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Diffusion and reaction in three-phase systems: Average transport equations and jump boundary conditions

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Abstract

A macroscopic modeling of diffusion and chemical reaction in double emulsion systems using the method of volume-averaging is presented. In this three-phase system, chemical reaction takes place in the drops and membrane phases (ω-region) while passive diffusion is considered in the continuous external phase (η-region). First, a *generalized one-equation model*, free of the usual length scale constraints, is derived in order to describe the solute transfer in both homogeneous regions and in the ω–η inter-region. The up-scaling in the ω-region is based in the local mass equilibrium assumption between the two phases. Equations in both homogeneous regions are deduced from the generalized one-equation model. Then, the jump boundary condition at the dividing surface is derived and associated closure problems are established in order to calculate the jump coefficients.

Keywords: Volume averaging; Closure problem; Jump condition; Local equilibrium; One-equation model; Liquid membrane

1. Introduction

This study deals with the analysis of diffusion and chemical reaction in a system composed by three phases (Fig. 1) where the external phase (γ-phase) contains dispersed drops called membrane phase (μ-phase), themselves containing small dispersed droplets (σ-phase). This system is similar to double emulsions which are used in many extraction processes such as hydrocarbons fractioning [1,2], recuperation of rare component ions [3], recovery of metals [4], purification of fatty esters [5], elimination of contaminants in aqueous streams [6], and the concentration of pharmaceuticals [7]. The so-called liquid surfactant membrane has been used for lactic acid extraction [8] and to explore enzymatic reactions [9]. Moreover, the study of gas dispersion and mass exchange between bubbles and emulsion phases, including interfacial mass transfer, (with and without chemical reaction) is essential in order to model mass transfer in fluidized beds [10,11]. In addition, a clear study of the rheology in double emulsion systems has been recently, performed by Pal [12]. These extraction processes involve the transport of a solute of interest (species A) from the external phase (γ-phase) to the droplets (σ-phase). The transport is based in the difference of solubility of the several phases and is increased by means of a reversible chemical reaction in the μ-phase while an irreversible reaction takes place in the σ-phase. This type of membrane separation represents a relatively new unit operation which, ultimately, is expected to replace a significant proportion of conventional separation processes [13]. Unlike classical process such as distillation, extraction, and crystallization, membrane separation generally does not involve phase transition and therefore requires lower energy consumption.

Theoretical studies of diffusion and reaction in double emulsions have been carried out [1,3,14–24] but most of the works have been focused in the solution of the differential equations. Most of the models are based in intuitive considerations that could lead to rough approximations and inaccurate interpretation of experimental results. In their large majority, these models implicitly consider average equations where macroscopic quantities are not explicitly related to local values and therefore prediction of the effective

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Nomenclature

Along the paper, "α" is used to indicate variables or parameters associated with the phase γ, μ or σ; "λ" with the region η or ω, and "i" with the species A, B or R.

$a_v^{\mu\sigma}$	droplet interfacial volumetric area (m^{-1})
A_∞	external surface of the large-scale averaging volume V_∞
A_λ	external surface of V_λ
$A_{\eta\omega}$	dividing surface between η- and ω-regions
$A_{\mu\alpha}$	surface of the μ–α interface in the averaging volume
$\mathbf{b}_\alpha$	vector that maps $\nabla\{C_A\}_\omega$ onto $\tilde{C}_{A\alpha}$ (m)
$\mathbf{b}_{i\alpha}$	vector that maps $\nabla\langle C_{i\alpha}\rangle^\alpha$ onto $\tilde{C}_{i\alpha}$, $i = B, R$ (m)
$\mathbf{b}_\alpha^\lambda$	vector that maps $\nabla\{C_A\}_\lambda$ onto $\tilde{C}_{A\alpha}$ (m)
$\{C_A\}$	generalized volume averaged concentration (mol/m^3)
$C_{i\alpha}$	local concentration of species $i(A, B, R)$ in the α-phase (mol/m^3)
$\mathcal{D}_{i\alpha}$	molecular diffusivity of species $i(A, B, R)$ in the α-phase (m^2/s)
$\mathbf{D}_A(\mathbf{x})$	position-dependent effective diffusivity tensor of species A in the generalized one-equation model (m^2/s)
$\mathbf{D}_{i\alpha}$	position dependent effective diffusivity tensor of species $i(A, B, R)$ in generalized average equation for $\langle C_{i\alpha}\rangle^\alpha$ (m^2/s)
$\mathbf{D}_{i\omega}$	effective diffusivity tensor of species $i(A, B, R)$ in the homogeneous ω-region (m^2/s)
h	half of the length of the unit cell for the inter-region (m)
k_σ	reaction rate constant in the σ-phase $(m^3\,(mol\,s)^{-1})$
k_μ	reaction rate constant in the μ-phase (s^{-1})
K_μ	equilibrium reaction constant μ-phase
$K_{eq}^{\mu\alpha}$	equilibrium distribution coefficient for the solute A between the μ-phase and α-phase; $\alpha = \sigma, \gamma$
$\langle K_{eq}^{\mu\alpha}\rangle_{\eta\omega}^{\alpha\mu}$	area average of $K_{eq}^{\mu\alpha}$; $\alpha = \sigma, \gamma$
$K_{eff}^{\eta\omega}$	effective equilibrium coefficient at the ω–η dividing surface
$\mathbf{I}$	unit tensor
ℓ	unit cell size (m)
ℓ_α	characteristic length for α-phase (m)
L	characteristic length for volume averaged properties (m)
$\mathbf{n}_{\alpha\beta}$	normal unit vector directed from the α-phase towards the β-phase
$\mathbf{n}_{\omega\eta}$	unit normal vector directed from the ω-region towards the η-region
$\mathbf{N}_{A\alpha}$	molar flux of species A corresponding to the α-phase ($mol/m^2\,s$)
$P_{\alpha\mu}$	membrane permeability at the $\alpha = \sigma, \gamma$ interface (m/s)
$\langle P_{\alpha\mu}\rangle_{\eta\omega}^{\alpha\mu}$	area average of $P_{\alpha\mu}$, m/s, $\alpha = \sigma, \gamma$
P_{eff}^λ	effective permeability in the λ-region (m/s)
r_0	radius of the averaging volume (m)
$R(\mathbf{x})$	position-dependent effective reaction rate $(mol\,(s\,m^3)^{-1})$
R_α	local reaction rate in the α-phase $(mol\,(s\,m^3)^{-1})$
s_α^λ	closure variable that maps $\{C_A\}_\lambda$ onto $\tilde{C}_{A\alpha}$; $\alpha = \sigma, \mu, \gamma, \lambda = \omega, \eta$
t	time (s)
t^*	characteristic process time (s)
$\mathcal{V}$	averaging volume (m^3)
V_∞	large-scale averaging volume (m^3)
V_α	volume of the α-phase contained in the averaging volume (m^3)
$\mathbf{x}$	position vector locating the centroid of averaging volume (m)
$\mathbf{y}_\alpha$	position vector used to locate points in the α-phase relative to the centroid of averaging volume (m)

Greek letters

$\varepsilon(\mathbf{x})$	position-dependent mixed-mode volume fraction defined in Eq. (39)
ε_α	volume fraction of the α-phase

Subscripts

s	identifies excess quantities
0	at the dividing surface
α	identifies a quantity associated to the α-phase, α(σ, μ, γ)
λ	identifies a quantity associated to the λ-region, λ(η, ω)

Special notation

$\tilde{\psi}_\alpha$	spatial local deviation of variable ψ_α from the average value $\langle\psi_\alpha\rangle^\alpha$
$\hat{\psi}_\alpha$	spatial macroscopic deviation of average variable $\langle\psi_\alpha\rangle^\alpha$
$\langle\psi_\alpha\rangle$	superficial average value of ψ_α
$\langle\psi_\alpha\rangle^\alpha$	intrinsic average value of ψ_α

coefficients is not considered. However, recent studies have been devoted to the development of multiscale models of three-phase systems (such as gas–liquid–solid) in fluidized beds [25]. Important improvements (in macroscopic modeling) have been achieved for diffusion and reaction in other three-phase systems such as biofilms or cellular systems [26,27] which are based in the application of the method of volume averaging [28]. In these cases, the effective diffusivity tensor involved in the macroscopic description is predicted by means of closure problems which have been solved for simplified geometries.

In the mentioned three-phase system, the concentration equation in the membrane phase (ω-region) has been represented by a "one average transport equation model", similar to the one obtained in Ref. [29]. This equation is coupled to the transport equation in the external η-region by appropriate boundary conditions. However, the length scale constraints imposed through the derivation of the single average equation in both the η- and ω-regions are not satisfied in the ω–η inter-region where rapid spatial variations of the effective properties are present. Several authors have shown, in the context of volume averaging method, that this difficulty can be solved by the introduction of a jump condition for the mass flux of concentration. This condition applies at the dividing surface that replaces the ω–η inter-region [30,31,37].

The objective of this work is to provide a macroscopic modeling analysis of diffusion and reaction in double emulsion systems and to derive the jump boundary condition at the dividing surface. This is done using the method of volume averaging. The paper is organized as follows: the local conservation equations for the three-phase system are presented in Section 2 and averaged in Section 3. Then, a generalized one-equation model is derived (Section 4) in order to describe the solute transfer in the whole three-phase system (both in the homogeneous ω- and η-regions and in the ω–η inter-region). The up-scaling in the ω-region is based in the local mass equilibrium assumption between droplets and liquid membrane. Equations in both homogeneous ω- and η-regions are deduced from the generalized equation. Finally, on the basis of previous studies [31–33] the macroscopic jump condition is derived in Section 5 and its closed form is presented in Section 6. The effective transport coefficients involved in this jump condition are related to closure variables which are solutions of associated boundary-value problems.

2. Local equations

Let us consider the three-phase system illustrated in Fig. 1 where two homogeneous regions are identified. The ω-region is composed by a continuous membrane phase (μ-phase) and small disperse droplets (σ-phase) while the η-region corresponds to the external continuous γ-phase surrounding the ω-region. In this three-phase system, it is assumed that species A is transferred from

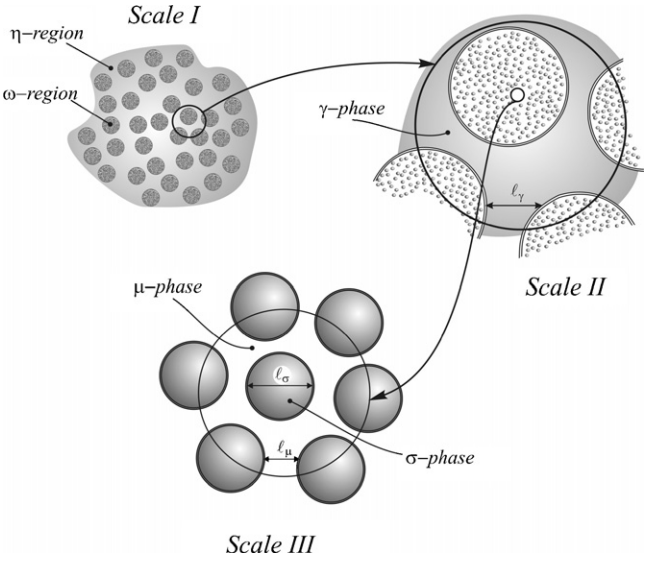

Fig. 1. Three-phase system. *Scale I* corresponds to the macroscopic system; *Scale II* represents a sample of the liquid membrane drops surrounded by the external γ-phase while *Scale III* illustrates droplets in the membrane phase.

the η-region to the ω-region. In this latter region an irreversible reaction ($A + R \rightarrow P$) takes place in the σ-phase while a reversible reaction $A \rightleftarrows B$ occurs in the μ-phase. The formulation of the problem is restricted to dilute solutions where convective transport is neglected. However, it captures the main characteristics that are pursued in a double emulsion separation system. The effect of convective transport in the γ-phase will be presented in a future work.

The local equations governing the diffusive mass transfer with chemical reactions process are

σ-phase

$$\frac{\partial C_{A\sigma}}{\partial t} = \nabla \cdot (\boldsymbol{\mathcal{D}}_{A\sigma} \nabla C_{A\sigma}) - R_\sigma, \tag{1}$$

$$\frac{\partial C_{R\sigma}}{\partial t} = \nabla \cdot (\boldsymbol{\mathcal{D}}_{R\sigma} \nabla C_{R\sigma}) - R_\sigma. \tag{2}$$

μ-phase

$$\frac{\partial C_{A\mu}}{\partial t} = \nabla \cdot (\boldsymbol{\mathcal{D}}_{A\mu} \nabla C_{A\mu}) - R_\mu, \tag{3}$$

$$\frac{\partial C_{B\mu}}{\partial t} = \nabla \cdot (\boldsymbol{\mathcal{D}}_{B\mu} \nabla C_{B\mu}) + R_\mu. \tag{4}$$

γ-phase

$$\frac{\partial C_{A\gamma}}{\partial t} = \nabla \cdot (\boldsymbol{\mathcal{D}}_{A\gamma} \nabla C_{A\gamma}). \tag{5}$$

The kinetics of the two chemical reactions occurring in the σ- and μ-phases are given, respectively by

$$R_\sigma = k_\sigma C_{A\sigma} C_{R\sigma}, \tag{6}$$

$$R_\mu = k_\mu \left(C_{A\mu} - \frac{C_{B\mu}}{K_\mu} \right). \tag{7}$$

Eq. (6) considers the possibility of increasing the separation capability of the system by eliminating the solute in the inner phase [14,23]. Eq. (7) includes the facilitated transport mechanism in the membrane phase [3,4,7]. In this way, although the two kinetic expressions have been taken to be simple, the essence of the separation problem is maintained. Eqs. (1)–(5) are associated to the following interfacial boundary conditions

at the $\sigma\mu$-interface,

$$-\mathbf{n}_{\mu\sigma} \cdot \boldsymbol{\mathcal{D}}_{A\mu} \nabla C_{A\mu} = -\mathbf{n}_{\mu\sigma} \cdot \boldsymbol{\mathcal{D}}_{A\sigma} \nabla C_{A\sigma} \tag{8}$$

$$-\mathbf{n}_{\sigma\mu} \cdot \boldsymbol{\mathcal{D}}_{A\sigma} \nabla C_{A\sigma} = P_{\sigma\mu} (C_{A\sigma} - K_{\mathrm{eq}}^{\mu\sigma} C_{A\mu}) \tag{9}$$

$$-\mathbf{n}_{\sigma\mu} \cdot \boldsymbol{\mathcal{D}}_{R\sigma} \nabla C_{R\sigma} = 0 \tag{10}$$

$$-\mathbf{n}_{\mu\sigma} \cdot \boldsymbol{\mathcal{D}}_{B\mu} \nabla C_{B\mu} = 0 \tag{11}$$

at the $\mu\gamma$-interface,

$$-\mathbf{n}_{\mu\gamma} \cdot \boldsymbol{\mathcal{D}}_{A\mu} \nabla C_{A\mu} = -\mathbf{n}_{\mu\gamma} \cdot \boldsymbol{\mathcal{D}}_{A\gamma} \nabla C_{A\gamma} \tag{12}$$

$$-\mathbf{n}_{\gamma\mu} \cdot \boldsymbol{\mathcal{D}}_{A\gamma} \nabla C_{A\gamma} = P_{\gamma\mu} (C_{A\gamma} - K_{\mathrm{eq}}^{\mu\gamma} C_{A\mu}) \tag{13}$$

$$-\mathbf{n}_{\mu\gamma} \cdot \boldsymbol{\mathcal{D}}_{B\mu} \nabla C_{B\mu} = 0. \tag{14}$$

Eqs. (8), (9), (12) and (13) have been derived following Wood and Whitaker [26]. For conciseness, details are not provided in the present paper but it can be shown that coefficients $P_{\sigma\mu}$, $P_{\gamma\mu}$, $K_{\mathrm{eq}}^{\mu\sigma}$ and $K_{\mathrm{eq}}^{\mu\gamma}$ are functions of local equilibrium constants. In the above equations $\mathbf{n}_{\mu\sigma}$ represents the unit normal vector directed from the μ-phase towards the σ-phase. In Eqs. (9) and (13), $K_{\mathrm{eq}}^{\mu\sigma}$ and $K_{\mathrm{eq}}^{\mu\gamma}$ are the equilibrium distribution coefficients for the solute A, while the membrane permeability of the $\sigma\mu$- and $\gamma\mu$-interfaces are given by $P_{\sigma\mu}$ and $P_{\gamma\mu}$, respectively. On the other hand, Eqs. (10), (11) and (14) indicate that the solutes B and R are restricted to the μ- and σ-phases, respectively. In order to provide a generalized one-equation model for the whole three-phase system, the local equations are up-scaled, in the next section, using the method of volume averaging.

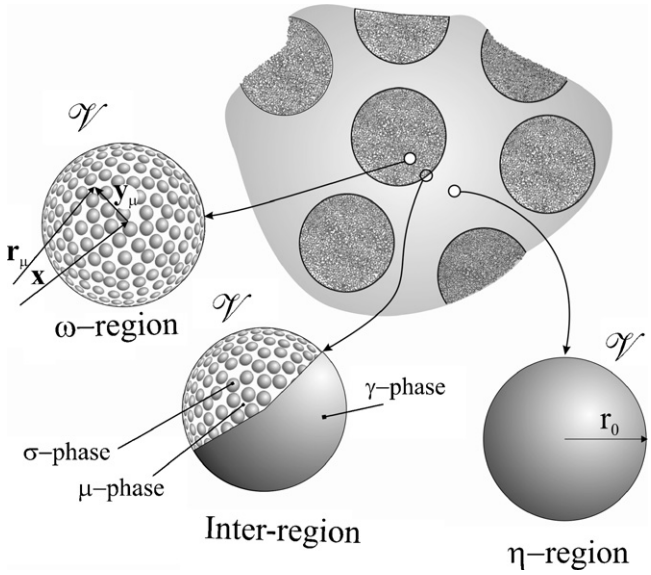

Fig. 2. Averaging volume of radius r_0 to obtain average concentrations and equations at *Scale II*.

3. Volume averaging

Let us consider an averaging volume $\mathcal{V}$ (Fig. 2) that can be located in the double emulsion system including the ω–η inter-region where rapid spatial variations of the geometric properties are present. In terms of this averaging volume, two averaging operators arise [28], namely the *superficial* average of a quantity ψ_μ, defined in the μ-phase

$$\langle \psi_\mu \rangle = \frac{1}{\mathcal{V}} \int_{V_\mu(\mathbf{x})} \psi_\mu \, \mathrm{d}V \tag{15}$$

and the *intrinsic* average, given by

$$\langle \psi_\mu \rangle^\mu = \frac{1}{V_\mu} \int_{V_\mu(\mathbf{x})} \psi_\mu \, \mathrm{d}V. \tag{16}$$

These two averages are related by

$$\langle \psi_\mu \rangle = \varepsilon_\mu(\mathbf{x}) \langle \psi_\mu \rangle^\mu \tag{17}$$

where $\varepsilon_\mu(\mathbf{x})$ is the volume fraction occupied by the μ-phase within the averaging volume. Although $\mathcal{V}$ is constant, it is important to note that the volumes of each phase may change with the location of the averaging volume, which is determined by the vector $\mathbf{x}$ (Fig. 2). This idea can be expressed more precisely by

$$\mathcal{V} = V_\sigma(\mathbf{x}) + V_\mu(\mathbf{x}) + V_\gamma(\mathbf{x}) \tag{18}$$

and therefore

$$\varepsilon_\sigma(\mathbf{x}) + \varepsilon_\mu(\mathbf{x}) + \varepsilon_\gamma(\mathbf{x}) = 1. \tag{19}$$

In Eq. (19), the spatial dependence of the three-phase volume fractions has been kept explicit since they undergo significant spatial variations in the inter-region. Notice that in the homogeneous ω-region only the σ- and μ-phases are present, and therefore $\varepsilon_\sigma + \varepsilon_\mu = 1$ and $\varepsilon_\gamma = 0$. On the other hand, in the homogeneous η-region $\varepsilon_\gamma = 1$ ($\varepsilon_\sigma = \varepsilon_\mu = 0$). Since the membrane phase (μ-phase) is in contact with the other two phases, the averaging procedure is first performed in Eqs. (3) and (4). In this way, an average form of Eqs. (1), (2) and (5) will be easily deduced from the average equation obtained for the membrane phase.

