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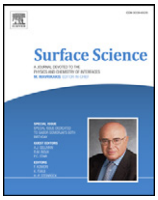

Capillary equilibrium and sintering kinetics in dispersed media and catalysts

Francis Delannay *

Institute of Mechanics, Materials and Civil Engineering, iMMC/IMAP, Université Catholique de Louvain, Louvain-la-Neuve B-1348, Belgium

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Dedicated to Professor Gabor A. Somorjai on the occasion of his 80th birthday

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ABSTRACT

The evolution of an aggregate of particles embedded in a fluid phase, no matter whether a liquid, a vapor, or a mixture of both, is determined by the dependence of the equilibrium interface area on porosity volume fraction. In system with open porosity, this equilibrium can be analyzed using a model representing the particles as a collection of cones of revolution, the number of which is the average particle coordination number. The accuracy of the model has been assessed using *in situ* X-ray microtomography. The model makes possible the computation of the driving force for sintering, commonly called sintering stress. It allows the mapping of the domains of relative density, coordination number, and dihedral angle that bring about aggregate densification or expansion. The contribution of liquid/vapor interfaces is enlightened, as well as the dependence of the equilibrium fluid phase distribution on particle size. Applied to foams and emulsions, the model provides insight into the relationship between osmotic pressure and coordination. Interface-governed transport mechanisms are considered dominant in the macroscopic viscosity. Both sintering stress and viscosity parameters strongly depend on particle size. The capacity of modeling the simultaneous particle growth is thus essential. The analysis highlights the microstructural parameters and material properties needed for kinetics simulation.

1. Introduction

Industrial heterogeneous catalysts consist of finely divided solid particles forming randomly packed aggregates with open, percolating porosity in which the fluid carrying reactants and products travels (Fig. 1) [1,2]. The “fluid” can be a vapor phase, a liquid phase, or two coexisting phases: a vapor with a liquid, or two immiscible liquids. If two fluid phases are involved, they may either share the porosity volume or, as represented in Fig. 1, be partitioned between the inner porosity and the external environment of the aggregate. In the latter case, their interface consists of menisci at the outlet of the pores. Capillary phenomena play an essential role in trickle-bed reactors and other multiphase reactors [3–5]. The evolution of the shape, size, and packing of the particles determines both the surface area developed by active catalytic species and the volume fraction and topology of the porosity, which affects the mechanics of fluid flow through the catalyst bed. The control of the kinetics of catalyst sintering becomes increasingly crucial today as catalyst microstructure evolves to the nanoscale [6]. The evolution of the system is governed by interface tensions and by the physical mechanisms of diffusion across the fluid, across the bulk of the particles, and along the various interfaces. These phenomena have been early investigated by G.A. Somorjai (e.g., [7,8]).

The purpose of the paper is to present an overview of a modeling approach developed in recent years for apprehending fluid distribution, coarsening kinetics, and densification kinetics in dispersed media. Although the approach focused primarily on materials processing by sintering, the paper aims at showing the insight offered by the approach into phenomena belonging to the realms of catalysts, emulsions, and foams.

Let us consider energetically isotropic systems consisting of solid particles and two fluids: a vapor phase and a liquid phase. Capillary equilibrium is then governed by four interface tensions: solid/solid, γ_{ss}; solid/vapor, γ_{sv}; solid liquid, γ_{sl}; and liquid/vapor γ_{lv}. These tensions define the equilibrium wetting angle $\theta = \arccos\left[(\gamma_{sv} - \gamma_{sl}) / \gamma_{lv}\right]$ [9] and the equilibrium dihedral angles $\psi_{sv} = 2\arccos\,(\gamma_{ss}/2\gamma_{sv})$ and $\psi_{sl} = 2\arccos\,(\gamma_{ss}/2\gamma_{sl})$. In the following, we use the subscript “fl” for designating indifferently liquid or vapor. When $\gamma_{sfl} \leq \gamma_{ss} / 2$, $\psi_{sfl} = 0$ and one takes $\gamma_{ss} = 2\gamma_{fl}$ because a thin interlayer of fluid is assumed to be sandwiched at the contact interface between particles. The evolution of the system is driven by the decrease in interfacial energy

