Jump Mass Transfer for
Double Emulsion Systems

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Abstract

The mass transfer condition that applies at the boundary between the \( \omega \)-region (globules and liquid membrane) and the \( \eta \)-region (external region) in a double emulsion system, was developed as a jump condition based on the non-local form of the volume averaged mass transport equation that is valid within the boundary region. Outside the boundary region this non-local form reduces to the classic volume averaged transport equation in the \( \omega \)-region and to the point in the \( \eta \)-region. The jump condition takes the form of a surface transport equation that contains terms representing the excess surface accumulation, diffusion, reaction, and a non-equilibrium source term, in addition to a term representing the exchange with the surrounding regions.

Keywords: Diffusion, Emulsion, Mass Transfer, Jump Condition, Multi-phase Flow, Liquid Membrane, Averaging Volume

1 Introduction

The method of averaging volume was used to derive the mass transport jump condition at the boundary between \( \omega \)-region and \( \eta \)-region for double emulsion systems (three-phase systems). In this study a volume-averaged mass transfer equation for species \( A \), \( B \) and \( R \) that are valid everywhere in this system and, in the \( \omega - \eta \) boundary was developed. These equations are based on the non-local form of the volume-average mass transport equation that is valid within the boundary region. Outside the boundary region this non-local form reduces to the classic volume-average transport equation, which is not valid within the boundary region.
In a previous study of systems with a boundary between a heterogeneous medium and a homogeneous fluid, flux jump condition was developed based on the non-local form of the volume averaged transport equations for momentum transfer \([6]-[8]\), for heat transfer \([9]-[10]\) and for mass transfer \([13]\).

The momentum transfer condition that applies at the boundary between a porous medium and a homogeneous fluid were developed by Ochoa-Tapia and Whitaker \([6]\) and their theoretical results were compared with experimental data \([7]\). These authors constructed the jump condition to join Darcys law with the Brinkman correction to Stokes equation, and this leads to a volume averaged velocity field that is continuous. The same investigators \([8]\) have presented another shear jump boundary condition where the inertia effects become important in the boundary region.

The heat transfer jump condition that applies at the boundary between a porous medium and a homogeneous fluid when the condition of local thermal equilibrium is not valid was developed by Ochoa-Tapia and Whitaker \([9]\). These authors applied separate transport equations to describe the behavior for each phase and found that the jump condition contained an excess surface heat exchange term that controls the manner in which the total flux is distributed between the two phases. Ochoa-Tapia and Whitaker \([10]\) developed the jump condition when local thermal equilibrium is imposed and found that the non-local form simplifies to the classic one-equation model for thermal energy transport.

The mass transfer jump condition at the boundary between a porous medium and a homogeneous fluid was developed by Valencia et al. \([13]\). These authors found that the jump conditions takes the form of surface transport equations that contains terms representing the excess surface accumulation, convection, diffusion, adsorption, non-equilibrium source term and, a term representing the exchange with the surrounding regions.

The stress, mass and flux jump conditions have an inherent problem, due that they involve unknown coefficients, which need to be fitten experimentally or numerically. Recently, Min and Kim \([5]\) developed a methodology to determine stress-jump coefficient and boundary heat transfer coefficient of the mathematical models presented in \([6]\) and \([9]\), respectively.

The jump condition at non-uniform boundaries and a closure problem to provide theoretical values of the effective reaction rate coefficient for a first order, irreversible reaction has been presented by Wood et al. \([15]\), while that Goyeau et al. \([4]\) have derived an explicit function for stress jump coefficient in a fluid-porous interface, which was considered as a heterogeneous porous layer. Following similar ideas, Valdes-Parada, et al. \([12]\), obtained the effective reaction rate coefficient involved in diffusive mass transfer between a microporous medium and a homogeneous fluid.

In this paper we construct the jump condition to mass transfer in a double
emulsion system with liquid membrane. The frameworks for the derivation of the mass transfer jump condition were established in the work of Espinosa-Paredes [2], specifically the one-equation model to globules and membrane in a double emulsion system was developed with chemical reaction and diffusion and convection effects.

2 Generalized Mass Transfer Equation

In this study we need a volume-averaged mass transfer equation for species $A$, $B$ and $R$ that are valid everywhere in this system and, in the $\omega - \eta$ boundary. We begin this process by locating an averaging volume at every point in space, and three of these averaging volumes are shown in Fig. 1.

Definition 2.1 This idea can be expressed more precisely in the next form

$$ V = V_\sigma(x) + V_\mu(x) + V_\gamma(x) $$

Therefore

$$ \varepsilon_\sigma(x) + \varepsilon_\mu(x) + \varepsilon_\gamma(x) = 1 \quad (1) $$

It should be noticed that although $V$ is constant, the volumes of each phase may change with the position of the averaging volume. It should be clear that the volume fractions $\varepsilon_\kappa(\kappa = \sigma, \mu, \gamma)$ are functions of the position, depending of the sampling point located by $x$. We noted that in the $\omega - \eta$ boundary $\varepsilon_\kappa$ undergoes significant changes over a distance equal to the radius of the averaging volume, $r_o$ (as is illustrated in the Fig. 2 in Ref. [2], where $\delta$ represents the thickness of the interfacial region, where there are rapid changes in $\varepsilon_\kappa$).