Applying the superficial average operator to Eq. (3) gives

$$\left\langle \frac{\partial C_{A\mu}}{\partial t} \right\rangle = \langle \nabla \cdot (\mathcal{D}_{A\mu} \nabla C_{A\mu}) \rangle - \langle R_\mu \rangle. \tag{20}$$

The initial statement of the problem assumes the microstructure to be time-independent, therefore V_μ is constant and integration and differentiation can be interchanged in the left hand side (LHS) of Eq. (20) leading to

$$\frac{\partial\langle C_{A\mu}\rangle}{\partial t} = \langle\nabla\cdot(\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu})\rangle - \langle R_\mu\rangle. \tag{21}$$

Applying the spatial averaging theorem [34] to the first term of the right hand side (RHS) of Eq. (21) yields

$$\frac{\partial\langle C_{A\mu}\rangle}{\partial t} = \nabla\cdot\langle\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu}\rangle + \frac{1}{\mathcal{V}}\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu}\,\mathrm{d}A + \frac{1}{\mathcal{V}}\int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu}\,\mathrm{d}A - \langle R_\mu\rangle \tag{22}$$

Assuming that $\boldsymbol{\mathcal{D}}_{A\mu}$ is constant within the averaging volume and using again the spatial averaging theorem leads to

$$\begin{aligned}\frac{\partial\langle C_{A\mu}\rangle}{\partial t} = {}& \nabla\cdot\left[\boldsymbol{\mathcal{D}}_{A\mu}\left(\nabla\langle C_{A\mu}\rangle + \frac{1}{\mathcal{V}}\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}C_{A\mu}\,\mathrm{d}A + \frac{1}{\mathcal{V}}\int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}C_{A\mu}\,\mathrm{d}A\right)\right]\\ &+\frac{1}{\mathcal{V}}\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu}\,\mathrm{d}A + \frac{1}{\mathcal{V}}\int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu}\,\mathrm{d}A - \langle R_\mu\rangle.\end{aligned} \tag{23}$$

In terms of intrinsic averaged quantities, Eq. (22) can be rewritten under the form

$$\varepsilon_\mu(\mathbf{x})\frac{\partial\langle C_{A\mu}\rangle^\mu}{\partial t} = \nabla\cdot[\varepsilon_\mu(\mathbf{x})\mathbf{D}_{A\mu}\cdot\nabla\langle C_{A\mu}\rangle^\mu] + \frac{1}{\mathcal{V}}\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu}\,\mathrm{d}A + \frac{1}{\mathcal{V}}\int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu}\,\mathrm{d}A - \varepsilon_\mu(\mathbf{x})\langle R_\mu\rangle^\mu \tag{24}$$

where we introduced the position-dependent diffusivity tensor $\mathbf{D}_{A\mu}$ given by

$$\mathbf{D}_{A\mu}\cdot\nabla\langle C_{A\mu}\rangle^\mu = \boldsymbol{\mathcal{D}}_{A\mu}\nabla\langle C_{A\mu}\rangle^\mu + \frac{\boldsymbol{\mathcal{D}}_{A\mu}}{V_\mu}\left[\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}(C_{A\mu}-\langle C_{A\mu}\rangle^\mu)\,\mathrm{d}A + \int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}(C_{A\mu}-\langle C_{A\mu}\rangle^\mu)\,\mathrm{d}A\right]. \tag{25}$$

Substituting Eq. (7) in Eq. (24) gives

$$\begin{aligned}\varepsilon_\mu(\mathbf{x})\frac{\partial\langle C_{A\mu}\rangle^\mu}{\partial t} = {}& \nabla\cdot[\varepsilon_\mu(\mathbf{x})\mathbf{D}_{A\mu}\cdot\nabla\langle C_{A\mu}\rangle^\mu] + \frac{1}{\mathcal{V}}\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu}\,\mathrm{d}A\\ &+\frac{1}{\mathcal{V}}\int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu}\,\mathrm{d}A - \varepsilon_\mu(\mathbf{x})k_\mu\left(\langle C_{A\mu}\rangle^\mu - \frac{\langle C_{B\mu}\rangle^\mu}{K_\mu}\right).\end{aligned} \tag{26}$$

To obtain the above equation, the spatial changes of k_μ and K_μ within the averaging volume have been neglected. At this stage, note that Eq. (26) has been derived without the use of any length scale constraints and therefore it is valid in both the homogeneous and heterogeneous regions. Finally, let us remark that, due to its lineal form, the average kinetics in Eq. (26) are of the same form than the point equation given by Eq. (7). This will not be the case for the average equation of the globular phase.

Similarly to species A, the average equation for species B is given by

$$\varepsilon_\mu(\mathbf{x})\frac{\partial\langle C_{B\mu}\rangle^\mu}{\partial t} = \nabla\cdot[\varepsilon_\mu(\mathbf{x})\mathbf{D}_{B\mu}\cdot\nabla\langle C_{B\mu}\rangle^\mu] + \varepsilon_\mu(\mathbf{x})k_\mu\left(\langle C_{A\mu}\rangle^\mu - \frac{\langle C_{B\mu}\rangle^\mu}{K_\mu}\right) \tag{27}$$

where $\mathbf{D}_{B\mu}$ has the same form as $\mathbf{D}_{A\mu}$ (Eq. (25)).

An analogous averaging procedure applied to Eqs. (1) and (5) leads to

$$\varepsilon_\gamma(\mathbf{x})\frac{\partial\langle C_{A\gamma}\rangle^\gamma}{\partial t} = \nabla\cdot[\varepsilon_\gamma(\mathbf{x})\mathbf{D}_{A\gamma}\cdot\nabla\langle C_{A\gamma}\rangle^\gamma] + \frac{1}{\mathcal{V}}\int_{A_{\mu\gamma}}\mathbf{n}_{\gamma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}\nabla C_{A\gamma}\,\mathrm{d}A \tag{28}$$

$$\varepsilon_\sigma(\mathbf{x})\frac{\partial\langle C_{A\sigma}\rangle^\sigma}{\partial t} = \nabla\cdot[\varepsilon_\sigma(\mathbf{x})\mathbf{D}_{A\sigma}\cdot\nabla\langle C_{A\sigma}\rangle^\sigma] + \frac{1}{\mathcal{V}}\int_{A_{\mu\sigma}}\mathbf{n}_{\sigma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\sigma}\nabla C_{A\sigma}\,\mathrm{d}A - \varepsilon_\sigma(\mathbf{x})k_\sigma\langle C_{A\sigma}\rangle^\sigma\langle C_{R\sigma}\rangle^\sigma - \varepsilon_\sigma(\mathbf{x})\langle R_\sigma\rangle^\sigma_{\mathrm{exc}} \tag{29}$$

where the following definition has been introduced

$$\mathbf{D}_{Ai}\cdot\nabla\langle C_{Ai}\rangle^i = \boldsymbol{\mathcal{D}}_{Ai}\nabla\langle C_{Ai}\rangle^i + \frac{\boldsymbol{\mathcal{D}}_{Ai}}{V_i}\int_{A_{i\mu}}\mathbf{n}_{i\mu}(C_{Ai}-\langle C_{Ai}\rangle^i)\,\mathrm{d}A \quad i=\sigma,\gamma. \tag{30}$$

In order to avoid the imposition of any length scale constraints, the following representation is adopted for the reaction term

$$\langle R_\sigma\rangle^\sigma = k_\sigma\langle C_{A\sigma}\rangle^\sigma\langle C_{R\sigma}\rangle^\sigma + \langle R_\sigma\rangle^\sigma_{\mathrm{exc}} \tag{31}$$

in which $\langle R_\sigma \rangle^\sigma_{\text{exc}}$ represents the excess reaction contribution. As shown in Appendix A, this term is found to be negligible in the homogeneous-ω region when local mass equilibrium is satisfied. Finally, averaging Eq. (2) and introducing the zero mass-flux interfacial condition yields

$$\varepsilon_\sigma(\mathbf{x})\frac{\partial\langle C_{R\sigma}\rangle^\sigma}{\partial t} = \nabla\cdot[\varepsilon_\sigma(\mathbf{x})\mathbf{D}_{R\sigma}\cdot\nabla\langle C_{R\sigma}\rangle^\sigma] - \varepsilon_\sigma(\mathbf{x})k_\sigma\langle C_{A\sigma}\rangle^\sigma\langle C_{R\sigma}\rangle^\sigma - \varepsilon_\sigma(\mathbf{x})\langle R_\sigma\rangle^\sigma_{\text{exc}}. \tag{32}$$

with $\mathbf{D}_{R\sigma}$ similar to $\mathbf{D}_{A\sigma}$.

4. Generalized one-equation model

In order to develop the one-equation model for diffusion and reaction of the solute A, we must recall the principle of local mass equilibrium, which is based in the assumption that the mass transfer process can be characterized by a single concentration. This principle has been used by Whitaker [35] to obtain a one-equation model in a micropore–macropore system. On the other hand, the principle of local mass equilibrium has been used to describe the diffusion and reaction process in cellular media, in terms of a one-equation model [26,29].

Keeping that idea in mind, the following equilibrium weighted average concentration is proposed for the generalized one-equation model

$$\{C_A\} = \varepsilon_\mu(\mathbf{x})\langle C_{A\mu}\rangle^\mu + \frac{\varepsilon_\sigma(\mathbf{x})}{K^{\mu\sigma}_{\text{eq}}}\langle C_{A\sigma}\rangle^\sigma + \frac{\varepsilon_\gamma(\mathbf{x})}{K^{\mu\gamma}_{\text{eq}}}\langle C_{A\gamma}\rangle^\gamma \tag{33}$$

along with the macroscopic spatial deviation concentrations given by

$$\hat{C}_{A\mu} = \langle C_{A\mu}\rangle^\mu - \{C_A\} \tag{34}$$

$$\hat{C}_{A\sigma} = \langle C_{A\sigma}\rangle^\sigma - K^{\mu\sigma}_{\text{eq}}\{C_A\} \tag{35}$$

$$\hat{C}_{A\gamma} = \langle C_{A\gamma}\rangle^\gamma - K^{\mu\gamma}_{\text{eq}}\{C_A\}. \tag{36}$$

These deviations are zero under local mass equilibrium conditions and are negligible when certain length scale constraints are satisfied. Using the above definitions in the result of adding Eqs. (26), (28) and (29) yields after some manipulations [36]

$$\varepsilon(\mathbf{x})\frac{\partial\{C_A\}}{\partial t} = \nabla\cdot[\mathbf{D}_A(\mathbf{x})\cdot\nabla\{C_A\}] - R(\mathbf{x}) - \underbrace{\frac{\partial\hat{\chi}(\mathbf{x})}{\partial t} + \nabla\cdot\hat{\mathbf{d}} - \hat{R}(\mathbf{x})}_{\text{non-equilibrium terms}} \tag{37}$$

where the following definitions have been introduced

Effective reaction rate term

$$R(\mathbf{x}) = \varepsilon_\sigma(\mathbf{x})k_\sigma K^{\mu\sigma}_{\text{eq}}\{C_A\}\langle C_{R\sigma}\rangle^\sigma + \varepsilon_\mu(\mathbf{x})k_\mu\left(\{C_A\} - \frac{\langle C_{B\mu}\rangle^\mu}{K_\mu}\right) \tag{38}$$

Mixed volume fraction

$$\varepsilon(\mathbf{x}) = \varepsilon_\mu(\mathbf{x}) + \varepsilon_\sigma(\mathbf{x})K^{\mu\sigma}_{\text{eq}} + \varepsilon_\gamma(\mathbf{x})K^{\mu\gamma}_{\text{eq}} \tag{39}$$

Position dependent diffusivity tensor

$$\mathbf{D}_A(\mathbf{x})\cdot\nabla\{C_A\} = (\varepsilon_\mu(\mathbf{x})\boldsymbol{\mathcal{D}}_{A\mu} + \varepsilon_\sigma(\mathbf{x})K^{\mu\sigma}_{\text{eq}}\boldsymbol{\mathcal{D}}_{A\sigma} + \varepsilon_\gamma(\mathbf{x})\boldsymbol{\mathcal{D}}_{A\gamma}K^{\mu\gamma}_{\text{eq}})\nabla\{C_A\} + \sum_{i=2}^{3}\int_{A_{\mu i}}\mathbf{n}_{\mu i} \times\left[\frac{\varepsilon_\mu(\mathbf{x})\boldsymbol{\mathcal{D}}_{A\mu}}{V_\mu}(C_{A\mu} - \langle C_{A\mu}\rangle^\mu) - \frac{\varepsilon_i(\mathbf{x})\boldsymbol{\mathcal{D}}_{Ai}}{V_i}(C_{Ai} - \langle C_{Ai}\rangle^i)\right]\mathrm{d}A \tag{40}$$

In addition, the non-equilibrium terms are given by

Non-equilibrium accumulation

$$\frac{\partial\hat{\chi}(\mathbf{x})}{\partial t} = \sum_{i=1}^{3}\varepsilon_i(\mathbf{x})\frac{\partial\hat{C}_{Ai}}{\partial t}, \tag{41}$$

Non-equilibrium diffusion

$$\hat{\mathbf{d}} = \sum_{i=1}^{3} \varepsilon_i(\mathbf{x}) \boldsymbol{\mathcal{D}}_{Ai} \nabla \hat{C}_{Ai}, \tag{42}$$

Non-equilibrium reaction

$$\hat{R}(\mathbf{x}) = \varepsilon_\sigma(\mathbf{x}) k_\sigma \hat{C}_{A\sigma} \langle C_{R\sigma} \rangle^\sigma + \varepsilon_\mu(\mathbf{x}) k_\mu \hat{C}_{A\mu} + \varepsilon_\sigma(\mathbf{x}) \langle R_\sigma \rangle^\sigma_{\text{exc}}. \tag{43}$$

Let us remark that expressions (39) and (40) have been obtained assuming that $K_{\text{eq}}^{\mu\sigma}$ and $K_{\text{eq}}^{\mu\gamma}$ are constants. In Eqs. (40)–(42) we have used $1 \equiv \mu$; $2 \equiv \sigma$; $3 \equiv \gamma$.

In addition, note that in both homogeneous regions, the following length scale constraints are satisfied

$$\ell_\sigma, \ell_\mu \ll r_0, \quad r_0^2 \ll L_{C1} L_\varepsilon \tag{44}$$

which allow simplifying Eq. (40) as shown later.

Eq. (37) is the generalized mass transfer equation for solute A valid everywhere in the whole system since its derivation does not involve the use of the usual length scale constraints at all. As consequence, Eq. (37) can be used to obtain the corresponding effective medium equations for the homogeneous portions of the system, this is carried out below.

4.1. Homogeneous η-region

This region is only composed by the γ-phase (i.e., $\varepsilon_\gamma(\mathbf{x}) = 1$ and $\varepsilon_\mu(\mathbf{x}) = \varepsilon_\sigma(\mathbf{x}) = 0$). When the averaging volume is small enough, ($\ell_\sigma, \ell_\mu \ll r_0$) [32], Eq. (37) reduces to

$$\frac{\partial \{C_A\}_\eta}{\partial t} = \nabla \cdot [\boldsymbol{\mathcal{D}}_{A\gamma} \nabla \{C_A\}_\eta] \tag{45}$$

where $\{C_A\}_\eta$ represents the concentration field in the η-region.

4.2. Homogeneous ω-region

In this two-phase region, the μ- and σ-phases have volume fractions with negligible spatial variations (i.e., $\varepsilon_\gamma(\mathbf{x}) = 0$; $\varepsilon_\mu(\mathbf{x}) = \varepsilon_{\mu\omega}$ and $\varepsilon_\sigma(\mathbf{x}) = \varepsilon_{\sigma\omega}$). This implies that the characteristic length constraints given in Eq. (44) are satisfied. Under such circumstances, Eq. (37) reduces to

$$\begin{aligned}(\varepsilon_{\mu\omega} + \varepsilon_{\sigma\omega} K_{\text{eq}}^{\mu\sigma}) \frac{\partial \{C_A\}_\omega}{\partial t} = {} & \nabla \cdot [\mathbf{D}_{A\omega} \cdot \nabla \{C_A\}_\omega] - \varepsilon_{\sigma\omega} k_\sigma K_{\text{eq}}^{\mu\sigma} \{C_A\}_\omega \langle C_{R\sigma} \rangle^\sigma_\omega - \varepsilon_{\mu\omega} k_\mu \left(\{C_A\}_\omega - \frac{\langle C_{B\mu} \rangle^\mu_\omega}{K_\mu} \right) \\ & - \varepsilon_{\sigma\omega} k_\sigma \langle \tilde{C}_{A\sigma} \tilde{C}_{R\sigma} \rangle^\sigma_\omega + \nabla \cdot [\varepsilon_{\sigma\omega} \boldsymbol{\mathcal{D}}_{A\sigma} \nabla \hat{C}_{A\sigma} + \varepsilon_{\mu\omega} \boldsymbol{\mathcal{D}}_{A\mu} \nabla \hat{C}_{A\mu}] - \varepsilon_{\mu\omega} k_\mu \hat{C}_{A\mu} \\ & - \varepsilon_{\sigma\omega} k_\sigma \hat{C}_{A\sigma} \langle C_{R\sigma} \rangle^\sigma_\omega - \varepsilon_{\mu\omega} \frac{\partial \hat{C}_{A\mu}}{\partial t} - \varepsilon_{\sigma\omega} \frac{\partial \hat{C}_{A\sigma}}{\partial t}\end{aligned} \tag{46}$$

Here, the diffusivity tensor $\mathbf{D}_{A\omega}$ is given by,

$$\mathbf{D}_{A\omega} \cdot \nabla \{C_A\}_\omega = D_{A\sigma\mu} \nabla \{C_A\}_\omega + \frac{1}{V} \int_{A_{\mu\sigma,\omega}} \mathbf{n}_{\mu\sigma} [\boldsymbol{\mathcal{D}}_{A\mu} \tilde{C}_{A\mu} - \boldsymbol{\mathcal{D}}_{A\sigma} \tilde{C}_{A\sigma}] \, \mathrm{d}A \tag{47}$$

where,

$$D_{A\sigma\mu} = \varepsilon_{\mu\omega} \boldsymbol{\mathcal{D}}_{A\mu} + \varepsilon_{\sigma\omega} K_{\text{eq}}^{\mu\sigma} \boldsymbol{\mathcal{D}}_{A\sigma} \tag{48}$$

and the spatial concentration deviations given by

$$\tilde{C}_{Ai} = C_{Ai} - \langle C_{Ai} \rangle^i_\omega \quad i = \mu, \sigma. \tag{49}$$

