IFPRI Project Proposal

Modeling Porosity Development during Drying of Liquids and Slurries

by

Reza Kharaghani

Otto von Guericke University Magdeburg
Chair of Thermal Process Engineering
Pore Networks and Drying Group

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Project Description

1. Current state of research and preliminary work

1.1. Current state of research

Fundamental knowledge on development of the **internal morphology** (e.g. porosity) of porous particles produced from drying of liquids and slurries is of great practical importance in the formulation of new particles or products. Application of this knowledge is not limited to the process example of spray drying considered here, but suited for many other types of solution gas-drive processes. Spray drying is considered here, because it offers a certain benchmark to other drying technologies, and because this is the method studied intensively and put widely into practice, among others, in the food, pharmaceutical and fine chemical industries. Despite this growing drying technology, however, a big challenge remains in producing powder products with improved primary and secondary properties with the best possible process efficiency.

Foaming the liquid feed is recognized as one of the promising directions in this respect. Droplets in spray dryers can be foamed (Fig. 1) by either injecting inert gas into the high-pressure feed or by reducing the liquid pressure after expansion of the feed at the outlet of the nozzle (see [1,2] and citations therein). An alternative to foaming droplets in spray dryers, is to produce stable foam by adding suitable surfactants (e.g. milk protein) in small amounts to the slurry feed. Then, the foam is layered on belts or drums and dried by hot air flow, or even by contact under freeze or vacuum conditions. Another way to create layered foam is to spray a slurry on the conveyer of a belt dryer, where the foam generation and drying takes place together. Here, layer thickness and structure are imposed by spray pre-drying and the speed of the conveyer.

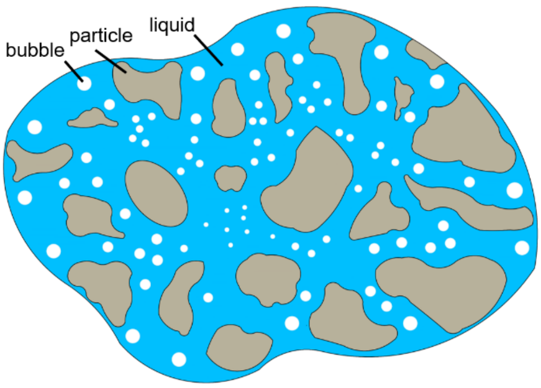

Fig. 1: Schematic illustration of many bubbles formed in a slurry droplet.

On one hand, these diverse options for tailoring foaming (which serves as a template for subsequent drying), choice of drying process, and selection of foam thickness and operating conditions create opportunities for better product quality and process efficiency in spray drying. On the other hand, they render the process complex and increase considerably the amount of research effort required to understand them. <u>Though numerous works on foam spray drying have appeared in the past few decades, but they are empirical and product-specific, and their results can hardly be universalized because of the absence of theoretical understanding and fundamental modeling background</u>.

At the scale of a single droplet/particle, the understanding and quantification of bubble nucleation and growth induced by pressure reduction in a liquid formulation during spray drying are commonly achieved by mathematical models, either written at continuum scale or pore scale (such as pore network or population balance). All the models account for the following mechanisms: Bubble nucleation, bubble growth and gas transport. Modeling of these mechanisms has both theoretical and practical challenges and interests. On the theoretical side, it is important to comprehend the interaction between nucleation, mass transfer and fluid transport (both gas and liquid) and the growth of the gas phase, not previously investigated in the context of foam spray drying. From the practical perspective, many unresolved issues, such as how the internal pore structure (pore size and pore size distribution) of dried particles is influenced by feed properties and process parameters.

At the pore scale, a liquid formulation is represented explicitly as a network of pores interconnected by constrictions called throats. A particle network complementary to the network of pores and throats represents the solid phase (see Fig. 2). The pores and throats have prescribed shapes but are random in size providing disorder of the void space. The pores and throats are connected to each other as required. All transport and phase change equations pertaining to both dispersed and continuous phases are modeled directly at the pore scale using fundamental physical laws. This description ensures that relevant effects are "visible", having over experimental measurements the decisive advantage that everything can also be explored and controlled.