Following the same procedure leading averaging mass transport equations presented in [2], we express the average to species (The point equations are given in Ref. [2]) as

$$ \varepsilon_\sigma \frac{\partial \langle c_{A\sigma} \rangle}{\partial t} = \nabla \cdot \left\{ \varepsilon_\sigma D_{A\sigma} \left[ \nabla \langle c_{A\sigma} \rangle + \frac{1}{V_\sigma} \int_{A_{\sigma\mu}} \mathbf{n}_{\sigma\mu} \tilde{c}_{A\sigma} \, dA \right] \right\} $$

$$ + \frac{1}{V_\sigma} \int_{A_{\sigma\mu}} \mathbf{n}_{\sigma\mu} \langle c_{A\sigma} \rangle \big|_{x+y} - \langle c_{A\sigma} \rangle \big|_x \, dA \right\} + \frac{1}{V} \int_{A_{\sigma\mu}} \mathbf{n}_{\sigma\mu} \cdot D_{A\sigma} \nabla c_{A\sigma} \, dA $$

$$ - k_\sigma \varepsilon_\sigma \langle c_{A\sigma} \rangle \langle c_{R\sigma} \rangle - k_\sigma \langle \tilde{c}_{A\sigma} \tilde{c}_{R\sigma} \rangle - k_\sigma \langle c_{A\sigma} c_{R\sigma} \rangle_{exc} $$

(2)

where
Definition 2.2 The excess reaction term for the convective terms is

$$\langle c_{A\sigma} c_{R\sigma} \rangle_{\text{exc}} = \langle c_{A\sigma} c_{R\sigma} \rangle - \varepsilon_\sigma \langle c_{A\sigma} \rangle^\sigma \langle c_{R\sigma} \rangle^\sigma - \langle \tilde{c}_{A\sigma} \tilde{c}_{R\sigma} \rangle$$

This term is introduced in Eq. (2) to avoid imposing length-scale constraints, with the idea that.

$$\langle C_{A\sigma} c_{R\sigma} \rangle_{\text{exc}} = 0 \quad , \quad \text{in the homogeneous regions} \quad (3)$$

The excess reaction term will not be equal to zero in the boundary, where the length-scale constraints developed by Carbonell and Whitaker [1] are not valid.

The non-local diffusion term in Eq. (2) was obtained as follow: The diffusion transport term is given by:

$$\langle D_{A\sigma} \nabla c_{A\sigma} \rangle = D_{A\sigma} \left[ \varepsilon_\sigma \nabla \langle c_{A\sigma} \rangle^\sigma + \langle c_{A\sigma} \rangle^\sigma \nabla \varepsilon_\sigma + \frac{1}{V} \int_{A_{\sigma \mu}} n_{\sigma \mu} c_{A\mu} dA \right] \quad (4)$$

In order to obtain a volume-average transport equation that contains only average quantities and spatial deviations, the interfacial area integral in this equation is developed as follow: from the volume-averaging theorem (Theorem 3.2 in Ref. [2]) we can obtain the result (Lemma 3.3 in Ref. [2]).

$$\frac{1}{V} \int_{A_{\sigma \mu}} n_{\sigma \mu} dA = -\nabla \varepsilon_\sigma \quad (5)$$

which can be used to write

$$\frac{1}{V} \int_{A_{\sigma \mu}} n_{\sigma \mu} \langle c_{A\sigma} \rangle^\sigma \big|_x dA = -\langle c_{A\sigma} \rangle^\sigma \big|_x \nabla \varepsilon_\sigma = -\langle c_{A\sigma} \rangle^\sigma \nabla \varepsilon_\sigma \quad (6)$$

It can be observed that the convention used here is that averaged quantities located outside an integral are always evaluated at the centroid unless there is some specific indication to the contrary. Use of this result together with Eq. (4) leads to the following expression for the diffusive transport:

$$\langle D_{A\sigma} \nabla c_{A\sigma} \rangle = D_{A\sigma} \left[ \varepsilon_\sigma \nabla \langle c_{A\sigma} \rangle^\sigma + \frac{1}{V} \int_{A_{\sigma \mu}} n_{\sigma \mu} (c_{A\sigma} \big|_{x+y} - \langle c_{A\sigma} \rangle^\sigma \big|_x) dA \right] \quad (7)$$

Use of the decomposition: $c_{A\sigma} = \langle c_{A\sigma} \rangle^\sigma + \tilde{c}_{A\sigma}$, yields the following representation for the diffusion transport term:

$$\langle D_{A\sigma} \nabla C_{A\sigma} \rangle = D_{A\sigma} \left[ \varepsilon_\sigma \nabla \langle c_{A\sigma} \rangle^\sigma + \frac{1}{V} \int_{A_{\sigma \mu}} n_{\sigma \mu} \tilde{c}_{A\sigma} dA \right.$$  

$$+ \frac{1}{V} \int_{A_{\sigma \mu}} n_{\sigma \mu} (\langle c_{A\sigma} \rangle^\sigma \big|_{x+y} - \langle c_{A\sigma} \rangle^\sigma \big|_x) dA \bigg] \quad (8)$$
The second integral on the right-hand side of this equation was identified as a non-local term, since it involves values of $\langle c_{A\sigma} \rangle^\sigma$ that are evaluated at points within the averaging volume that are not located at the centroid. This term could be negligible in homogeneous regions if some appropriate length-scale constraints are imposed.

