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A Non-equilibrium Approach to Model Dynamic Composite Systems with Interface Transport [⋆]

Aarón Romo-Hernandez [*] **Denis Dochain** [*] **B. Erik Ydstie** [**]
Nicolas Hudon [***]

[*] *ICTEAM, Université Catholique de Louvain, B-1348, Louvain-la-Neuve, Belgium (e-mail: aaron.romo,denis.dochain@uclouvain.be).*
[**] *Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA (e-mail: ydstie@cmu.edu).*
[***] *Department of Chemical Engineering, Queen's University, Kingston, ON, K7L 3N6 Canada (e-mail: nicolas.hudon@queensu.ca).*

Abstract: In this note, we derive a dynamical model that tracks the evolution of the internal energy, the volume and the molar compositions of composite systems. The proposed modeling approach considers interface transport using a non-equilibrium thermodynamic perspective and predicts dynamical trajectories to thermodynamic equilibrium. Both closed and open systems are considered and, for both cases, it is shown that expected equilibrium properties are recovered. Numerical simulations based on the proposed model show the potential of the proposed non-equilibrium approach for open and closed multiphase systems.

Keywords: Non-equilibrium thermodynamics, Multiphase systems, Modeling, Composite systems

1. INTRODUCTION

In recent years, most process control studies using thermodynamics have considered homogeneous reacting systems, see for example (Hoang and Dochain, 2013) and references therein. A key objective treated in the literature has been to study the dynamics of systems in a neighborhood of a thermodynamic equilibrium, taking advantage of thermostatic principles. The objective of the present study consists in analyzing non-homogeneous systems, and, in the present note, we consider the problem of modeling such systems using a composite systems approach.

In general, the thermodynamic equilibrium in a composite system is defined using thermostatic principles. Roughly speaking, a non-reactive closed system is said to be in thermodynamic equilibrium when a particular set of properties (temperature, pressure and chemical potential) are homogeneous inside the boundaries of the system (Callen, 1985). When spatial variations in these properties appear, the system will go to a non-equilibrium state. Hence, heat and mass fluxes will occur to compensate for the inhomogeneities, as the system goes back to the equilibrium.

Thermostatic principles become somehow limited when it comes to describe non-homogeneous, non-stationary systems. In this instance, non-equilibrium thermodynamics (NET) turns particularly useful. Applying a NET approach, it is possible to: (*1*) Describe the transport processes in systems that are out of global equilibrium; and (*2*) Quantify the entropy, the energy and the work produced (or lost) as transport phenomena are occurring (de Groot and Mazur, 1984; Kjelstrup and Bedeaux, 2008). Some examples of systems that can be modeled using a NET perspective include: Liquid-liquid separators; Multiphase reactors; Distillation columns; and Evaporation units in transient regime.

The link between system theory and thermodynamics has been established in the literature for different specific non-homogeneous chemical units. For example, one of the first works on dynamic characterization of multiphase systems can be traced back to Rosenbrock (1963), in which Lyapunov second method was used to prove that a non-ideal binary distillation column operates at a unique asymptotically stable steady state. Rouchon and Creff (1993) proved, by using irreversible thermodynamic principles, that an adiabatic flash drum operates under a dynamic stable regime as a consequence of thermodynamic stability. In the survey presented by Skogestad (1997), equilibrium multiplicity, limit cycles and instability are reported for distillation columns. Recently, Aggarwal and Ydstie (2013) extended the results from (Rouchon and Creff, 1993) to prove exponential stability of a flash unit and asymptotic stability for a distillation column. García-Sandoval et al. (2015) developed a passivity-based approach to emphasize the stability in a gaseous phase reactor that can interact with its surroundings.

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All the properties of a thermodynamic system are determined once its extensive variables are known: Internal energy; Volume; and Molar composition. In this paper, we derive a dynamical model to recover the extensive properties of a composite system, taking the interface transport into account. This leads to a general model where no assumptions on the pressure (isobaric), volume (isochoric), nor the temperature (isothermal) on each subsystem are required. To model a non-homogeneous composite system, we need to consider input and output flows for each phase of the system, denoted $(\mathcal{F}_i^j, Q^j)$. A new term, that corresponds to the transport between the different compartments of the system ($\mathbf{R}$) is considered in the present study. This term models the thermodynamic effects of the interaction between phases in a dynamical model of the system. Figure 1 provides a representation of a simple non-equilibrium composite system.

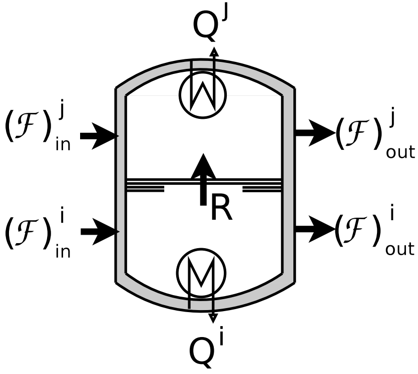

Fig. 1. Composite system with interface transport

The paper is organized as follows. Section 2 presents the interphase transport as a function of the extensive variables for a closed composite system that does not exchange matter with its environment. Assuming local thermodynamic equilibrium, Section 3 extends the model to an open system. Section 4 presents numerical simulations for the open and closed systems. Finally, Section 5 summarizes the contribution and discusses future work.

