma}\nabla^2\mathbf{b}_{\sigma\sigma} - \frac{\varepsilon_\sigma^{-1}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma}\nabla\mathbf{b}_{\sigma\sigma} dA \quad (\text{A.80})$$

At $\mathcal{A}_{\gamma\mu}$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu\sigma} = -\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\gamma}\nabla\mathbf{b}_{\gamma\sigma} \quad (\text{A.81})$$

$$-\mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma}\nabla\mathbf{b}_{\gamma\sigma} = P_{\gamma\mu}(\mathbf{b}_{\gamma\sigma} - K_{\mu\gamma}^{eq}\mathbf{b}_{\mu\sigma}) \quad (\text{A.82})$$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu}\nabla\mathbf{b}_{B\sigma} = 0 \quad (\text{A.83})$$

At $\mathcal{A}_{\mu\sigma}$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu\sigma} = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma}\nabla\mathbf{b}_{\sigma\sigma} - \mathbf{n}_{\mu\sigma}\mathcal{D}_{A\sigma} \quad (\text{A.84})$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma}\nabla\mathbf{b}_{\sigma\sigma} = P_{\sigma\mu}(\mathbf{b}_{\sigma\sigma} - K_{\mu\sigma}^{eq}\mathbf{b}_{\mu\sigma}) + \mathbf{n}_{\sigma\mu}\mathcal{D}_{A\sigma} \quad (\text{A.85})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu}\nabla\mathbf{b}_{B\sigma} = 0 \quad (\text{A.86})$$

Periodicity and restriction:

$$\mathbf{b}_{j\sigma}(\mathbf{r} + \mathbf{l}_k) = \mathbf{b}_{j\sigma}(\mathbf{r}), \quad k = 1, 2; \quad j = \gamma, \mu, \sigma, B \quad (\text{A.87})$$

$$\langle \mathbf{b}_{j\sigma} \rangle^j = 0, \quad j = \gamma, \mu, \sigma, B \quad (\text{A.88})$$

Problem IV (source $\nabla\langle C_{B\mu}\rangle^\mu$):

In γ -phase

$$0 = \mathcal{D}_{A\gamma}\nabla^2\mathbf{b}_{\gamma B} - \frac{\varepsilon_\gamma^{-1}}{\gamma} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma}\nabla\mathbf{b}_{\gamma B} dA \quad (\text{A.89})$$

In μ -phase,

$$0 = \mathcal{D}_{A\mu}\nabla^2\mathbf{b}_{\mu B} - \frac{\varepsilon_\mu^{-1}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu B} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu B} dA \right) \quad (\text{A.90})$$

$$0 = \mathcal{D}_{B\mu}\nabla^2\mathbf{b}_{BB} \quad (\text{A.91})$$

In σ -phase:

$$0 = \mathcal{D}_{A\sigma}\nabla^2\mathbf{b}_{\sigma B} - \frac{\varepsilon_\sigma^{-1}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma}\nabla\mathbf{b}_{\sigma B} dA \quad (\text{A.92})$$

At $\mathcal{A}_{\gamma\mu}$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu B} = -\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\gamma}\nabla\mathbf{b}_{\gamma B} \quad (\text{A.93})$$

$$-\mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma}\nabla\mathbf{b}_{\gamma B} = P_{\gamma\mu}(\mathbf{b}_{\gamma B} - K_{\mu\gamma}^{eq}\mathbf{b}_{\mu B}) \quad (\text{A.94})$$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu}\nabla\mathbf{b}_{BB} = \mathbf{n}_{\mu\gamma}\mathcal{D}_{B\mu} \quad (\text{A.95})$$

At $\mathcal{A}_{\mu\sigma}$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu}\nabla\mathbf{b}_{\mu B} = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma}\nabla\mathbf{b}_{\sigma B} \quad (\text{A.96})$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma}\nabla\mathbf{b}_{\sigma B} = P_{\sigma\mu}(\mathbf{b}_{\sigma B} - K_{\mu\sigma}^{eq}\mathbf{b}_{\mu B}) \quad (\text{A.97})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu}\nabla\mathbf{b}_{BB} = \mathbf{n}_{\mu\sigma}\mathcal{D}_{B\mu} \quad (\text{A.98})$$

Periodicity and restriction:

$$\mathbf{b}_{jB}(\mathbf{r} + \mathbf{l}_k) = \mathbf{b}_{jB}(\mathbf{r}), \quad k = 1, 2; \quad j = \gamma, \mu, \sigma, B \quad (\text{A.99})$$

$$\langle \mathbf{b}_{jB} \rangle^j = 0, \quad j = \gamma, \mu, \sigma, B \quad (\text{A.100})$$

Problem V (source $\langle C_{A\gamma} \rangle^\gamma - K_{\mu\gamma}^{eq} \langle C_{A\mu} \rangle^\mu$):

In γ -phase

$$0 = \mathcal{D}_{A\gamma} \nabla^2 s_\gamma^{\mu\gamma} - \frac{\varepsilon_\gamma^{-1}}{\gamma} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla s_\gamma^{\mu\gamma} dA \quad (\text{A.101})$$

In μ -phase,

$$0 = \mathcal{D}_{A\mu} \nabla^2 s_\mu^{\mu\gamma} - \frac{\varepsilon_\mu^{-1}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla s_\mu^{\mu\gamma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla s_\mu^{\mu\gamma} dA \right) \quad (\text{A.102})$$

$$0 = \mathcal{D}_{B\mu} \nabla^2 s_B^{\mu\gamma} \quad (\text{A.103})$$

In σ -phase:

$$0 = \mathcal{D}_{A\sigma} \nabla^2 s_\sigma^{\mu\gamma} - \frac{\varepsilon_\sigma^{-1}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla s_\sigma^{\mu\gamma} dA \quad (\text{A.104})$$

At $\mathcal{A}_{\gamma\mu}$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla s_\mu^{\mu\gamma} = -\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\gamma} \nabla s_\gamma^{\mu\gamma} \quad (\text{A.105})$$

$$-\mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla s_\gamma^{\mu\gamma} = P_{\gamma\mu} (1 + s_\gamma^{\mu\gamma} - K_{\mu\gamma}^{eq} s_\mu^{\mu\gamma}) \quad (\text{A.106})$$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu} \nabla s_B^{\mu\gamma} = 0 \quad (\text{A.107})$$

At $\mathcal{A}_{\mu\sigma}$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla s_\mu^{\mu\gamma} = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla s_\sigma^{\mu\gamma} \quad (\text{A.108})$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla s_\sigma^{\mu\gamma} = P_{\sigma\mu} (s_{\sigma\gamma} - K_{\mu\gamma}^{eq} s_\mu^{\mu\gamma}) \quad (\text{A.109})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla s_B^{\mu\gamma} = 0 \quad (\text{A.110})$$

Periodicity and restriction:

$$s_j^{\mu\gamma}(\mathbf{r} + \mathbf{l}_k) = s_j^{\mu\gamma}(\mathbf{r}), \quad k = 1, 2; \quad j = \gamma, \mu, B, \sigma \quad (\text{A.111})$$

$$\langle s_j^{\mu\gamma} \rangle^j = 0, \quad j = \gamma, \mu, B, \sigma \quad (\text{A.112})$$

$$k_{\gamma}^{\mu\gamma} = -\frac{\mathcal{D}A_{\gamma}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \nabla s_{\gamma}^{\mu\gamma} dA \quad (\text{A.113})$$

$$k_{\mu_1}^{\mu\gamma} = \frac{\mathcal{D}A_{\mu}}{\mathcal{V}} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \nabla s_{\mu}^{\mu\gamma} dA \quad (\text{A.114})$$

$$k_{\sigma}^{\mu\gamma} = -\frac{\mathcal{D}A_{\sigma}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla s_{\sigma}^{\mu\gamma} dA \quad (\text{A.115})$$

$$k_{\mu_2}^{\mu\gamma} = \frac{\mathcal{D}A_{\mu}}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \nabla s_{\mu}^{\mu\gamma} dA \quad (\text{A.116})$$

Additionally, one can deduced the following relations: sabiendo que

$$k_{\gamma}^{\mu\gamma} = k_{\mu_1}^{\mu\gamma} = a_{v_1} k_1^{\mu\gamma} \quad (\text{A.117})$$

$$k_{\sigma}^{\mu\gamma} = k_{\mu_2}^{\mu\gamma} = a_{v_2} k_2^{\mu\gamma} \quad (\text{A.118})$$

Problem VI (source $\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu$):

In γ -phase

$$0 = \mathcal{D}_{A\gamma} \nabla^2 s_\gamma^{\mu\sigma} - \frac{\varepsilon_\gamma^{-1}}{\gamma} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla s_\gamma^{\mu\sigma} dA \quad (\text{A.119})$$