In Eq. (46), we have used, $\langle C_{A\mu} \rangle^\mu_\omega \gg \tilde{C}_{A\mu}$ and $\langle C_{A\sigma} \rangle^\sigma_\omega \gg \tilde{C}_{A\sigma}$ which is only valid when the length constraints given by Eq. (44) are satisfied. In order to derive the one-equation model, with the only dependent variable $\{C_A\}_\omega$, the following restrictions are imposed

$$\varepsilon_{\mu\omega} \frac{\partial \hat{C}_{A\mu}}{\partial t} + \varepsilon_{\sigma\omega} \frac{\partial \hat{C}_{A\sigma}}{\partial t} \ll \nabla \cdot [\mathbf{D}_{A\omega} \cdot \nabla \{C_A\}_\omega], \tag{50}$$

$$\varepsilon_{\sigma\omega}\mathcal{D}_{A\sigma}\nabla\hat{C}_{A\sigma}+\varepsilon_{\mu\omega}\mathcal{D}_{A\mu}\nabla\hat{C}_{A\mu}\ll\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega, \tag{51}$$

$$\varepsilon_{\mu\omega}k_\mu\hat{C}_{A\mu}+\varepsilon_{\sigma\omega}k_\sigma\hat{C}_{A\sigma}\langle C_{R\sigma}\rangle^\sigma_\omega\ll\nabla\cdot[\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega]. \tag{52}$$

Note that these restrictions are proposed on the basis that the macroscopic deviation terms are negligible with respect to the diffusive terms in the one-equation model. For conciseness, the length scale constraints allowing the restrictions given in Eqs. (50)–(52) are presented in Appendix A. As consequence Eq. (46) becomes

$$(\varepsilon_{\mu\omega}+\varepsilon_{\sigma\omega}K^{\mu\sigma}_{\rm eq})\frac{\partial\{C_A\}_\omega}{\partial t}=\nabla\cdot[D_{A\sigma\mu}\nabla\{C_A\}_\omega]+\nabla\cdot\left\{\frac{1}{\mathcal{V}}\int_{A_{\mu\sigma,\omega}}\mathbf{n}_{\mu\sigma}[\mathcal{D}_{A\mu}\tilde{C}_{A\mu}-\mathcal{D}_{A\sigma}\tilde{C}_{A\sigma}]\,{\rm d}A\right\}$$
$$-\varepsilon_{\sigma\omega}k_\sigma K^{\mu\sigma}_{\rm eq}\{C_A\}_\omega\langle C_{R\sigma}\rangle^\sigma_\omega-\varepsilon_{\sigma\omega}k_\sigma\langle\tilde{C}_{A\sigma}\tilde{C}_{R\sigma}\rangle^\sigma_\omega-\varepsilon_{\mu\omega}k_\mu\left(\{C_A\}-\frac{\langle C_{B\mu}\rangle^\mu}{K_\mu}\right) \tag{53}$$

On the other hand, the associated closure problem for the concentration deviation variables [29] suggest that

$$\tilde{C}_{Aj}=\mathbf{b}_j\cdot\nabla\{C_A\}_\omega,\quad j=\sigma,\mu \tag{54}$$

$$\tilde{C}_{R\sigma}=\mathbf{b}_{R\sigma}\cdot\nabla\langle C_{R\sigma}\rangle^\sigma_\omega \tag{55}$$

and therefore Eq. (53) takes the form

$$(\varepsilon_{\mu\omega}+\varepsilon_{\sigma\omega}K^{\mu\sigma}_{\rm eq})\frac{\partial\{C_A\}_\omega}{\partial t}=\nabla\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega)-\varepsilon_{\mu\omega}k_\mu\left(\{C_A\}_\omega-\frac{\langle C_{B\mu}\rangle^\mu_\omega}{K_\mu}\right)-\varepsilon_{\sigma\omega}k_\sigma K^{\mu\sigma}_{\rm eq}\langle C_{R\sigma}\rangle^\sigma_\omega\{C_A\}_\omega$$
$$-\varepsilon_{\sigma\omega}k_\sigma\langle\mathbf{b}_{R\sigma}\mathbf{b}_\sigma\rangle^\sigma_\omega:\nabla\nabla\langle C_{R\sigma}\rangle^\sigma_\omega\{C_A\}_\omega \tag{56}$$

where the effective diffusivity tensor for species A in the ω-region, takes the form

$$\mathbf{D}_{A\omega}=D_{A\sigma\mu}\mathbf{I}+\frac{1}{\mathcal{V}}\int_{A_{\mu\sigma,\omega}}\mathbf{n}_{\sigma\mu}(\mathcal{D}_{A\sigma}\mathbf{b}_\sigma-\mathcal{D}_{A\mu}\mathbf{b}_\mu)\,{\rm d}A. \tag{57}$$

Furthermore, if the following length scale constraint is satisfied

$$\frac{\ell_\sigma\ell_\mu}{L^2}\ll1 \tag{58}$$

Then, Eq. (56) finally reduces to the one-equation model for the homogeneous ω-region

$$(\varepsilon_{\mu\omega}+\varepsilon_{\sigma\omega}K^{\mu\sigma}_{\rm eq})\frac{\partial\{C_A\}_\omega}{\partial t}=\nabla\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega)-\langle R\rangle_\omega \tag{59}$$

where

$$\langle R\rangle_\omega=\varepsilon_{\mu\omega}k_\mu\left(\{C_A\}_\omega-\frac{\langle C_{B\mu}\rangle^\mu_\omega}{K_\mu}\right)+\varepsilon_{\sigma\omega}k_\sigma K^{\mu\sigma}_{\rm eq}\langle C_{R\sigma}\rangle^\sigma_\omega\{C_A\}_\omega \tag{60}$$

The components of the effective diffusivity tensor $\mathbf{D}_{A\omega}$, have been previously computed for several configurations [29]. In Eq. (60), $\langle C_{B\mu}\rangle^\mu_\omega$ and $\langle C_{R\sigma}\rangle^\sigma_\omega$ are the solutions of the average equations for species B and R, respectively,

$$\varepsilon_{\mu\omega}\frac{\partial\langle C_{B\mu}\rangle^\mu_\omega}{\partial t}=\nabla\cdot[\varepsilon_{\mu\omega}\mathbf{D}_{B\omega}\cdot\nabla\langle C_{B\mu}\rangle^\mu_\omega]+\varepsilon_{\mu\omega}k_\mu\left(\{C_A\}_\omega-\frac{\langle C_{B\mu}\rangle^\mu_\omega}{K_\mu}\right), \tag{61}$$

$$\varepsilon_{\sigma\omega}\frac{\partial\langle C_{R\sigma}\rangle^\sigma_\omega}{\partial t}=\nabla\cdot[\varepsilon_{\sigma\omega}\mathbf{D}_{R\omega}\cdot\nabla\langle C_{R\sigma}\rangle^\sigma_\omega]-\varepsilon_{\sigma\omega}k_\sigma K^{\mu\sigma}_{\rm eq}\{C_A\}_\omega\langle C_{R\sigma}\rangle^\sigma_\omega \tag{62}$$

which have been obtained from Eqs. (27) and (32) with the use of following restrictions

$$\nabla\cdot[\varepsilon_{\mu\omega}\mathbf{D}_{B\omega}\cdot\nabla\langle C_{B\mu}\rangle^\mu_\omega]\gg\varepsilon_{\mu\omega}k_\mu\hat{C}_{A\mu}, \tag{63}$$

$$\nabla\cdot[\varepsilon_{\sigma\omega}\mathbf{D}_{R\omega}\cdot\nabla\langle C_{R\sigma}\rangle^\sigma_\omega]\gg\varepsilon_{\sigma\omega}k_\sigma\hat{C}_{A\sigma}\langle C_{R\sigma}\rangle^\sigma_\omega. \tag{64}$$

In Eqs. (61) and (62) the effective diffusivity tensors are defined by

$$\mathbf{D}_{B\omega}=\mathcal{D}_{B\mu}\mathbf{I}+\frac{\mathcal{D}_{B\mu}}{V_\mu}\int_{A_{\mu\sigma,\omega}}\mathbf{n}_{\mu\sigma}\mathbf{b}_{B\sigma}\,{\rm d}A, \tag{65}$$

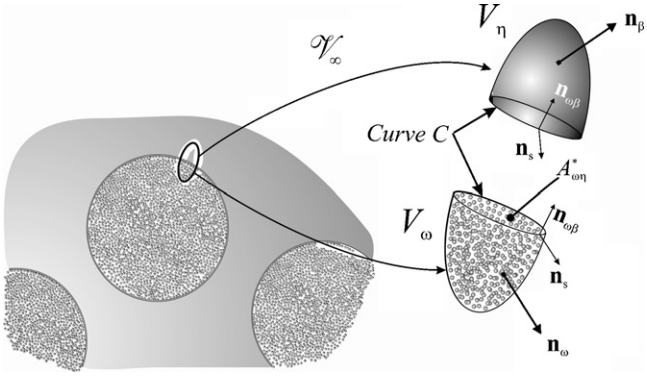

Fig. 3. Large scale averaging volume at the ω–η inter-region that includes the interfacial mass transfer resistance between the γ- and μ-phases.

$$\mathbf{D}_{R\omega} = \mathcal{D}_{R\sigma}\mathbf{I} + \frac{\mathcal{D}_{R\sigma}}{V_\sigma}\int_{A_{\mu\sigma,\omega}} \mathbf{n}_{\sigma\mu}\mathbf{b}_{R\sigma}\,\mathrm{d}A. \tag{66}$$

Let us note that Eq. (59) is only valid whenever the local mass equilibrium assumption is satisfied. According to the analysis performed in Appendix A, the length scale constraints leading to this assumption are more likely to be satisfied in the homogeneous portions of the ω-region, but they actually fail in the ω–η inter-region. This is the reason why it is necessary to derive the corresponding jump boundary conditions that match Eqs. (45) and (60) at the dividing surface. This is carried out in following sections.

5. Jump boundary condition

In order to derive the jump boundary conditions we first define a large-scale averaging volume $\mathcal{V}_\infty$. It is located at the ω–η inter-region (Fig. 3) and contains portions of both homogeneous regions, such as

$$\mathcal{V}_\infty = V_\omega + V_\eta. \tag{67}$$

On the other hand, the area that defines this volume is expressed as

$$\mathcal{A}_\infty = A_\omega + A_\eta \tag{68}$$

where A_ω and A_η denote the external surface areas of the volumes V_ω and V_η, respectively. The integration of Eq. (37) over $\mathcal{V}_\infty$ and the use of the divergence theorem yield

$$\begin{aligned}
&\int_{V_\omega}\left(\varepsilon(\mathbf{x})\frac{\partial\{C_A\}}{\partial t} + \frac{\partial\hat{\chi}(\mathbf{x})}{\partial t}\right)\mathrm{d}V + \int_{V_\eta}\left(\varepsilon(\mathbf{x})\frac{\partial\{C_A\}}{\partial t} + \frac{\partial\hat{\chi}(\mathbf{x})}{\partial t}\right)\mathrm{d}V \\
&\quad= \int_{A_\omega}\mathbf{n}_\omega\cdot[\mathbf{D}_A(\mathbf{x})\cdot\nabla\{C_A\} + \hat{\mathbf{d}}]\,\mathrm{d}A + \int_{A_\eta}\mathbf{n}_\eta\cdot[\mathbf{D}_A(\mathbf{x})\cdot\nabla\{C_A\} + \hat{\mathbf{d}}]\,\mathrm{d}A \\
&\qquad- \int_{V_\omega}[R(\mathbf{x}) + \hat{R}(\mathbf{x})]\,\mathrm{d}V - \int_{V_\eta}[R(\mathbf{x}) + \hat{R}(\mathbf{x})]\,\mathrm{d}V
\end{aligned} \tag{69}$$

For convenience, the equilibrium and non-equilibrium accumulation, diffusion and reaction terms were combined accordingly. Similarly, integrating Eqs. (45) and (59) over the volumes V_η and V_ω, respectively leads to

$$\int_{V_\eta}\frac{\partial\{C_A\}_\eta}{\partial t}\,\mathrm{d}V = \int_{A_\eta}\mathbf{n}_\eta\cdot(\mathcal{D}_{A\gamma}\nabla\{C_A\}_\eta)\,\mathrm{d}A + \int_{A^*_{\eta\omega}}\mathbf{n}_{\eta\omega}\cdot[\mathcal{D}_{A\gamma}\nabla\{C_A\}_\eta]\,\mathrm{d}A \tag{70}$$

$$\int_{V_\omega}(\varepsilon_{\mu\omega} + \varepsilon_{\sigma\omega}K^{\mu\sigma}_{\mathrm{eq}})\frac{\partial\{C_A\}_\omega}{\partial t}\,\mathrm{d}V = \int_{A_\omega}\mathbf{n}_\omega\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega)\,\mathrm{d}A + \int_{A^*_{\eta\omega}}\mathbf{n}_{\omega\eta}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega)\,\mathrm{d}A - \int_{V_\omega}\langle R\rangle_\omega\,\mathrm{d}V \tag{71}$$

In the above equations, $A^*_{\eta\omega}$ represents the portion of dividing surface $A_{\omega\eta}$ contained within $\mathcal{V}_\infty$, where the macroscopic jump boundary condition is imposed. The location of this surface can be arbitrarily chosen as the position $\mathbf{x}=\mathbf{x}_0$ where the γ-phase volume fraction is equal to the mean of the corresponding values in the homogeneous regions. The dividing surface must include the effect of the interfacial mass transfer resistance between the γ- and μ-phases. Subtracting Eqs. (70) and (71)

from Eq. (69) leads to

$$\int_{V_\omega}\left(\varepsilon(\mathbf{x})\frac{\partial\{C_A\}}{\partial t}+\frac{\partial\hat{\chi}(\mathbf{x})}{\partial t}-(\varepsilon_{\mu\omega}+\varepsilon_{\sigma\omega}K_{\mathrm{eq}}^{\mu\sigma})\frac{\partial\{C_A\}_\omega}{\partial t}\right)\mathrm{d}V+\int_{V_\eta}\left(\varepsilon(\mathbf{x})\frac{\partial\{C_A\}}{\partial t}+\frac{\partial\hat{\chi}(\mathbf{x})}{\partial t}-\frac{\partial\{C_A\}_\eta}{\partial t}\right)\mathrm{d}V$$
$$=\int_{A_\omega}\mathbf{n}_\omega\cdot[\mathbf{D}_A(\mathbf{x})\cdot\nabla\{C_A\}+\hat{\mathbf{d}}-\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega]\,\mathrm{d}A+\int_{A_\eta}\mathbf{n}_\eta\cdot[\mathbf{D}_A(\mathbf{x})\cdot\nabla\{C_A\}+\hat{\mathbf{d}}-\mathcal{D}_{A\gamma}\nabla\{C_A\}_\eta]\,\mathrm{d}A$$
$$-\int_{A^*_{\eta\omega}}\mathbf{n}_{\omega\eta}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega-\mathcal{D}_{A\gamma}\nabla\{C_A\}_\eta)\,\mathrm{d}A-\int_{V_\omega}(R(\mathbf{x})+\hat{R}-\langle R\rangle_\omega)\,\mathrm{d}V-\int_{V_\eta}(R(\mathbf{x})+\hat{R})\,\mathrm{d}V \tag{72}$$

whose form suggests introducing the following excess terms:

Excess of surface accumulation

$$\int_{A^*_{\omega\eta}}\varepsilon_s\frac{\partial\{C_A\}_s}{\partial t}\,\mathrm{d}A=\int_{V_\omega}\left(\varepsilon(\mathbf{x})\frac{\partial\{C_A\}}{\partial t}+\frac{\partial\hat{\chi}(\mathbf{x})}{\partial t}-(\varepsilon_{\mu\omega}+\varepsilon_{\sigma\omega}K_{\mathrm{eq}}^{\mu\sigma})\frac{\partial\{C_A\}_\omega}{\partial t}\right)\mathrm{d}V$$
$$+\int_{V_\eta}\left(\varepsilon(\mathbf{x})\frac{\partial\{C_A\}}{\partial t}+\frac{\partial\hat{\chi}(\mathbf{x})}{\partial t}-\frac{\partial\{C_A\}_\eta}{\partial t}\right)\mathrm{d}V \tag{73}$$

Excess of surface conductive transport

$$\oint_C\mathbf{n}_s\cdot(\varepsilon_s\mathbf{D}_s\cdot\nabla_s\{C_A\}_s)\,\mathrm{d}\sigma=\int_{A_\omega}\mathbf{n}_\omega\cdot[\mathbf{D}_A(\mathbf{x})\cdot\nabla\{C_A\}+\hat{\mathbf{d}}-\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega]\,\mathrm{d}A+\int_{A_\eta}\mathbf{n}_\eta\cdot[\mathbf{D}_A(\mathbf{x})\cdot\nabla\{C_A\}$$
$$+\hat{\mathbf{d}}-\mathcal{D}_{A\gamma}\nabla\{C_A\}_\eta]\,\mathrm{d}A \tag{74}$$

Excess of surface reaction rate

$$\int_{A^*_{\omega\eta}}\langle R\rangle_s\,\mathrm{d}A=\int_{V_\omega}(R(\mathbf{x})+\hat{R}(\mathbf{x})-\langle R\rangle_\omega)\,\mathrm{d}V+\int_{V_\eta}(R(\mathbf{x})+\hat{R}(\mathbf{x}))\,\mathrm{d}V \tag{75}$$

In Eq. (74) $\mathbf{n}_s$ is the outwardly unit normal vector to the *Curve C* (Fig. 3), ε_s is the excess surface volume fraction, $\mathbf{D}_s$ represents the excess surface diffusivity tensor, and ∇_s is the superficial nabla operator defined by $\nabla_s=(\mathbf{I}-\mathbf{n}_{\eta\omega}\mathbf{n}_{\eta\omega})\cdot\nabla$. The use of Eqs. (73)–(75) into Eq. (72) yields, after making use of the surface divergence theorem [39]

$$\underbrace{\varepsilon_s\frac{\partial\{C_A\}_s}{\partial t}}_{\text{surface accumulation}}-\underbrace{\nabla_s\cdot(\varepsilon_s\mathbf{D}_s\cdot\nabla_s\{C_A\}_s)}_{\text{surface transport excess}}=\underbrace{-\mathbf{n}_{\omega\eta}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega-\mathcal{D}_{A\gamma}\nabla\{C_A\}_\eta)}_{\text{surface diffusive exchange}}-\underbrace{\langle R\rangle_s}_{\text{excess reaction}}\quad\text{at } A_{\eta\omega} \tag{76}$$

In many practical situations, the excess of surface transport and accumulation are negligible with respect to the surface diffusive exchange. Related to this assumption there are certain length scale constraints that must be satisfied. This will be further discussed elsewhere. Therefore, Eq. (76) can be reduced to

$$-\mathbf{n}_{\omega\eta}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega-\mathcal{D}_{A\gamma}\nabla\{C_A\}_\eta)=\langle R\rangle_s\quad\text{at } A_{\eta\omega} \tag{77}$$

Furthermore, when the excess of surface reaction is negligible compared to the surface diffusive transport, Eq. (77) reduces to the flux continuity condition

$$-\mathbf{n}_{\eta\omega}\cdot\mathcal{D}_{A\gamma}\nabla\{C_A\}_\eta=-\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega)\,\text{at } A_{\eta\omega}. \tag{78}$$

When this is not the case, one should follow the works of Wood et al. [33] and Valdés-Parada et al. [31] in order to express the excess of reaction rate as a function of properties measurable in the homogeneous regions. Moreover, from Section 5 in Valdés-Parada et al. [31], it can be stated that Eq. (78) is a valid assumption whenever the following inequality is satisfied

$$\frac{1}{\mathcal{V}}\int_{V_\mu}\langle R\rangle_\omega\,\mathrm{d}V\gg\frac{1}{\mathcal{V}}\int_{A^*_{\omega\eta}}\langle R\rangle_s\,\mathrm{d}A. \tag{79}$$

At this stage, an additional boundary condition is still necessary in order to completely define the problem at the inter-region. Eq. (78) suggests imposing continuity of the weighted average concentration at the dividing surface, $\{C_A\}_\eta\big|_{\mathbf{x}_0}=\{C_A\}_\omega\big|_{\mathbf{x}_0}$. As

consequence, this does not account for the mass transfer resistance between μ and γ phases at $\mathbf{x}=\mathbf{x}_0$. This is the reason why, we here follow Wood et al. [33] to express the mass-flux continuity condition as

$$-\mathbf{n}_{\eta\omega}\cdot\mathcal{D}_{A\gamma}\nabla\{C_A\}_\eta=-\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega)=\mathbf{n}_{\eta\omega}\cdot\langle\mathbf{N}_A\rangle_s \tag{80}$$

where $\langle\mathbf{N}_A\rangle_s$ represents the excess of surface diffusion flux defined by

$$\mathbf{n}_{\eta\omega}\cdot\langle\mathbf{N}_A\rangle_s=\frac{1}{A_{\eta\omega}(\mathbf{x}_0)}\int_{A_{\eta\omega}(\mathbf{x}_0)}\mathbf{n}_s\cdot\mathbf{N}_{As}\,\mathrm{d}A=\langle\mathbf{n}_s\cdot\mathbf{N}_{As}\rangle_{\eta\omega}. \tag{81}$$

In Eq. (81) $A_{\eta\omega}(\mathbf{x}_0)$ is the area of the averaging volume when the centroid is located at the dividing surface [33]. In general, this area is composed of two contributions, namely the $\sigma\mu$-interface and the $\gamma\mu$-interface. Using, Eqs. (8) and (9), (12) and (13) in Eq. (81) yields

$$-\mathbf{n}_{\eta\omega}\cdot\mathcal{D}_{A\gamma}\nabla\{C_A\}_\eta=-\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega)=\langle P_{\sigma\mu}(C_{A\sigma}-K_{\mathrm{eq}}^{\mu\sigma}C_{A\mu})\rangle_{\eta\omega}^{\sigma\mu}+\langle P_{\gamma\mu}(C_{A\gamma}-K_{\mathrm{eq}}^{\mu\gamma}C_{A\mu})\rangle_{\eta\omega}^{\gamma\mu} \tag{82}$$

The closed form of Eq. (82) is derived in the next section. It will be shown that the closed concentration jump condition involves effective coefficients that can be computed from the solution of the associated closure problems.