2. CLOSED MULTIPHASE SYSTEMS

2.1 System and Variables Description

We first consider a closed composite system, as depicted in Figure 2 (right). We assume that the c chemical components in the system can move from one chamber to the other. To build up our model, the following assumptions are considered:

1. Each phase is homogeneous and it is locally in thermodynamic equilibrium;
2. Each phase consists of a mixture of ideal gases;
3. The volume of each subsystem can change; however; and
4. The total volume of the system is constant.

With some modifications, the model could be used to represent a non-equilibrium flash unit or a liquid-liquid separation process.

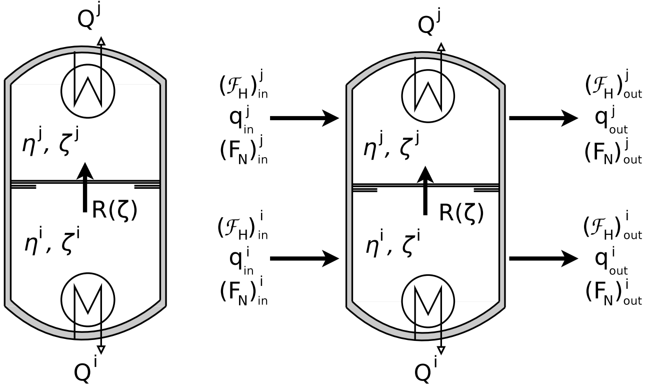

Fig. 2. Left: closed vessel with two chambers; Right: open vessel with two chambers.

We consider the following variables:

- Q^k corresponds to the heat exchange between the phase k and the environment (J/s);
- $\boldsymbol{\eta^k} = \left[U^k, N_1^k, \ldots, N_c^k\right]'$ is a vector that contains extensive variables of phase k: Internal energy (J); and Mole numbers of each component (mol), respectively;
- $\boldsymbol{\zeta^k} = \left[(\frac{1}{T})^k, -(\frac{\mu_1}{T})^k, \ldots, -(\frac{\mu_c}{T})^k\right]'$ is a vector that contains intensive variables of phase k: The temperature T (K); and The chemical potential of component i, μ_i (J/mol); and
- $\mathbf{R}(\boldsymbol{\zeta}) = [R_Q(\boldsymbol{\zeta}), R_{N_1}(\boldsymbol{\zeta}), \ldots, R_{N_c}(\boldsymbol{\zeta})]'$ corresponds to the interface flowrate transport from phase i to phase j: Heat flow (J/s); and Molar flow (mol/s), respectively.

We denote the driving force vector as $\boldsymbol{\zeta} \in \mathbb{R}^{c+1}$. It is a function of the intensive variables of the phases in contact $\boldsymbol{\zeta} = \boldsymbol{\zeta}(\boldsymbol{\zeta^i}, \boldsymbol{\zeta^k})$.

2.2 Interface Flow

Heat and mass can be transferred through the interface of the system. The flux vector is denoted by $\mathbf{J} = [J_Q, J_{N_1}, \ldots, J_{N_c}]'$, where J_Q, and J_{N_k} are the heat flux, and the molar flux of component k through the interface, respectively. If Ω is the contact area between phases, assuming that the flux is uniform, then the flow from phase i to phase j is

$$\mathbf{R} = \iint_{\Omega} \mathbf{J} \cdot \mathbf{dA} = \Omega \mathbf{J}.$$

At thermodynamic equilibrium, both the driving forces vector and the flux vector are zero (Prigogine, 1955). Therefore, near thermodynamic equilibrium, there is a linear relationship between the fluxes and the driving forces:

$$\mathbf{J} = \mathrm{L}\boldsymbol{\zeta}, \qquad L \succeq 0,$$

where L is a positive definite matrix of dimension $(c+1)$ (Prigogine, 1955). Moreover, when local thermodynamic equilibrium is assumed at each phase, we can write (Callen, 1985)

$$\boldsymbol{\zeta} = \nabla_{\boldsymbol{\eta^j}} S = \nabla_{\boldsymbol{\eta^j}} S^j - \nabla_{\boldsymbol{\eta^i}} S^i = (\boldsymbol{\zeta^j} - \boldsymbol{\zeta^i}), \qquad (1)$$

where $S = S(\boldsymbol{\eta^i}, \boldsymbol{\eta^j})$ is the Entropy Fundamental Relation for the composite system [1]. When the driving forces ζ_k are

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[1] Equation (1) is only valid for local thermodynamic equilibrium at each phase. A future perspective could be to consider $\zeta = \nabla_{\eta^j}(P)$ for some general potential function $P(\eta)$.