Chemical Engineering Science 61 (2006) 1692–1704

Chemical
Engineering Science

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Diffusive mass transfer between a microporous medium and an homogeneous fluid: Jump boundary conditions

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Received 9 July 2005; received in revised form 28 September 2005; accepted 3 October 2005

Abstract

The method of volume averaging is used to derive the diffusive mass transfer boundary conditions for transport between the micro-pores (ω-region) and the fluid in the macro-pores (η-region) in a catalyst pellet. In this configuration, the mass jump boundary condition between the homogeneous regions takes the form

$$-\mathbf{n}_{\eta\omega}\cdot(D_\gamma\nabla\langle c_{A\gamma}\rangle_\eta^\gamma)+\mathbf{n}_{\eta\omega}\cdot(\varepsilon_\gamma\mathbf{D}_\omega\cdot\nabla\langle c_{A\gamma}\rangle_\omega^\gamma)=K_{\text{eff}}\langle c_{A\gamma}\rangle_\omega^\gamma,$$

where K_{eff} is the effective reaction rate coefficient at the inter-region. In this study, a closure is derived in order to predict this average jump coefficient as a function of the microstructure of the porous layer and the Thiele modulus. The jump coefficient predicted for three inter-region structures is presented.

Keywords: Closure problem; Diffusion; Homogenization; Microstructure; Porous media; Reaction jump coefficient

1. Introduction

The derivation of macroscopic conservation equations for transport phenomena in multiphase systems has been the subject of intense research activity in the last decades. Usually, average equations are obtained using up-scaling procedures such as homogenization (Sanchez-Palencia, 1986) or the method of volume averaging (Whitaker, 1999). In many practical systems the configuration is composed by an homogeneous fluid region and an adjacent porous layer saturated by the same fluid (Beavers and Joseph, 1967). In that case, one of the most challenging problems lies in the determination of appropriate large-scale boundary conditions at the fluid-porous inter-region. Indeed, in this transition region, the length scale constraints used to perform the up-scaling in the homogeneous porous layer are not satisfied due to significant spatial variations of the porous structure. This difficulty has been addressed by deriving jump boundary conditions at the fluid-porous dividing surface for momentum (Ochoa-Tapia and Whitaker, 1995a,b, 1998b), heat transfer (Prat, 1989, 1990, 1992; Sahraoui and Kaviany, 1993, 1994; Ochoa-Tapia and Whitaker, 1997, 1998a) or mass transport (Valencia-López et al., 2003). However, these jump conditions involve coefficients whose physical meaning is not well understood and up to now they have been considered as adjustable parameters. Recently, Goyeau et al. (2003) have described the inter-region as a non-homogeneous interfacial porous layer and derived an explicit expression for the stress jump coefficient involved in the momentum transport. However, this latter methodology includes the knowledge of the spatial variation of the effective properties in the inter-region.

Actually, in the context of the volume averaging method, the exact determination of such a coefficient taking into account the microstructure of the non-homogeneous porous layer needs the derivation of an associated closure problem. Such type of analysis has been presented by Wood et al. (2000) to obtain an effective reaction rate coefficient at non-uniform catalytic surfaces. In this paper this analysis is extended to more

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0009-2509/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.ces.2005.10.005

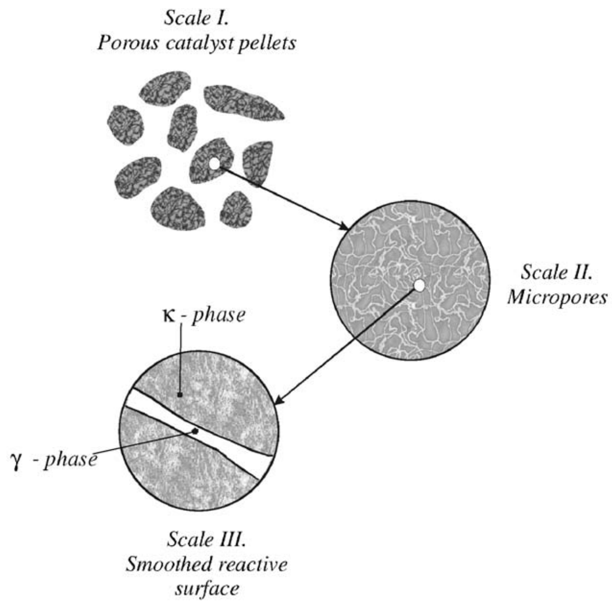

Fig. 1. Scales of interest in a porous catalyst.