The procedure leading to the $\sigma$-phase mass transport equation can be repeated for the $\mu$-phase beginning with Eq. (3) and (4), then the average equations for this phase are:

$$
\varepsilon_\mu \frac{\partial \langle c_{A\mu} \rangle^\mu}{\partial t} = \nabla \cdot \left\{ \varepsilon_\mu D_{A\mu} \left[ \nabla \langle c_{A\mu} \rangle^\mu + \frac{1}{V_\mu} \int_{A_\mu} n_{\mu\sigma} \tilde{c}_{A\mu} dA \right. \right.
$$

$$
+ \frac{1}{V_\mu} \int_{A_{\mu\gamma}} n_{\mu\gamma} c_{A\mu} dA + \frac{1}{V_\mu} \int_{A_\mu} n_{\mu\sigma} (\langle c_{A\mu} \rangle^\mu \bigg|_{x+y} - \langle c_{A\mu} \rangle^\mu \bigg|_x) dA
$$

$$
+ \frac{1}{V_\mu} \int_{A_{\mu\gamma}} n_{\mu\gamma} (\langle c_{A\mu} \rangle^\mu \bigg|_{x+y} - \langle c_{A\mu} \rangle^\mu \bigg|_x) dA \left. \right] + \frac{1}{V_\mu} \int_{A_\mu} n_{\mu\sigma} \cdot D_{A\mu} \nabla c_{A\mu} dA
$$

$$
+ \frac{1}{V_\mu} \int_{A_{\mu\gamma}} n_{\mu\gamma} \cdot D_{A\mu} \nabla c_{A\mu} dA - \varepsilon_\mu k_\mu \left( \langle c_{A\mu} \rangle^\mu - \frac{1}{K_\mu} \langle c_{B\mu} \rangle^\mu \right) \right)
$$

(9)

$$
\varepsilon_\mu \frac{\partial \langle c_{B\mu} \rangle^\mu}{\partial t} = \nabla \cdot \left\{ D_{B\mu} \varepsilon_\mu \left[ \nabla \langle c_{B\mu} \rangle^\mu + \frac{1}{V_\mu} \int_{A_{\mu\sigma}} n_{\mu\sigma} \tilde{c}_{B\mu} dA \right. \right.
$$

$$
+ \frac{1}{V_\mu} \int_{A_{\mu\gamma}} n_{\mu\gamma} \tilde{c}_{B\mu} dA + \frac{1}{V_\mu} \int_{A_\mu} n_{\mu\sigma} (\langle c_{B\mu} \rangle^\mu \bigg|_{x+y} - \langle c_{B\mu} \rangle^\mu \bigg|_x) dA
$$

$$
+ \frac{1}{V_\mu} \int_{A_{\mu\gamma}} n_{\mu\gamma} (\langle c_{B\mu} \rangle^\mu \bigg|_{x+y} - \langle c_{B\mu} \rangle^\mu \bigg|_x) dA \left. \right] - \varepsilon_\mu k_\mu \left( \langle c_{A\mu} \rangle^\mu - \frac{1}{K_\mu} \langle c_{B\mu} \rangle^\mu \right) \right)
$$

(10)

It is important to note that we have not imposed any length-scale constraints to obtain Eqs. (2), (9) and (10). Therefore, these equations are valid everywhere in the multiphase system, including the inter-region between the $\omega$-region and $\eta$-region for double emulsion systems.

In order to derive the jump condition, we need to obtain an equation that is valid at any place of the three-phase system of the double emulsion.

**Definition 2.3** The concentration for the individual phases are related to each other by a simple algebraic relation.

$$
\{c_A\} = \varepsilon_\mu \langle c_{A\mu} \rangle^\mu + \frac{\varepsilon_\sigma}{K_{eq}^{\mu\sigma}} \langle c_{A\sigma} \rangle^\sigma + \frac{\varepsilon_\gamma}{K_{eq}^{\mu\gamma}} \langle c_{A\gamma} \rangle^\gamma
$$
where \( \langle c_{A\kappa} \rangle \) with \( \kappa = \sigma, \mu, \gamma \) is the intrinsic volume average concentration of \( A \) in the phase \( \kappa \), and \( \varepsilon_\kappa \) is the volume fraction of \( \kappa \)-phase.

**Definition 2.4** The macroscopic spatial deviation concentration in the \( \omega \)-region are given by

\[
\hat{c}_{A\sigma} = \langle c_{A\sigma} \rangle - K_{eq}^{\mu\sigma} \{ c_A \}
\]

\[
\hat{c}_{A\mu} = \langle c_{A\mu} \rangle - \{ c_A \}
\]

\[
\hat{c}_{A\gamma} = \langle c_{A\gamma} \rangle - K_{eq}^{\mu\sigma} \{ c_A \}
\]

When these representations are used in Eqs. (2), (9) and (10), and the results added, one obtain

\[
(\varepsilon_\sigma K_{eq}^{\mu\sigma} + \varepsilon_\mu + \varepsilon_\gamma K_{eq}^{\mu\gamma}) \frac{\partial \{ c_A \}}{\partial t} + \nabla \cdot (\varepsilon_\gamma K_{eq}^{\mu\gamma} \langle v_\gamma \rangle \gamma \{ c_A \})
\]

\[
= \nabla \cdot [(D_A + D_D) \cdot \nabla \{ c_A \}] - (\varepsilon_\sigma k_\sigma K_{eq}^{\mu\sigma} \langle c_{R\sigma} \rangle \sigma + \varepsilon_\mu k_\mu) \{ c_A \}_\omega
\]

\[
+ \frac{\varepsilon_\mu k_\mu}{K_\mu} \langle c_{B\mu} \rangle - \varepsilon_\sigma k_\sigma \langle \tilde{c}_{A\sigma} \tilde{c}_{R\sigma} \rangle - k_\sigma \langle c_{A\sigma} c_{R\sigma} \rangle_{exc} + \Psi_A
\]