In μ -phase,

$$0 = \mathcal{D}_{A\mu} \nabla^2 s_\mu^{\mu\sigma} - \frac{\varepsilon_\mu^{-1}}{\gamma} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla s_\mu^{\mu\sigma} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla s_\mu^{\mu\sigma} dA \right) \quad (\text{A.120})$$

$$0 = \mathcal{D}_{B\mu} \nabla^2 s_B^{\mu\sigma} \quad (\text{A.121})$$

In σ -phase:

$$0 = \mathcal{D}_{A\sigma} \nabla^2 s_\sigma^{\mu\sigma} - \frac{\varepsilon_\sigma^{-1}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla s_\sigma^{\mu\sigma} dA \quad (\text{A.122})$$

At $\mathcal{A}_{\gamma\mu}$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla s_\mu^{\mu\sigma} = -\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\gamma} \nabla s_\gamma^{\mu\sigma} \quad (\text{A.123})$$

$$-\mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla s_\gamma^{\mu\sigma} = P_{\gamma\mu} (s_\gamma^{\mu\sigma} - K_{\mu\gamma}^{eq} s_\mu^{\mu\sigma}) \quad (\text{A.124})$$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu} \nabla s_B^{\mu\sigma} = 0 \quad (\text{A.125})$$

At $\mathcal{A}_{\mu\sigma}$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla s_\mu^{\mu\sigma} = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla s_\sigma^{\mu\sigma} \quad (\text{A.126})$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla s_\sigma^{\mu\sigma} = P_{\sigma\mu} (1 + s_\sigma^{\mu\sigma} - K_{\mu\sigma}^{eq} s_\mu^{\mu\sigma}) \quad (\text{A.127})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla s_B^{\mu\sigma} = 0 \quad (\text{A.128})$$

Periodicity and restriction:

$$s_j^{\mu\sigma}(\mathbf{r} + \mathbf{l}_k) = s_j^{\mu\sigma}(\mathbf{r}), \quad k = 1, 2; \quad j = \gamma, \mu, B, \sigma \quad (\text{A.129})$$

$$\langle s_j^{\mu\sigma} \rangle^j = 0, \quad j = \gamma, \mu, B, \sigma \quad (\text{A.130})$$

$$k_{\gamma}^{\mu\sigma} = -\frac{\mathcal{D}_{A\gamma}}{\gamma} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \nabla s_{\gamma}^{\mu\sigma} dA \quad (\text{A.131})$$

$$k_{\mu_1}^{\mu\sigma} = \frac{\mathcal{D}_{A\mu}}{\gamma} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \nabla s_{\mu}^{\mu\sigma} dA \quad (\text{A.132})$$

$$k_{\sigma}^{\mu\sigma} = -\frac{\mathcal{D}_{A\sigma}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla s_{\sigma}^{\mu\sigma} dA \quad (\text{A.133})$$

$$k_{\mu_2}^{\mu\sigma} = \frac{\mathcal{D}_{A\mu}}{\gamma} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \nabla s_{\mu}^{\mu\sigma} dA \quad (\text{A.134})$$

$$(\text{A.135})$$

where:

$$k_{\gamma}^{\mu\sigma} = k_{\mu_1}^{\mu\sigma} = a_{v_1} k_1^{\mu\sigma} \quad (\text{A.136})$$

$$k_{\sigma}^{\mu\sigma} = k_{\mu_2}^{\mu\sigma} = a_{v_2} k_2^{\mu\sigma} \quad (\text{A.137})$$

These six closure problems, can be summarized into the following one

Problem i , ($i=1, 2, 3, 4, 5, 6$)

$$\text{In } \gamma\text{-phase} \quad 0 = \mathcal{D}_{A\gamma} \nabla^2 \phi_{\gamma i} + f_{\gamma i} \quad (\text{A.138})$$

$$\text{In } \mu\text{-phase,} \quad (\text{A.139})$$

$$\text{species } A : \quad 0 = \mathcal{D}_{A\mu} \nabla^2 \phi_{\mu i} + f_{\mu i} \quad (\text{A.140})$$

$$\text{species } B : \quad 0 = \mathcal{D}_{B\mu} \nabla^2 \phi_{B i} \quad (\text{A.141})$$

$$\text{In } \sigma\text{-phase:} \quad 0 = \mathcal{D}_{A\sigma} \nabla^2 \phi_{\sigma i} + f_{\sigma i} \quad (\text{A.142})$$

Boundary conditions:

$$\text{At } \mathcal{A}_{\gamma\mu}: \quad \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\gamma} \nabla \phi_{\gamma i} - \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \phi_{\mu i} = g_i^I \quad (\text{A.143})$$

$$-\mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla \phi_{\gamma i} - P_{\gamma\mu} (\phi_{\gamma i} - K_{\mu\gamma}^{eq} \phi_{\mu i}) = g_i^{II} \quad (\text{A.144})$$

$$-\mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{B\mu} \nabla \phi_{B i} = g_i^{III} \quad (\text{A.145})$$

$$\text{At } \mathcal{A}_{\mu\sigma}: \quad \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla \phi_{\sigma i} - \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \phi_{\mu i} = h_i^I \quad (\text{A.146})$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \phi_{\sigma i} - P_{\sigma\mu}(\phi_{\sigma i} - K_{\mu\gamma}^{eq} \phi_{\mu i}) = h_i^{II} \quad (\text{A.147})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \phi_{B i} = h_i^{III} \quad (\text{A.148})$$

Periodicity and restriction:

$$\phi_{ji}(\mathbf{r} + \mathbf{l}_k) = \phi_{ji}(\mathbf{r}), \quad k = 1, 2; \quad j = \gamma, \mu, B, \sigma \quad (\text{A.149})$$

$$\langle \phi_{j\sigma} \rangle^j = 0, \quad j = \gamma, \mu, B, \sigma \quad (\text{A.150})$$

where ϕ_{ji} ($j = \gamma, \mu, B, \sigma; i = 1, 2, 3, 4, 5, 6$) represent scalar and vectorial fields according to: $\phi_{j1} = \mathbf{b}_{j\gamma}$, $\phi_{j2} = \mathbf{b}_{j\mu}$, $\phi_{j3} = \mathbf{b}_{jB}$, $\phi_{j4} = \mathbf{b}_{j\sigma}$, $\phi_{j5} = s_{j\gamma}$, $\phi_{j6} = s_{j\sigma}$

In addition, in Eqs. (A.138)-(A.148) we introduced:

$$\begin{aligned} f_{ji} = & -\frac{\delta_{j\gamma}\varepsilon_\gamma^{-1}}{\mathcal{V}} \int_{A_{\gamma\mu}(\mathbf{x})} \mathbf{n}_{\gamma\mu} \cdot \mathcal{D}_{A\gamma} \nabla \phi_{\gamma i} dA \\ & -\frac{\delta_{j\mu}\varepsilon_\mu^{-1}}{\mathcal{V}} \left(\int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \cdot \mathcal{D}_{A\mu} \nabla \phi_{\mu i} dA + \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \phi_{\mu i} dA \right) \\ & -\frac{\delta_{j\sigma}\varepsilon_\sigma^{-1}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \phi_{\sigma i} dA \end{aligned} \quad (\text{A.151})$$

$$g_i^I = \mathbf{n}_{\mu\gamma} (-\delta_{1i} \mathcal{D}_{A\gamma} + \delta_{2i} \mathcal{D}_{A\mu}) \quad (\text{A.152})$$

$$g_i^{II} = \delta_{1i} \mathbf{n}_{\gamma\mu} \mathcal{D}_{A\gamma} + \delta_{5i} P_{\gamma\mu} \quad (\text{A.153})$$

$$g_i^{III} = \delta_{3i} \mathbf{n}_{\mu\gamma} \mathcal{D}_{B\mu} \quad (\text{A.154})$$

$$h_i^I = \mathbf{n}_{\mu\sigma} (\delta_{2i} \mathcal{D}_{A\mu} - \delta_{4i} \mathcal{D}_{A\sigma}) \quad (\text{A.155})$$

$$h_i^{II} = \delta_{4i} \mathbf{n}_{\sigma\mu} \mathcal{D}_{A\sigma} + \delta_{6i} P_{\sigma\mu} \quad (\text{A.156})$$

$$h_i^{III} = \delta_{6i} \mathbf{n}_{\mu\sigma} \mathcal{D}_{B\mu} \quad (\text{A.157})$$

Appendix B

Closed problem for the two region modeling approach

B.1 The Closure Problem (ω -region)

This section is devoted to obtain a *closed form* of the averaged equations presented in the chapter 5, and this means that a representation for the spatial deviation concentrations has to be developed. As mentioned, the details of the derivation and formal solution of the closure problem are quite lengthy, thus, some repetitive steps, that were already developed in detail in Appendix A, are omitted in this section.

