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# Densification rate in a granular mechanical sintering model based on flux balance

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## Abstract

Properties of a solid state sintering model developed for the study of nuclear fuel sintering are studied (chemical potential at surfaces expression and along a grain boundary). They generalize classical sintering laws in symmetrical cases with a constant grain boundary mean curvature (rounded or plane grain boundary). The shrinkage rate is discussed for classical analytical models with their geometrical assumptions, and their tacit assumptions are emphasized. With our model, morphology of grains resulting from their fabrication route can be taken into account. Flux balance along the triple line gives an insight to sinterability of powders due to their morphology.

**Keywords:** sintering, model, powder, morphology, chemical potential

## I. Introduction

Sinterability of powders for nuclear fuel pellets is of major importance for fuel fabrication. This property does not only depend on the chemical composition of the material (Pu or Am contents of the MOX material) and on the thermodynamic conditions of sintering but also on the morphology of the powder – both on the crystallite scale and on that of aggregates (Guillet & Gu  rin, 2009; Mihaila, 2012). Models have shown attempts to tackle the influence of morphology on sintering (Eggersdorfer, Kadau, Herrmann, & Pratsinisa, 2012; Wakai & Brakke, 2013).

The study presented hereafter deals with the effect of crystallite morphology upon the shrinkage rate of two crystallites in contact. Such a law can be used for instance in macroscopic models based on the discrete element method (Yan, Martin, Guillon, & Bouvard, 2013) or based on non-smooth contact dynamics (Martin, Contribution   

la modélisation du frittage à l'état solide, 2014; Martin, Guessasma, Léchelle, Fortin, Saleh, & Adenot, 2014) to get an insight upon its macroscopic consequences on the macroscopic shrinkage rate. In any case this study gives a hint on the way shrinkage may be influenced by the morphology of crystallites (Nkou Bouala, et al., 2014).

Literature (Coblenz, Dynys, Cannon, & L., 1980; Parhami, McMeeking, Cocks, & Suo, 1999; Delannay & Missiaen, 2009; Bouvard & McMeeking, 1996) gives analytical laws or numerical treatment of models to account for the shrinkage rate. These models are generally based on the assumption that particles (crystallites) are spherical and that the initial grain boundary is a plane. In that case two symmetry elements make the problem simpler, they are the rotation axis and the symmetry plane perpendicular to this axis. In order for the model to make it possible to predict the evolution of curved grain boundaries, for instance in the third stage of sintering, where neighboring grains may coalesce and lead to a non-regularly curved grain boundary, a more general approach is required.

A model on a sub-granular scale was proposed. Its main specific feature is the way chemical potential of atoms is computed within this framework. The chemical potential definition is valid both at interfaces of crystallites and in the bulk of grains and makes it possible to take into account both bulk, surface and grain boundary diffusion. The chemical potential term can include other contributions such as the electric field contribution (Munir, Anselmi-Tamburini, & Ohyanagi, 2006; Olevsky & Froyen, 2006) and mechanical boundary conditions may match those of Spark Plasma Sintering (SPS) in which sintering is pressure assisted (Mourad & Garikipati, 2006).

In the framework of the modelling of sintering on a sub-granular scale, a local densification law has been derived in the case of two grains. Predictions of the shrinkage rate can be obtained with the classical Herring and Gibbs-Thomson chemical potentials (i.e. with an interface defined chemical potential), or with the chemical potential we have proposed which is defined everywhere both in the bulk of grains or at interfaces. Tacit assumptions of classical models are emphasized. Consequences upon morphological effects on the shrinkage rate are analyzed on the crystallite scale.

## **II. Model description**

Two crystallites in contact are considered as schemed in Figure 1. Each possesses a free surface  $\Gamma_1$  (resp.  $\Gamma_2$ ) and they share a grain boundary (GB) denoted  $\Gamma_{1/2}$  the thickness of which is  $\delta_{GB}$ .