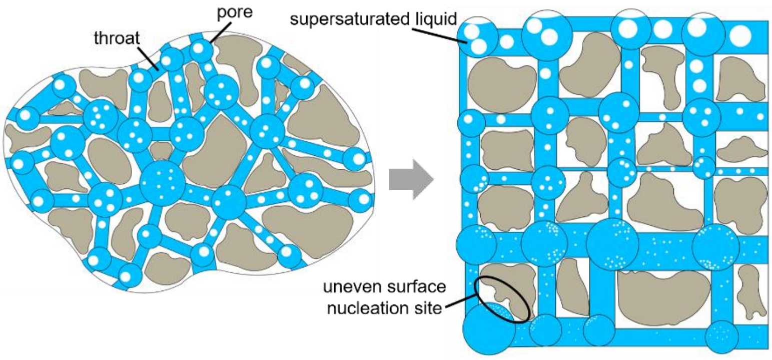

Fig. 2: Representation of a liquid droplet by networks of pores and particles.

Pore network models (PNMs) were originally developed to simulate immiscible, non-reactive flow in unsaturated porous media [3]. Later on, they were further tailored and refined to account for more complex pore-scale phenomena. These include (first-order) phase transitions (such as evaporation and condensation) [4,5] and chemical reactions (such as precipitation and dissolution) [6]. Efforts were also made to incorporate the physical effects [7] and structural properties [8] into the PNMs. The PNMs for drying we have at our disposal have been steadily advanced during the recent years. Those PNMs however assume the liquid to be free of bubbles, the pore space to be stationary, and the temperature field to be uniform. Bubble formation and transport in porous media has been study by PNMs, but only in the context of secondary oil recovery [9,10] and only for situations where there is no dynamic change of the network structure during the process.

1.2. Preliminary own work

There is a long record of modeling and simulation studies as well as experimental investigations of fluid transport phenomena in porous media in the Pore Networks and Drying Group at the Chair of Thermal Process Engineering in Magdeburg. This comprises drying, wetting as well as solid formation and accumulation in porous materials. Drying and related themes will be in the focus as they are of key importance for this project.

Early investigation has shown PNMs can now accurately predict kinetics and quality aspects of these processes [11,12]. Also, advanced PNMs have been developed that can simulate the dynamics of dissolved solid transport and accumulation in a porous structure during impregnation and subsequent drying [13]. Besides the modeling and simulation of these processes, the X-ray microtomography and image analysis techniques have been employed to assess the results obtained from the pore network simulations for drying of beds packed with glass beads [14]. Thermo-gravimetric experiments at the level of single droplets [15] and particles [16] have been carried out to acquire kinetic data.

To model bubble formation and transport, the ideas and algorithmic tricks developed to model solid transport and accumulation in drying porous media will be adapted and improved. The applicant’s experience in this respect will be essential for the development of algorithms. Board experience with the use of X-ray microtomography, and with the processing and evaluation of respective data, is also available from other applications of this imaging technique.

2. Objectives and work program

2.1. Objectives

Aim of this project is to develop reliable models that can be used as powerful tools to predict the pore structure formation and development in gas-saturated liquids and slurries during evaporative drying. Models will be deterministic and discrete, able of representing micro-scale events and processes which include capillarity combined with liquid flow (where the gas molecules are dissolved in liquid) and gas phase diffusion as well as the liquid-to-gas phase change. The latter occurs by two consecutive processes, *in situ* nucleation and bubble growth, which, in turn, results in redistribution of the liquid by capillarity. An important feature of these models is that they can provide possibilities to manipulate by the development of bubbles the pore structure of slurries, increasing product porosity, which may result in superior application properties (better rehydration and instant behaviour).

Central scientific questions to be addressed in this project are as follows:

- What are adjoining and competitive mechanisms that control bubble formation (nucleation and growth) and transport in a single liquid droplet?

- What is the influence of the pressure drop and the supersaturation (fixed or constant rate of increase) on the development of pore structure (i.e. patterns and rates of bubble growth) of a single liquid droplet?
- What are the influence of process conditions (fast and slow drying) and of formulations (e.g. initial concentration of solid particles and liquid viscosity) on the development of pore structure of a single liquid droplet?
- What are the possibilities to manipulate the development of internal structure of a certain formulation during drying?

There is no overlap between present proposal and other applicant's projects. More details on the WPs follow, with a bar graph at the end.