First to obtaining the spatial deviation concentrations, Eq. 5.15 can be rewritten as:

$$\tilde{C}_{i\lambda}|_{\mathbf{r}_\lambda} = C_{i\lambda}|_{\mathbf{r}_\lambda} - \langle C_{i\lambda} \rangle^\lambda|_{\mathbf{r}_\lambda}, \quad (\text{B.1})$$

where $\mathbf{r}_\lambda = \mathbf{x} + \mathbf{y}_\lambda$, is the position vector of locating points of the λ -phase ($\lambda = \mu, \sigma$) within the domain averaging, with respect to an external reference frame. Base on Eq. B.1 one can obtain the governing equations for spatial deviation concentrations by subtracting the average equation when $\mathbf{x} \rightarrow \mathbf{r}_\lambda$ (Eqs. 5.27, 5.35 and 5.40), to the local equations (Eqs. 5.1-5.3), also evaluated in \mathbf{r}_λ , thus, the transport equations for the spatial deviation concentrations can be expressed as

In μ -phase:

Species A:

$$\begin{aligned} \frac{\partial \tilde{C}_{A\mu}}{\partial t} = & \nabla \cdot (\mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu}) - \varepsilon_\mu^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{A\mu} dA \right) \right] - k_\mu \left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu} \right) \\ & - \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} dA \right) - \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \langle C_{A\mu} \rangle^\mu dA \right) \\ & - \varepsilon_\mu^{-1} \nabla \varepsilon_\mu \cdot \mathcal{D}_{A\mu} \nabla \langle C_{A\mu} \rangle^\mu \end{aligned} \quad (\text{B.2})$$

Species B:

$$\begin{aligned} \frac{\partial \tilde{C}_{B\mu}}{\partial t} = & \nabla \cdot (\mathcal{D}_{B\mu} \nabla \tilde{C}_{B\mu}) + \varepsilon_\mu^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{B\mu}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{B\mu} dA \right) \right] + k_\mu \left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu} \right) \\ & - \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \tilde{C}_{B\mu} dA \right) - \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \langle C_{B\mu} \rangle^\mu dA \right) \\ & - \varepsilon_\mu^{-1} \nabla \varepsilon_\mu \cdot \mathcal{D}_{B\mu} \nabla \langle C_{B\mu} \rangle^\mu \end{aligned} \quad (\text{B.3})$$

In σ -phase:

$$\begin{aligned} \frac{\partial \tilde{C}_{A\sigma}}{\partial t} = & \nabla \cdot (\mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma}) - k_\sigma \tilde{C}_{A\sigma} - \varepsilon_\sigma^{-1} \nabla \cdot \left[\frac{\mathcal{D}_{A\sigma}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \tilde{C}_{A\sigma} dA \right] \\ & - \frac{\varepsilon_\sigma^{-1}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma} dA \\ & - \frac{\varepsilon_\sigma^{-1}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \langle C_{A\sigma} \rangle^\sigma dA + \varepsilon_\sigma^{-1} \nabla \varepsilon_\sigma \cdot \mathcal{D}_{A\sigma} \nabla \langle C_{A\sigma} \rangle^\sigma \end{aligned} \quad (\text{B.4})$$

Eqs. B.2 - B.4 contain averaged local and non-local sources, in the same way as the non-closed averaged equations, Eqs. 5.27, 5.35 and 5.40. In order to remove these averaged concentrations from the area integrals, the following expansions in Taylor series about the centroid of the averaging volume (\mathbf{x}), are proposed for the averaged concentrations $\langle C_{i,\lambda} \rangle^\lambda$:

$$\langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{r}_\lambda} = \underbrace{\langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}}}_{\mathbf{O}(\langle C_{i,\lambda} \rangle^\lambda)} + \underbrace{\mathbf{y}_\lambda \cdot \nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}}}_{\mathbf{O}(\frac{r_0}{L} \langle C_{i,\lambda} \rangle^\lambda)} + \underbrace{\frac{1}{2} \mathbf{y}_\lambda \mathbf{y}_\lambda : \nabla \nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}} + \dots}_{\mathbf{O}(\frac{r_0^2}{L^2} \langle C_{i,\lambda} \rangle^\lambda)} \quad (\text{B.5})$$

$$\nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{r}_\lambda} = \underbrace{\nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}}}_{\mathbf{O}(\nabla \langle C_{i,\lambda} \rangle^\lambda)} + \underbrace{\mathbf{y}_\lambda \cdot \nabla \nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}} + \dots}_{\mathbf{O}(\frac{r_0}{L} \nabla \langle C_{i,\lambda} \rangle^\lambda)} \quad (\text{B.6})$$

In Eqs. B.5 and B.6 the estimates of order of magnitude of the first terms of the series have been included, one can observe that it has been assumed that the characteristic length associated with spatial variations of $\langle C_{i,\lambda} \rangle^\lambda$ and $\nabla \langle C_{i,\lambda} \rangle^\lambda$ are of the same order of magnitude which is the large length-scale L . In order to solve the closure problem, the following length-scale constraints are imposed.

$$r_0 \ll L \quad (\text{B.7})$$

$$r_0^2 \ll L^2 \quad (\text{B.8})$$

Consequently, Eqs. B.5 - B.6 lead to the following

$$\mathbf{O} \left(\langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{r}_\lambda} - \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}} \right) \ll 1 \quad (\text{B.9})$$

$$\mathbf{O} \left(\nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{r}_\lambda} - \nabla \langle C_{i,\lambda} \rangle^\lambda|_{\mathbf{x}} \right) \ll 1 \quad (\text{B.10})$$

Under these conditions, one can remove the averaged quantities from the area integrals in Eqs. B.2 - B.4. Then, to simplify this equations, it should be provided the order of magnitude estimates of some terms and one can notice that, on the basis of the length scale constraint,

$$\ell_\sigma \ll \ell_\mu \ll L, \quad (\text{B.11})$$

the following inequalities are satisfied for Eqs. B.2 - B.4,

$$\varepsilon_\mu^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{A\mu}}{\gamma} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \tilde{C}_{A\mu} dA \right) \ll \mathcal{D}_{A\mu} \nabla^2 \tilde{C}_{A\mu} \quad (\text{B.12})$$

$$\varepsilon_\mu^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{A\mu}}{\gamma} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{A\mu} dA \right) \ll \mathcal{D}_{A\mu} \nabla^2 \tilde{C}_{A\mu}, \quad (\text{B.13})$$

i. e. the non-local diffusion term is smaller than diffusion term since $\ell_\mu \ll L$. And exactly for the equation of species B as one can see in the next expressions:

$$\varepsilon_\mu^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{B\mu}}{\gamma} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\gamma} \tilde{C}_{B\mu} dA \right) \ll \mathcal{D}_{B\mu} \nabla^2 \tilde{C}_{B\mu} \quad (\text{B.14})$$

$$\varepsilon_\mu^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{B\mu}}{\gamma} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \tilde{C}_{B\mu} dA \right) \ll \mathcal{D}_{B\mu} \nabla^2 \tilde{C}_{B\mu} \quad (\text{B.15})$$

Since $\ell_\sigma \ll L$, the last inequality is given by

$$\varepsilon_\sigma^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{A\sigma}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \tilde{C}_{A\sigma} dA \right) \ll \mathcal{D}_{A\sigma} \nabla^2 \tilde{C}_{A\sigma} \quad (\text{B.16})$$

In addition, as a final simplification, we limit the closure problem as quasi-steady. The constraint associated to this simplification is:

$$\frac{\mathcal{D}_{A\lambda} t^*}{\ell_\lambda^2} \gg 1 \quad (\text{B.17})$$

In this way, Eqs. B.2 - B.4 take the form of the closure problem, given by

In μ -phase

Species A:

$$0 = \underbrace{\mathcal{D}_{A\mu} \nabla^2 \tilde{C}_{A\mu}}_{\text{diffusion}} - \underbrace{k_\mu \left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu} \right)}_{\text{reaction}} - \underbrace{\frac{\varepsilon_\mu^{-1}}{\gamma} \left(\int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} dA \right)}_{\text{non-local flux}} \quad (\text{B.18})$$

Species B:

$$0 = \underbrace{\mathcal{D}_{B\mu} \nabla^2 \tilde{C}_{B\mu}}_{\text{diffusion}} + \underbrace{k_\mu \left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu} \right)}_{\text{reaction}} \quad (\text{B.19})$$

In σ -phase:

$$0 = \underbrace{\mathcal{D}_{A\sigma} \nabla^2 \tilde{C}_{A\sigma}}_{\text{diffusion}} - \underbrace{k_\sigma \tilde{C}_{A\sigma}}_{\text{reaction}} - \underbrace{\frac{\varepsilon_\sigma^{-1}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma} dA}_{\text{non local flux}} \quad (\text{B.20})$$

From Eqs. 5.6 - 5.8 and the decomposition represented by Eq. B.1 one can obtain the interfacial boundary conditions for the closure problem, which can be express as

At $\mathcal{A}_{\mu\sigma}$

$$\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma} - \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \tilde{C}_{A\mu} = \underbrace{\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \langle C_{A\mu} \rangle^\mu - \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla \langle C_{A\sigma} \rangle^\sigma}_{\text{surface diffusive source}} \quad (\text{B.21})$$

$$\begin{aligned} -\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \tilde{C}_{A\sigma} - P_{\sigma\mu} (\tilde{C}_{A\sigma} - K_{\mu\sigma}^{eq} \tilde{C}_{A\mu}) &= \underbrace{P_{\sigma\mu} (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu)}_{\text{surface exchange source}} \\ &+ \underbrace{\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \langle C_{A\sigma} \rangle^\sigma}_{\text{surface diffusive source}} \end{aligned} \quad (\text{B.22})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \tilde{C}_{B\mu} = \underbrace{\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \langle C_{B\mu} \rangle^\mu}_{\text{surface diffusive source}} \quad (\text{B.23})$$

Eqs. B.18 -B.23 represent the closure problem, however we have no intention of solving it over the entire macroscopic region. Instead, we want to solve for $\tilde{C}_{i\lambda}$ in some representative region and use the computed results in Eqs. 5.16, 5.17 and 5.18 to affect the closure.