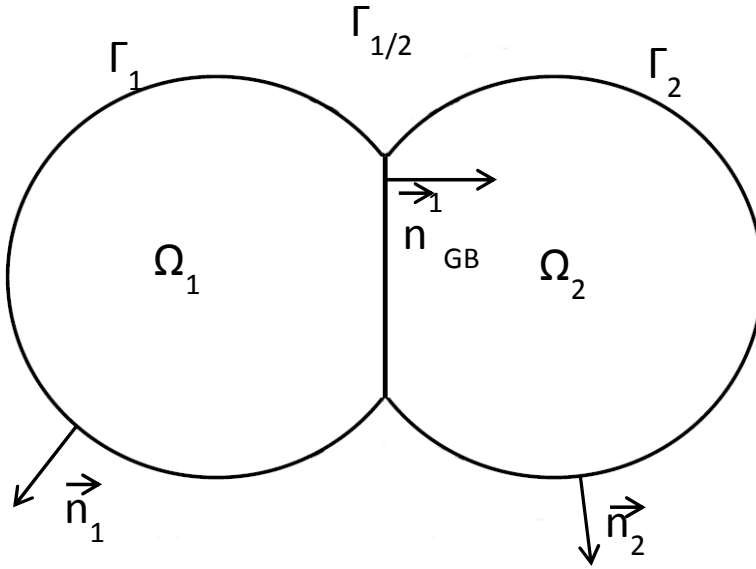


Figure 1: schematics of a contact between two sintering grains - notations

If  $\sigma$  is the stress tensor, boundary conditions used to compute the displacement field are of von Neumann type at free surfaces  $\Gamma_1$  and  $\Gamma_2$  due to Laplace law. In the framework of Herring approximation (Herring, 1951) they read:

$$\bar{\bar{\sigma}}(\vec{n}) \cdot \vec{n} = -p_{gas} - \left\{ 2\gamma_{SV}\kappa_m + \frac{1}{R_1} \frac{\partial^2 \gamma_{SV}}{\partial^2 n_1} + \frac{1}{R_2} \frac{\partial^2 \gamma_{SV}}{\partial^2 n_2} \right\} \quad (1)$$

with  $p_{gas}$  the pressure of the outer gas,  $n_1$  (resp.  $n_2$ ) the outer normal,  $\gamma_{SV}$  the solid/vapor surface energy,  $\kappa_m$  the local mean solid/vapor curvature defined as  $\frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$  and  $R_1$  and  $R_2$  are the local principal curvature radii. When surface energy does not vary with outer surface local direction the latter expression simplifies into Gibbs-Thomson's law:

$$\bar{\bar{\sigma}}(\vec{n}) \cdot \vec{n} = -p_{gas} - \{2\gamma_{SV}\kappa_m\} \quad (2)$$

For  $\Gamma_{1/2}$  grain boundary the boundary condition reads:

$$\bar{\bar{\sigma}}_1(\vec{n}_1) \cdot \vec{n}_1 = \bar{\bar{\sigma}}_2(\vec{n}_1) \cdot \vec{n}_1 - 2\gamma_{GB}\kappa_{GB} \quad (3)$$

corresponding to a finite jump in stress across the interface (i.e. over a  $\delta_{GB}$  wide area).

For materials with a surface energy varying with orientation, the chemical potential of atoms and vacancies in the vicinity of an interface,  $\mu$  is given by (Philibert, 1990):

$$\mu = \mu_A - \mu_V = \mu_{bulk}^0 + \Omega \left\{ \gamma_{SV} \left[ \frac{1}{R_1} + \frac{1}{R_2} \right] + \frac{1}{R_1} \frac{\partial^2 \gamma_{SV}}{\partial^2 n_1} + \frac{1}{R_2} \frac{\partial^2 \gamma_{SV}}{\partial^2 n_2} \right\} \quad (4)$$

where  $A$  denotes an atom and  $V$  a vacancy, and  $\Omega$  the atomic (resp. molar) volume, which reads more simply in the isotropic case :

$$\mu = \mu_A - \mu_V = \mu_{bulk}^0 + \Omega \gamma_{SV} \left[ \frac{1}{R_1} + \frac{1}{R_2} \right] \quad (5)$$

Shrinkage rate is linked to the normal velocity of interfaces, hence to flows of matter. These latter depend on the chemical potential accordingly to Onsager law (Philibert, 1990):

$$\vec{J}_A = -L_{AA} \nabla \left( \frac{\mu}{T} \right) \quad (6)$$

with T temperature and  $L_{AA}$  Onsager's coefficient. In our solid state sintering model (Ajdour, 2006; Martin, 2014) the chemical potential is defined at any place in the grains (bulk or interfaces) by:

$$\mu = \mu_{bulk}^0 - \frac{\Omega}{3} \text{tr}(\sigma) - \frac{1}{2} \Omega (\sigma : \varepsilon) \quad (7)$$

with  $\varepsilon$  the strain tensor. Our materials show an elastic limit thrice higher than the stress due to surface curvature at any temperature along the thermal cycle (Fossati, 2012) so that free sintering can be modeled with an elastic constitutive law:

$$\varepsilon = s : \sigma \quad (8)$$

with s the compliance matrix. Its terms are small enough so that the density of elastic energy can be regarded as a small second order term in  $\sigma$ . If stress is hydrostatic at boundaries  $\sigma$  is close to  $\sigma_i = -p_{gas} - \gamma_{SV} \left[ \frac{1}{R_1} + \frac{1}{R_2} \right]$  ( $i \in \{1,2,3\}$  with Voigt notations) and meets the expression of Gibbs-Thomson of the chemical potential. The approach differs from Wakai's (Wakai & Brakke, 2013) by the fact that the stress field is computed by solving Navier-Lamé equations with Laplace boundary conditions and non-translation and non-rotation as algebraic conditions.