6. Closed jump boundary condition

In order to have a useful form of the jump condition, the point concentration values involved in RHS of Eq. (82) must be expressed in terms of the weighted average concentrations $\{C_A\}_\eta$ and $\{C_A\}_\omega$. For this, let us first introduce Gray's [40] spatial decomposition

$$C_{A\alpha}=\langle C_{A\alpha}\rangle^\alpha+\tilde{C}_{A\alpha},\quad \alpha=\sigma,\mu,\gamma \tag{83}$$

into Eq. (82) to get

$$\begin{aligned}-\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega)=&\langle P_{\sigma\mu}(\tilde{C}_{A\sigma}-K_{\mathrm{eq}}^{\mu\sigma}\tilde{C}_{A\mu})\rangle_{\eta\omega}^{\sigma\mu}+\langle P_{\gamma\mu}(\tilde{C}_{A\gamma}-K_{\mathrm{eq}}^{\mu\gamma}\tilde{C}_{A\mu})\rangle_{\eta\omega}^{\gamma\mu}+\langle P_{\sigma\mu}(\langle C_{A\sigma}\rangle^\sigma-K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle^\mu)\rangle_{\eta\omega}^{\sigma\mu}\\&+\langle P_{\gamma\mu}(\langle C_{A\gamma}\rangle^\gamma-K_{\mathrm{eq}}^{\mu\gamma}\langle C_{A\mu}\rangle^\mu)\rangle_{\eta\omega}^{\gamma\mu}.\end{aligned} \tag{84}$$

It is clear that the terms in the RHS of the above equation must be expressed in terms of the weighted average concentrations $\{C_A\}_\omega$ and $\{C_A\}_\eta$. The needed expressions result from the closure problem derived in Appendix B. Actually, the intrinsic average concentration $\langle C_{A\gamma}\rangle^\gamma$ can easily be written in terms of $\{C_A\}_\eta$ while $\langle C_{A\sigma}\rangle^\sigma$ and $\langle C_{A\mu}\rangle^\mu$ are expressed in terms of $\{C_A\}_\omega$ by introducing Eqs. (C.4) and (C.5) into Eq. (84), leading to

$$-\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega)=\langle P_{\sigma\mu}(\tilde{C}_{A\sigma}-K_{\mathrm{eq}}^{\mu\sigma}\tilde{C}_{A\mu})\rangle_{\eta\omega}^{\sigma\mu}+\langle P_{\gamma\mu}(\tilde{C}_{A\gamma}-K_{\mathrm{eq}}^{\mu\gamma}\tilde{C}_{A\mu})\rangle_{\eta\omega}^{\gamma\mu}+\langle P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma}\rangle_{\eta\omega}^{\gamma\mu}(\{C_A\}_\eta|_{\mathbf{x}_0}-\{C_A\}_\omega|_{\mathbf{x}_0}). \tag{85}$$

Here, it has been assumed that the following restraint is satisfied at the dividing surface

$$\{C_A\}_\omega|_{\mathbf{x}_0}\gg\left(\langle C_{A\mu}\rangle^\mu|_{\mathbf{x}_0}-\frac{1}{K_{\mathrm{eq}}^{\mu\sigma}}\langle C_{A\sigma}\rangle^\sigma|_{\mathbf{x}_0}\right). \tag{86}$$

The derivation of the constraints associated to the above inequality is given in Appendix C. On the other hand, the deviations $\tilde{C}_{A\alpha}(\alpha=\sigma,\mu,\gamma)$ in Eq. (85) are written in terms of the weighted average concentrations according to the boundary-value problem presented in Appendix B,

$$\tilde{C}_{A\alpha}=s_\alpha^\omega\{C_A\}_\omega|_{\mathbf{x}_0}+s_\alpha^\eta\{C_A\}_\eta|_{\mathbf{x}_0}+\mathbf{b}_\alpha^\omega\cdot\nabla\{C_A\}_\omega|_{\mathbf{x}_0}+\mathbf{b}_\alpha^\eta\cdot\nabla\{C_A\}_\eta|_{\mathbf{x}_0} \tag{87}$$

where s_α^λ and $\mathbf{b}_\alpha^\lambda$ ($\alpha=\sigma,\mu,\gamma$; $\lambda=\omega,\eta$) are the closure variables. These latter are the solutions of the closure problems stated in the same appendix. Introducing Eq. (87) into Eq. (85) yields

$$\begin{aligned}-\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega)=&\langle P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma}\rangle_{\eta\omega}^{\gamma\mu}(\{C_A\}_\eta|_{\mathbf{x}_0}-\{C_A\}_\omega|_{\mathbf{x}_0})+(\langle P_{\sigma\mu}(s_\sigma^\omega-K_{\mathrm{eq}}^{\mu\sigma}s_\mu^\omega)\rangle_{\eta\omega}^{\sigma\mu}+\langle P_{\gamma\mu}(s_\gamma^\omega-K_{\mathrm{eq}}^{\mu\gamma}s_\mu^\omega)\rangle_{\eta\omega}^{\gamma\mu})\{C_A\}_\omega|_{\mathbf{x}_0}\\&+(\langle P_{\sigma\mu}(s_\sigma^\eta-K_{\mathrm{eq}}^{\mu\sigma}s_\mu^\eta)\rangle_{\eta\omega}^{\sigma\mu}+\langle P_{\gamma\mu}(s_\gamma^\eta-K_{\mathrm{eq}}^{\mu\gamma}s_\mu^\eta)\rangle_{\eta\omega}^{\gamma\mu})\{C_A\}_\eta|_{\mathbf{x}_0}.\end{aligned} \tag{88}$$

In the above equation, the terms containing $\nabla\{C_A\}_\omega|_{\mathbf{x}_0}$ and $\nabla\{C_A\}_\eta|_{\mathbf{x}_0}$ were neglected on the basis of order of magnitude estimates (Appendix D). In the same appendix, it is also shown that Eq. (88) can be expressed more conveniently as

$$-\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega|_{\mathbf{x}_0})=P_{\mathrm{eff}}^\eta(\{C_A\}_\eta|_{\mathbf{x}_0}-K_{\mathrm{eff}}^{\eta\omega}\{C_A\}_\omega|_{\mathbf{x}_0})\quad\text{at } A_{\eta\omega} \tag{89}$$

where P^{η}_{eff} represents the effective permeability in the η-region, while $K^{\eta\omega}_{\text{eff}}$ is the effective equilibrium coefficient at the inter-region. Indeed, under thermodynamic equilibrium conditions, $K^{\eta\omega}_{\text{eff}} = 1$. As shown in Appendix D, both P^{η}_{eff} and $K^{\eta\omega}_{\text{eff}}$ are functions of closure variables s^{λ}_{α} ($\alpha = \sigma, \mu, \gamma; \lambda = \omega, \eta$). The boundary value problems for s^{λ}_{α} can be obtained from Eqs. (B.36)–(B.55) in a unit cell representing the inter-region (Appendix B). The structure of these problems are similar to the one previously solved by Nozad et al. [41] to compute the effective conductivity for heat transfer in the bulk of a two-phase medium. Methodologies for the solution of this type of problems have been presented previously [28].

Finally, the closed set of equations describing the macroscopic mass transport of species A in this three-phase system, is given by

Differential equations

$$\frac{\partial\{C_A\}_{\eta}}{\partial t} = \nabla\cdot[\mathcal{D}_{A\gamma}\nabla\{C_A\}_{\eta}] \quad \text{in the } \eta\text{-region} \tag{90}$$

$$(\varepsilon_{\mu\omega} + \varepsilon_{\sigma\omega}K^{\mu\sigma}_{\text{eq}})\frac{\partial\{C_A\}_{\omega}}{\partial t} = \nabla\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_{\omega}) - \langle R\rangle_{\omega} \quad \text{in the } \omega\text{-region} \tag{91}$$

Boundary conditions

$$-\mathbf{n}_{\eta\omega}\cdot\mathcal{D}_{A\gamma}\nabla\{C_A\}_{\eta}|_{\mathbf{x}_0} = -\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_{\omega}|_{\mathbf{x}_0}) \quad \text{at } A_{\eta\omega} \tag{92}$$

$$-\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_{\omega}|_{\mathbf{x}_0}) = P^{\eta}_{\text{eff}}(\{C_A\}_{\eta}|_{\mathbf{x}_0} - K^{\eta\omega}_{\text{eff}}\{C_A\}_{\omega}|_{\mathbf{x}_0}) \quad \text{at } A_{\eta\omega}. \tag{93}$$

7. Conclusions

In this paper the average equations governing the separation of solute A in a three-phase system have been derived using the volume averaging method. First, a generalized one-equation model (Eq. (37)) was derived in order to describe the solute mass transfer in both homogeneous regions and in the inter-region. Conservation equations in the homogeneous continuous and dispersed regions were obtained from the generalized one-equation model assuming local mass equilibrium in the ω-region. The volume average concentration and effective parameters have been precisely defined in terms of local quantities. Order of magnitude analyses have been performed to determine the length scale constraints associated to the macroscopic model.

Then, in order to fully describe the solute transport at the dividing surface, a concentration jump boundary condition was derived following the general methodology recently proposed by Valdés-Parada et al. [31]. Associated closure problems for the determination of the effective jump coefficients were obtained. One of the main features of the results is that the jump is in the concentration and not necessarily in the diffusive flux. Indeed, when the surface transport and the excess of chemical reaction are negligible the continuity of the concentration flux is obtained.

The concentration jump condition contains effective transport coefficients which are expressed in terms of average concentrations and closure variables. These latter are obtained by solving the associated boundary-value problems presented in Appendix B. It is worth mentioning that, in the statement of the closure problem, some length scale constraints were imposed as consequence of assuming local mass equilibrium. However, overly severe length scale constraints were avoided in the derivation of the jump condition by proposing a combination of equilibrium and non-equilibrium terms in the definitions of the excess properties.

Finally, this study enables a better understanding of the assumptions and validity of the equations modeling mass diffusion and reaction in three-phase systems. The influence of the microstructure in the jump coefficients can be assessed by solving the closure problems within representative unit cells of the inter-region. In subsequent papers, the analysis will include convective effects in the γ-phase. This will allow proposing a more realistic model for separation in double emulsion systems.

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Appendix A. Local equilibrium constraints in the homogeneous ω-region

In this section, the length scale constraints under which the assumption of local mass equilibrium is valid in the homogeneous ω-region are developed. The one-equation model will be valid if the restrictions given by Eqs. (50)–(52) are satisfied. In order to obtain a more useful form of these restrictions, we follow the procedure developed by Whitaker [35] for local thermal equilibrium.

Locating the centroid of the averaging volume ($\mathbf{x}$) in the homogeneous ω-region allows simplifying Eqs. (33)–(35) to

$$\{C_A\}_{\omega} = \varepsilon_{\mu\omega}\langle C_{A\mu}\rangle^{\mu}_{\omega} + \frac{\varepsilon_{\sigma\omega}}{K^{\mu\sigma}_{\text{eq}}}\langle C_{A\sigma}\rangle^{\sigma}_{\omega} \tag{A.1}$$

$$\hat{C}_{A\mu\omega} = \langle C_{A\mu}\rangle^{\mu}_{\omega} - \{C_A\}_{\omega} \tag{A.2}$$

$$\hat{C}_{A\sigma\omega} = \langle C_{A\sigma}\rangle^{\sigma}_{\omega} - K^{\mu\sigma}_{\mathrm{eq}}\{C_A\}_{\omega} \tag{A.3}$$

Substituting Eq. (A.1) in Eqs. (A.2) and (A.3) gives

$$\hat{C}_{A\mu\omega} = \frac{\varepsilon_{\sigma\omega}}{K^{\mu\sigma}_{\mathrm{eq}}}(K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega}) \tag{A.4}$$

$$\hat{C}_{A\sigma\omega} = -\varepsilon_{\mu\omega}(K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega}) \tag{A.5}$$

which can be used to write the intrinsic averages in the μ- and σ-phases in terms of the difference $K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega}$ and the weighted average concentration $\{C_A\}_{\omega}$ as

$$\langle C_{A\mu}\rangle^{\mu}_{\omega} = \frac{\varepsilon_{\sigma\omega}}{K^{\mu\sigma}_{\mathrm{eq}}}(K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega}) + \{C_A\}_{\omega} \tag{A.6}$$

$$\langle C_{A\sigma}\rangle^{\sigma}_{\omega} = K^{\mu\sigma}_{\mathrm{eq}}\{C_A\}_{\omega} - \varepsilon_{\mu\omega}(K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega}) \tag{A.7}$$

Using Eqs. (A.4) and (A.5), the restrictions for local-mass equilibrium in the homogeneous ω-region can written as follows

$$\frac{\varepsilon_{\mu\omega}\varepsilon_{\sigma\omega}}{K^{\mu\sigma}_{\mathrm{eq}}}(1 - K^{\mu\sigma}_{\mathrm{eq}})\frac{\partial(K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega})}{\partial t} \ll \nabla\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_{\omega}), \tag{A.8}$$

$$\frac{\varepsilon_{\mu\omega}\varepsilon_{\sigma\omega}}{K^{\mu\sigma}_{\mathrm{eq}}}(\boldsymbol{\mathcal{D}}_{A\mu} - K^{\mu\sigma}_{\mathrm{eq}}\boldsymbol{\mathcal{D}}_{A\sigma})\nabla(K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega}) \ll \mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_{\omega}, \tag{A.9}$$

$$(k_{\mu} - k_{\sigma}K^{\mu\sigma}_{\mathrm{eq}}\langle C_{R\sigma}\rangle^{\sigma}_{\omega})\frac{\varepsilon_{\sigma\omega}\varepsilon_{\mu\omega}}{K^{\mu\sigma}_{\mathrm{eq}}}(K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega}) \ll \nabla\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_{\omega}). \tag{A.10}$$

which, using order of magnitude estimates, become

$$\frac{L_C L_{C1}}{\mathrm{D}_{A\omega}t^*}\frac{\varepsilon_{\mu\omega}\varepsilon_{\sigma\omega}}{K^{\mu\sigma}_{\mathrm{eq}}}(1 - K^{\mu\sigma}_{\mathrm{eq}})\frac{(K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega})}{\{C_A\}_{\omega}} \ll 1, \tag{A.11}$$

$$\frac{\varepsilon_{\mu\omega}\varepsilon_{\sigma\omega}}{K^{\mu\sigma}_{\mathrm{eq}}}\frac{(\boldsymbol{\mathcal{D}}_{A\mu} - K^{\mu\sigma}_{\mathrm{eq}}\boldsymbol{\mathcal{D}}_{A\sigma})}{\mathrm{D}_{A\omega}}\frac{(K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega})}{\{C_A\}_{\omega}} \ll 1, \tag{A.12}$$

$$\frac{L_C L_{C1}}{\mathrm{D}_{A\omega}}(k_{\mu} - k_{\sigma}K^{\mu\sigma}_{\mathrm{eq}}\langle C_{R\sigma}\rangle^{\sigma}_{\omega})\frac{\varepsilon_{\sigma\omega}\varepsilon_{\mu\omega}}{K^{\mu\sigma}_{\mathrm{eq}}}\frac{(K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega})}{\{C_A\}_{\omega}} \ll 1. \tag{A.13}$$

In order to estimate $(K^{\mu\sigma}_{\mathrm{eq}}\langle C_{A\mu}\rangle^{\mu}_{\omega} - \langle C_{A\sigma}\rangle^{\sigma}_{\omega})/\{C_A\}_{\omega}$, let us express the spatially-smoothed equations for the μ- and σ-phases, in the homogeneous ω-region, as

$$\varepsilon_{\mu\omega}\frac{\partial\langle C_{A\mu}\rangle^{\mu}_{\omega}}{\partial t} = \nabla\cdot\left(\varepsilon_{\mu\omega}\boldsymbol{\mathcal{D}}_{A\mu}\nabla\langle C_{A\mu}\rangle^{\mu}_{\omega} + \frac{\boldsymbol{\mathcal{D}}_{A\mu}}{\boldsymbol{\mathcal{V}}}\int_{A_{\mu\sigma,\omega}}\mathbf{n}_{\mu\sigma}\tilde{C}_{A\mu}\,\mathrm{d}A\right) + \frac{1}{\boldsymbol{\mathcal{V}}}\int_{A_{\mu\sigma,\omega}}\mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu}\,\mathrm{d}A - \varepsilon_{\mu\omega}k_{\mu}\times\left(\langle C_{A\mu}\rangle^{\mu}_{\omega} - \frac{\langle C_{B\mu}\rangle^{\mu}_{\omega}}{K_{\mu}}\right) \tag{A.14}$$

$$\varepsilon_{\sigma\omega}\frac{\partial\langle C_{A\sigma}\rangle^{\sigma}_{\omega}}{\partial t} = \nabla\cdot\left[\varepsilon_{\sigma\omega}\boldsymbol{\mathcal{D}}_{A\sigma}\nabla\langle C_{A\sigma}\rangle^{\sigma}_{\omega} + \frac{\boldsymbol{\mathcal{D}}_{A\sigma}}{\boldsymbol{\mathcal{V}}}\int_{A_{\sigma\mu,\omega}}\mathbf{n}_{\sigma\mu}\tilde{C}_{A\sigma}\,\mathrm{d}A\right] + \frac{1}{\boldsymbol{\mathcal{V}}}\int_{A_{\sigma\mu,\omega}}\mathbf{n}_{\sigma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\sigma}\nabla C_{A\sigma}\,\mathrm{d}A - \varepsilon_{\sigma\omega}k_{\sigma}\langle C_{A\sigma}\rangle^{\sigma}_{\omega}\langle C_{R\sigma}\rangle^{\sigma}_{\omega} - \varepsilon_{\sigma\omega}k_{\sigma}\langle\tilde{C}_{A\sigma}\tilde{C}_{R\sigma}\rangle^{\sigma}_{\omega} \tag{A.15}$$