B.1.1 Closure variables

Given the nature of the boundary-value problem for $\tilde{C}_{i\lambda}$, the solution of the spatial deviation concentration, in terms of the sources present in Eqs. B.21 - B.23, are defined as

$$\tilde{C}_{A\mu} = \mathbf{b}_{\mu\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{\mu\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{\mu B} \cdot \nabla \langle C_{B\mu} \rangle^\mu + s_\mu (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu) \quad (\text{B.24})$$

$$\tilde{C}_{B\mu} = \mathbf{b}_{B\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{B\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{BB} \cdot \nabla \langle C_{B\mu} \rangle^\mu + s_B (\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu) \quad (\text{B.25})$$

$$\tilde{C}_{A\sigma} = \mathbf{b}_{\sigma\mu} \cdot \nabla \langle C_{A\mu} \rangle^\mu + \mathbf{b}_{\sigma\sigma} \cdot \nabla \langle C_{A\sigma} \rangle^\sigma + \mathbf{b}_{\sigma B} \cdot \nabla \langle C_{B\mu} \rangle^\mu - s_\sigma (K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu - \langle C_{A\sigma} \rangle^\sigma) \quad (\text{B.26})$$

In Eqs. B.24 - B.26, the variables \mathbf{b}_{ji} , s_j , where $j = \mu, B, \sigma$ and $i = \mu, \sigma, B$ are the closure variables. The closure variables are determined by solving the corresponding boundary-value problems that result from substituting Eqs. B.24 - B.26 into the closure problem, Eqs. B.18 - B.20.

B.2 Boundary-value problems (ω -region)

Problem I (source $\nabla\langle C_{A\mu}\rangle^\mu$):

In μ -phase,

$$\text{species } A: \quad 0 = \mathcal{D}_{A\mu} \nabla^2 \mathbf{b}_{\mu\mu} - k_\mu \left(\mathbf{b}_{\mu\mu} - \frac{\mathbf{b}_{B\mu}}{K_\mu} \right) - \frac{\varepsilon_\mu^{-1}}{\gamma} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \mathbf{b}_{\mu\mu} dA \quad (\text{B.27})$$

$$\text{species } B: \quad 0 = \mathcal{D}_{B\mu} \nabla^2 \mathbf{b}_{B\mu} + k_\mu \left(\mathbf{b}_{\mu\mu} - \frac{\mathbf{b}_{B\mu}}{K_\mu} \right) \quad (\text{B.28})$$

$$\text{In } \sigma\text{-phase:} \quad 0 = \mathcal{D}_{A\sigma} \nabla^2 \mathbf{b}_{\sigma\mu} - k_\sigma \mathbf{b}_{\sigma\mu} - \frac{\varepsilon_\sigma^{-1}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma\mu} dA \quad (\text{B.29})$$

At $\mathcal{A}_{\mu\sigma}$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \mathbf{b}_{\mu\mu} = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma\mu} + \mathbf{n}_{\mu\sigma} \mathcal{D}_{A\mu} \quad (\text{B.30})$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma\mu} = P_{\sigma\mu} (\mathbf{b}_{\sigma\mu} - K_{\mu\gamma}^{eq} \mathbf{b}_{\mu\mu}) \quad (\text{B.31})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \mathbf{b}_{B\mu} = 0 \quad (\text{B.32})$$

Periodicity and restriction:

$$\mathbf{b}_{j\mu}(\mathbf{r} + \mathbf{l}_k) = \mathbf{b}_{j\mu}(\mathbf{r}), \quad k = 1, 2; \quad j = \mu, \sigma, B \quad (\text{B.33})$$

$$\langle \mathbf{b}_{j\mu} \rangle^j = 0, \quad j = \mu, \sigma, B \quad (\text{B.34})$$

Problem II (source $\nabla\langle C_{A\sigma}\rangle^\sigma$):

In μ -phase,

$$\text{species } A : \quad 0 = \mathcal{D}_{A\mu} \nabla^2 \mathbf{b}_{\mu\sigma} - k_\mu \left(\mathbf{b}_{\mu\sigma} - \frac{\mathbf{b}_{B\sigma}}{K_\mu} \right) - \frac{\varepsilon_\mu^{-1}}{\gamma} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \mathbf{b}_{\mu\sigma} dA \quad (\text{B.35})$$

$$\text{species } B : \quad 0 = \mathcal{D}_{B\sigma} \nabla^2 \mathbf{b}_{B\sigma} + k_\mu \left(\mathbf{b}_{\mu\mu} - \frac{\mathbf{b}_{B\sigma}}{K_\mu} \right) \quad (\text{B.36})$$

$$\text{In } \sigma\text{-phase:} \quad 0 = \mathcal{D}_{A\sigma} \nabla^2 \mathbf{b}_{\sigma\sigma} - k_\sigma \mathbf{b}_{\sigma\sigma} - \frac{\varepsilon_\sigma^{-1}}{\gamma} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma\sigma} dA \quad (\text{B.37})$$

At $\mathcal{A}_{\mu\sigma}$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \mathbf{b}_{\mu\sigma} = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma\sigma} - \mathbf{n}_{\mu\sigma} \mathcal{D}_{A\sigma} \quad (\text{B.38})$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma\sigma} = P_{\sigma\mu} (\mathbf{b}_{\sigma\sigma} - K_{\mu\sigma}^{eq} \mathbf{b}_{\mu\sigma}) + \mathbf{n}_{\sigma\mu} \mathcal{D}_{A\sigma} \quad (\text{B.39})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \mathbf{b}_{B\sigma} = 0 \quad (\text{B.40})$$

Periodicity and restriction:

$$\mathbf{b}_{j\sigma}(\mathbf{r} + \mathbf{l}_k) = \mathbf{b}_{j\sigma}(\mathbf{r}), \quad k = 1, 2; \quad j = \mu, \sigma, B \quad (\text{B.41})$$

$$\langle \mathbf{b}_{j\sigma} \rangle^j = 0, \quad j = \mu, \sigma, B \quad (\text{B.42})$$

Problem III (source $\nabla\langle C_{B\mu}\rangle^\mu$):

In μ -phase,

$$\text{species } A: \quad 0 = \mathcal{D}_{A\mu} \nabla^2 \mathbf{b}_{\mu B} - k_\mu \left(\mathbf{b}_{\mu B} - \frac{\mathbf{b}_{BB}}{K_\mu} \right) - \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \mathbf{b}_{\mu B} dA \quad (\text{B.43})$$

$$\text{species } B: \quad 0 = \mathcal{D}_{B\mu} \nabla^2 \mathbf{b}_{BB} + k_\mu \left(\mathbf{b}_{\mu B} - \frac{\mathbf{b}_{BB}}{K_\mu} \right) \quad (\text{B.44})$$

$$\text{In } \sigma\text{-phase:} \quad 0 = \mathcal{D}_{A\sigma} \nabla^2 \mathbf{b}_{\sigma B} - k_\sigma \mathbf{b}_{\sigma B} - \frac{\varepsilon_\sigma^{-1}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma B} dA \quad (\text{B.45})$$

At $\mathcal{A}_{\mu\sigma}$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla \mathbf{b}_{\mu B} = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma B} \quad (\text{B.46})$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla \mathbf{b}_{\sigma B} = P_{\sigma\mu} (\mathbf{b}_{\sigma B} - K_{\mu\gamma}^{eq} \mathbf{b}_{\mu B}) \quad (\text{B.47})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla \mathbf{b}_{BB} = \mathbf{n}_{\mu\sigma} \mathcal{D}_{B\mu} \quad (\text{B.48})$$

Periodicity and restriction:

$$\mathbf{b}_{jB}(\mathbf{r} + \mathbf{l}_k) = \mathbf{b}_{jB}(\mathbf{r}), \quad k = 1, 2; \quad j = \mu, \sigma, B \quad (\text{B.49})$$

$$\langle \mathbf{b}_{jB} \rangle^j = 0, \quad j = \mu, \sigma, B \quad (\text{B.50})$$