$$E_{\text{interface}} = \gamma_{ss}A_{ss} + \gamma_{sv}A_{sv} + \gamma_{sl}A_{sl} + \gamma_{lv}A_{lv} \qquad (1)$$

where A_{ss}, A_{sv}, A_{sl}, and A_{lv} are interface areas. Foams and emulsions are other types of dispersed media, which may be represented by Fig. 1 on condition that so-called “particles” are vapor bubbles in foams and liquid droplets in emulsions. Their capillary equilibrium obeys the

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* IMAP, Place Sainte Barbe 2 bte L5.02.02, Louvain-la-Neuve 1348, Belgium.
E-mail address: Francis.delannay@uclouvain.be.

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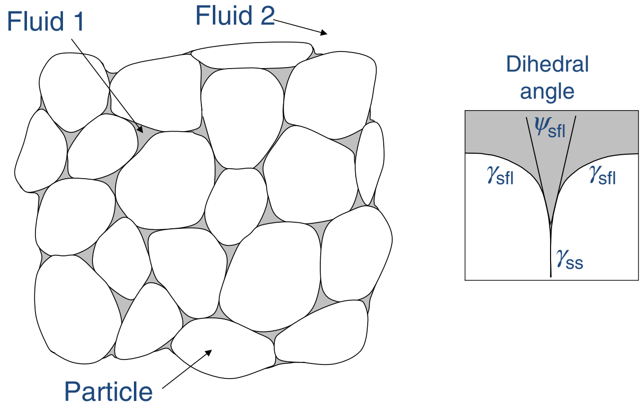

Fig. 1. Aggregate of particles with two fluid phases separated by menisci at the outlet of the pores; definition of dihedral angle $\psi_{sfl} = 2\arccos(\gamma_{ss}/2\gamma_{sfl})$.

same principles as for solid aggregates [10]. Interfaces between bubbles and droplets being fully wetted by the percolating liquid, dihedral angle is zero in foams and emulsions.

In the following, the so-called "relative density," denoted ρ, is the total volume of solid particles, liquid droplets, or vapor bubbles divided by the total volume of the aggregate. No contact exists between the particles below a certain critical relative density, denoted ρ_0, which is close to 0.62 in monodispersed random aggregates [11,12]. In isotropic systems at capillary equilibrium, particles are then perfect spheres freely floating in the fluid phase. These spheres can grow only by Oswald ripening via mass transport through the fluid phase. When ρ increases above ρ_0, interparticle contact areas increase while porosity remains open, forming a fully interconnected network of channels which percolates throughout the aggregate. Interparticle mass transport mechanisms can then occur also via the bulk of the particles and along their contact interfaces. The pore channels network becomes unstable when ρ exceeds a second critical value, denoted ρ_{pc}, at which porosity subdivides into closed pores isolated from one another.

In this paper, the analysis of the thermodynamics and kinetics of evolution of the aggregate is limited to the process starting at the initial formation of contacts between the particles and finishing at the closure of the pores: neither the evolution of isolated particles by Oswald ripening nor the sintering process after pore closure are considered. The subject is addressed in three steps. Section 2 analyses the equilibrium area of the interfaces without paying attention to the kinetics. The basic principles underlying the modeling of the equilibrium configuration of interfaces are introduced while giving reference to literature for mathematical details. We describe first aggregates in which porosity contains only one fluid phase – either vapor or liquid – and subsequently aggregates containing both a liquid and a vapor. We present two examples of validation of computational results by comparison with direct characterization of interfaces by microtomography. Section 3 focuses on the driving force for the evolution of the system, commonly called "sintering stress," in the presence of one or two fluid phases. The influence of particle size on the phenomenon of liquid migration in a graded aggregate is enlightened. A parallel is made with the concept of "osmotic pressure," which is the corresponding driving force in foams and emulsions. Finally, Section 4 deals with the modeling of sintering kinetics via the modeling of the mass transport mechanisms that determine the macroscopic viscosity opposing the sintering pressure. Only interface-governed transport mechanisms are considered in some detail. The discussion highlights the importance of faithful, validated values for the various microstructural parameters and material properties that enter into the computational models.