In addition, from the closure problems, presented in Ref. [29], we have

$$\tilde{C}_{A\sigma} = \mathbf{b}_{\sigma}\cdot\nabla\{C_A\}_{\omega};\ \tilde{C}_{A\mu} = \mathbf{b}_{\mu}\cdot\nabla\{C_A\}_{\omega};\ \tilde{C}_{R\sigma} = \mathbf{b}_{R\sigma}\cdot\nabla\langle C_{R\sigma}\rangle^{\sigma} \tag{A.16}$$

which allow writing Eqs. (A.14) and (A.15) only in terms of averaged quantities

$$\frac{\partial\langle C_{A\mu}\rangle_\omega^\mu}{\partial t} = \nabla\cdot(\boldsymbol{\mathcal{D}}_{A\mu}\nabla\langle C_{A\mu}\rangle_\omega^\mu) + \varepsilon_{\mu\omega}^{-1}\nabla\varepsilon_{\mu\omega}\cdot(\boldsymbol{\mathcal{D}}_{A\mu}\nabla\langle C_{A\mu}\rangle_\omega^\mu) + \varepsilon_{\mu\omega}^{-1}\nabla\cdot\left(\frac{\boldsymbol{\mathcal{D}}_{A\mu}}{\mathcal{V}}\left[\int_{A_{\mu\sigma,\omega}}\mathbf{n}_{\mu\sigma}\mathbf{b}_\mu\,\mathrm{d}A\right]\cdot\nabla\{C_A\}_\omega\right)$$
$$+\frac{a_{v\omega}h_\omega}{\varepsilon_{\mu\omega}}(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma) - k_\mu\left(\langle C_{A\mu}\rangle_\omega^\mu - \frac{\langle C_{B\mu}\rangle_\omega^\mu}{K_\mu}\right) \tag{A.17}$$

$$\frac{\partial\langle C_{A\sigma}\rangle_\omega^\sigma}{\partial t} = \nabla\cdot\left[\boldsymbol{\mathcal{D}}_{A\sigma}\nabla\langle C_{A\sigma}\rangle_\omega^\sigma\right] + \varepsilon_{\sigma\omega}^{-1}\nabla\varepsilon_{\sigma\omega}\cdot\left[\boldsymbol{\mathcal{D}}_{A\sigma}\nabla\langle C_{A\sigma}\rangle_\omega^\sigma\right] + \varepsilon_{\sigma\omega}^{-1}\nabla\cdot\left[\frac{\boldsymbol{\mathcal{D}}_{A\sigma}}{\mathcal{V}}\left[\int_{A_{\sigma\mu,\omega}}\mathbf{n}_{\sigma\mu}\mathbf{b}_\sigma\mathrm{d}A\right]\cdot\nabla\{C_A\}_\omega\right]$$
$$-\frac{a_{v\omega}h_\omega}{\varepsilon_{\sigma\omega}}(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma) - k_\sigma\langle C_{A\sigma}\rangle_\omega^\sigma\langle C_{R\sigma}\rangle_\omega^\sigma - k_\sigma\langle\mathbf{b}_\sigma\mathbf{b}_{R\sigma}\rangle_\omega^\sigma : \nabla\{C_A\}_\omega\nabla\langle C_{R\sigma}\rangle^\sigma \tag{A.18}$$

where, following Quintard and Whitaker [38], we have used

$$\frac{1}{\mathcal{V}}\int_{A_{\mu\sigma,\omega}}\mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla C_{A\mu}\,\mathrm{d}A = a_{v\omega}h_\omega(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma) \tag{A.19}$$

and $a_{v\omega}h_\omega$ is a volumetric film mass transfer coefficient. Substituting Eqs. (A.6) and (A.7) in Eqs. (A.17) and (A.18), respectively give

$$\varepsilon_{\sigma\omega}\frac{\partial(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)}{\partial t} + K_{\mathrm{eq}}^{\mu\sigma}\frac{\partial\{C_A\}_\omega}{\partial t}$$
$$= \nabla\cdot(\boldsymbol{\mathcal{D}}_{A\mu}\varepsilon_{\sigma\omega}\nabla(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)) + \nabla\cdot K_{\mathrm{eq}}^{\mu\sigma}\left[\boldsymbol{\mathcal{D}}_{A\mu}\mathbf{I} + \frac{\boldsymbol{\mathcal{D}}_{A\mu}}{V_\mu}\int_{A_{\mu\sigma,\omega}}\mathbf{n}_{\mu\sigma}\mathbf{b}_\mu\,\mathrm{d}A\right]\cdot\nabla\{C_A\}_\omega$$
$$+[\varepsilon_{\mu\omega}^{-1}K_{\mathrm{eq}}^{\mu\sigma}a_{v\omega}h_\omega - \varepsilon_{\sigma\omega}k_\mu](K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma) - k_\mu K_{\mathrm{eq}}^{\mu\sigma}\{C_A\}_\omega + K_{\mathrm{eq}}^{\mu\sigma}k_\mu\frac{\langle C_{B\mu}\rangle_\omega^\mu}{K_\mu} \tag{A.20}$$

$$K_{\mathrm{eq}}^{\mu\sigma}\frac{\partial\{C_A\}_\omega}{\partial t} - \varepsilon_{\mu\omega}\frac{\partial(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)}{\partial t}$$
$$= -\nabla\cdot[\varepsilon_{\mu\omega}\boldsymbol{\mathcal{D}}_{A\sigma}\nabla(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)] + \nabla\cdot\left[\boldsymbol{\mathcal{D}}_{A\sigma}K_{\mathrm{eq}}^{\mu\sigma}\mathbf{I} + \frac{\boldsymbol{\mathcal{D}}_{A\sigma}}{V_\sigma}\int_{A_{\sigma\mu,\omega}}\mathbf{n}_{\sigma\mu}\mathbf{b}_\sigma\,\mathrm{d}A\right]\cdot\nabla\{C_A\}_\omega$$
$$-[a_{v\omega}h_\omega\varepsilon_{\sigma\omega}^{-1} - k_\sigma\langle C_{R\sigma}\rangle_\omega^\sigma\varepsilon_{\mu\omega}](K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma) - k_\sigma\langle C_{R\sigma}\rangle_\omega^\sigma K_{\mathrm{eq}}^{\mu\sigma}\{C_A\}_\omega - k_\sigma\langle\mathbf{b}_\sigma\mathbf{b}_{R\sigma}\rangle_\omega^\sigma : \nabla\{C_A\}_\omega\nabla\langle C_{R\sigma}\rangle_\omega^\sigma \tag{A.21}$$

Note that in the above equations we have neglected the spatial variations of the volume fractions. Subtracting Eq. (A.21) from Eq. (A.20) yields

$$\frac{\partial(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)}{\partial t} = \nabla\cdot[D_{A\sigma\mu}\nabla(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)] + \nabla$$
$$\times\cdot\left[(\boldsymbol{\mathcal{D}}_{A\mu} - \boldsymbol{\mathcal{D}}_{A\sigma})K_{\mathrm{eq}}^{\mu\sigma}\mathbf{I} + \frac{\boldsymbol{\mathcal{D}}_{A\mu}}{V_{\mu,\omega}}\int_{A_{\mu\sigma,\omega}}\mathbf{n}_{\mu\sigma}K_{\mathrm{eq}}^{\mu\sigma}\mathbf{b}_\mu\mathrm{d}A + \frac{\boldsymbol{\mathcal{D}}_{A\sigma}}{V_{\sigma,\omega}}\int_{A_{\sigma\mu,\omega}}\mathbf{n}_{\mu\sigma}\mathbf{b}_\sigma\mathrm{d}A\right]\cdot\nabla\{C_A\}_\omega$$
$$+[\varepsilon_{\mu\omega}^{-1}K_{\mathrm{eq}}^{\mu\sigma}a_{v\omega}h_\omega + a_{v\omega}h_\omega\varepsilon_{\sigma\omega}^{-1} - \varepsilon_{\sigma\omega}k_\mu - k_\sigma\langle C_{R\sigma}\rangle_\omega^\sigma\varepsilon_{\mu\omega}](K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)$$
$$+(k_\sigma\langle C_{R\sigma}\rangle_\omega^\sigma - k_\mu)K_{\mathrm{eq}}^{\mu\sigma}\{C_A\}_\omega + K_{\mathrm{eq}}^{\mu\sigma}k_\mu\frac{\langle C_{B\mu}\rangle_\omega^\mu}{K_\mu} + k_\sigma\langle\mathbf{b}_\sigma\mathbf{b}_{R\sigma}\rangle_\omega^\sigma : \nabla\{C_A\}_\omega\nabla\langle C_{R\sigma}\rangle_\omega^\sigma \tag{A.22}$$

where we have used the following definition

$$D_{A\sigma\mu} = \varepsilon_{\mu\omega}\boldsymbol{\mathcal{D}}_{A\sigma} + \boldsymbol{\mathcal{D}}_{A\mu}\varepsilon_{\sigma\omega} \tag{A.23}$$

However, from the closure problem statement, it is possible to obtain

At the $\sigma\mu$-interface,

$$K_{\mathrm{eq}}^{\mu\sigma}\mathbf{b}_\mu = \mathbf{b}_\sigma + \mathbf{n}_{\sigma\mu}\alpha(K_{\mathrm{eq}}^{\mu\sigma})^2 + \mathbf{n}_{\sigma\mu}\cdot\alpha K_{\mathrm{eq}}^{\mu\sigma}\nabla\mathbf{b}_\sigma \tag{A.24}$$

In this way, let us define $\mathbf{C}_{\mu\sigma} = C_{\mu\sigma}\mathbf{I}$, where

$$\begin{aligned}\frac{\mathbf{C}_{\mu\sigma}}{\mathcal{D}_{A\mu}-\mathcal{D}_{A\sigma}} &= \frac{\mathcal{D}_{A\mu}}{\varepsilon_{\mu\omega}\mathcal{V}}\int_{A_{\mu\sigma,\omega}}\mathbf{n}_{\mu\sigma}K_{\mathrm{eq}}^{\mu\sigma}\mathbf{b}_\mu\,\mathrm{d}A + \frac{\mathcal{D}_{A\sigma}}{\varepsilon_{\sigma\omega}\mathcal{V}}\int_{A_{\sigma\mu,\omega}}\mathbf{n}_{\mu\sigma}\mathbf{b}_\sigma\,\mathrm{d}A\\ &= \left[\frac{D_{A\sigma\mu}}{\varepsilon_{\mu\omega}\varepsilon_{\sigma\omega}}\right]\frac{1}{\mathcal{V}}\int_{A_{\sigma\mu,\omega}}\mathbf{n}_{\mu\sigma}\mathbf{b}_\sigma\,\mathrm{d}A + \frac{\mathcal{D}_{A\mu}\alpha K_{\mathrm{eq}}^{\mu\sigma}}{\varepsilon_{\mu\omega}\mathcal{V}}\int_{A_{\mu\sigma,\omega}}\mathbf{n}_{\mu\sigma}\mathbf{n}_{\sigma\mu}\cdot(K_{\mathrm{eq}}^{\mu\sigma}\mathbf{I}+\nabla\mathbf{b}_\sigma)\,\mathrm{d}A\end{aligned} \tag{A.25}$$

So that Eq. (A.22) can be put as

$$\begin{aligned}&\frac{\partial(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)}{\partial t} - \nabla\cdot[D_{A\sigma\mu}\nabla(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)]\\ &-[(\varepsilon_{\mu\omega}^{-1}K_{\mathrm{eq}}^{\mu\sigma}+\varepsilon_{\sigma\omega}^{-1})a_{v\omega}h_\omega - \varepsilon_{\sigma\omega}k_\mu - k_\sigma\langle C_{R\sigma}\rangle_\omega^\sigma\varepsilon_{\mu\omega}](K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)\\ &\quad= \nabla\cdot[(\mathcal{D}_{A\mu}-\mathcal{D}_{A\sigma})(K_{\mathrm{eq}}^{\mu\sigma}\mathbf{I}+\mathbf{C}_{\mu\sigma})]\cdot\nabla\{C_A\}_\omega + (k_\sigma\langle C_{R\sigma}\rangle_\omega^\sigma - k_\mu)K_{\mathrm{eq}}^{\mu\sigma}\{C_A\}_\omega\\ &+K_{\mathrm{eq}}^{\mu\sigma}k_\mu\frac{\langle C_{B\mu}\rangle_\omega^\mu}{K_\mu} + k_\sigma\langle\mathbf{b}_\sigma\mathbf{b}_{R\sigma}\rangle_\omega^\sigma : \nabla\{C_A\}_\omega\nabla\langle C_{R\sigma}\rangle_\omega^\sigma\end{aligned} \tag{A.26}$$

The order of magnitude of the LHS of Eq. (A.26) is

$$\begin{aligned}&\frac{\partial(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)}{\partial t} - \nabla\cdot[D_{A\sigma\mu}\nabla(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)] - [(\varepsilon_{\mu\omega}^{-1}K_{\mathrm{eq}}^{\mu\sigma}+\varepsilon_{\sigma\omega}^{-1})a_{v\omega}h_\omega - \varepsilon_{\sigma\omega}k_\mu - k_\sigma\langle C_{R\sigma}\rangle_\omega^\sigma\varepsilon_{\mu\omega}]\\ &\times(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma) = \left\{\mathbf{O}\left(\frac{1}{t^*}\right) + \mathbf{O}\left(\frac{D_{A\sigma\mu}}{L_{C1}L_C}\right) + \mathbf{O}\left(\frac{a_{v\omega}h_\omega}{\varepsilon_{\sigma\omega}\varepsilon_{\mu\omega}}\right) + \mathbf{O}(\varepsilon_{\sigma\omega}k_\mu + k_\sigma\langle C_{R\sigma}\rangle_\omega^\sigma\varepsilon_{\mu\omega})\right\}\\ &\times(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma)\end{aligned} \tag{A.27}$$

While the order of magnitude estimate of the LHS of Eq. (A.26) is given by

$$\begin{aligned}&\nabla\cdot[(\mathcal{D}_{A\mu}-\mathcal{D}_{A\sigma})(K_{\mathrm{eq}}^{\mu\sigma}\mathbf{I}+\mathbf{C}_{\mu\sigma})]\cdot\nabla\{C_A\}_\omega + (k_\sigma\langle C_{R\sigma}\rangle_\omega^\sigma - k_\mu)K_{\mathrm{eq}}^{\mu\sigma}\{C_A\}_\omega + k_\sigma\langle\mathbf{b}_\sigma\mathbf{b}_{R\sigma}\rangle_\omega^\sigma : \nabla\{C_A\}_\omega\nabla\langle C_{R\sigma}\rangle_\omega^\sigma\\ &\quad= \left\{\mathbf{O}\frac{(\mathcal{D}_{A\mu}-\mathcal{D}_{A\sigma})(K_{\mathrm{eq}}^{\mu\sigma}+C_{\mu\sigma})}{L_CL_{C1}} + \mathbf{O}(k_\sigma\langle C_{R\sigma}\rangle_\omega^\sigma - k_\mu)K_{\mathrm{eq}}^{\mu\sigma} + \mathbf{O}\left(\frac{k_\sigma\langle C_{R\sigma}\rangle_\omega^\sigma\ell_\sigma^2}{L_C^2}\right)\right\}\{C_A\}_\omega\end{aligned} \tag{A.28}$$

To obtain Eqs. (A.27) and (A.28) we have considered that

$$\frac{\langle C_{B\mu}\rangle_\omega^\mu}{K_\mu} = \mathbf{O}(\langle C_{A\mu}\rangle_\omega^\mu) = \mathbf{O}\left(\frac{\varepsilon_{\sigma\omega}}{K_{\mathrm{eq}}^{\mu\sigma}}(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma) + \{C_A\}_\omega\right),\quad \mathbf{b}_\sigma\mathbf{b}_{R\sigma} = \mathbf{O}(\ell_\sigma^2) \tag{A.29}$$

Substituting the estimates given in Eqs. (A.27) and (A.28) in Eq. (A.26) gives

$$\begin{aligned}\frac{K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma}{\{C_A\}_\omega} &= \mathbf{O}\left(\frac{\ell_{\sigma\mu}^2}{L_CL_{C1}}\right)\\ &\times\frac{\{((\mathcal{D}_{A\mu}-\mathcal{D}_{A\sigma})(K_{\mathrm{eq}}^{\mu\sigma}+C_{\mu\sigma})/D_{A\sigma\mu}) + (L_{C1}/L_C)[(\Phi_\sigma^2-\Phi_\mu^2)K_{\mathrm{eq}}^{\mu\sigma} + \Phi_\sigma^2\mathbf{O}(\ell_\sigma^2/L_C^2)]\}}{\{1+\mathbf{O}(\ell_{\sigma\mu}^2/D_{A\sigma\mu}t^*) + \mathbf{O}(\ell_{\sigma\mu}^2/L_{C1}L_C) + \mathbf{O}(\varepsilon_{\sigma\omega}\Phi_\mu^2 + \Phi_\sigma^2\varepsilon_{\mu\omega})\ell_{\sigma\mu}^2/L_C^2\}}\end{aligned} \tag{A.30}$$

where we have employed the mixed-mode small length scale is given by

$$\ell_{\sigma\mu}^2 = \frac{\varepsilon_{\sigma\omega}\varepsilon_{\mu\omega}D_{A\sigma\mu}}{a_{v\omega}h_\omega} \tag{A.31}$$

and the large-scale Thiele modulus

$$\Phi_\sigma^2 = \frac{k_\sigma \langle C_{R\sigma}\rangle^\sigma L_C^2}{D_{A\sigma\mu}}, \qquad \Phi_\mu^2 = \frac{k_\mu L_C^2}{D_{A\sigma\mu}} \tag{A.32}$$

In most processes, unless the interfacial mass transfer resistance governs the macroscopic transport, the following estimates are reasonable

$$\frac{\ell_{\sigma\mu}^2}{L_C L_{C1}} \ll 1 \tag{A.33}$$

$$\frac{\ell_{\sigma\mu}^2}{D_{A\sigma\mu} t^*} \ll 1 \tag{A.34}$$

Therefore, Eq. (A.30) reduces to

$$\frac{K_{\text{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle_\omega^\mu - \langle C_{A\sigma}\rangle_\omega^\sigma}{\{C_A\}_\omega} = \mathbf{O}\left(\frac{\ell_{\sigma\mu}^2}{L_C L_{C1}}\right) \tag{A.35}$$

The use of this result in the restrictions given in Eqs. (A.8)–(A.10) leads to the desired length scale constraints

$$\frac{\varepsilon_{\mu\omega}\varepsilon_{\sigma\omega}(1 - K_{\text{eq}}^{\mu\sigma})\ell_{\sigma\mu}^2}{D_{A\omega} K_{\text{eq}}^{\mu\sigma} t^*} \ll 1 \tag{A.36}$$

$$\frac{\varepsilon_{\mu\omega}\varepsilon_{\sigma\omega}(\boldsymbol{\mathcal{D}}_{A\mu} - K_{\text{eq}}^{\mu\sigma}\boldsymbol{\mathcal{D}}_{A\sigma})}{K_{\text{eq}}^{\mu\sigma} D_{A\omega}}\left(\frac{\ell_{\sigma\mu}^2}{L_C L_{C1}}\right) \ll 1 \tag{A.37}$$

$$(\Phi_\mu^2 - K_{\text{eq}}^{\mu\sigma}\Phi_\sigma^2)\frac{D_{A\sigma\mu}\varepsilon_{\sigma\omega}\varepsilon_{\mu\omega}}{D_{A\omega} K_{\text{eq}}^{\mu\sigma}}\left(\frac{\ell_{\sigma\mu}^2}{L_C^2}\right) \ll 1 \tag{A.38}$$

From the above equations, it can be concluded that the assumption of local mass equilibrium is valid when:

- Either $\varepsilon_{\mu\sigma}$ or $\varepsilon_{\sigma\omega}$ is much less than the unity.
- The difference between the physicochemical coefficients of the σ-phase and the μ-phase is negligible.
- Constraints (A.33) and (A.34) are satisfied.