2.2. Work program including proposed research methods

The work program is organized with three work packages in the first funding period (WP1 to WP3 for the first three project years, for which funding is here requested) and further two work packages in the second funding period of the project (WP4 and WP6 for the next three project years). Funding for the second project period will be requested timely before the end of the first period by a project continuation proposal, based on the achieved results. Consequently, WP4-WP6 are only described in a brief introductory manner.

First project period, with WP1 to WP3

WP1, Discrete modeling of bubble formation and transport: Discrete modeling and simulation of *bubble formation (nucleation and growth) and transport* in liquid media lay the foundation for all subsequent development and analysis. They will be conducted in already available, heavily to modify discrete pore network models. This challenging task is approached by considering a liquid medium composed of water or other volatile solvents capable of dissolving or dispersing solid particles. Such medium is conceptualized as a two-dimensional network of pores and of particles, the latter being complementary to the former. Pores are initially filled by a supersaturated liquid and the size of pores follows a probability density function. An a priori constant *superstation* (later on, linear gas concentration profiles between the open and the opposite closed network side are imposed) is specified at all pores. If this supersaturation surpasses at the particular pore (because of the liquid pressure decline), the nucleation sites are activated, and the host pore becomes occupied by vapor. For

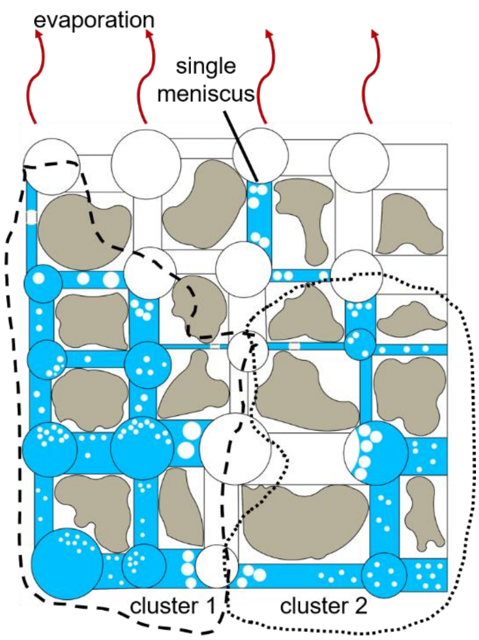

Fig. 3: Representation of a foamed pore network. Liquid is disintegrated into clusters of different size due to evaporative drying.

modeling convenience, nucleation sites are randomly distributed on the pores and they are activated when the local supersaturation is surpassed. The one-dimensional advection-diffusion equation is solved to describe the mass transfer of dissolved gas in the liquid-occupied pore space. As boundary conditions, the gas concentration on the interface of each cluster is spatially constant and the liquid pressure decline rate is given. The discrete model to be developed at this stage of the project will be versatile enough so that it can be generically applied to liquid media with different physical and structural properties. In a consultation with the IFPRI members liquid media and soluble gases will be specified and, hence, respective discrete simulations will be carried out. Here, properties that can be varied, among others, are: Initial solid mass fraction, liquid density and viscosity, dissolved gas density and viscosity, solubility constant, and diffusion coefficient. Isothermal conditions are assumed and possibly important inertial and gravity effects are neglected. Periodic boundary conditions are used to make the results independent from medium size and, thus, enable representative simulations with relatively small physical domain and a reasonable number of pores. Results from WP1 are evaluated upon the effect of pressure reduction (rate) on patterns and rates of bubble growth, to be used for the development of a new discrete drying model in WP2 and then in the new upgraded drying model in WP3.

WP2, Extension of discrete model for drying: Building on bubble formation and transport formulations from WP1, a *discrete drying model* will be developed. In WP1, bubble growth is activated at fixed supersaturation, where the liquid pressure is instantly lowered to a constant value, which remains subsequently unchanged. By contrast, bubble growth in WP2 is driven by liquid evaporation. Bubble transport is similar to WP1, but dynamic transitions and modified initial conditions are also investigated. Consequently, bubble sizes and patterns (single cluster or multiple clusters) are expected to be influenced by drying conditions, as well as by the gas concentration and the pore structure. Results go in the development of an improved discrete drying model in WP3.