In this equation \( D_A \) and \( D_D \) represents the effective diffusivity tensor and dispersion tensor, respectively, which are defined as:

\[
D_A \cdot \nabla \{ c_A \} = \left[ (\varepsilon_\sigma K_{eq}^{\mu\sigma} D_{A\sigma} + \varepsilon_\mu D_{A\mu} + \varepsilon_\gamma K_{eq}^{\mu\gamma} D_{A\gamma} ) \nabla \{ c_A \} \right]
\]

\[
+ \left( \varepsilon_\sigma K_{eq}^{\mu\sigma} \Phi_\sigma + \varepsilon_\mu \Phi_\mu + \varepsilon_\gamma K_{eq}^{\mu\gamma} \Phi_\gamma \right)
\]

\[
D_D \cdot \nabla \{ c_A \} = -\nabla \cdot \langle \tilde{v}_\gamma \tilde{c}_{A\gamma} \rangle - \nabla \cdot \langle v_\gamma c_{A\gamma} \rangle_{exc}
\]

where

\[
\Phi_\sigma = \frac{1}{V_\sigma} \int_{A_{\sigma\mu}} n_{\sigma\mu} \tilde{c}_{A\sigma} dA + \frac{1}{V_\sigma} \int_{A_{\sigma\mu}} n_{\sigma\mu} \left( \langle c_{A\sigma} \rangle |_{x+y} - \langle c_{A\sigma} \rangle |_x \right) dA
\]

\[
\Phi_\mu = \frac{1}{V_\mu} \int_{A_{\mu\sigma}} n_{\mu\sigma} \tilde{c}_{A\mu} dA + \frac{1}{V_\mu} \int_{A_{\mu\sigma}} n_{\mu\sigma} \tilde{c}_{A\mu} dA
\]

\[
+ \frac{1}{V_\mu} \int_{A_{\mu\sigma}} n_{\mu\sigma} \left( \langle c_{A\mu} \rangle |_{x+y} - \langle c_{A\mu} \rangle |_x \right) dA
\]
+ \frac{1}{V_{\mu}} \int_{A_{\mu}} \mathbf{n}_{\mu} \left( \langle c_{A\mu} \rangle_{x+y} - \langle c_{A\mu} \rangle_{x} \right) dA \\

\Phi_\gamma = \frac{1}{V_{\mu}} \int_{A_{\gamma}} \mathbf{n}_{\gamma} \tilde{c}_{A\gamma} dA + \frac{1}{V_{\mu}} \int_{A_{\mu\gamma}} \mathbf{n}_{\mu\gamma} \left( \langle c_{A\gamma} \rangle_{x+y} - \langle c_{A\gamma} \rangle_{x} \right) dA \tag{16}

and \( \Psi_A \) represents the non-equilibrium concentration source, it is defined as follows

\[ \Psi_A = - \left[ \varepsilon_\sigma \frac{\partial \hat{c}_{A\sigma}}{\partial t} + \varepsilon_\mu \frac{\partial \hat{c}_{A\mu}}{\partial t} + \varepsilon_\gamma \frac{\partial \hat{c}_{A\gamma}}{\partial t} \right] \]

\[ - \nabla \cdot \left( \varepsilon_\sigma D_{A\sigma} \nabla \hat{c}_{A\sigma} + \varepsilon_\mu D_{A\mu} \nabla \hat{c}_{A\mu} + \varepsilon_\gamma D_{A\gamma} \nabla \hat{c}_{A\gamma} \right) \]  

\[ + \nabla \cdot \left( \varepsilon_\gamma \langle \mathbf{v}_\gamma \rangle \nabla \hat{c}_{A\gamma} \right) + (\varepsilon_\sigma k_\sigma \hat{c}_{R\sigma} \hat{c}_{A\sigma} + \varepsilon_\mu k_\mu \hat{c}_{A\mu}) \right] \]

This idea is better emphasize if one observes that the last integral term in Eqs. (14) to (17) represent the non-local contribution to the diffusive transport, and it is negligible when the tensor \( D_A \) reduces to the classical representation for the effective diffusivity tensor \[14\].