Problem IV (source $\langle C_{A\sigma} \rangle^\sigma - K_{\mu\sigma}^{eq} \langle C_{A\mu} \rangle^\mu$):

In μ -phase,

$$\text{species } A : \quad 0 = \mathcal{D}_{A\mu} \nabla^2 s_\mu - k_\mu \left(s_\mu - \frac{s_B}{K_\mu} \right) - \frac{\varepsilon_\mu^{-1}}{\mathcal{V}} \int_{A_{\mu\sigma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla s_\mu dA \quad (\text{B.51})$$

$$\text{species } B : \quad 0 = \mathcal{D}_{B\mu} \nabla^2 s_B + k_\mu \left(s_\mu - \frac{s_B}{K_\mu} \right) \quad (\text{B.52})$$

$$\text{In } \sigma\text{-phase:} \quad 0 = \mathcal{D}_{A\sigma} \nabla^2 s_\sigma - k_\sigma s_\sigma - \frac{\varepsilon_\sigma^{-1}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla s_\sigma dA \quad (\text{B.53})$$

At $\mathcal{A}_{\mu\sigma}$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\mu} \nabla s_\mu = -\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{A\sigma} \nabla s_\sigma \quad (\text{B.54})$$

$$-\mathbf{n}_{\sigma\mu} \cdot \mathcal{D}_{A\sigma} \nabla s_\sigma = P_{\sigma\mu} (1 + s_\sigma - K_{\mu\gamma}^{eq} s_\mu) \quad (\text{B.55})$$

$$-\mathbf{n}_{\mu\sigma} \cdot \mathcal{D}_{B\mu} \nabla s_B = 0 \quad (\text{B.56})$$

Periodicity and restriction:

$$s_{j\sigma}(\mathbf{r} + \mathbf{l}_k) = s_{j\sigma}(\mathbf{r}), \quad k = 1, 2; \quad j = \mu, B, \sigma \quad (\text{B.57})$$

$$\langle s_{j\sigma} \rangle^j = 0, \quad j = \mu, B, \sigma \quad (\text{B.58})$$

$$k_\mu = \frac{\mathcal{D}_{A\mu}}{\mathcal{V}} \int_{A_{\mu\gamma}(\mathbf{x})} \mathbf{n}_{\mu\sigma} \cdot \nabla s_{\mu\sigma} dA \quad (\text{B.59})$$

$$k_\sigma = -\frac{\mathcal{D}_{A\sigma}}{\mathcal{V}} \int_{A_{\sigma\mu}(\mathbf{x})} \mathbf{n}_{\sigma\mu} \cdot \nabla s_\sigma dA \quad (\text{B.60})$$

Additionally, one can deduced the following relation

$$k_\sigma = k_\mu = a_v k \quad (\text{B.61})$$

B.3 Large-scale closure problem

The objective of this section is to obtain a *closed form* of the large-scale averaged equations, Eqs. 5.67, 5.69 and 5.70, and this means that we need develop a representation for the large-scale spatial deviation concentrations. To achieve it, Eq. 5.66 can be rewritten as

$$\tilde{C}_{A,\eta}|_{\mathbf{x}+\mathbf{y}_\eta} = C_{A,\eta}|_{\mathbf{x}+\mathbf{y}_\eta} - \{C_{A,\eta}\}^\eta|_{\mathbf{x}+\mathbf{y}_\eta}, \quad (\text{B.62})$$

and Eq. 5.68 can be rewritten as

$$\tilde{C}_{j\beta\omega}|_{\mathbf{x}+\mathbf{y}_\omega} = \langle C_{j\beta} \rangle_\omega^\beta|_{\mathbf{x}+\mathbf{y}_\omega} - \{ \langle C_{j\beta} \rangle_\omega^\beta \}^\omega|_{\mathbf{x}+\mathbf{y}_\omega}, \quad j = A, B; \beta = \mu, \sigma, \quad (\text{B.63})$$

where $\mathbf{r}_\lambda = \mathbf{x} + \mathbf{y}_\lambda$, is the position vector of locating points of the η or ω -region within the domain averaging, with respect to an external reference. Base on Eq. B.62 one can obtain the governing equation for the spatial deviation concentration for η -region by subtracting the averaged equation, Eqs. 5.67, when $\mathbf{x} \rightarrow \mathbf{r}_\eta$, to the local equation, Eqs. 5.48, also evaluated in \mathbf{r}_η . This equations is defined as

$$\begin{aligned} \frac{\partial \tilde{C}_{A\eta}}{\partial t} = & \nabla \cdot (\mathcal{D}_{A\eta} \nabla \tilde{C}_{A\eta}) - \varepsilon_\eta^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{A\eta}}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \tilde{C}_{A\eta} dA \right) \\ & - \frac{\varepsilon_\eta^{-1}}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \tilde{C}_{A\eta} dA \\ & - \frac{\varepsilon_\eta^{-1}}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \{C_{A\eta}\}^\eta dA - \varepsilon_\eta^{-1} \nabla \varepsilon_\eta \cdot \mathcal{D}_{A\eta} \{C_{A\eta}\}^\eta \end{aligned} \quad (\text{B.64})$$

Similarly, base on Eq. B.63 one can obtain the governing equation for the spatial deviation concentration for η -region by subtracting the averaged equations, Eqs. 5.69, ?? and 5.70, when $\mathbf{x} \rightarrow \mathbf{r}_\omega$, to the local equations, Eqs. 5.49, 5.50 and 5.51 also evaluated in \mathbf{r}_ω , respectively. This equations are defined as

Species A:

$$\begin{aligned}
 \underbrace{\varepsilon_\mu \frac{\partial \tilde{C}_{A\mu\omega}}{\partial t}}_{\text{accumulation}} &= \underbrace{\nabla \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \tilde{C}_{A\mu\omega})}_{\text{diffusion}} \\
 &\quad - \underbrace{\nabla \cdot \left(\frac{\varepsilon_\omega^{-1}}{\gamma} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \tilde{C}_{A\mu\omega}) dA \right)}_{\text{non-local diffusion}} \\
 &\quad - \underbrace{\frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \tilde{C}_{A\mu\omega}) dA \right)}_{\text{non-local flux}} \\
 &\quad - \underbrace{\frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega) dA \right)}_{\text{interfacial flux source}} \\
 &\quad - \underbrace{\varepsilon_\omega^{-1} \nabla \varepsilon_\omega \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega)}_{\text{diffusive source}} \\
 &\quad - \underbrace{\varepsilon_\mu k_\mu \left(\tilde{C}_{A\mu\omega} - \frac{\tilde{C}_{B\mu\omega}}{K_\mu} \right)}_{\text{reaction}} + \underbrace{a_v k (\tilde{C}_{A\sigma\omega} - K_{\mu\sigma}^{eq} \tilde{C}_{A\mu\omega})}_{\text{exchange term}} \tag{B.65}
 \end{aligned}$$

and finally,

$$\begin{aligned}
 \varepsilon_\sigma \frac{\partial \tilde{C}_{A\sigma\omega}}{\partial t} &= \nabla \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \tilde{C}_{A\sigma\omega}) \\
 &\quad - \nabla \cdot \left(\frac{\varepsilon_\omega^{-1}}{\gamma} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\sigma\sigma} \tilde{C}_{A\sigma\omega}) dA \right) \\
 &\quad - \frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \tilde{C}_{A\sigma\omega}) dA \right) \\
 &\quad - \frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega) dA \right) \\
 &\quad - \varepsilon_\omega^{-1} \nabla \varepsilon_\omega \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\omega) \\
 &\quad - \varepsilon_\sigma k_\sigma \tilde{C}_{A\sigma\omega} + a_v k (\tilde{C}_{A\sigma\omega} - K_{\mu\sigma}^{eq} \tilde{C}_{A\mu\omega}) \tag{B.66}
 \end{aligned}$$

