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Multi-scale distributed parameter model of an adsorption column using a bond graph approach

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Abstract

In this paper we present a model of an adsorption column in order to illustrate a generic port-based modelling methodology (bond graphs) and its extension to multi-scale non-uniform (distributed parameters) models. This "energy-flow" model is derived from a graph representation of the power exchanges at each physical scale and on an explicit formulation of the multi-scale coupling.

Keywords: multi-scale modelling, adsorption column, Stefan-Maxwell diffusion, distributed parameter model, port-based Hamiltonian systems.

1. Introduction

Many approaches of computer aided modelling in process engineering are based on a structured modelling approach using sets of balance equations, constitutive equations and constraints (see for instance Giorgiadis et al. (2002)). Mangold et al. (2002) proposed a block-diagram approach which also applies to distributed parameter systems. This block-diagram is composed of the *components elements* (representing the storage of conserved quantities) and the *coupling elements* (defining the fluxes between components) related by bidirectional signal flows (composed of potentials and fluxes). In this approach causality is thus assigned once for all which harms the reusability of the submodels, the submodels have to be re-defined for each new set of boundary conditions (i.e. for each new configuration of the interconnection with the environment). The goal of this paper is to present, on the example of an adsorption column, a port-based model using a novel extension of the *bond graph* language to *multi-scale* and *non-uniform* models. This paper also extends previous work on structured modelling for chemical engineering using bond graph for finite dimensional systems (Breedveld et al., 2003) (Couenne et al. 2004). It will be shown how the bond graph model represents the basic thermodynamic properties, conservation laws at each scale and the multiscale coupling in terms of a *network* of multiport elements *acausally* related by edges (bonds) indicating the identity of pairs of power conjugated variables (intensive and variations of extensive variables). It will be shown how this approach leads to a simple an easily re-usable graphical description of the system which is an interesting modelling alternative to sets of partial differential equations and boundary conditions.

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We shall illustrate the bond graph modelling approach on the example of an isothermal model of the mass transfer phenomena in the adsorption process (used for the separation of gaseous mixture by adsorption (Ruthven, 1994)). If a zeolite is used as adsorbent medium, the mass transfer phenomena description may be decomposed at three different scales[1]: namely the column scale, the pellet scale and the crystal scale, as it is represented in the Figure 1 for a binary gas mixture where constituent A is adsorbed faster than B.

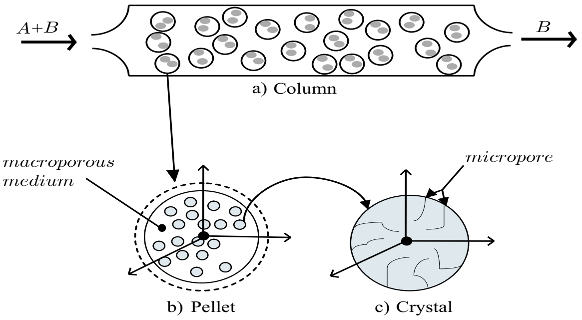

Figure 1. Schematic representation of a column a), packed with absorbent pellets b), themselves constituted by crystals c), associated with the three scales

The bond graph model presented herafter is restricted to the description of the two smaller scales consisting of the macroporous medium (pellet) and the microporous medium.

2. Model of the microporous scale

Let us first briefly summarize the thermodynamical models and conservation law. The thermodynamic model of mass transfer in porous media is given by the Stefan-Maxwell's law completed by considering the vacant sites of the solid as a (pseudo-) species n+1 (Krishna and Wesselingh 1997) (Krishna 1990). We assume furthermore that each molecule which lies in the micropore is adsorbed or in other words that in the adsorbed phase, there is no possibility of two different molecules to undergo a counter-exchange at an adsorption site. Hence the diffusion equation can be then written:

$$-\frac{q_i D_i^s}{RT}\nabla_{T,P}\mu_i^{ads} = N_i^{ads} \tag{1}$$

where μ_i^{ads} denotes the chemical potential of species i (in the adsorbed phase), $\nabla_{P,T}$ (μ) its gradient at constant temperature T and pressure P, N_i^{ads} the total molar flux of species i in the diffusing mixture, q_i the molar concentration of adsorbed species i in the mixture and D_i^s a Stefan-Maxwell diffusivity coefficient (in the micropore). The second principle is expressed as the dissipativity of the relation (1).

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[1] This is a classical approach justified by the physical sizes of the objects. For instance according to DaSilva and Rodrigues (2001), the radius of a crystal is of an order of magnitude of 1 μm and the radius of a pellet approximately 0.8 mm for 13X CECA zeolite.

Secondly the thermodynamic properties of the mixture in the micropore medium is given by the expression of the chemical potentials of the components *i* at some temperature *T* and pressure *P*. We have assumed that only one of the components is diffusing at the microscale (i.e. is penetrating the crystals) using Langmuir's model:

$$\mu_i^{ads} = \mu_i^0(T,P) + RT\ln\left(\frac{q_i}{P(k_1 - k_2 q_i)}\right) \tag{2}$$

where $\mu_i^0(T,P)$ denotes the chemical potential of pure component *i* at standard state and k_1 and k_2 are two constants.