### III. Resultst and Discussion : shrinkage rate

The advantage of our expression also compared with other mechanical models (Bruchon, Pino-Munoz, Valdivieso, & Drapier, 2012) is the differentiability of the chemical potential within a grain (between the bulk and the interfaces) so that both bulk, surface and grain boundary diffusion phenomena can be described with the same chemical potential.

For any surface S belonging to a free interface  $\Gamma_i$ , Ficks's second law gives the movements of the interfaces (Léchelle, Martin, Boyer, & Saikouk, 2014) :

$$\iint_S \vec{V}_{int} \cdot \vec{n}_i dS = \Omega \iint_S (\vec{J}_V \cdot \vec{n}_i + \text{div}_S(\vec{J}_S)) dS \quad (9)$$

With  $V_{int}$  the interface velocity,  $\text{div}_S$  the surface divergence operator and  $J_s$  the surface flow. The mass of quasi-incompressible matter produced along the grain boundary by grain 1 per time unit and transferred towards direction of grain 2 through a unit surface of the grain boundary is (Martin, 2014):

$$\dot{V}_1 = -\Omega (\vec{J}_{GB_1}^\perp \cdot \vec{n}_{GB}^1) - \Omega \text{div}_S(\vec{J}_{GB_1}^\parallel) \quad (10)$$

$\vec{J}_{GB_1}^\perp$ , respectively  $\vec{J}_{GB_1}^\parallel$ , are the grain boundary flux perpendicular resp. parallel to the grain boundary as shown in Figure 2. Their respective diffusion coefficients are those obtained by the study of grain growth and by tracer diffusion experiments.

The expression of the velocity of the interface in the case of Gibbs-Thomson's law can be written as follows:

$$v_n = \Omega (\vec{J}_{GB_1}^\perp + \vec{J}_{GB_1}^\parallel) \cdot \vec{n}_{GB}^1 - \frac{\delta_{GB} \gamma_{GB} D_{GB}^\parallel}{kT} \Delta_S \kappa_m \quad (11)$$

with  $\delta_{GB}$  the grain boundary thickness. In the case of our model bulk diffusion also depends on stress, so that:

$$\vec{J}_{GB_l}^\perp = \frac{D_{GB}^\parallel}{kT \Omega} \left( \frac{1}{3} \sum_{i=1}^3 \sigma_i + \frac{1}{2} \sum_{k=1}^6 \sum_{l=1}^6 \vec{\nabla}(\sigma_k \sigma_l) \right) \quad (12)$$

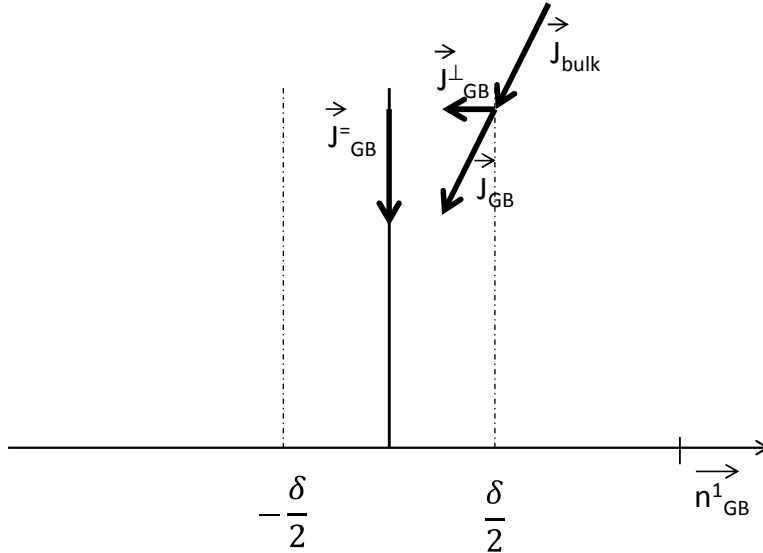


Figure 2 : definition of volume (or bulk) and grain boundary fluxes

Relation (11) is valid even if grain boundary curvature is not constant and gives a local value of the interface velocity along the grain boundary.