Eqs. B.64 - B.3 contain averaged local and non-local sources, in the same way as the regional non-closed averaged equations, Eqs. 5.67, 5.69 and 5.70. In order to remove

these averaged concentrations from the area integrals, the following expansions in Taylor series about the centroid of the regional averaging volume (\mathbf{x}), are proposed for the regional averaged concentrations. Concerning to η -region the Taylor series have the form

$$\{C_{A,\eta}\}^\eta|_{\mathbf{r}_\eta} = \underbrace{\{C_{A,\eta}\}^\eta|_{\mathbf{x}}}_{\mathcal{O}(\{C_{A,\eta}\}^\eta)} + \underbrace{\mathbf{y}_\eta \cdot \nabla \{C_{A,\eta}\}^\eta|_{\mathbf{x}}}_{\mathcal{O}(\frac{R_0}{\mathcal{L}}\{C_{A,\eta}\}^\eta)} + \underbrace{\frac{1}{2}\mathbf{y}_\eta\mathbf{y}_\eta : \nabla\nabla \{C_{A,\eta}\}^\eta|_{\mathbf{x}} + \dots}_{\mathcal{O}(\frac{R_0^2}{\mathcal{L}^2}\{C_{A,\eta}\}^\eta)} \quad (\text{B.67})$$

$$\{C_{A,\eta}\}^\eta|_{\mathbf{r}_\eta} = \underbrace{\nabla \{C_{A,\eta}\}^\eta|_{\mathbf{x}}}_{\mathcal{O}(\nabla\{C_{A,\eta}\}^\eta)} + \underbrace{\mathbf{y}_\eta \cdot \nabla\nabla \{C_{A,\eta}\}^\eta|_{\mathbf{x}} + \dots}_{\mathcal{O}(\frac{R_0}{\mathcal{L}}\nabla\{C_{A,\eta}\}^\eta)}, \quad (\text{B.68})$$

and for the ω -region have the next form

$$\{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega|_{\mathbf{r}_\omega} = \underbrace{\{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega|_{\mathbf{x}}}_{\mathcal{O}(\{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega)} + \underbrace{\mathbf{y}_\omega \cdot \nabla \{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega|_{\mathbf{x}}}_{\mathcal{O}(\frac{R_0}{\mathcal{L}}\{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega)} + \underbrace{\frac{1}{2}\mathbf{y}_\omega\mathbf{y}_\omega : \nabla\nabla \{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega|_{\mathbf{x}} + \dots}_{\mathcal{O}(\frac{R_0^2}{\mathcal{L}^2}\{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega)} \quad (\text{B.69})$$

$$\{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega|_{\mathbf{r}_\omega} = \underbrace{\nabla \{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega|_{\mathbf{x}}}_{\mathcal{O}(\nabla\{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega)} + \underbrace{\mathbf{y}_\omega \cdot \nabla\nabla \{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega|_{\mathbf{x}} + \dots}_{\mathcal{O}(\frac{R_0}{\mathcal{L}}\nabla\{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega)} \quad (\text{B.70})$$

In Eqs. B.67 - B.70 the estimates of order of magnitude of the first terms of the series have been included; one can observe that it has been assumed that the characteristic length associated with spatial variations of $\{C_{A,\eta}\}^\eta$ and $\{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega$, and $\nabla\{\langle C_{j\beta} \rangle_\omega^\beta\}^\omega$ and $\nabla\{C_{A,\eta}\}^\eta$ are of the same order of magnitude which is the large length-scale \mathcal{L} . In order to solve the closure problem, the following length-scale constraints are imposed.

$$R_0 \ll \mathcal{L} \quad (\text{B.71})$$

$$R_0^2 \ll \mathcal{L}^2 \quad (\text{B.72})$$

Consequently, Eqs. B.67 - B.70 lead to the following

$$\mathbf{O}\left(\{C_{A,\eta}\}^\eta|_{\mathbf{r}_\eta} - \{C_{A,\eta}\}^\eta|_{\mathbf{x}}\right) \ll 1 \quad (\text{B.73})$$

$$\mathbf{O}\left(\nabla\{C_{A,\eta}\}^\eta|_{\mathbf{r}_\eta} - \nabla\{C_{A,\eta}\}^\eta|_{\mathbf{x}}\right) \ll 1 \quad (\text{B.74})$$

$$\mathbf{O}\left(\{\langle C_{j\beta}\rangle_\omega^\beta|_{\mathbf{r}_\omega} - \{\langle C_{j\beta}\rangle_\omega^\beta|_{\mathbf{x}}\}\right) \ll 1 \quad (\text{B.75})$$

$$\mathbf{O}\left(\nabla\{\langle C_{j\beta}\rangle_\omega^\beta|_{\mathbf{r}_\omega} - \nabla\{\langle C_{j\beta}\rangle_\omega^\beta|_{\mathbf{x}}\}\right) \ll 1 \quad (\text{B.76})$$

Under these conditions, one can remove the averaged quantities from the area integrals in Eqs. B.64 - B.3. Then, to simplify this equations, it should be provided the order of magnitude estimates of some terms and one can notice that, on the basis of the length scale constraint,

$$\ell_\eta \ll \ell_\omega \ll \mathcal{L}, \quad (\text{B.77})$$

the following inequalities are satisfied for Eqs. B.2 - B.4

$$\underbrace{\varepsilon_\eta^{-1} \nabla \cdot \left(\frac{\mathcal{D}_{A\eta}}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \tilde{C}_{A\eta} dA \right)}_{\text{non-local diffusion}} \ll \underbrace{\mathcal{D}_{A\eta} \nabla^2 \tilde{C}_{A\eta}}_{\text{diffusion}} \quad (\text{B.78})$$

$$\nabla \cdot \left(\frac{\varepsilon_\omega^{-1}}{\mathcal{V}} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \tilde{C}_{A\mu\omega}) dA \right) \ll \nabla \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \tilde{C}_{A\mu\omega}) \quad (\text{B.79})$$

$$\nabla \cdot \left(\frac{\varepsilon_\omega^{-1}}{\mathcal{V}} \int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\sigma\sigma} \tilde{C}_{A\sigma\omega}) dA \right) \ll \nabla \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \tilde{C}_{A\sigma\omega}) \quad (\text{B.80})$$

As a final simplification, we limit the analysis to situations when the spatial deviations of the concentration can be assumed to be quasi-steady. The constraint associated to this simplification is:

$$\frac{\mathcal{D}_{A\eta} t^*}{\ell_\eta^2} \gg 1 \quad (\text{B.81})$$

$$\frac{\mathbf{D}_{ii} t^*}{\ell_\omega^2} \gg \mathbf{1}; \quad i = \mu, \sigma \quad (\text{B.82})$$

In this way, Eqs. B.64 - B.3 take the form of the closure problem:

In η -region

$$0 = \nabla \cdot (\mathcal{D}_{A\eta} \nabla \tilde{C}_{A\eta}) - \frac{\varepsilon_\eta^{-1}}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \tilde{C}_{A\eta} dA \quad (\text{B.83})$$

In ω -region

$$0 = \nabla \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \tilde{C}_{A\mu\omega}) - \frac{\varepsilon_\omega^{-1}}{\mathcal{V}} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \tilde{C}_{A\mu\omega}) dA \right) - \varepsilon_\mu k_\mu \left(\tilde{C}_{A\mu\omega} - \frac{\tilde{C}_{B\mu\omega}}{K_\mu} \right) - (a_v k)_\mu (\tilde{C}_{A\sigma\omega} - K_{\mu\sigma}^{eq} \tilde{C}_{A\mu\omega}) \quad (\text{B.84})$$

$$0 = \nabla \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \tilde{C}_{A\sigma\omega}) - \frac{\varepsilon_\omega^{-1}}{\mathcal{V}} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \tilde{C}_{A\sigma\omega}) dA \right) - \varepsilon_\sigma k_\sigma \tilde{C}_{A\sigma\omega} - (a_v k)_\sigma (\tilde{C}_{A\sigma\omega} - K_{\mu\sigma}^{eq} \tilde{C}_{A\mu\omega}) \quad (\text{B.85})$$

At the interface between η -region and ω -region ($\mathcal{A}_{\eta\omega}$):

$$-(\mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{\mu\mu} \cdot \nabla \tilde{C}_{A\mu\omega}) = -\mathbf{n}_{\omega\eta} \cdot \mathcal{D}_{A\eta} \nabla \tilde{C}_{A\eta} \underbrace{-\mathbf{n}_{\omega\eta} \cdot \mathcal{D}_{A\eta} \nabla \{C_{A\eta}\}^\eta}_{\text{surface diffusive source}} + \underbrace{\mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{\mu\mu} \cdot \nabla \{\{C_{A\mu}\}_\omega^\mu\}^\omega}_{\text{surface diffusive source}} \quad (\text{B.86})$$

$$-\mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \tilde{C}_{A\eta} = P_{\eta\omega} (\tilde{C}_{A\eta} - K_{\eta\omega}^{eq} \tilde{C}_{A\mu\omega}) \underbrace{+\mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \{C_{A\eta}\}^\eta}_{\text{surface diffusive source}} + \underbrace{P_{\eta\omega} (\{C_{A\eta}\}^\eta - K_{\eta\omega}^{eq} \{\{C_{A\mu}\}_\omega^\mu\}^\omega)}_{\text{surface exchange source}} \quad (\text{B.87})$$

$$-\mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{BB} \cdot \nabla \tilde{C}_{B\mu\omega} = \underbrace{\mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{BB} \cdot \nabla \{\{C_{B\mu}\}_\omega^\mu\}^\omega}_{\text{surface diffusive source}} \quad (\text{B.88})$$