Appendix B. Derivation of closure problem for jump condition

In this appendix, the boundary-value problems for the variables that map the average concentrations onto the local concentration spatial variations are presented. Since the jump boundary condition (82) is expressed in terms of point variables, let us first use the Gray's [40] spatial decomposition

$$C_{A\alpha} = \langle C_{A\alpha}\rangle^\alpha + \tilde{C}_{A\alpha}, \tag{B.1}$$

in Eq. (82) to obtain

$$\begin{aligned} -\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega) = {} & \langle P_{\sigma\mu}(\langle C_{A\sigma}\rangle^\sigma - K_{\text{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle^\mu + \tilde{C}_{A\sigma} - K_{\text{eq}}^{\mu\sigma}\tilde{C}_{A\mu})\rangle_{\eta\omega}^{\sigma\mu} \\ & + \langle P_{\gamma\mu}(\langle C_{A\gamma}\rangle^\gamma - K_{\text{eq}}^{\mu\gamma}\langle C_{A\mu}\rangle^\mu + \tilde{C}_{A\gamma} - K_{\text{eq}}^{\mu\gamma}\tilde{C}_{A\mu})\rangle_{\eta\omega}^{\gamma\mu} \end{aligned} \tag{B.2}$$

In addition, each one of the concentration spatial deviations $\tilde{C}_{A\alpha}$ can be related to the average concentrations by writing associated local deviation problems. These can be obtained by subtracting from the point equations (1)–(5) the respective non-closed macroscopic equations [(32), (26–29)], to obtain

σ-phase

$$\begin{aligned} \frac{\partial\tilde{C}_{A\sigma}}{\partial t} = {} & \boldsymbol{\mathcal{D}}_{A\sigma}\nabla^2\tilde{C}_{A\sigma} - \frac{1}{V_\sigma(\mathbf{x})}\int_{A_{\mu\sigma}}\mathbf{n}_{\sigma\mu}\cdot\mathbf{D}_{A\sigma}\nabla\tilde{C}_{A\sigma}\,\mathrm{d}A - \varepsilon_\sigma^{-1}(\mathbf{x})\nabla\cdot\left[\frac{\boldsymbol{\mathcal{D}}_{A\sigma}}{\boldsymbol{\mathcal{V}}}\int_{A_{\sigma\mu}}\mathbf{n}_{\sigma\mu}\Delta\langle C_{A\sigma}\rangle^\sigma\,\mathrm{d}A\right] \\ & - k_\sigma C_{A\sigma}C_{R\sigma} + k_\sigma\langle C_{A\sigma}C_{R\sigma}\rangle^\sigma \end{aligned} \tag{B.3}$$

$$\frac{\partial \tilde{C}_{R\sigma}}{\partial t} = \boldsymbol{\mathcal{D}}_{R\sigma}\nabla^2\tilde{C}_{R\sigma} - \varepsilon_\sigma^{-1}(\mathbf{x})\nabla\varepsilon_\sigma(\mathbf{x})\cdot[\boldsymbol{\mathcal{D}}_{R\sigma}\nabla\langle C_{R\sigma}\rangle^\sigma] - \varepsilon_\sigma^{-1}(\mathbf{x})\nabla\cdot\left[\frac{\boldsymbol{\mathcal{D}}_{R\sigma}}{\boldsymbol{\mathcal{V}}}\int_{A_{\sigma\mu}}\mathbf{n}_{\sigma\mu}\nabla\langle C_{R\sigma}\rangle^\sigma\,\mathrm{d}A\right] - k_\sigma C_{A\sigma}C_{R\sigma} + k_\sigma\langle C_{A\sigma}C_{R\sigma}\rangle^\sigma \tag{B.4}$$

μ-phase

$$\frac{\partial \tilde{C}_{A\mu}}{\partial t} = \boldsymbol{\mathcal{D}}_{A\mu}\nabla^2\tilde{C}_{A\mu} - k_\mu\left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu}\right) - \frac{1}{V_\mu(\mathbf{x})}\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla\tilde{C}_{A\mu}\,\mathrm{d}A - \frac{1}{V_\mu(\mathbf{x})}\int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla\tilde{C}_{A\mu}\mathrm{d}A - \varepsilon_\mu^{-1}(\mathbf{x})\nabla\cdot\left(\frac{\boldsymbol{\mathcal{D}}_{A\mu}}{\boldsymbol{\mathcal{V}}}\left[\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}\Delta\langle C_{A\mu}\rangle^\mu\,\mathrm{d}A + \int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}\Delta\langle C_{A\mu}\rangle^\mu\,\mathrm{d}A\right]\right). \tag{B.5}$$

$$\frac{\partial \tilde{C}_{B\mu}}{\partial t} = \boldsymbol{\mathcal{D}}_{B\mu}\nabla^2\tilde{C}_{B\mu} + \varepsilon_\mu^{-1}(\mathbf{x})\nabla\varepsilon_\mu(\mathbf{x})\cdot[\boldsymbol{\mathcal{D}}_{B\mu}\nabla\langle C_{B\mu}\rangle^\mu] + k_\mu\left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu}\right) + \varepsilon_\mu^{-1}(\mathbf{x})\nabla\cdot\left[\frac{\boldsymbol{\mathcal{D}}_{B\mu}}{\boldsymbol{\mathcal{V}}}\left(\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}\Delta\langle C_{B\mu}\rangle^\mu\,\mathrm{d}A + \int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}\Delta\langle C_{B\mu}\rangle^\mu\,\mathrm{d}A\right)\right] \tag{B.6}$$

γ-phase

$$\frac{\partial \tilde{C}_{A\gamma}}{\partial t} = \boldsymbol{\mathcal{D}}_{A\gamma}\nabla^2\tilde{C}_{A\gamma} - \varepsilon_\gamma^{-1}(\mathbf{x})\nabla\cdot\left[\frac{\boldsymbol{\mathcal{D}}_{A\gamma}}{\boldsymbol{\mathcal{V}}}\int_{A_{\gamma\mu}}\mathbf{n}_{\gamma\mu}\Delta\langle C_{A\gamma}\rangle^\gamma\,\mathrm{d}A\right] - \frac{1}{V_\gamma(\mathbf{x})}\int_{A_{\mu\gamma}}\mathbf{n}_{\gamma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}\nabla\tilde{C}_{A\gamma}\,\mathrm{d}A \tag{B.7}$$

In the above equations, we have already imposed the following length scale constraint, that can be satisfied based on the disparity of the local and macroscopic length scales

$$\frac{\ell_\alpha}{L} \ll 1, \quad \alpha = \sigma, \mu, \gamma \tag{B.8}$$

and introduced the following definitions,

$$\Delta\langle C_{i\alpha}\rangle^\alpha = \langle C_{i\alpha}\rangle^\alpha|_{\mathbf{x}+\mathbf{y}_\alpha} - \langle C_{i\alpha}\rangle^\alpha|_{\mathbf{x}}, \quad i = A, B, R; \ \alpha = \sigma, \mu, \gamma \tag{B.9}$$

The interfacial boundary conditions associated with Eqs. (B.3)–(B.7) are obtained by substituting the concentration spatial decompositions in Eqs. (8)–(13)

At the σμ-interface

$$\mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\sigma}\nabla\tilde{C}_{A\sigma} - \mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla\tilde{C}_{A\mu} = \underbrace{\mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla\langle C_{A\mu}\rangle^\mu - \mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\sigma}\nabla\langle C_{A\sigma}\rangle^\sigma}_{\text{surface diffusive source}} \tag{B.10}$$

$$-\mathbf{n}_{\sigma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\sigma}\nabla\tilde{C}_{A\sigma} - P_{\sigma\mu}(\tilde{C}_{A\sigma} - K_{\mathrm{eq}}^{\mu\sigma}\tilde{C}_{A\mu}) = \underbrace{\mathbf{n}_{\sigma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\sigma}\nabla\langle C_{A\sigma}\rangle^\sigma}_{\text{surface diffusive source}} + \underbrace{P_{\sigma\mu}(\langle C_{A\sigma}\rangle^\sigma - K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle^\mu)}_{\text{surface exchange source}} \tag{B.11}$$

$$-\mathbf{n}_{\sigma\mu}\cdot\boldsymbol{\mathcal{D}}_{R\sigma}\nabla\tilde{C}_{R\sigma} = \mathbf{n}_{\sigma\mu}\cdot\boldsymbol{\mathcal{D}}_{R\sigma}\nabla\langle C_{R\sigma}\rangle^\sigma \tag{B.12}$$

$$-\mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{B\mu}\nabla\tilde{C}_{B\mu} = \mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{B\mu}\nabla\langle C_{B\mu}\rangle^\mu \tag{B.13}$$

At the μγ-interface

$$\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}\nabla\tilde{C}_{A\gamma} - \mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla\tilde{C}_{A\mu} = \underbrace{\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla\langle C_{A\mu}\rangle^\mu - \mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}\nabla\langle C_{A\gamma}\rangle^\gamma}_{\text{surface diffusive source}} \tag{B.14}$$

$$-\mathbf{n}_{\gamma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}\nabla\tilde{C}_{A\gamma} - P_{\gamma\mu}(\tilde{C}_{A\gamma} - K_{\mathrm{eq}}^{\mu\gamma}\tilde{C}_{A\mu}) = \underbrace{\mathbf{n}_{\gamma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}\nabla\langle C_{A\gamma}\rangle^\gamma}_{\text{surface diffusive source}} + \underbrace{P_{\gamma\mu}(\langle C_{A\gamma}\rangle^\gamma - K_{\mathrm{eq}}^{\mu\gamma}\langle C_{A\mu}\rangle^\mu)}_{\text{surface exchange source}} \tag{B.15}$$

$$-\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{B\mu}\nabla\tilde{C}_{B\mu} = \mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{B\mu}\nabla\langle C_{B\mu}\rangle^\mu \tag{B.16}$$

Using Taylor series expansions of the intrinsic average concentrations about the centroid of the averaging volume [28], the concentration difference defined by Eq. (B.9) can be assumed negligible when the following constrains are satisfied

$$\frac{r_0}{L} \ll 1; \quad \frac{r_0^2}{L^2} \ll 1; \quad \frac{\ell_\mu}{10L}\varepsilon_{\mu\omega} \ll 1; \quad \frac{\varepsilon_{\mu\omega}}{20}\frac{\ell_\mu r_0}{L^2} \ll 1 \tag{B.17}$$

Therefore, Eqs. (B.3)–(B.7) can be written as,

σ-phase

$$\mathcal{D}_{A\sigma}\nabla^2\tilde{C}_{A\sigma} = \frac{1}{V_\sigma(\mathbf{x})}\int_{A_{\mu\sigma}} \mathbf{n}_{\sigma\mu}\cdot\mathcal{D}_{A\sigma}\nabla\tilde{C}_{A\sigma}\,\mathrm{d}A + k_\sigma\tilde{C}_{A\sigma}\langle C_{R\sigma}\rangle^\sigma + k_\sigma\langle C_{A\sigma}\rangle^\sigma\tilde{C}_{R\sigma} + k_\sigma\tilde{C}_{A\sigma}\tilde{C}_{R\sigma} - k_\sigma\langle\tilde{C}_{A\sigma}\tilde{C}_{R\sigma}\rangle^\sigma \tag{B.18}$$

$$\mathcal{D}_{R\sigma}\nabla^2\tilde{C}_{R\sigma} = \varepsilon_\sigma^{-1}(\mathbf{x})\nabla\varepsilon_\sigma(\mathbf{x})\cdot[\mathcal{D}_{R\sigma}\nabla\langle C_{R\sigma}\rangle^\sigma] + k_\sigma\tilde{C}_{A\sigma}\langle C_{R\sigma}\rangle^\sigma + k_\sigma\langle C_{A\sigma}\rangle^\sigma\tilde{C}_{R\sigma} + k_\sigma\tilde{C}_{A\sigma}\tilde{C}_{R\sigma} - k_\sigma\langle\tilde{C}_{A\sigma}\tilde{C}_{R\sigma}\rangle^\sigma \tag{B.19}$$

μ-phase

$$\mathcal{D}_{A\mu}\nabla^2\tilde{C}_{A\mu} = k_\mu\left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu}\right) + \frac{1}{V_\mu(\mathbf{x})}\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\mu}\nabla\tilde{C}_{A\mu}\,\mathrm{d}A + \frac{1}{V_\mu(\mathbf{x})}\int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\mu}\nabla\tilde{C}_{A\mu}\,\mathrm{d}A \tag{B.20}$$

$$\mathcal{D}_{B\mu}\nabla^2\tilde{C}_{B\mu} = -\varepsilon_\mu^{-1}(\mathbf{x})\nabla\varepsilon_\mu(\mathbf{x})\cdot[\mathcal{D}_{B\mu}\nabla\langle C_{B\mu}\rangle^\mu] - k_\mu\left(\tilde{C}_{A\mu} - \frac{\tilde{C}_{B\mu}}{K_\mu}\right) \tag{B.21}$$

γ-phase

$$\mathcal{D}_{A\gamma}\nabla^2\tilde{C}_{A\gamma} = \frac{1}{V_\gamma(\mathbf{x})}\int_{A_{\mu\gamma}}\mathbf{n}_{\gamma\mu}\cdot\mathcal{D}_{A\gamma}\nabla\tilde{C}_{A\gamma}\,\mathrm{d}A \tag{B.22}$$

In the above equations we have imposed the following length scale constraints,

$$\frac{\mathcal{D}_{i\alpha}t^*}{\ell_\alpha^2} \gg 1 \quad \alpha = \sigma, \mu, \gamma \quad i = A, B, R \tag{B.23}$$

which allowed neglecting the accumulation terms in Eqs. (B.18)–(B.22). Moreover, the characteristic length of the deviations makes possible to neglect, for the purposes of the closure problem, the reaction terms in comparison to the diffusive contributions. Let us highlight that, according to Wood and Whitaker [42] (see Appendix A.2 therein), it is reasonable to neglect the reaction rate at the level of the closure problem even if it plays an important role at the macroscopic level. Indeed, as long as the following constraints are satisfied

$$\frac{\mathcal{D}_{A\sigma}}{\ell_\sigma^2 k_\sigma\tilde{C}_{R\sigma}} \gg 1, \quad \frac{\mathcal{D}_{A\sigma}\tilde{C}_{A\sigma}}{\ell_\sigma^2\langle C_{A\sigma}\rangle^\sigma\tilde{C}_{R\sigma}} \gg 1, \quad \frac{\mathcal{D}_{A\sigma}}{\ell_\sigma^2\langle C_{R\sigma}\rangle^\sigma} \gg 1, \quad \frac{\mathcal{D}_{A\mu}}{\ell_\mu^2 k_\mu[1 - \tilde{C}_{B\mu}/K_\mu\tilde{C}_{A\mu}]} \gg 1. \tag{B.24}$$

the deviation equations and boundary conditions for species A take the form

σ-phase

$$\mathcal{D}_{A\sigma}\nabla^2\tilde{C}_{A\sigma} = \frac{\varepsilon_\sigma^{-1}(\mathbf{x})}{\mathcal{V}}\int_{A_{\mu\sigma}}\mathbf{n}_{\sigma\mu}\cdot\mathcal{D}_{A\sigma}\nabla\tilde{C}_{A\sigma}\,\mathrm{d}A, \tag{B.25}$$

μ-phase

$$\mathcal{D}_{A\mu}\nabla^2\tilde{C}_{A\mu} = \frac{\varepsilon_\mu^{-1}(\mathbf{x})}{\mathcal{V}}\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\mu}\nabla\tilde{C}_{A\mu}\,\mathrm{d}A + \frac{\varepsilon_\mu^{-1}(\mathbf{x})}{\mathcal{V}}\int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\mu}\nabla\tilde{C}_{A\mu}\,\mathrm{d}A \tag{B.26}$$

γ-phase

$$\mathcal{D}_{A\gamma}\nabla^2\tilde{C}_{A\gamma} = \frac{\varepsilon_\gamma^{-1}(\mathbf{x})}{\mathcal{V}}\int_{A_{\mu\gamma}}\mathbf{n}_{\gamma\mu}\cdot\mathcal{D}_{A\gamma}\nabla\tilde{C}_{A\gamma}\,\mathrm{d}A \tag{B.27}$$

At the σμ-interface

$$\mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\sigma}\nabla\tilde{C}_{A\sigma} - \mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\mu}\nabla\tilde{C}_{A\mu} = \underbrace{\mathbf{n}_{\mu\sigma}\cdot(\mathcal{D}_{A\mu} - \mathcal{D}_{A\sigma}K_{\mathrm{eq}}^{\mu\sigma})\nabla\{C_A\}_\omega|_{\mathbf{x}_0}}_{\text{diffusive source}} \tag{B.28}$$

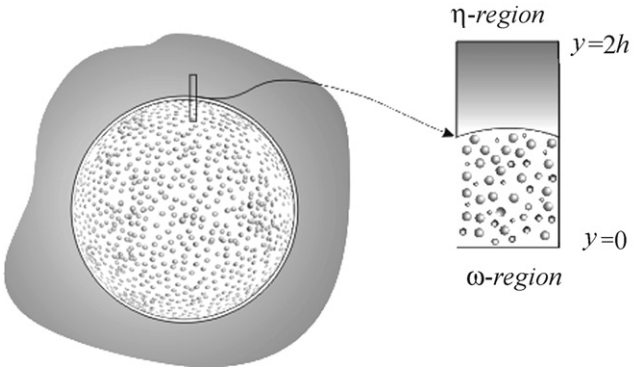

Fig. B.1. Representative unit cell for the inter-region.

$$-\mathbf{n}_{\sigma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\sigma}\nabla\tilde{C}_{A\sigma}-P_{\sigma\mu}(\tilde{C}_{A\sigma}-K_{\mathrm{eq}}^{\mu\sigma}\tilde{C}_{A\mu})=\underbrace{\mathbf{n}_{\sigma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\sigma}K_{\mathrm{eq}}^{\mu\sigma}\nabla\{C_A\}_{\omega}|_{\mathbf{x}_0}}_{\text{diffusive source}} \tag{B.29}$$

At the $\mu\gamma$-interface

$$\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}\nabla\tilde{C}_{A\gamma}-\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla\tilde{C}_{A\mu}=\underbrace{\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla\{C_A\}_{\omega}|_{\mathbf{x}_0}}_{\text{diffusive source}}-\underbrace{\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}K_{\mathrm{eq}}^{\mu\gamma}\nabla\{C_A\}_{\eta}|_{\mathbf{x}_0}}_{\text{diffusive source}} \tag{B.30}$$

$$-\mathbf{n}_{\gamma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}\nabla\tilde{C}_{A\gamma}-P_{\gamma\mu}(\tilde{C}_{A\gamma}-K_{\mathrm{eq}}^{\mu\gamma}\tilde{C}_{A\mu})=\underbrace{\mathbf{n}_{\gamma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}K_{\mathrm{eq}}^{\mu\gamma}\nabla\{C_A\}_{\eta}\big|_{\mathbf{x}_0}}_{\text{diffusive source}}+\underbrace{P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma}(\{C_A\}_{\eta}|_{\mathbf{x}_0}-\{C_A\}_{\omega}|_{\mathbf{x}_0})}_{\text{exchange source}} \tag{B.31}$$