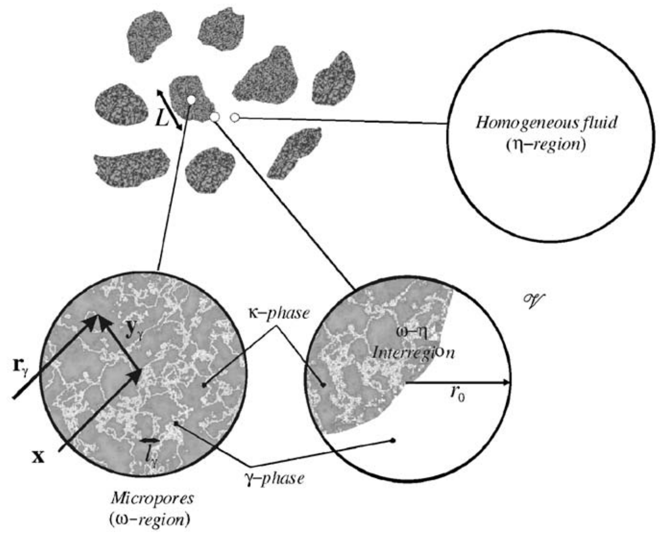

Fig. 2. Volume averaging at *Scale II*.

complicated systems, in particular we will deal with the transport between a micro-pore and a fluid in a macro-pore (Fig. 1). The objective is to derive the appropriate mass flux boundary conditions (including the jump coefficients) for this system. The methodology here outlined may also be applied to other situations, for example, the analysis of the stress jump condition in the problem of Beavers and Joseph (1967) or the mass transfer in double emulsions, in fact the case under study can be regarded as a special case of the double emulsion system. In future works we will analyze these and other transport processes.

Indeed, the problem under consideration concerns the mass transport in a packed bed reactor with micro–macro porous pellets. In order to model a fixed bed or other type of reactor, it is necessary to define boundary conditions for the transport between the catalytic pellets and the fluid flowing through. However, to derive them accurately, the analysis must start with a boundary value problem governing the transport between the micro-porous region and the fluid in the macro-pores (see *Scale I* in Fig. 1). At this scale interfacial boundary conditions have not been properly obtained.

2. Volume averaging

The point and average jump conditions for *Scale III* were developed by Wood et al. (2000) assuming that the reaction takes place only at the γ–κ interface where γ and κ represent the solid and fluid phases, respectively. This is the initial statement for the derivation presented in this paper. Under these circumstances, the average concentration conservation equation and interfacial boundary condition at *Scale III* are (Wood et al., 2000)

$$\frac{\partial \langle c_{A\gamma}\rangle^{\gamma}_{III}}{\partial t} = \nabla \cdot (D_\gamma \nabla \langle c_{A\gamma}\rangle^{\gamma}_{III}) \quad \text{in the } \gamma\text{-phase}, \tag{1}$$

$$-\mathbf{n}_{\gamma\kappa} \cdot D_\gamma \nabla \langle c_{A\gamma}\rangle^{\gamma}_{III} = k\langle c_{A\gamma}\rangle^{\gamma}_{III} \quad \text{at the } \gamma\text{–}\kappa \text{ interface}, \tag{2}$$

where $\mathbf{n}_{\gamma\kappa}$ is unit normal vector directed from the γ-phase towards the κ-phase. In order to simplify the nomenclature the above equations are now written as

$$\frac{\partial c_{A\gamma}}{\partial t} = \nabla \cdot (D_\gamma \nabla c_{A\gamma}) \quad \text{in the } \gamma\text{-phase}, \tag{3}$$

$$-\mathbf{n}_{\gamma\kappa} \cdot D_\gamma \nabla c_{A\gamma} = k c_{A\gamma} \quad \text{at the } \gamma\text{–}\kappa \text{ interface}. \tag{4}$$

The average equations and boundary conditions at *Scale II* are obtained using the averaging volume $\mathscr{V}$ represented in Fig. 2.

As shown in this figure, $\mathscr{V}$ can be located in the homogeneous parts of the system: micro-pore ω-region or fluid in the macro-pore η-region. It can also be located at the ω–η inter-region where rapid spatial variations of the geometric properties are present.

In order to provide useful average quantities the characteristic length scales of the system must satisfy

$$l_\gamma \ll r_0 \ll L, \tag{5}$$

where l_γ and L are the length scales associated to the micro- and macro-pores, respectively, and r_0 denotes the size of the averaging volume (Fig. 2). According to Whitaker (1999), the *superficial* average of a quantity ψ_γ defined in the γ-phase is

$$\langle \psi_\gamma \rangle = \frac{1}{\mathscr{V}} \int_{V_\gamma(\mathbf{x})} \psi_\gamma \, \mathrm{d}V \tag{6}$$

while the *intrinsic* average is given by

$$\langle \psi_\gamma \rangle^{\gamma} = \frac{1}{V_\gamma(\mathbf{x})} \int_{V_\gamma(\mathbf{x})} \psi_\gamma \, \mathrm{d}V. \tag{7}$$

These two averages are related as follows:

$$\langle \psi_\gamma \rangle = \varepsilon_\gamma(\mathbf{x}) \langle \psi_\gamma \rangle^{\gamma}. \tag{8}$$