Thirdly, the *dynamic model* of the adsorption process in the microporous medium is then obtained by considering the conservation law:

$$\frac{\partial q_i}{\partial t} = -\beta_i = -div(N_i^{ads}) \tag{3}$$

together with the two closure equations (1) and (2) leading to a "complete set" of partial differential equations.

The bond graph model in the figure 2 represents the dynamical model of the microporous medium as the interconnection of five multiport elements which represents the elementary physical phenomena (and corresponds to some reorganization of the relations presented above).

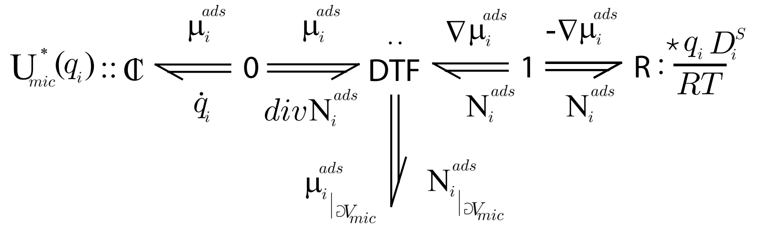

Figure 3. Bond Graph representation of the adsorption process at the microporous scale.

They are related by oriented edges called *bonds* which are associated with a pair of conjugated variables *(f,e)* endowed with a product with unit being power: $\langle e,f\rangle = \int_Z e.f\,dz$ on the spatial domain *Z*. This is very similar to the bilateral signal flow relating blocks in (Mangold et al. 2002); however it differs firstly as it is an acausal relation between multiports (it only tells about the identity of shared variables) and secondly by the choice of conjugated variables with respect to energy. **The element, denoted by the symbol C**, has the pair of conjugated port (external) variables $\left(\frac{\partial q_i}{\partial t}, \mu_i^{ads}\right)$ and represents the thermodynamic property of the mixture defined by the equation (2). **The element denoted by 0** denotes the balance equation: $\frac{\partial q_i}{\partial t} = -\beta_i$ as well as the assumption of local equilibrium. **The element denoted by R** represents the diffusion in the micoporous scale, defined by the dissipative relation (1) relating the two conjugated variables $\left(N_i^{ads}, \nabla_{T,P}\mu_i^{ads}\right)$. **The element denoted by 1**, the dual of a "0-junction", ensures the respect of sign convention.

The central **element denoted by DTF** represents the interconnection between the storage, dissipative and boundary parts of the model. It combines two adjoint differential relations, namely the definition of the generating force as the gradient of the chemical potential $\nabla_{T,P}\mu_i^{ads}$ and of the conservation law (3) by the divergence of the flux. Furthermore it defines the two boundary variables obtained by Stoke's theorem applied to a micropore volume V_{mic} :

$$\int_{V_{mic}} \mu_i^{ads} \cdot div(N_i^{ads}) + \int_{V_{mic}} grad(\mu_i^{ads}) \cdot N_i^{ads} = \left(\mu_i^{ads} N_i^{ads}\right)\Big|_{\partial V_{mic}} \tag{4}$$

where ∂V_{mic} denotes the boundary of the micropore, i.e. the interface with the macroporous scale (which shall be used for the interconnection of the two scales). The constitutive equation (4) expresses also the continuity of power at its ports (Maschke and van der Schaft 2004).

3. Model of the macroporous scale and coupling

In the macropore we only consider the bulk diffusion in gaseous phase and therefore use Maxwell-Stefan's diffusion equation (Krishna and Wesselingh 1997):

$$-\frac{y_i}{RT}\nabla_{T,P}\mu_i^{mac} = \sum_{j=1;\, j\neq i}^{n} \frac{y_j N_i^{mac} - y_i N_j^{mac}}{c_{tot} D_{i,j}} \tag{5}$$

where y_j denotes the molar fraction of species j (in the gaseous phase), N_i^{mac} the molar flux of species i (gaseous phase), c_{tot} the total molar concentration of the fluid mixture, $D_{i,j}$ the Stefan-Maxwell diffusivity (in the macropore) between species i and j. It is important to notice that the Maxwell-Stefan equation gives rise to an *implicit* relation between the molar fluxes N_i^{mac} and the chemical potential gradients $\nabla_{P,T}$ (μ_i^{mac}). The dynamic model of diffusion process in the pellet is then given by the balance equation (consisting of a conservation law augmented with a distributed source term):

$$\frac{\partial c_i}{\partial t} = -\mathrm{div}(N_i^{mac}) + f_i^{mac} \tag{6}$$

where c_i denotes the concentration of species i (gaseous phase), f_i^{mac} the flow of species i per unit of volume. The distributed source term f_i^{mac} accounts for the molar flow coming out of a microporous medium at the considered point in the spatial macroporous domain. The balance equation (6) augmented with the diffusion equation (5) and the thermodynamical properties of the mixture in the macropore medium analoguous to (2), gives the total dynamical model of the pellet.