According to the previous line of thought, we define \( D^* \) as the total dispersion tensor, and it is used to replace \( D_A + D_D \) in Eq. (11). Then, the generalized mass transport equation is given by

\[ (\varepsilon_\sigma K_{eq}^{\mu\sigma} + \varepsilon_\mu + \varepsilon_\gamma K_{eq}^{\mu\gamma}) \frac{\partial \{ c_A \}}{\partial t} + \nabla \cdot (\varepsilon_\gamma K_{eq}^{\mu\gamma} \langle \mathbf{v}_\gamma \rangle \{ c_A \}) \]

\[ = \nabla \cdot (D^* \cdot \nabla \{ c_A \}) - (\varepsilon_\sigma k_\sigma K_{eq}^{\mu\sigma} \langle c_{R\sigma} \rangle_{\sigma} + \varepsilon_\mu k_\mu) \{ c_A \} \]

\[ + \frac{\varepsilon_\mu k_\mu}{K_\mu} (c_{B\mu})_{\mu} - \varepsilon_\sigma k_\sigma \langle \hat{c}_{A\sigma} \hat{c}_{R\sigma} \rangle - k_\sigma \langle c_{A\sigma} c_{R\sigma} \rangle_{exc} + \Psi_A \]  

The equations that are valid in the homogeneous \( \omega- \) region and homogeneous \( \eta- \) region are listed to continuation:

\( \omega- \) region

\[ (\varepsilon_\sigma K_{eq}^{\mu\sigma} + \varepsilon_\mu \omega) \frac{\partial \{ c_A \}_\omega}{\partial t} = D_{A\omega} \cdot \nabla \{ c_A \}_\omega \]

\[ - (\varepsilon_\sigma k_\sigma K_{eq}^{\mu\sigma} \langle c_{R\sigma} \rangle_{\omega} + \varepsilon_\mu \omega k_\mu) \{ c_A \}_\omega + \frac{\varepsilon_\mu \omega k_\mu}{K_\mu} (c_{B\mu})_{\mu\omega} \] \tag{19}

\( \eta- \) region

\[ \frac{\partial \{ c_A \}_\eta}{\partial t} + \nabla \cdot (\langle \mathbf{v}_\gamma \rangle \{ c_A \}_\eta) = \nabla \cdot (D_{A\gamma} \nabla \{ c_A \}_\eta) \] \tag{20}

These equations were derived in Ref. [2].
3 Jump Condition

The coefficients and the non-equilibrium source in the generalized transport equation given by Eq. (18) undergoes extremely rapid variations in the boundary region. To avoid the difficulty associated with these rapid variations, we will apply the transport equations that are valid in the homogeneous parts of the $\omega$ and $\eta$-regions to the entire space occupied by the $\omega$ and $\eta$-regions. For example, this means that the computed values of $\{c_A\}_\omega$ and $\{c_A\}_\eta$ in the boundary region will not be equal to the value of $\{c_A\}$ that would be determined by Eq. (18). We have indicated this situation in Fig. 2 where concentration profiles when $\mathbf{n}_{\omega\eta} \cdot \mathbf{D}^* \cdot \mathbf{n}_{\omega\eta} > D_\beta$. It is important to understand that the profiles for $\{c_A\}_\omega$ and $\{c_A\}_\eta$ are not extrapolations, but are solutions to the transport equations that are valid in the homogeneous $\omega$ and $\eta$-regions and applied everywhere, while $\{c_A\}$ is continuous in the boundary region, as illustrated in Fig. 2. It should be clear that the fluid volume fraction $\varepsilon_\gamma$ is a continuous function of position, that takes the value $\varepsilon_\gamma\eta$ in the homogeneous fluid region and $\varepsilon_\gamma\omega$ in the homogeneous membrane phase (as is illustrated in Fig. 2 of the Ref. [2]). Therefore, the superficial concentration $\{c_A\}$ is also continuous everywhere in the two-phase system including the inter-region neighborhood.

In this analysis we will make use of the idea that the generalized mass transport must be satisfied within the large-scale averaging volume $V_\infty$ shown in Fig. 1.

**Definition 3.1** The volume of the $\omega$ and $\eta$ regions contained in $V_\infty$ are designated by $V_\omega$ and $V_\eta$, respectively, thus we have

$$V_\infty = V_\omega(t) + V_\eta(t)$$

**Definition 3.2** The area of the surface, $A_\infty$, that defines the large-scale averaging volume can also be represented in terms of the bounding surfaces located in the $\omega$- and $\eta$-regions according to

$$A_\infty = A_\omega + A_\eta$$

The procedure to develop a jump condition associate with the $\omega$-$\eta$ boundary is given by Ochoa-Tapia and Whitaker [6]. One first integrates the equations that are valid in the homogeneous $\omega$ and $\eta$ regions over $V_\omega$ and $V_\eta$. Next, one integrates the generalized mass transport equations over $V_\infty$ and the former integrals are subtracted from the latter to eventually obtain a jump condition. The use of this jump condition in conjunction with the equations that are valid in the homogeneous $\omega$ and $\eta$-regions, but applied everywhere in those...
regions, provide a solution for which the generalized mass transport equations are satisfied on the average.

To develop the jump condition for the mass transport process, we first integrate Eqs. (19) and (20) over volumes $V_\omega$ and $V_\eta$, respectively, and then add them to obtain:

$$
\int_{V_\omega} \left( \varepsilon_{\sigma} K_{eq}^{\mu\sigma} + \varepsilon_{\mu} \right) \frac{\partial \{c_A\}}{\partial t} dV + \int_{V_\eta} \frac{\partial \{c_A\}}{\partial t} dV
$$

$$
+ \int_{A_\eta} \mathbf{n}_\eta \cdot \left( \langle \mathbf{v}_\gamma \rangle \{c_A\}_\eta - D_{A\gamma} \nabla \{c_A\}_\eta \right) dA
$$

$$
- \int_{A_\omega} \mathbf{n}_\omega \cdot \left( D_{A\omega} \cdot \nabla \{c_A\}_\omega - \langle \mathbf{v}_\gamma \rangle \{c_A\}_\eta \right) dA
$$

$$
= \int_{A_\omega} \mathbf{n}_\omega \cdot \left( D_{A\omega} \cdot \nabla \{c_A\}_\omega \right) dA
$$

$$
- \int_{V_\infty} \left[ \varepsilon_{\sigma} k_{eq}^\sigma \langle R_\sigma \rangle^\sigma + \varepsilon_{\mu} k_{\mu} \right] \{c_A\}_\omega - \frac{\varepsilon_{\mu} k_{\mu}}{K_{\mu}} \langle c_{B\mu} \rangle^\mu dV
$$