For a plane grain boundary  $\Delta_S = \Delta$  (classical Laplace's operator). If in addition grains are symmetrical with respect to the grain boundary, the symmetry of the problem leads to  $v_n=0$  so that:  $\Delta_S \mu = 0$ , and  $\mu$  is a second order polynomial of the distance from the grain boundary center. In that case the flux is nul in the center on symmetry grounds and linear with the distance from the grain boundary, its divergence is a constant and can be estimated from its difference between the triple line and the center of the grain boundary. Thus classical results are found back.

If S is taken as the whole grain boundary, Kirchhoff analogue for matter flow at triple point T reads:

$$\vec{J}_{S_1} \cdot \vec{n}_{t_1} = -\vec{J}_{GB_1} \cdot \vec{n}_{t_{GB}} \quad (13)$$

with  $\vec{n}_{t_1}$  (resp.  $\vec{n}_{t_2}, \vec{n}_{t_{GB}}$ ) the outer normal of the triple line for a surface element belonging to surface  $\Gamma_1$  (resp.  $\Gamma_2, \Gamma_{GB}$ ) which is tangent to  $\Gamma_1$  (resp.  $\Gamma_2, \Gamma_{GB}$ ) (see Figure 3). So that:

$$\dot{V}_1 = -\Omega \iint_{\Gamma_{S_1}} \vec{J}_{GB_1}^\perp dS - \Omega \oint_{\Delta} \vec{J}_{GB_1}^\perp dl = -\Omega \iint_{\Gamma_{S_1}} \vec{J}_{GB_1}^\perp dS + \Omega \oint_{\Delta} \vec{J}_{S_1}^\perp dl \quad (14)$$

And the shrinkage rate averaged on the grain boundary is:  $h = \frac{1}{S} (\dot{V}_1 + \dot{V}_2)$ . If diffusion perpendicular to the grain boundary can be neglected the shrinkage rate only depends on the change in mean curvature at the surface of crystallites in the vicinity of the triple line, i.e. on the morphology of crystallites, or indirectly on the fabrication route of the powder. The higher the changes in curvature radii are, the fastest the shrinkage should begin.

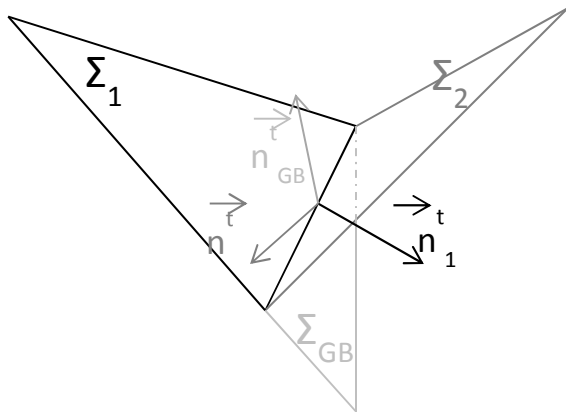


Figure 3: Kirchhoff's analogue of current law: geometry of discretized surfaces in the vicinity of a triple point

Application of relation (4) to spherical rigid grains with a negative neck the curvature radius with a constrained geometry by classical models (Parhami & McMeeking, A network model for initial stage sintering, 1998) does not make it possible to account for the initial nor changing morphology of grains. For rigid grains, with a constant

curvature grain boundary with an absence of diffusion perpendicular to the grain boundary ( $\overrightarrow{J_{GB}^\perp}=0$ ) the shrinkage rate would be zero:  $\dot{h} = 0$ . The latter conclusions are changed when grains are no more considered as rigid, but for instance elastic at a given (quasi-static time step) during the sintering process since in that case the chemical potential in the bulk of grains is no more constant ( $\mu_{bulk} = f(\sigma) \neq \mu^0$ ).

#### IV. Conclusion

The compatibility of a solid state sintering model under development presented in Ajdour's and Martin's works (Ajdour, 2006; Martin, 2014), with other models with assumptions on geometry was shown. Its compatibility with Gibbs-Thomson's law was also shown.

Predictions of the shrinkage rate in the symmetrical case show that this rate only depends on the geometry of crystallites at their surface in the vicinity of the triple line, i.e. to the morphology of crystallites resulting from their fabrication route (Nkou Bouala, et al., 2014). In a more general case (absence of symmetry of the grain boundary) our model can be used to predict shrinkage rates.

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