B.4 Closure variables

Given the nature of the boundary-value problem for $\tilde{C}_{i\lambda}$, the solution of the spatial deviation concentration, in terms of the sources present in Eqs. B.86 - B.88, are defined as

$$\begin{aligned}\tilde{C}_{A\eta} = & \mathbf{b}_{\eta\eta} \cdot \nabla \{C_{A\eta}\}^\eta + \mathbf{b}_{\eta\omega} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega + \mathbf{b}_{\eta\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\sigma \\ & + \mathbf{b}_{\eta B} \cdot \nabla \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega - s_\eta (\{C_{A\eta}\}^\eta - K_{\eta\omega}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega)\end{aligned}\quad (\text{B.89})$$

$$\begin{aligned}\tilde{C}_{A\mu\omega} = & \mathbf{b}_{\mu\eta} \cdot \nabla \{C_{A\eta}\}^\eta + \mathbf{b}_{\mu\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega + \mathbf{b}_{\mu\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\sigma \\ & + \mathbf{b}_{\mu B} \cdot \nabla \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega + s_\omega (\{C_{A\eta}\}^\eta - K_{\eta\omega}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega)\end{aligned}\quad (\text{B.90})$$

$$\begin{aligned}\tilde{C}_{B\mu\omega} = & \mathbf{b}_{B\eta} \cdot \nabla \{C_{A\eta}\}^\eta + \mathbf{b}_{B\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega + \mathbf{b}_{B\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\sigma \\ & + \mathbf{b}_{BB} \cdot \nabla \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega + s_B (\{C_{A\eta}\}^\eta - K_{\eta\omega}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega)\end{aligned}\quad (\text{B.91})$$

$$\begin{aligned}\tilde{C}_{A\sigma\omega} = & \mathbf{b}_{\sigma\eta} \cdot \nabla \{C_{A\eta}\}^\eta + \mathbf{b}_{\sigma\mu} \cdot \nabla \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega + \mathbf{b}_{\sigma\sigma} \cdot \nabla \{ \langle C_{A\sigma} \rangle_\omega^\sigma \}^\sigma \\ & + \mathbf{b}_{\sigma B} \cdot \nabla \{ \langle C_{B\mu} \rangle_\omega^\mu \}^\omega + s_\sigma (\{C_{A\eta}\}^\eta - K_{\eta\omega}^{eq} \{ \langle C_{A\mu} \rangle_\omega^\mu \}^\omega)\end{aligned}\quad (\text{B.92})$$

In Eqs. B.89 - B.92, the variables \mathbf{b}_{ji} , s_j , where $j = \eta, \mu, B, \sigma$ and $i = \eta, \mu, B, \sigma$ are the closure variables. The closure variables are determined by solving the corresponding boundary-value problems that result from substituting Eqs. B.89 - B.92 into Eqs. B.83 - B.85.

B.5 Boundary-value problems (Large-scale)

Problem I (source $\nabla\{C_{A\eta}\}^\eta$):

In η -region

$$0 = \nabla \cdot (\mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\eta}) - \frac{\varepsilon_\eta^{-1}}{\gamma} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\eta} dA \quad (\text{B.93})$$

In ω -region

μ -phase:

$$\begin{aligned} 0 = & \nabla \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu\eta}) - \frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu\eta}) dA \right) \\ & + (a_v k) (\mathbf{b}_{\sigma\eta} - K_{\mu\sigma}^{eq} \mathbf{b}_{\mu\eta}) - \varepsilon_\mu k_\mu \left(\mathbf{b}_{\mu\eta} - \frac{\mathbf{b}_{B\eta}}{K_\mu} \right) \end{aligned} \quad (\text{B.94})$$

σ -phase:

$$\begin{aligned} 0 = & \nabla \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \mathbf{b}_{\sigma\eta}) - \frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \mathbf{b}_{\sigma\eta}) dA \right) \\ & + (a_v k) (\mathbf{b}_{\sigma\eta} - K_{\mu\sigma}^{eq} \mathbf{b}_{\mu\eta}) - \varepsilon_\sigma k_\sigma \mathbf{b}_{\sigma\eta} \end{aligned} \quad (\text{B.95})$$

At the interface between η -region and ω -region ($\mathcal{A}_{\eta\omega}$):

$$- \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu\eta}) = - \mathbf{n}_{\omega\eta} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\eta} - \mathbf{n}_{\omega\eta} \mathcal{D}_{A\eta} \quad (\text{B.96})$$

$$- \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\eta} = P_{\eta\omega} (\mathbf{b}_{\eta\eta} - K_{\eta\omega}^{eq} \mathbf{b}_{\mu\eta}) + \mathbf{n}_{\eta\omega} \mathcal{D}_{A\eta} \quad (\text{B.97})$$

$$- \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{BB} \cdot \nabla \mathbf{b}_{B\eta} = 0 \quad (\text{B.98})$$

Periodicity and restriction:

$$\mathbf{b}_{j\eta}(\mathbf{r} + \mathbf{l}_k) = \mathbf{b}_{j\gamma}(\mathbf{r}), \quad k = 1, 2; \quad j = \eta, \mu, \sigma, B \quad (\text{B.99})$$

$$\langle \mathbf{b}_{j\eta} \rangle^j = 0, \quad j = \eta, \mu, \sigma, B \quad (\text{B.100})$$

Problem II (source $\nabla\{\langle C_{A\mu} \rangle_\omega^\mu\}$):

In η -region

$$0 = \nabla \cdot (\mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\mu}) - \frac{\varepsilon_\eta^{-1}}{\gamma} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\mu} dA \quad (\text{B.101})$$

In ω -region

μ -phase:

$$\begin{aligned} 0 = & \nabla \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu\mu}) - \frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu\mu}) dA \right) \\ & + (a_\nu k) (\mathbf{b}_{\sigma\mu} - K_{\mu\sigma}^{eq} \mathbf{b}_{\mu\mu}) - \varepsilon_\mu k_\mu \left(\mathbf{b}_{\mu\mu} - \frac{\mathbf{b}_{B\mu}}{K_\mu} \right) \end{aligned} \quad (\text{B.102})$$

σ -phase:

$$\begin{aligned} 0 = & \nabla \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \mathbf{b}_{\sigma\mu}) - \frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \mathbf{b}_{\sigma\mu}) dA \right) \\ & - (a_\nu k)_\sigma (K_{\mu\sigma}^{eq} \mathbf{b}_{\mu\mu} - \mathbf{b}_{\sigma\mu}) - \varepsilon_\sigma k_\sigma \mathbf{b}_{\sigma\eta} \end{aligned} \quad (\text{B.103})$$

At the interface between η -region and ω -region ($\mathcal{A}_{\eta\omega}$):

$$- \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu\mu}) = - \mathbf{n}_{\omega\eta} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\mu} - \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{\mu\mu} \quad (\text{B.104})$$

$$- \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\mu} = P_{\eta\omega} (\mathbf{b}_{\eta\mu} - K_{\eta\omega}^{eq} \mathbf{b}_{\mu\mu}) \quad (\text{B.105})$$

$$- \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{BB} \cdot \nabla \mathbf{b}_{B\mu} = 0 \quad (\text{B.106})$$

Periodicity and restriction:

$$\mathbf{b}_{j\mu}(\mathbf{r} + \mathbf{l}_k) = \mathbf{b}_{j\gamma}(\mathbf{r}), \quad k = 1, 2; \quad j = \gamma, \mu, \sigma, B \quad (\text{B.107})$$

$$\langle \mathbf{b}_{j\mu} \rangle^j = 0, \quad j = \mu, \mu, \sigma, B \quad (\text{B.108})$$

Problem III (source $\nabla\{\langle C_{A\sigma} \rangle_\omega^\sigma\}^\omega$):

In η -region

$$0 = \nabla \cdot (\mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\sigma}) - \frac{\varepsilon_\eta^{-1}}{\gamma} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\sigma} dA \quad (\text{B.109})$$

In ω -region

μ -phase:

$$\begin{aligned} 0 = & \nabla \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu\sigma}) - \frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu\sigma}) dA \right) \\ & + (a_v k)_\mu (\mathbf{b}_{\sigma\sigma} - K_{\mu\sigma}^{eq} \mathbf{b}_{\mu\sigma}) - \varepsilon_\mu k_\mu \left(\mathbf{b}_{\mu\sigma} - \frac{\mathbf{b}_{B\sigma}}{K_\mu} \right) \end{aligned} \quad (\text{B.110})$$

σ -phase:

$$\begin{aligned} 0 = & \nabla \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \mathbf{b}_{\sigma\sigma}) - \frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \mathbf{b}_{\sigma\sigma}) dA \right) \\ & + (a_v k)_\sigma (K_{\mu\sigma}^{eq} \mathbf{b}_{\mu\sigma} - \mathbf{b}_{\sigma\sigma}) - \varepsilon_\sigma k_\sigma \mathbf{b}_{\sigma\sigma} \end{aligned} \quad (\text{B.111})$$

At the interface between η -region and ω -region ($\mathcal{A}_{\eta\omega}$):

$$- \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu\mu}) = - \mathbf{n}_{\omega\eta} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\mu} - \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{\mu\sigma} \quad (\text{B.112})$$

$$- \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\mu} = P_{\eta\omega} (\mathbf{b}_{\eta\mu} - K_{\eta\omega}^{eq} \mathbf{b}_{\mu\mu}) \quad (\text{B.113})$$

$$- \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{BB} \cdot \nabla \mathbf{b}_{B\mu} = 0 \quad (\text{B.114})$$