In the above equations we have accepted the validity of the length scale constraints introduced in Appendix C, under which the assumption of local mass equilibrium is valid at the closure level. Notice that, by neglecting the reaction rate contribution, only the boundary-value problem for the spatial deviations of species A has to be considered and not those corresponding to species B and R. This problem has to be solved in a representative unit cell of the inter-region (Fig. B.1). Its height ($2h$) must be large enough in order to impose the following boundary conditions

$$\text{At } y=2h,\quad \tilde{C}_{A\sigma}=0,\quad \tilde{C}_{A\mu}=0,\quad \tilde{C}_{A\gamma}=0 \tag{B.32}$$

$$\text{At } y=0\quad \tilde{C}_{A\sigma}=\tilde{C}_{A\sigma\omega},\quad \tilde{C}_{A\mu}=\tilde{C}_{A\mu\omega},\quad \tilde{C}_{A\gamma}=0 \tag{B.33}$$

which are the deviation values in both homogeneous regions. Assuming that the width of the unit cell is small enough in order to neglect the curvature effects of the membrane, we can impose periodicity conditions in the tangential direction of the dividing surface

$$\tilde{C}_{A\alpha}(\mathbf{r}+\ell_k)=\tilde{C}_{A\alpha}(\mathbf{r})\quad k=1,2;\ \ \alpha=\sigma,\mu,\gamma. \tag{B.34}$$

The sources in Eqs. (B.28)–(B.31) suggest the following form for the spatial concentration deviations

$$\tilde{C}_{A\alpha}=s_{\alpha}^{\omega}\{C_A\}_{\omega}+s_{\alpha}^{\eta}\{C_A\}_{\eta}+\mathbf{b}_{\alpha}^{\omega}\cdot\nabla\{C_A\}_{\omega}+\mathbf{b}_{\alpha}^{\eta}\cdot\nabla\{C_A\}_{\eta}\quad(\text{for}\,\alpha=\sigma,\mu,\gamma) \tag{B.35}$$

Using these expressions in Eqs. (B.25)–(B.34) gives rise to the boundary-value problems for the closure variables s_{α}^{ω}, s_{α}^{η}, $\mathbf{b}_{\alpha}^{\omega}$ and $\mathbf{b}_{\alpha}^{\eta}$. The associated differential equations (for these four closure coefficients) have the same form. Therefore, the set of differential equations can be written in compact form as

Differential equations:

σ-phase

$$\nabla^2\varphi_{\sigma}=\frac{1}{V_{\sigma}(\mathbf{x}_0)}\int_{A_{\mu\sigma}}\mathbf{n}_{\sigma\mu}\cdot\nabla\varphi_{\sigma}\,\mathrm{d}A, \tag{B.36}$$

μ-phase

$$\nabla^2\varphi_{\mu}=\frac{1}{V_{\mu}(\mathbf{x}_0)}\int_{A_{\mu\sigma}}\mathbf{n}_{\mu\sigma}\cdot\nabla\varphi_{\mu}\,\mathrm{d}A+\frac{1}{V_{\mu}(\mathbf{x}_0)}\int_{A_{\mu\gamma}}\mathbf{n}_{\mu\gamma}\cdot\nabla\varphi_{\mu}\,\mathrm{d}A \tag{B.37}$$

γ-phase

$$\nabla^2\varphi_\gamma = \frac{1}{V_\gamma(\mathbf{x}_0)}\int_{A_{\mu\gamma}} \mathbf{n}_{\gamma\mu}\cdot\nabla\varphi_\gamma\,\mathrm{d}A \tag{B.38}$$

where φ_α represents the closure coefficients according to

$$\varphi_\alpha = s_\alpha^\omega, s_\alpha^\eta, \mathbf{b}_\alpha^\omega, \mathbf{b}_\alpha^\eta, \quad \alpha = \sigma, \mu, \gamma \tag{B.39}$$

However the boundary conditions to which Eqs. (B.36)–(B.38) are subjected cannot be summarized easily. They are

At the σμ-interface

$$\mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\sigma}\nabla s_\sigma^\lambda = \mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\mu}\nabla s_\mu^\lambda \quad \lambda = \omega, \eta, \tag{B.40}$$

$$\mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\sigma}\nabla\mathbf{b}_\sigma^\omega - \mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\mu}\nabla\mathbf{b}_\mu^\omega = \mathbf{n}_{\mu\sigma}(\mathcal{D}_{A\mu} - \mathcal{D}_{A\sigma}K_{\mathrm{eq}}^{\mu\sigma}) \tag{B.41}$$

$$\mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\sigma}\nabla\mathbf{b}_\sigma^\eta = \mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\mu}\nabla\mathbf{b}_\mu^\eta \tag{B.42}$$

$$-\mathbf{n}_{\sigma\mu}\cdot\mathcal{D}_{A\sigma}\nabla s_\sigma^\lambda = P_{\sigma\mu}(s_\sigma^\lambda - K_{\mathrm{eq}}^{\mu\sigma}s_\mu^\lambda) \quad \lambda = \omega, \eta \tag{B.43}$$

$$-\mathbf{n}_{\sigma\mu}\cdot\mathcal{D}_{A\sigma}\nabla\mathbf{b}_\sigma^\omega - P_{\sigma\mu}(\mathbf{b}_\sigma^\omega - K_{\mathrm{eq}}^{\mu\sigma}\mathbf{b}_\mu^\omega) = \mathbf{n}_{\sigma\mu}\mathcal{D}_{A\sigma}K_{\mathrm{eq}}^{\mu\sigma} \tag{B.44}$$

$$-\mathbf{n}_{\sigma\mu}\cdot\mathcal{D}_{A\sigma}\nabla\mathbf{b}_\sigma^\eta = P_{\sigma\mu}(\mathbf{b}_\sigma^\eta - K_{\mathrm{eq}}^{\mu\sigma}\mathbf{b}_\mu^\eta) \tag{B.45}$$

At the μγ-interface

$$\mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\gamma}\nabla s_\gamma^\lambda = \mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\mu}\nabla s_\mu^\lambda \quad \lambda = \omega, \eta \tag{B.46}$$

$$\mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\gamma}\nabla\mathbf{b}_\gamma^\omega - \mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\mu}\nabla\mathbf{b}_\mu^\omega = \mathbf{n}_{\mu\gamma}\mathcal{D}_{A\mu} \tag{B.47}$$

$$\mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\gamma}\nabla\mathbf{b}_\gamma^\eta - \mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\mu}\nabla\mathbf{b}_\mu^\eta = -\mathbf{n}_{\mu\gamma}\mathcal{D}_{A\gamma}K_{\mathrm{eq}}^{\mu\gamma} \tag{B.48}$$

$$-\mathbf{n}_{\gamma\mu}\cdot\mathcal{D}_{A\gamma}\nabla s_\gamma^\omega - P_{\gamma\mu}(s_\gamma^\omega - K_{\mathrm{eq}}^{\mu\gamma}s_\mu^\omega) = -P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma} \tag{B.49}$$

$$-\mathbf{n}_{\gamma\mu}\cdot\mathcal{D}_{A\gamma}\nabla s_\gamma^\eta - P_{\gamma\mu}(s_\gamma^\eta - K_{\mathrm{eq}}^{\mu\gamma}s_\mu^\eta) = P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma} \tag{B.50}$$

$$-\mathbf{n}_{\gamma\mu}\cdot\mathcal{D}_{A\gamma}\nabla\mathbf{b}_\gamma^\omega = P_{\gamma\mu}(\mathbf{b}_\gamma^\omega - K_{\mathrm{eq}}^{\mu\gamma}\mathbf{b}_\mu^\omega) \tag{B.51}$$

$$-\mathbf{n}_{\gamma\mu}\cdot\mathcal{D}_{A\gamma}\nabla\mathbf{b}_\gamma^\eta - P_{\gamma\mu}(\mathbf{b}_\gamma^\eta - K_{\mathrm{eq}}^{\mu\gamma}\mathbf{b}_\mu^\eta) = \mathbf{n}_{\gamma\mu}\mathcal{D}_{A\gamma}K_{\mathrm{eq}}^{\mu\gamma} \tag{B.52}$$

$$\text{At } \ y = 2h \quad \varphi_\alpha = 0 \tag{B.53}$$

$$\text{At } \ y = 0, \quad \mathbf{b}_\sigma^\omega = \mathbf{b}_\sigma, \quad \mathbf{b}_\mu^\omega = \mathbf{b}_\mu, \quad \varphi_\gamma = 0, \quad s_\alpha^\omega = s_\alpha^\eta = 0, \quad \mathbf{b}_\alpha^\eta = \mathbf{b}_\alpha^\eta = \mathbf{0}, \quad \alpha = \sigma, \mu, \gamma \tag{B.54}$$

Periodicity

$$\varphi_\alpha(\mathbf{r} + \ell_k) = \varphi_\alpha(\mathbf{r}) \quad k = 1, 2;\ \alpha = \sigma, \mu, \gamma. \tag{B.55}$$

In addition, in Eq. (B.54) we have used Eq. (54). This concludes the analysis.

Appendix C. Local mass equilibrium for the closure problem of the jump condition

In this section, the length scale constraints associated to the validity of the local mass equilibrium in V_ω in the inter-region are derived. The analysis is based in the analogous case of heat transfer in porous media described by Whitaker (Chapter 2, in Ref. [28]). In Section 4 we introduced the following expression,

$$\{C_A\}_\omega|_{\mathbf{x}_0} = \varepsilon_\mu(\mathbf{x}_0)\langle C_{A\mu}\rangle^\mu|_{\mathbf{x}_0} + \frac{\varepsilon_\sigma(\mathbf{x}_0)}{K_{\mathrm{eq}}^{\mu\sigma}}\langle C_{A\sigma}\rangle^\sigma|_{\mathbf{x}_0} \tag{C.1}$$

Associated to this weighted average, the following macroscopic deviations arise

$$\hat{C}_{A\mu}|_{\mathbf{x}_0} = \langle C_{A\mu}\rangle^\mu|_{\mathbf{x}_0} - \{C_A\}_\omega|_{\mathbf{x}_0} \tag{C.2}$$

$$\hat{C}_{A\sigma}|_{\mathbf{x}_0} = \langle C_{A\sigma}\rangle^\sigma|_{\mathbf{x}_0} - K_{\mathrm{eq}}^{\mu\sigma}\{C_A\}_\omega|_{\mathbf{x}_0} \tag{C.3}$$

Combining Eqs. (C.1)–(C.3) gives,

$$\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} = \{C_A\}_{\omega}|_{\mathbf{x}_0} + \varepsilon_{\sigma}(\mathbf{x}_0)\left(\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \frac{1}{K_{\mathrm{eq}}^{\mu\sigma}}\langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0}\right) \tag{C.4}$$

$$\langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0} = K_{\mathrm{eq}}^{\mu\sigma}\{C_A\}_{\omega}\big|_{\mathbf{x}_0} - \varepsilon_{\mu}(\mathbf{x}_0)K_{\mathrm{eq}}^{\mu\sigma}\left(\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \frac{1}{K_{\mathrm{eq}}^{\mu\sigma}}\langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0}\right) \tag{C.5}$$

In order to develop the restraints behind the assumption of local mass equilibrium, let us substitute Eqs. (C.4) and (C.5) in the interfacial boundary conditions for the spatial deviations of species A to obtain,

At the $\mu\sigma$-interface

$$\begin{aligned}\mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\sigma}\nabla\tilde{C}_{A\sigma} - \mathbf{n}_{\mu\sigma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla\tilde{C}_{A\mu} &= \mathbf{n}_{\mu\sigma}\cdot(\boldsymbol{\mathcal{D}}_{A\mu} - \boldsymbol{\mathcal{D}}_{A\sigma}K_{\mathrm{eq}}^{\mu\sigma})\nabla\{C_A\}_{\omega}|_{\mathbf{x}_0}\\ &\quad + \mathbf{n}_{\mu\sigma}\cdot\nabla\left[D_{A\mu\sigma}\left(\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \frac{1}{K_{\mathrm{eq}}^{\mu\sigma}}\langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0}\right)\right]\end{aligned} \tag{C.6}$$

$$\begin{aligned}-\mathbf{n}_{\sigma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\sigma}\nabla\tilde{C}_{A\sigma} - P_{\sigma\mu}(\tilde{C}_{A\sigma} - K_{\mathrm{eq}}^{\mu\sigma}\tilde{C}_{A\mu}) &= \mathbf{n}_{\sigma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\sigma}\nabla(K_{\mathrm{eq}}^{\mu\sigma}\{C_A\}_{\omega}|_{\mathbf{x}_0}) - P_{\sigma\mu}K_{\mathrm{eq}}^{\mu\sigma}\left(\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \frac{1}{K_{\mathrm{eq}}^{\mu\sigma}}\langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0}\right)\\ &\quad - \mathbf{n}_{\sigma\mu}\cdot\nabla\left[\boldsymbol{\mathcal{D}}_{A\sigma}\varepsilon_{\mu}(\mathbf{x}_0)K_{\mathrm{eq}}^{\mu\sigma}\left(\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \frac{1}{K_{\mathrm{eq}}^{\mu\sigma}}\langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0}\right)\right]\end{aligned} \tag{C.7}$$

At the $\mu\gamma$-interface

$$\begin{aligned}\mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}\nabla\tilde{C}_{A\gamma} - \mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla\tilde{C}_{A\mu} &= \mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\mu}\nabla\{C_A\}_{\omega}|_{\mathbf{x}_0} - \mathbf{n}_{\mu\gamma}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}K_{\mathrm{eq}}^{\mu\gamma}\nabla\{C_A\}_{\eta}|_{\mathbf{x}_0}\\ &\quad + \mathbf{n}_{\mu\gamma}\cdot\nabla\left[\boldsymbol{\mathcal{D}}_{A\mu}\varepsilon_{\sigma}(\mathbf{x}_0)\left(\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \frac{1}{K_{\mathrm{eq}}^{\mu\sigma}}\langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0}\right)\right]\end{aligned} \tag{C.8}$$

$$\begin{aligned}-\mathbf{n}_{\gamma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}\nabla\tilde{C}_{A\gamma} - P_{\gamma\mu}(\tilde{C}_{A\gamma} - K_{\mathrm{eq}}^{\mu\gamma}\tilde{C}_{A\mu}) &= \mathbf{n}_{\gamma\mu}\cdot\boldsymbol{\mathcal{D}}_{A\gamma}K_{\mathrm{eq}}^{\mu\gamma}\nabla\{C_A\}_{\eta}|_{\mathbf{x}_0} + P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma}(\{C_A\}_{\eta}|_{\mathbf{x}_0} - \{C_A\}_{\omega}|_{\mathbf{x}_0})\\ &\quad - P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma}\varepsilon_{\sigma}(\mathbf{x}_0)\left(\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \frac{1}{K_{\mathrm{eq}}^{\mu\sigma}}\langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0}\right)\end{aligned} \tag{C.9}$$

Where we have introduced the following definition,

$$D_{A\mu\sigma} = \boldsymbol{\mathcal{D}}_{A\mu}\varepsilon_{\sigma}(\mathbf{x}_0) + \boldsymbol{\mathcal{D}}_{A\sigma}\varepsilon_{\mu}(\mathbf{x}_0)K_{\mathrm{eq}}^{\mu\sigma} \tag{C.10}$$

From Eqs. (C.6)–(C.9) it is obtained that the local mass equilibrium is valid at the closure level, if the following inequalities are satisfied,

$$(\boldsymbol{\mathcal{D}}_{A\mu} - \boldsymbol{\mathcal{D}}_{A\sigma}K_{\mathrm{eq}}^{\mu\sigma})\nabla\{C_A\}_{\omega}|_{\mathbf{x}_0} \gg \nabla\left[\frac{D_{A\mu\sigma}}{K_{\mathrm{eq}}^{\mu\sigma}}(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0})\right] \tag{C.11}$$

$$\nabla\{C_A\}_{\omega}\big|_{\mathbf{x}_0} \gg \nabla\left[\frac{\varepsilon_{\sigma}(\mathbf{x}_0)}{K_{\mathrm{eq}}^{\mu\sigma}}(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0})\right] \tag{C.12}$$

$$(\tilde{C}_{A\sigma},\, K_{\mathrm{eq}}^{\mu\sigma}\tilde{C}_{A\mu}) \gg (K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0}) \tag{C.13}$$

$$\{C_A\}_{\omega}|_{\mathbf{x}_0} \gg \frac{\varepsilon_{\sigma}(\mathbf{x}_0),\, \varepsilon_{\mu}(\mathbf{x}_0)}{K_{\mathrm{eq}}^{\mu\sigma}}(K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0}) \tag{C.14}$$

In addition, from Appendix A, the following estimates are obtained

$$\frac{K_{\mathrm{eq}}^{\mu\sigma}\langle C_{A\mu}\rangle^{\mu}|_{\mathbf{x}_0} - \langle C_{A\sigma}\rangle^{\sigma}|_{\mathbf{x}_0}}{\{C_A\}_{\omega}|_{\mathbf{x}_0}} = \mathbf{O}\left(\frac{\ell_{\sigma\mu}^2}{L^2}\right) \tag{C.15}$$

here,

$$\ell_{\sigma\mu}^2 = \frac{\varepsilon_\sigma(\mathbf{x}_0)\varepsilon_\mu(\mathbf{x}_0)D_{A\mu\sigma}}{a_v(\mathbf{x}_0)h(\mathbf{x}_0)} \tag{C.16}$$

From Eq. (C.15), the following length scale constraints are obtained when this estimate is substituted in Eqs. (C.11), (C.12) and (C.14),

$$\frac{K_{\text{eq}}^{\mu\sigma}(\mathcal{D}_{A\mu} - \mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma})}{D_{A\mu\sigma}} \gg \frac{\ell_{\sigma\mu}^2}{L^2} \tag{C.17}$$

$$\frac{K_{\text{eq}}^{\mu\sigma}}{\varepsilon_\sigma(\mathbf{x}_0),\, \varepsilon_\mu(\mathbf{x}_0)} \gg \frac{\ell_{\sigma\mu}^2}{L^2} \tag{C.18}$$

Notice that the above equations are automatically satisfied if the physical properties of the two phases are equal (i.e., $\mathcal{D}_{A\mu} \to \mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma}$) or only one phase is present. If these length scale constraints are satisfied in the inter-region, then Eqs. (C.6)–(C.9) are simplified to,

At the $\mu\sigma$-interface

$$\mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\sigma}\nabla\tilde{C}_{A\sigma} - \mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\mu}\nabla\tilde{C}_{A\mu} = \mathbf{n}_{\mu\sigma}\cdot(\mathcal{D}_{A\mu} - \mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma})\nabla\{C_A\}_\omega|_{\mathbf{x}_0} \tag{C.19}$$

$$-\mathbf{n}_{\sigma\mu}\cdot\mathcal{D}_{A\sigma}\nabla\tilde{C}_{A\sigma} - P_{\sigma\mu}(\tilde{C}_{A\sigma} - K_{\text{eq}}^{\mu\sigma}\tilde{C}_{A\mu}) = \mathbf{n}_{\sigma\mu}\cdot\mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma}\nabla\{C_A\}_\omega|_{\mathbf{x}_0} - P_{\sigma\mu}K_{\text{eq}}^{\mu\sigma}\left(\langle C_{A\mu}\rangle^\mu|_{\mathbf{x}_0} - \frac{1}{K_{\text{eq}}^{\mu\sigma}}\langle C_{A\sigma}\rangle^\sigma|_{\mathbf{x}_0}\right) \tag{C.20}$$