The various unit vectors used in this result are identified in Fig. 3. To obtain Eq. (21) we have used the divergence theorem to change several of the volume integrals to area integrals. In this result, we have also used $A_{\omega\eta} = A_{\eta\omega}$ to represent the area of dividing inter-region contained within the volume $V_\infty$, and the convention associated with the unit normal vectors at the dividing surface is $\mathbf{n}_{\omega\eta} = -\mathbf{n}_{\eta\omega}$. The next step requires that we integrate Eq. (18) over the volume identified by $V_\infty$, thus the following result is obtained:

$$
\int_{V_\eta} \left( \varepsilon_{\sigma} K_{eq}^{\mu\sigma} + \varepsilon_{\mu} \right) \frac{\partial \{c_A\}}{\partial t} dV
$$

$$
+ \int_{V_\omega} \left( \varepsilon_{\sigma} K_{eq}^{\mu\sigma} + \varepsilon_{\mu} \right) \frac{\partial \{c_A\}}{\partial t} dV
$$

$$
- \int_{A_\omega} \mathbf{n}_\omega \cdot \left( D_{A\omega} \cdot \nabla \{c_A\}_\omega - \varepsilon_{\gamma} K_{eq}^{\gamma\gamma} \langle \mathbf{v}_\gamma \rangle^\gamma \{c_A\}_\omega \right) dA
$$

$$
- \int_{A_\eta} \mathbf{n}_\eta \cdot \left( D_{A\eta} \cdot \nabla \{c_A\}_\eta - \varepsilon_{\gamma} K_{eq}^{\gamma\gamma} \langle \mathbf{v}_\gamma \rangle^\gamma \{c_A\}_\eta \right) dA
$$

$$
= - \int_{V_\omega} \left( \varepsilon_{\sigma} k_{\sigma} K_{eq}^{\mu\sigma} \langle R_\sigma \rangle^\sigma + \varepsilon_{\mu} k_{\mu} \right) \{c_A\}_\omega dV
$$

$$
- \int_{V_\eta} \left( \varepsilon_{\sigma} k_{\sigma} K_{eq}^{\mu\sigma} \langle R_\sigma \rangle^\sigma + \varepsilon_{\mu} k_{\mu} \right) \{c_A\}_\eta dV
$$

$$
- \int_{V_\omega} \left( \varepsilon_{\sigma} k_{\sigma} \langle c_{A\sigma} c_{R\sigma} \rangle + k_{\sigma} \langle c_{A\sigma} c_{R\sigma} \rangle_{exc} - \frac{\varepsilon_{\mu} k_{\mu}}{K_{\mu}} \langle c_{B\mu} \rangle^\mu \right) dV
$$
When we subtract Eq. (21) from Eq. (22), we obtain the lengthy result, that is given below:

\[- \int_{V_{\eta}} \left( \varepsilon_{\sigma} k_{\sigma} \left( c_{A \sigma} c_{R \sigma} \right) + k_{\sigma} \left( c_{A \sigma} c_{R \sigma} \right)_{\text{exc}} - \frac{\varepsilon_{\mu} k_{\mu}}{K_{\mu}} \left( c_{B \mu} \right) \right) \right) dV\]

\[+ \int_{V_{\omega}} \Psi_{A} dV + \int_{V_{\eta}} \Psi_{A} dV \tag{22}\]

The type of terms containing integrals in the surfaces \(A_{\omega}\) and \(A_{\eta}\), are the characteristics that leads Gibbs \([3]\) to first define excess functions at phase interfaces; an explanation that is applicable to the particular problem under investigation is given elsewhere \([6]\). The excess surface accumulation associated with Eq. (23) is defined next.

**Definition 3.3** Excess surface accumulation

\[\int_{A_{\omega}} \varepsilon_{\omega} \frac{\partial \{ c_{A} \}}{\partial t} dA\]

\[= \frac{d}{dt} \int_{V_{\omega}(t)} \left( \varepsilon_{\sigma} K_{eq}^{\mu \sigma} + \varepsilon_{\mu} + \varepsilon_{\gamma} K_{eq}^{\mu \gamma} \right) \{ c_{A} \} - \left( \varepsilon_{\sigma \omega} K_{eq}^{\mu \sigma} + \varepsilon_{\mu \omega} \right) \{ c_{A} \}_{\omega} dV\]

\[- \int_{A_{\omega}} n_{\omega} \cdot \left( D_{A}^{*} \cdot \nabla \left\{ c_{A} \right\} - D_{A \omega} \cdot \nabla \left\{ c_{A} \right\}_{\omega} - \varepsilon_{\gamma} K_{eq}^{\mu \gamma} \left\{ v_{\gamma} \right\} \left\{ c_{A} \right\} \right) dA\]