2. Interface shape equilibrium

2.1. Modeling principles

The volume of a randomly packed aggregate of particles may be subdivided into an ensemble of Voronoï cells built by tracing the median planes between the centers of gravity of the particles (Fig. 2a). We will represent the average particle size by the radius R_p of a sphere with volume equal to the average particle volume in the aggregate. The average particle coordination number, n_c, can be defined as the average number of faces of the cells. Accordingly, n_c is non-integer and vary depending on the random packing density. If we leave aside the effects due to particle size distribution, we may analyze the system by considering only an "average Voronoï cell" of volume $4\pi R_p^3/(3\rho)$ containing a particle with average size R_p and average coordination n_c. The average Voronoï cell is an assemblage of n_c pyramids of which the apex is at the center of gravity of the particle. As long as porosity forms a continuous three-dimensional network of pore channels (Fig. 2a), the n_c pyramids may be approximated by n_c identical cones of revolution (Fig. 2b). The opening angle β at the apex of the cone is related to n_c as

$$\beta = \arccos\left(1 - \frac{2}{n_c}\right) \tag{2}$$

and the height H of the cone is a simple function of R_p, n_c, and ρ [13]. The interparticle interface is then a circle of radius $R_{contact}$. For symmetry, the particle/fluid interface meets the external surface of the cone at 90°. The critical particle volume fraction at which particle contact reduces to a point ($R_{contact} = 0$) is

$$\rho_0 = \frac{(n_c - 2)^2}{n_c(n_c - 1)}. \tag{3}$$

Eq. (3) closely corresponds to the volume fraction in regular periodic arrangements of spheres with $n_c = 4, 6, 8$, or 12 [13].

In random aggregates, the increase of ρ induces simultaneously a rearrangement of the grains, which causes a monotonic increase of n_c, from about 6 when particles enter in contact to about 14 at $\rho = 1$. Several authors have developed computational models aiming at capturing this increase of n_c with ρ [14–16]. Nevertheless, the phenomenon, and in particular the role of dihedral angle, remains ill understood. In the lack of a predictive law based on physical mechanisms, we must rely on empirical laws such as the relationship proposed German [17] on the basis of an extensive review of literature data:

$$n_c = 2 + 11\rho^2 \tag{4}$$

Glicksman [18,19] has shown that, for random polycrystals (i.e., $\rho = 1$), the mathematical condition for having grains with flat interfaces (i.e., grains at equilibrium with respect to one another) is $n_c = 13.397$.

If $\psi_{sfl} \leq 60°$, triple line boundaries (along the edges of the cell of Fig. 2a) remain wetted by the fluid phase, and Fig. 2a can then represent the system up to the disappearance of porosity. If $\psi_{sfl} > 60°$, the pore channel network becomes unstable when ρ exceeds ρ_{pc}, the value of which can be predicted on the basis of the Plateau–Rayleigh instability criterion [20,21]. At capillary equilibrium, closed pores assume the shape of regular spherical tetrahedrons localized at the points of meeting of four triple lines (i.e., at the vertices of the Voronoï cell) [22,23].

Let us assume that we start with an aggregate made by compaction of a bed of solid particles. Unless $\psi_{sfl} = 0$ at equilibrium, the evolution to equilibrium chemical bonding at the interface brings about, as a corollary, the formation of the equilibrium dihedral angle ψ_{sfl} along the triple line. As illustrated in Fig. 3a, this creates a "neck" at the contact between the particles. The subsequent evolution of the solid skeleton is driven by the overall decrease in interface energy. At given volume of the two phases, minimum particle/fluid interface area is reached when the curvature of