At the $\mu\gamma$-interface

$$\mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\gamma}\nabla\tilde{C}_{A\gamma} - \mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\mu}\nabla\tilde{C}_{A\mu} = \mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\mu}\nabla\{C_A\}_\omega|_{\mathbf{x}_0} - \mathbf{n}_{\mu\gamma}\cdot\mathcal{D}_{A\gamma}K_{\text{eq}}^{\mu\gamma}\nabla\{C_A\}_\eta|_{\mathbf{x}_0} \tag{C.21}$$

$$-\mathbf{n}_{\gamma\mu}\cdot\mathcal{D}_{A\gamma}\nabla\tilde{C}_{A\gamma} - P_{\gamma\mu}(\tilde{C}_{A\gamma} - K_{\text{eq}}^{\mu\gamma}\tilde{C}_{A\mu}) = \mathbf{n}_{\gamma\mu}\cdot\mathcal{D}_{A\gamma}K_{\text{eq}}^{\mu\gamma}\nabla\{C_A\}_\eta|_{\mathbf{x}_0} + P_{\gamma\mu}K_{\text{eq}}^{\mu\gamma}(\{C_A\}_\eta|_{\mathbf{x}_0} - \{C_A\}_\omega|_{\mathbf{x}_0}) \tag{C.22}$$

In order to develop the constraints associated with Eq. (C.13), let us assume that

$$\tilde{C}_{A\sigma} = \mathbf{O}(K_{\text{eq}}^{\mu\sigma}\tilde{C}_{A\mu}) \tag{C.23}$$

Following Whitaker [28] it is desirable to distribute the surface diffusive source $\nabla\{C_A\}_\omega|_{\mathbf{x}_0}$ in a manner consistent with the above equation. To this end, a weighting parameter $\varphi \in [0,1]$ is introduced, this allows distributing the flux as

$$\mathbf{n}_{\mu\sigma}\cdot\mathcal{D}_{A\sigma}\nabla\tilde{C}_{A\sigma} = \varphi[\mathbf{n}_{\mu\sigma}\cdot(\mathcal{D}_{A\mu} - \mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma})\nabla\{C_A\}_\omega|_{\mathbf{x}_0}] \tag{C.24}$$

$$\mathbf{n}_{\sigma\mu}\cdot\mathcal{D}_{A\mu}\nabla\tilde{C}_{A\mu} = (1-\varphi)[\mathbf{n}_{\mu\sigma}\cdot(\mathcal{D}_{A\mu} - \mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma})\nabla\{C_A\}_\omega|_{\mathbf{x}_0}] \tag{C.25}$$

From the above equations, the following order of magnitude estimates are obtained

$$\tilde{C}_{A\sigma} = \mathbf{O}\left[\varphi\ell_\sigma\frac{(\mathcal{D}_{A\mu} - \mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma})}{\mathcal{D}_{A\sigma}}\nabla\{C_A\}_\omega|_{\mathbf{x}_0}\right] \tag{C.26}$$

$$\tilde{C}_{A\mu} = \mathbf{O}\left[(1-\varphi)\ell_\mu\frac{(\mathcal{D}_{A\mu} - \mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma})}{\mathcal{D}_{A\mu}}\nabla\{C_A\}_\omega|_{\mathbf{x}_0}\right] \tag{C.27}$$

The order of magnitude of the weight φ is obtained by substituting Eqs. (C.26) and (C.27) in Eq. (C.23) as,

$$\varphi = \mathbf{O}\left[\frac{\ell_\mu\mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma}}{\ell_\sigma\mathcal{D}_{A\mu} + \ell_\mu\mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma}}\right] \tag{C.28}$$

and, as consequence,

$$\tilde{C}_{A\sigma} = \mathbf{O}(K_{\text{eq}}^{\mu\sigma}\tilde{C}_{A\mu}) = \mathbf{O}\left[\frac{\ell_\sigma\ell_\mu K_{\text{eq}}^{\mu\sigma}(\mathcal{D}_{A\mu} - \mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma})}{\ell_\sigma\mathcal{D}_{A\mu} + \ell_\mu\mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma}}\nabla\{C_A\}_\omega|_{\mathbf{x}_0}\right] \tag{C.29}$$

This result allows determining from Eq. (C.13) (taking in account the estimate in Eq. (C.15)) the following length scale constraint

$$\frac{\ell_\sigma\ell_\mu K_{\text{eq}}^{\mu\sigma}(\mathcal{D}_{A\mu} - \mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma})}{\ell_{\sigma\mu}(\ell_\sigma\mathcal{D}_{A\mu} + \ell_\mu\mathcal{D}_{A\sigma}K_{\text{eq}}^{\mu\sigma})} \gg \left(\frac{\ell_{\sigma\mu}}{L}\right) \tag{C.30}$$

For many practical systems the left hand side of the above equation is of the order of one, therefore, if $\ell_{\mu\sigma} \ll L$, then the assumption of local mass equilibrium is satisfied at the closure problem level for the $\mu\sigma$-interface.

Appendix D. Simplifications and order of magnitude analysis for the closed jump condition

In this appendix the simplification of the closed jump boundary condition (Eq. (88))

$$
\begin{aligned}
-\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega) = {} & \langle P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma}\rangle_{\eta\omega}^{\gamma\mu}(\{C_A\}_\eta|_{\mathbf{x}_0}-\{C_A\}_\omega|_{\mathbf{x}_0}) + (\langle P_{\sigma\mu}(s_\sigma^\omega - K_{\mathrm{eq}}^{\mu\sigma}s_\mu^\omega)\rangle_{\eta\omega}^{\sigma\mu} + \langle P_{\gamma\mu}(s_\gamma^\omega - K_{\mathrm{eq}}^{\mu\gamma}s_\mu^\omega)\rangle_{\eta\omega}^{\gamma\mu})\{C_A\}_\omega|_{\mathbf{x}_0} \\
& + (\langle P_{\sigma\mu}(s_\sigma^\eta - K_{\mathrm{eq}}^{\mu\sigma}s_\mu^\eta)\rangle_{\eta\omega}^{\sigma\mu} + \langle P_{\gamma\mu}(s_\gamma^\eta - K_{\mathrm{eq}}^{\mu\gamma}s_\mu^\eta)\rangle_{\eta\omega}^{\gamma\mu})\{C_A\}_\eta|_{\mathbf{x}_0} + (\langle P_{\sigma\mu}(\mathbf{b}_\sigma^\omega - K_{\mathrm{eq}}^{\mu\sigma}\mathbf{b}_\mu^\omega)\rangle_{\eta\omega}^{\sigma\mu} \\
& + \langle P_{\gamma\mu}(\mathbf{b}_\gamma^\omega - K_{\mathrm{eq}}^{\mu\gamma}\mathbf{b}_\mu^\omega)\rangle_{\eta\omega}^{\gamma\mu})\cdot\nabla\{C_A\}_\omega|_{\mathbf{x}_0} + (\langle P_{\sigma\mu}(\mathbf{b}_\sigma^\eta - K_{\mathrm{eq}}^{\mu\sigma}\mathbf{b}_\mu^\eta)\rangle_{\eta\omega}^{\sigma\mu} \\
& + \langle P_{\gamma\mu}(\mathbf{b}_\gamma^\eta - K_{\mathrm{eq}}^{\mu\gamma}\mathbf{b}_\mu^\eta)\rangle_{\eta\omega}^{\gamma\mu})\cdot\nabla\{C_A\}_\eta|_{\mathbf{x}_0}
\end{aligned}
\tag{D.1}
$$

is performed by showing that the two last terms in the RHS of the above equation are negligible. Indeed, an order of magnitude analysis, based in the results of Appendix B, yields

$$
\begin{aligned}
& (\langle P_{\sigma\mu}(\mathbf{b}_\sigma^\omega - K_{\mathrm{eq}}^{\mu\sigma}\mathbf{b}_\mu^\omega)\rangle_{\eta\omega}^{\sigma\mu} + \langle P_{\gamma\mu}(\mathbf{b}_\gamma^\omega - K_{\mathrm{eq}}^{\mu\gamma}\mathbf{b}_\mu^\omega)\rangle_{\eta\omega}^{\gamma\mu})\cdot\nabla\{C_A\}_\omega|_{\mathbf{x}_0} \\
& \quad = \mathbf{O}\left[\left(\frac{K_{\mathrm{eq}}^{\mu\sigma}\mathcal{D}_{A\sigma}P_{\sigma\mu}(1-\ell_\sigma/\ell_\mu)}{P_{\sigma\mu}\ell_\sigma\mathcal{D}_{A\mu}-(P_{\sigma\mu}K_{\mathrm{eq}}^{\mu\sigma}\ell_\mu-\mathcal{D}_{A\mu})\mathcal{D}_{A\sigma}} + \frac{\mathcal{D}_{A\gamma}P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma}}{P_{\gamma\mu}\ell_\gamma\mathcal{D}_{A\mu}-(P_{\gamma\mu}\ell_\mu K_{\mathrm{eq}}^{\mu\gamma}-\mathcal{D}_{A\mu})\mathcal{D}_{A\gamma}}\right)\mathcal{D}_{A\mu}\frac{\ell_\mu}{L}\{C_A\}_\omega|_{\mathbf{x}_0}\right]
\end{aligned}
\tag{D.2}
$$

$$
\begin{aligned}
& (\langle P_{\sigma\mu}(\mathbf{b}_\sigma^\eta - K_{\mathrm{eq}}^{\mu\sigma}\mathbf{b}_\mu^\eta)\rangle_{\eta\omega}^{\sigma\mu} + \langle P_{\gamma\mu}(\mathbf{b}_\gamma^\eta - K_{\mathrm{eq}}^{\mu\gamma}\mathbf{b}_\mu^\eta)\rangle_{\eta\omega}^{\gamma\mu})\cdot\nabla\{C_A\}_\eta|_{\mathbf{x}_0} \\
& \quad = \mathbf{O}\left[\left(\frac{P_{\sigma\mu}(\ell_\sigma\mathcal{D}_{A\mu}/\mathcal{D}_{A\sigma}-K_{\mathrm{eq}}^{\mu\sigma}\ell_\mu)-\mathcal{D}_{A\mu}}{(\mathcal{D}_{A\mu}-K_{\mathrm{eq}}^{\mu\gamma}P_{\gamma\mu}\ell_\mu)\mathcal{D}_{A\gamma}+P_{\gamma\mu}\mathcal{D}_{A\mu}\ell_\gamma}\right)P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma}\mathcal{D}_{A\gamma}\frac{\ell_\gamma}{L}\{C_A\}_\eta|_{\mathbf{x}_0}\right]
\end{aligned}
\tag{D.3}
$$

Therefore, if the length scale constraints,

$$
\left(\frac{K_{\mathrm{eq}}^{\mu\sigma}\mathcal{D}_{A\sigma}P_{\sigma\mu}(1-\ell_\sigma/\ell_\mu)}{P_{\sigma\mu}\ell_\sigma\mathcal{D}_{A\mu}-(P_{\sigma\mu}K_{\mathrm{eq}}^{\mu\sigma}\ell_\mu-\mathcal{D}_{A\mu})\mathcal{D}_{A\sigma}} + \frac{\mathcal{D}_{A\gamma}P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma}}{P_{\gamma\mu}\ell_\gamma\mathcal{D}_{A\mu}-(P_{\gamma\mu}\ell_\mu K_{\mathrm{eq}}^{\mu\gamma}-\mathcal{D}_{A\mu})\mathcal{D}_{A\gamma}}\right)\mathcal{D}_{A\mu}\frac{\ell_\mu}{L} \ll 1
\tag{D.4}
$$

$$
\left(\frac{P_{\sigma\mu}(\ell_\sigma\mathcal{D}_{A\mu}/\mathcal{D}_{A\sigma}-K_{\mathrm{eq}}^{\mu\sigma}\ell_\mu)-\mathcal{D}_{A\mu}}{(\mathcal{D}_{A\mu}-K_{\mathrm{eq}}^{\mu\gamma}P_{\gamma\mu}\ell_\mu)\mathcal{D}_{A\gamma}+P_{\gamma\mu}\mathcal{D}_{A\mu}\ell_\gamma}\right)P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma}\mathcal{D}_{A\gamma}\frac{\ell_\gamma}{L} \ll 1
\tag{D.5}
$$

are satisfied at the inter-region, the jump condition simplifies to

$$
\begin{aligned}
-\mathbf{n}_{\eta\omega}\cdot(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega) = {} & \langle P_{\gamma\mu}K_{\mathrm{eq}}^{\mu\gamma}\rangle_{\eta\omega}^{\gamma\mu}(\{C_A\}_\eta|_{\mathbf{x}_0}-\{C_A\}_\omega|_{\mathbf{x}_0}) + (\langle P_{\sigma\mu}(s_\sigma^\omega - K_{\mathrm{eq}}^{\mu\sigma}s_\mu^\omega)\rangle_{\eta\omega}^{\sigma\mu} + \langle P_{\gamma\mu}(s_\gamma^\omega - K_{\mathrm{eq}}^{\mu\gamma}s_\mu^\omega)\rangle_{\eta\omega}^{\gamma\mu})\{C_A\}_\omega|_{\mathbf{x}_0} \\
& + (\langle P_{\sigma\mu}(s_\sigma^\eta - K_{\mathrm{eq}}^{\mu\sigma}s_\mu^\eta)\rangle_{\eta\omega}^{\sigma\mu} + \langle P_{\gamma\mu}(s_\gamma^\eta - K_{\mathrm{eq}}^{\mu\gamma}s_\mu^\eta)\rangle_{\eta\omega}^{\gamma\mu})\{C_A\}_\eta|_{\mathbf{x}_0}.
\end{aligned}
\tag{D.6}
$$

Substituting the local permeabilities and equilibrium coefficients' spatial decompositions [33]

$$
P_{\alpha\mu} = \langle P_{\alpha\mu}\rangle_{\eta\omega}^{\alpha\mu} + \tilde{P}_{\alpha\mu}
\tag{D.7}
$$

$$
K_{\mathrm{eq}}^{\alpha\mu} = \langle K_{\mathrm{eq}}^{\alpha\mu}\rangle_{\eta\omega}^{\alpha\mu} + \tilde{K}_{\mathrm{eq}}^{\alpha\mu}
\tag{D.8}
$$

in Eq. (D.6) leads to [28],

$$
-\mathbf{n}_{\eta\omega}.(\mathbf{D}_{A\omega}\cdot\nabla\{C_A\}_\omega|_{\mathbf{x}_0}) = P_{\mathrm{eff}}^\eta(\{C_A\}_\eta|_{\mathbf{x}_0} - K_{\mathrm{eff}}^{\eta\omega}\{C_A\}_\omega|_{\mathbf{x}_0}),
\tag{D.9}
$$

at the dividing surface.

In the above equation we have introduced the following effective coefficients

Effective permeability of the η-region

$$
\begin{aligned}
P_{\mathrm{eff}}^\eta = {} & P_{\mathrm{eff}} + \langle P_{\sigma\mu}\rangle_{\eta\omega}^{\sigma\mu}\langle\tilde{K}_{\mathrm{eq}}^{\mu\sigma}s_\mu^\eta\rangle_{\eta\omega}^{\sigma\mu} + \langle P_{\gamma\mu}\rangle_{\eta\omega}^{\gamma\mu}\langle\tilde{K}_{\mathrm{eq}}^{\mu\gamma}s_\mu^\eta\rangle_{\eta\omega}^{\gamma\mu} + \langle\tilde{P}_{\sigma\mu}s_\sigma^\eta\rangle_{\eta\omega}^{\sigma\mu} + \langle\tilde{P}_{\gamma\mu}s_\gamma^\eta\rangle_{\eta\omega}^{\gamma\mu} - \langle\tilde{P}_{\sigma\mu}s_\mu^\eta\rangle_{\eta\omega}^{\sigma\mu}\langle K_{\mathrm{eq}}^{\mu\sigma}\rangle_{\eta\omega}^{\sigma\mu} \\
& - \langle\tilde{P}_{\gamma\mu}s_\mu^\eta\rangle_{\eta\omega}^{\gamma\mu}\langle K_{\mathrm{eq}}^{\mu\gamma}\rangle_{\eta\omega}^{\gamma\mu} - \langle\tilde{P}_{\sigma\mu}\tilde{K}_{\mathrm{eq}}^{\mu\sigma}s_\mu^\eta\rangle_{\eta\omega}^{\sigma\mu} - \langle\tilde{P}_{\gamma\mu}\tilde{K}_{\mathrm{eq}}^{\mu\gamma}s_\mu^\eta\rangle_{\eta\omega}^{\gamma\mu}
\end{aligned}
\tag{D.10}
$$

Effective permeability of the ω-region

$$P_{\text{eff}}^{\omega} = P_{\text{eff}} - \langle P_{\sigma\mu}\rangle_{\eta\omega}^{\sigma\mu}\langle \tilde{K}_{\text{eq}}^{\mu\sigma} s_{\mu}^{\omega}\rangle_{\eta\omega}^{\sigma\mu} - \langle P_{\gamma\mu}\rangle_{\eta\omega}^{\gamma\mu}\langle \tilde{K}_{\text{eq}}^{\mu\gamma} s_{\mu}^{\omega}\rangle_{\eta\omega}^{\gamma\mu} - \langle \tilde{P}_{\sigma\mu} s_{\sigma}^{\omega}\rangle_{\eta\omega}^{\sigma\mu} - \langle \tilde{P}_{\gamma\mu} s_{\gamma}^{\omega}\rangle_{\eta\omega}^{\gamma\mu} + \langle \tilde{P}_{\gamma\mu} s_{\mu}^{\omega}\rangle_{\eta\omega}^{\gamma\mu}\langle K_{\text{eq}}^{\mu\gamma}\rangle_{\eta\omega}^{\gamma\mu} + \langle \tilde{P}_{\sigma\mu} s_{\mu}^{\omega}\rangle_{\eta\omega}^{\sigma\mu}\langle K_{\text{eq}}^{\mu\sigma}\rangle_{\eta\omega}^{\sigma\mu} + \langle \tilde{P}_{\gamma\mu}\tilde{K}_{\text{eq}}^{\mu\gamma} s_{\mu}^{\omega}\rangle_{\eta\omega}^{\gamma\mu} + \langle \tilde{P}_{\sigma\mu}\tilde{K}_{\text{eq}}^{\mu\sigma} s_{\mu}^{\omega}\rangle_{\eta\omega}^{\sigma\mu} \tag{D.11}$$

Effective equilibrium coefficient of the ω–η inter-region

$$K_{\text{eff}}^{\eta\omega} = \frac{P_{\text{eff}}^{\omega}}{P_{\text{eff}}^{\eta}} \tag{D.12}$$

here $P_{\text{eff}} = \langle P_{\gamma\mu}\rangle_{\eta\omega}^{\gamma\mu}\langle K_{\text{eq}}^{\mu\gamma}\rangle_{\eta\omega}^{\gamma\mu} + \langle \tilde{P}_{\gamma\mu}\tilde{K}_{\text{eq}}^{\mu\gamma}\rangle_{\eta\omega}^{\gamma\mu}$ can be computed from the local spatial distribution of $P_{\gamma\mu}$ and $K_{\text{eq}}^{\mu\gamma}$.

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