Its Bond Graph representation is shown in Figure 3. One may note that it is almost identical to the bond graph of the figure 2: the main phenomena are identical, only their constitutive relations vary. Furthermore the element 0, representing the balance equation (6) has now three ports. The additional port corresponds to the coupling with the microporous scale though a distributed source term. This time the boundary output of the DTF enables the coupling with the gaseous phase in the adsorption column.

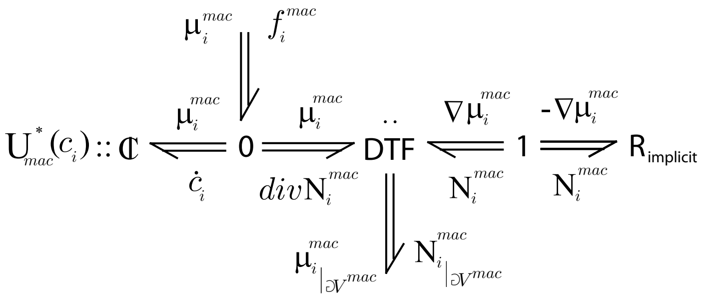

Figure 3. Bond Graph model of the diffusion at the macroporous scale.

4. Multiport element coupling two scales

The hypothesis of separation of the scales between the pellets (macroporous medium) and the crystal (microporous medium) here reduces to consider that a pellet is made of a sufficiently great number of crystals of much smaller size in order to abstract a crystal to a point of the macroporous scale.

In this case the coupling between the macropore scale and the micropore scale is stated classically with two equations :

- *identity of the chemical potentials* at the boundary of the two scales :

$$\mu_i^{ads}(x,z)\Big|_{z\in\partial V^{mic}} = \mu_i^{mac}(x)1_{\partial V^{mic}}(z) \tag{7}$$

where $x\in V^{mac}$ states for the pellet spatial domain, $z\in V^{mic}$ the crystal spatial domain, ∂V^{mic} denotes the boundary of the microporous scale and $1_{\partial V\mathrm{mic}}(z)$ has the value 1 in ∂V^{mic} and 0 elsewhere.

- *continuity of molar flux* at the boundary of the two scales :

$$f_i^{mac}(x)+\left(\int_{\partial V^{mic}(x)} N_i^{ads}(x,z)\mathrm{d}S(z)\right).\rho(x)=0 \tag{8}$$

where $\rho(x)$ denotes the volumetric density of crystals in the pellet (with $x\in V^{mac}$, the spatial domain of a pellet), $f_i^{mac}(x)$ the volumetric density flux variable at the macropore scale and $N_i^{ads}(x,z)$ the flux variable of the micropore scale.

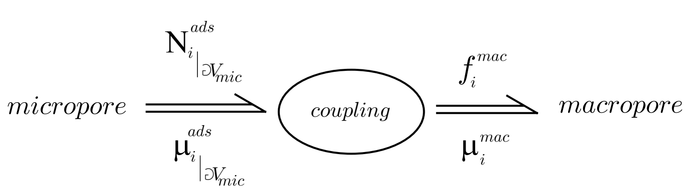

Figure 4. Bond Graph representation of the multiscale coupling element.

This two coupling equations (7) and (8) may be represented as the **power continuous 2-port bond graph element** shown in Figure 4. The complete bond graph model is obtained by coupling the submodels of figure 2 and 3 by the 2-port element of figure 5.

5. Conclusions

In this paper we have presented a Bond Graph model of an adsorption column derived directly from its thermodynamical description. The methodology presented exhibits some interesting features :

- The model is stated independently of the particular geometries of the adsorption columns, pellets and crystal. These geometric specifications may be addressed at the end of the physical modelling process as the derived equations and interconnection structure are “geometry-independent”.
- The model is a network model where each element represents a specific phenomenon which may be identified from a thermodynamics point of view. For instance, in our model, constitutive equations of these subsystems are directly related to the Stefan-Maxwell law for diffusion, the Gibbs-Duhem equation and the Langmuir’s model for potentials. The interconnection structure relating these subsystems expresses material balances and multi-scale coupling.

Consequently the derived model requires few parameters and these parameters have a clear physical meaning. It suggests a discretization method which preserves the invariants of the interconnection structure and dissipativity of the elements. Such discretization methodologies exists and appear to be very efficient in representing the qualitative behaviour of complex dynamical models (see Budd and Piggott 2003 for a review of these methods). Moreover the bond graph model is acausal, hence postpones the choice of boundary conditions (for instance depending here on the model of the gaseous phase in the adsorption column) and is thus clearly reusable.

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