Periodicity and restriction:

$$\mathbf{b}_{j\sigma}(\mathbf{r} + \mathbf{l}_k) = \mathbf{b}_{j\sigma}(\mathbf{r}), \quad k = 1, 2; \quad j = \gamma, \mu, \sigma, B \quad (\text{B.115})$$

$$\langle \sigma b_{j\mu} \rangle^j = 0, \quad j = \gamma, \mu, \sigma, B \quad (\text{B.116})$$

Problem IV (source $\nabla\{\langle C_{B\mu}^\mu \rangle^\omega\}$):

In η -region

$$0 = \nabla \cdot (\mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta B}) - \frac{\varepsilon_\eta^{-1}}{\mathcal{V}} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta B} dA \quad (\text{B.117})$$

In ω -region

μ -phase:

$$\begin{aligned} 0 = \nabla \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu B}) - \frac{\varepsilon_\omega^{-1}}{\mathcal{V}} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu B}) dA \right) \\ - (a_\nu k)_\mu (\mathbf{b}_{\sigma B} - K_{\mu\sigma}^{eq} \mathbf{b}_{\mu B}) - \varepsilon_\mu k_\mu \left(\mathbf{b}_{\mu B} - \frac{\mathbf{b}_{BB}}{K_\mu} \right) \end{aligned} \quad (\text{B.118})$$

σ -phase:

$$\begin{aligned} 0 = \nabla \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \mathbf{b}_{\sigma B}) - \frac{\varepsilon_\omega^{-1}}{\mathcal{V}} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla \mathbf{b}_{\sigma B}) dA \right) \\ + (a_\nu k)_\sigma (K_{\mu\sigma}^{eq} \mathbf{b}_{\mu B} - \mathbf{b}_{\sigma B}) - \varepsilon_\sigma k_\sigma \mathbf{b}_{\sigma B} \end{aligned} \quad (\text{B.119})$$

At the interface between η -region and ω -region ($\mathcal{A}_{\eta\omega}$):

$$-\mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla \mathbf{b}_{\mu\mu}) = -\mathbf{n}_{\omega\eta} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\mu} \quad (\text{B.120})$$

$$-\mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla \mathbf{b}_{\eta\mu} = P_{\eta\omega} (\mathbf{b}_{\eta\mu} - K_{\eta\omega}^{eq} \mathbf{b}_{\mu\mu}) \quad (\text{B.121})$$

$$-\mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{BB} \cdot \nabla \mathbf{b}_{B\mu} = \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{BB} \quad (\text{B.122})$$

Periodicity and restriction:

$$\mathbf{b}_{jB}(\mathbf{r} + \mathbf{l}_k) = \mathbf{b}_{jB}(\mathbf{r}), \quad k = 1, 2; \quad j = \gamma, \mu, \sigma, B \quad (\text{B.123})$$

$$\langle \sigma \mathbf{b}_{jB} \rangle^j = 0, \quad j = \gamma, \mu, \sigma, B \quad (\text{B.124})$$

Problem V (source $(\{C_{A\eta}\}^\eta - K_{\eta\omega}^{eq}\{\langle C_{A\mu}\rangle_\omega^\mu\})$):

In η -region

$$0 = \nabla \cdot (\mathcal{D}_{A\eta} \nabla s_\eta) - \frac{\varepsilon_\eta^{-1}}{\gamma} \int_{A_{\eta\omega}(\mathbf{x})} \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla s_\eta dA \quad (\text{B.125})$$

In ω -region

μ -phase:

$$\begin{aligned} 0 = & \nabla \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla s_\mu) - \frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla s_\mu) dA \right) \\ & + (a_v k)_\mu (K_{\mu\sigma}^{eq} s_\mu - s_\sigma) - \varepsilon_\mu k_\mu \left(s_\mu - \frac{s_B}{K_\mu} \right) \end{aligned} \quad (\text{B.126})$$

σ -phase:

$$\begin{aligned} 0 = & \nabla \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla s_\sigma) - \frac{\varepsilon_\omega^{-1}}{\gamma} \left(\int_{A_{\omega\eta}(\mathbf{x})} \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\sigma\sigma} \cdot \nabla s_\sigma) dA \right) \\ & + (a_v k)_\sigma (K_{\mu\sigma}^{eq} s_\mu - s_\sigma) - \varepsilon_\sigma k_\sigma s_\sigma \end{aligned} \quad (\text{B.127})$$

At the interface between η -region and ω -region ($\mathcal{A}_{\eta\omega}$):

$$- \mathbf{n}_{\omega\eta} \cdot (\mathbf{D}_{\mu\mu} \cdot \nabla s_\mu) = - \mathbf{n}_{\omega\eta} \cdot \mathcal{D}_{A\eta} \nabla s_\eta \quad (\text{B.128})$$

$$- \mathbf{n}_{\eta\omega} \cdot \mathcal{D}_{A\eta} \nabla s_\eta = P_{\eta\omega} (1 + s_\eta - K_{\eta\omega}^{eq} s_\mu) \quad (\text{B.129})$$

$$- \mathbf{n}_{\omega\eta} \cdot \mathbf{D}_{BB} \cdot \nabla s_B = 0 \quad (\text{B.130})$$

Periodicity and restriction:

$$s_j(\mathbf{r} + \mathbf{l}_k) = s_j(\mathbf{r}), \quad k = 1, 2; \quad j = \eta, \mu, \sigma, B \quad (\text{B.131})$$

$$\langle s_j \rangle^j = 0, \quad j = \eta, \mu, \sigma, B \quad (\text{B.132})$$

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Titre : Modélisation macroscopique des émulsions doubles

Mots clés : Émulsion double, méthode de la prise de moyenne, non équilibre local massique

Résumé : Les séparations à l'aide de membranes liquides sous forme d'émulsions doubles (DE) ont fait l'objet de nombreuses études compte tenu des applications potentielles notamment dans le domaine de la récupération des métaux, la séparation des gaz, l'élimination des composés organiques, l'élimination des polluants ou les bioséparations. Les difficultés de mise en œuvre de tels procédés ne relèvent pas de la complexité technique des installations mais avant tout dans la bonne compréhension des phénomènes couplés qui se produisent au sein de ces systèmes. Depuis leur invention, des progrès ont été réalisés ans la modélisation des procédés de séparation mais une description fine des mécanismes de diffusion-réaction au sein des émulsions doubles reste à établir.

L'objectif de cette thèse est précisément de décrire le transport d'un soluté avec réaction chimique au sein d'un système DE à l'aide d'une modélisation macroscopique par changement d'échelle permettant la prise en compte des mécanismes à l'échelle locale.

La méthode de la prise de moyenne a été utilisée pour établir rigoureusement les équations moyennes dans le cas où l'équilibre massique local n'est pas satisfait (non-équilibre local massique, NLME).

L'émulsion double a été modélisée de deux manières différentes : un premier modèle consiste à considérer l'émulsion comme un système à un seul domaine composé de trois phases et défini à l'aide d'une seule échelle caractéristique. Le deuxième modèle distingue deux régions dont l'une résulte d'une homogénéisation de la phase interne.

Les deux modélisations macroscopique font intervenir les propriétés effectives dont la détermination passe par la résolution des problèmes de fermeture associés.

Enfin, ces deux modèles sont comparés dans le cas d'un procédé de séparation par agitation d'une émulsion double au sein d'un réservoir.

Title : Macroscopic modeling of double emulsion systems

Keywords : Double emulsion, method of volume averaging, non-local mass equilibrium

Abstract : Liquid membrane separations as Double Emulsions (DE) have been extensively examined for potential application in fields such as metal recovery, gas separation, organic compound removal, pollutant removal, and bioseparations. The difficulties in the application of these processes do not consist in sophisticated equipment or installation but in a good understanding of the complex phenomena that occur inside these systems. Since its invention, efforts have been made for successful modeling of DE process separation; however, information about the diffusion and reaction phenomena inside the DE has not been included in the mathematical descriptions in detail yet. Therefore, the objective of this thesis is to describe the solute transport with chemical reaction through DE systems by means of rigorous modeling that can provide with valuable information from the micro-scale to be applied at the macro-scale. To accomplish this, a DE system has been analyzed as a three-phase system characterized by more than one disparate

length scales. The method of volume averaging has been used to derive rigorous averaged equations in the context of the non-local mass equilibrium (NLME). The structure of the DES has been studied from two different perspectives: 1) the DES as a single domain where concentration changes occur in the same length scale and 2) the DES consists in two homogeneous regions where concentration changes occur at two different length scales. As a result of these different standpoints of representing the system, two different averaged macroscopic models were obtained: the three-phase and the two-region models. Both models present effective coefficients that include information about the micro-scale. These latter are related to closure variables which are solutions of associated boundary-value problems. Finally, an analysis of a DE-containing separation process in a stirred tank by applying both models was made.