\[- \int_{A_{\eta}} n_{\eta} \cdot \left[ D_{A}^{*} \cdot \nabla \left\{ c_{A} \right\} - D_{A \gamma} \cdot \nabla \left\{ c_{A} \right\}_{\eta} - \left( v_{\gamma} \right) \left( \varepsilon_{\gamma} K_{eq}^{\mu \gamma} \left\{ c_{A} \right\} - \varepsilon_{\gamma} \left\{ c_{A} \right\}_{\eta} \right) \right] dA\]

\[= - \int_{A_{\omega \eta}} n_{\omega \eta} \cdot \left( D_{A \omega} \cdot \nabla \left\{ c_{A} \right\}_{\omega} - D_{A \gamma} \cdot \nabla \left\{ c_{A} \right\}_{\eta} - \left( v_{\gamma} \right) \left\{ c_{A} \right\}_{\eta} \right) dA \tag{23}\]
Jump mass transfer for double emulsion systems

\[ + \frac{d}{dt} \int_{V_{\eta}(t)} \left[ (\varepsilon_\sigma K_{eq}^{\mu\sigma} + \varepsilon_\mu + \varepsilon_\gamma K_{eq}^{\mu\gamma}) \{c_A\} - \{c_A\}_\eta \right] dV \]

Here the transport theorem was applied where the interface velocity is equal to zero, and \( \{c_A\}_s \) is the surface concentration.

**Definition 3.4** *Excess surface transport*

\[ \oint_C n_s \cdot N_A d\zeta \]

\[ = - \int_{A_{\omega}(t)} n_\omega \cdot (D_A^* \cdot \nabla \{c_A\}) - D_{A\omega} \cdot \nabla \{c_A\}_\omega - \varepsilon_\gamma K_{eq}^{\mu\gamma} \langle v_\gamma \rangle^{\gamma} \{c_A\} dA \]

\[ - \int_{A_\eta(t)} n_\eta \cdot \left[ D_A^* \cdot \nabla \{c_A\} - D_{A\eta} \nabla \{c_A\}_\eta - \langle v_\gamma \rangle^{\gamma} (\varepsilon_\gamma K_{eq}^{\mu\gamma} \{c_A\} - \varepsilon_\gamma \{c_A\}_\eta) \right] dA \]

In this equation, as can be observed in Fig. 3, \( C \) represents a closed curve lying on the dividing surface, \( A_{\omega\eta} \), while \( n_s \) represents the unit vector that is tangent to the \( \omega - \eta \) boundary and normal to the curve \( C \), and \( \zeta \) represents the arc length along this curve.

**Definition 3.5** *Excess surface reaction*

\[ - \int_{A_{\omega\eta}} R_A dA \]

\[ = - \int_{V_\omega} (\varepsilon_\sigma k_\sigma K_{eq}^{\mu\sigma} \langle c_{R\sigma} \rangle^\sigma + \varepsilon_\mu k_\mu) \{c_A\} dV \]

\[ + \int_{V_\omega} \left[ (\varepsilon_\sigma k_\sigma K_{eq}^{\mu\sigma} \langle c_{R\sigma} \rangle^\sigma + \varepsilon_\mu k_\mu) \{c_A\}_\omega - \frac{\varepsilon_\mu k_\mu}{K_\mu} \langle c_{B\mu} \rangle_\omega \right] dV \]

\[ - \int_{V_\omega} \left( \varepsilon_\sigma k_\sigma \langle c_{A\sigma} c_{R\sigma} \rangle + k_\sigma \langle c_{A\sigma} c_{R\sigma} \rangle_{exc} - \frac{\varepsilon_\mu k_\mu}{K_\mu} \langle c_{B\mu} \rangle^\sigma \right) dV \]

**Definition 3.6** *Non-equilibrium excess surface*

\[ \int_{A_{\omega\eta}} \Psi_A dA = \int_{V_\omega} \Psi_A dV + \int_{V_\eta} \Psi_A dV \]

in which \( \Psi \) is defined earlier by Eq. (17). This definition according with previous works [10] suggests that the non-equilibrium surface excess could be represented as

\[ \Psi_A = \delta \Psi_A \]  

(24)
where $\delta$ represents the thickness associated with the boundary region and can be estimated as the root of the norm of the permeability tensor in Darcy's law. Substituting Definitions 3.3-3.6 into Eq. (23), lead to the following result

$$
\int_{A_{\omega \eta}} \varepsilon_{\omega \eta} \frac{\partial \{c_A\}_s}{\partial t} dA
$$

$$
= - \int_{A_{\omega \eta}} n_{\omega \eta} \cdot \left( D_{A\omega} \cdot \nabla \{c_A\}_\omega - D_{A\eta} \nabla \{c_A\}_\eta - \langle \mathbf{v}_\gamma \rangle \{c_A\}_\eta \right) dA 
$$

$$
- \int_{A_{\omega \eta}} R_{As} dA + \int_{A_{\omega \eta}} \Psi_{As} dA
$$

where

$$
\oint_{C} n_{s} \cdot N_{As} d\zeta = \int_{A_{\omega \eta}} \nabla_{s} \cdot N_{As} dA
$$