WP3, Adaptive discrete model for drying: Based on the hypothesis from the literature review, the development of liquid-gas interfaces at the medium open surface leads to a decrease in the liquid pressure that essentially initiates a macroscopic liquid pressure gradient and thus solid tension

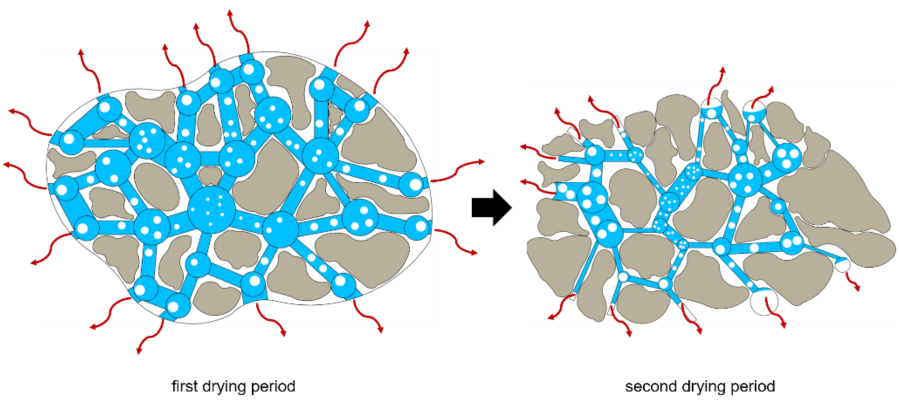

Fig. 4: Drying of a foamed pore network with evolving microstructure.

build-up. As a consequence, liquid is pumped by capillary action from the core of the medium towards its open surface. This liquid flow is limited by viscous effects, which play a dominant role when drying is very fast and/or pore size is very small. For modeling this (macroscopic) non-uniform shrinkage an algorithm will be developed. A challenging task in such model is the liquid redistribution during bubble transport and solid motion. To simply the algorithm, only a small displacement will be allowed so that there is an overlap between old and new element positions. From the new solid element positions, the new pore radii are calculated. For every element, the saturation of neighbouring throats has to be checked. Then, the liquid to be shifted shall be distributed according to the conductance of the neighbour throats. If these throats are to be fully saturated, the liquid will be accommodated in throats with hydraulic connections and liquid-gas interface – such a pore refilling algorithm would require imbibition (or wetting) rules.

Envisaged second project period, with WP4 to WP6

WP4, Realistic porous structures and experiments: The algorithms for modeling pore structure formation and development shall successively be extended to pore networks which are complementary to solid elements with high dispersions. Such solid elements shall be generated numerically using the discrete element method, for instance. Later on, this algorithm shall be advanced to account for irregular pore structures that are directly constructed from the real data to be measured using X-ray microtomography and/or scanning electron microscopy. Many of the premises upon which discrete models are developed, namely the onset of nucleation from different sites of supersaturated liquids and patterns by which bubbles grow, are confirmed by visualization experiments in transparent micromodels (first isothermal and later on in the presence of positive or negative thermal gradient) and single droplet experiments under vacuum conditions.

WP5, Model extension and incorporation of physical effects: Because discrete simulations to be conducted in the first funding period correspond to two-dimensional networks, finite size effects are strong and may result in unrealistic numerical values of quantities such as gas saturation. Therefore, three-dimensional discrete models will be developed with extension to non-isothermal situations of drying. Moreover, a discrete model will be developed for bubble growth that accounts for time-varying saturation in the far-field.

WP6, Final revision and check of discrete models: Developed algorithms for drying liquids in the presence of bubbles from the first period of the project are upgraded according to measurements and extensions made in WP5 and WP6. Thus, final version of discrete models, alongside with respective additional validations will be delivered.

Table 1: Distribution of work (PNM: pore network model) and time schedule for the proposed project (Abbreviations: WP: work package).

	1	2	3	4	1	2	3	4	1	2	3	4	1/2	3/4	1/2	3/4	1/2	3/4
First project period																		
WP1: Models of bubble formation and transport	■	■	■															
WP2: Models of drying in the presence of bubbles			■	■	■	■	■	■										
WP3: Adaptive models of drying in the presence of bubbles							■	■	■	■	■	■						
Second project period																		
WP4: Realistic porous structures and experiments													■	■				
WP5: Physical effects incorporation														■	■	■		
WP6: Upgraded models for bubble formation and transport and for drying																■	■	■

3. Literature

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