Using the surface divergence theorem to write all of the terms under the same area integral, and then requiring that the integrated to be zero, we obtain a surface transport equation, or a jump condition:

$$
\frac{\partial \{c_A\}_s}{\partial t} + \nabla_{s} \cdot N_{As}
$$

$$
= - n_{\omega \eta} \cdot \left[ \left( D_{A\omega} \cdot \nabla \{c_A\}_\omega - D_{A\eta} \nabla \{c_A\}_\eta \right) - \langle \mathbf{v}_\gamma \rangle \{c_A\}_\eta \right] 
$$

$$
+ R_{As} + \Psi_{As}
$$

\text{Excess surface transport}

\text{Excess surface reaction}

\text{Non-equilibrium excess surface}

We must remember that at this point it has not been imposed any condition on the average concentration at the dividing surface of the porous and fluid regions. Therefore, based on the continuity of the fields $\{c_A\}$ and $\{c_A\}_\kappa$ (with $\kappa = \omega, \eta$) shown in Fig. 2, we chose to impose the continuity of the intrinsic average concentrations at the $\omega - \eta$ boundary

$$
\{c_A\}_\omega = \{c_A\}_\eta, \quad \text{at the } \omega - \eta \text{ boundary}
$$

(28)

This also implies that the surface concentration must satisfy

$$
\{c_A\}_s = \{c_A\}_\eta = \{c_A\}_\omega, \quad \text{at the } \omega - \eta \text{ boundary}
$$

(29)

If the excess surface transport, reaction and the non-equilibrium terms are neglected, the boundary condition takes the form

$$
- n_{\omega \eta} \cdot \left[ \left( D_{A\omega} \cdot \nabla \{c_A\}_\omega - D_{A\eta} \nabla \{c_A\}_\eta \right) - \langle \mathbf{v}_\gamma \rangle \{c_A\}_\eta \right] = 0
$$

(30)
4 General Form of the Jump Condition

On the basis of the definitions of the excess surface terms given by Definitions 3.3-3.6 the following representations are proposed

*Excess surface accumulation*

\[ \varepsilon \omega \frac{\partial \{ c_A \}_s}{\partial t} = \gamma_a (\varepsilon \sigma \mu \sigma K_{eq}^{\mu \sigma} + \varepsilon \mu \omega) \frac{\partial \{ c_A \}_\omega}{\partial t} \quad (31) \]

*Excess surface transport*

\[ \nabla_s \cdot \mathbf{N}_{As} = \gamma_b n_{\omega \eta} \cdot \mathbf{N}_A \quad (32) \]

where

\[ n_{\omega \eta} \cdot \mathbf{N}_A = -n_{\omega \eta} \cdot \left[ (\gamma_c D_A^* - D_{A,\omega}) \cdot \nabla - \gamma_d \varepsilon \gamma K_{eq}^{\mu \gamma} \langle \mathbf{v}_\gamma \rangle \right] \{ c_A \}_\omega + n_{\omega \eta} \cdot \left[ (\gamma_e D_A^* - D_{A,\gamma} \mathbf{l}) \cdot \nabla - \langle \mathbf{v}_\gamma \rangle \gamma \varepsilon \gamma (\gamma_f K_{eq}^{\mu \gamma} - 1) \right] \{ c_A \}_\eta \quad (33) \]

In Eqs. (31)-(33), \( \gamma_a, \gamma_b, \gamma_c, \gamma_d, \) and \( \gamma_e \) are dimensionless parameters of order one. Using this equations into Eq. (27) yields

\[ \gamma_a (\varepsilon \sigma \omega K_{eq}^{\mu \sigma} + \varepsilon \mu \omega) \frac{\partial \{ c_A \}_\omega}{\partial t} + \gamma_b n_{\omega \eta} \cdot \mathbf{N}_A \]

\[ = -n_{\omega \eta} \cdot \left[ (\mathbf{D}_{A,\omega} \cdot \nabla \{ c_A \}_\omega - D_{A,\gamma} \nabla \{ c_A \}_\eta) - \langle \mathbf{v}_\gamma \rangle \gamma \{ c_A \}_\eta \right] 
+ \mathbf{R}_{As} \quad \text{Excess surface reaction} 
+ \mathbf{\Psi}_{As} \quad \text{Non-equilibrium excess surface} \]

The parameters \( \gamma_a, \gamma_b \) can be obtained using the method of the Goyeau et al. [4], which was applied in Ref. [12] or with the method given by Min and Kim [5]. This equation is the mass jump condition that couples the Eq. (19) and Eq. (20) for \( \omega \)-region and \( \eta \)-region, respectively.

5 Main Results

In this study we have derived a jump condition [Eq. (34)] for boundary between the \( \omega \)-region made by globules and liquid membrane and the \( \eta \)-region that represents the external region in a double emulsion system. The development is based on generalized, non-local form of the volume averaged mass transport equation that is valid within the boundary region. Outside the boundary region
this non-local form reduces to the classic volume averaged transport equation in the $\omega$–region [Eq. (19)] and to the point in the $\eta$–region [Eq. (20)]. The jump condition takes the form of a surface transport equation that contains terms representing the excess surface accumulation, diffusion, reaction, and a non-equilibrium source term, in addition to a term representing the exchange with the surrounding regions. The mass jump condition contains two adjustable parameters that can be determined by experimental studies or by means of theoretical method (e.g. [4], [5]).

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**References**


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Figure 1. Averaging volumes.
Figure 2. Continuity of the global spatial average concentration.
Figure 3. Unit vectors