IFPRI Proposal: Modelling Porosity Development During Drying of Liquids and Slurries

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Vision

The IFPRI award will fund a PhD studentship, used to develop a multi-physics mesoscale model for the evolution of porosity in spray-dried particles. The mesoscale model will be complemented by molecular dynamics simulation to establish the parameters required for an exemplar system of spray-dried lactose-water droplets initially saturated with N_2 or CO_2 gas. Results will be compared to experimental samples from the IFPRI partners, and predictive capabilities will be used to suggest further experiments for model validation. The work will provide a flexible framework that enables future studies of alternative material systems and drying configurations.

The Research Environment

Mulheran's group comprises PhD students and Postdoctoral Researchers working on a range of materials modelling projects. Its work is funded by the Industrial Biotechnology Innovation Centre (www.ibioic.com), as well as the UKRI's NERC, BBSRC and Innovate UK funding councils. All projects involve collaboration with experimentalists and company partners that range from local SMEs to large multinational companies.

Many of the current projects in the group utilise biomolecular simulation, with which it has much experience [1]. Examples of these projects include: the development of novel biopolymer films with antimicrobial properties [2]; the development of novel vaccines [3]; understanding the antimicrobial mechanisms of novel lipid nanoparticles; understanding the mechanism of peptide fertility treatments. These are complemented by molecular simulation of small molecule systems such as glycine, used as a model system for understanding heterogeneous crystallisation [4].

In addition to molecular simulations, Mulheran's group is also active in mesoscale modelling, including the evolution of packed bed structures during pharmaceutical filtration (in collaboration with AstraZeneca); the control of polymer crystallisation using filler particles [5]; and the modelling of gelation to create mesoporous materials with a range of applications including gas adsorbents (see Figure 1).

The research environment within the Department of Chemical and Process Engineering at The University of Strathclyde is a vibrant one. Molecular simulation is a widely used tool, with researchers from several groups meeting fortnightly to discuss methodology and analysis strategies, and to help each other to produce high quality research. The supportive ethos extends throughout the Department, where PhD students organise their own series of seminars. All PhD students undertake a bespoke PGCert training program (for a detailed explanation of the program please refer to: (https://www.strath.ac.uk/studywithus/postgraduateresearch/researcherdevelopment/forstudents/pgcertinresearcherprofessionaldevelopment/) in addition to their ultimate doctoral degree. The training on offer includes transferable skills as well as discipline-specific research skills. For researchers in Mulheran's group, the latter includes bespoke training in the use of high performance computing and molecular dynamics simulation, delivered by a long-term collaborator Dr Karina Kubiak-Ossowska, who is the Training Officer for the ARCHIE-WeSt supercomputing centre at Strathclyde (www.archie-west.ac.uk). Mulheran is the Director of ARCHIE-WeSt, and is the Deputy Head of Department (Research and Knowledge Exchange) for Chemical and Process Engineering.

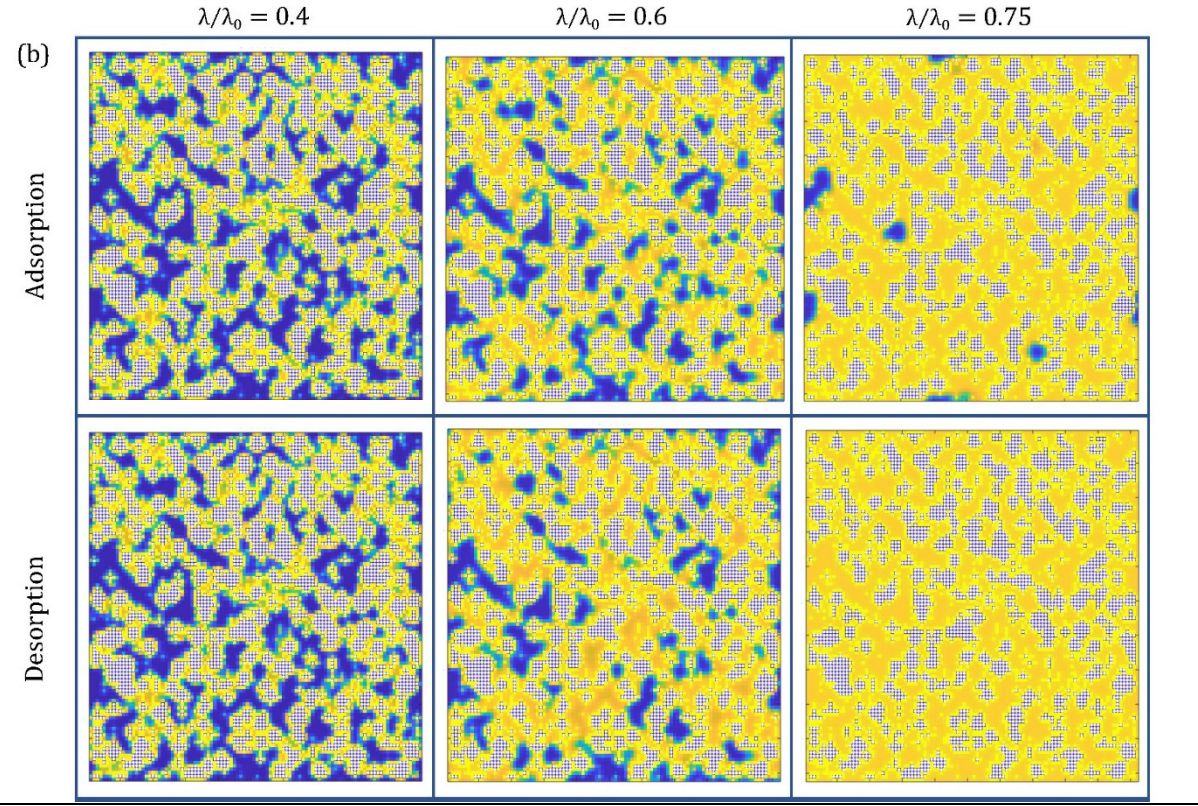

Figure 1. Gas adsorption/desorption in model gel structures. The pores in the simulated gel structure are coloured dark blue, and the yellow indicates the nitrogen gas density at various pressures (indicated by λ), using mean field calculations. The methodology explains the hysteresis between adsorption and desorption isotherms found experimentally, and allows the pore size distribution to be related to material growth parameters, including reactant and catalyst concentrations in the starting sol [6].

Background

Figure 2 illustrates the mesoscale model to be developed in the project. The droplet formed during the spraying process will incorporate gas bubbles nucleate during the concomitant pressure drop. We can model the initial distribution of bubbles and their sizes in (a) using Voronoi cells, which is an approach that has proved very informative during island nucleation and growth during thin film deposition process [7]. In (b), the situation at a later time is illustrated. Here the bubbles have coarsened by the diffusion of the gas from smaller bubbles (with higher pressure) to larger ones (lower pressure). Gas also diffuses to the outside of the droplet. The need to model the transport of gas through the solution is indicated by the yellow arrows. At the same time, the droplet dries by the transport of the solvent from the interior of the droplet to the exterior (indicated by the blue arrow), creating a density gradient which in turn influences gas diffusion. It is also apparent that the evaporation of the solvent at the droplet surface will also reduce the temperature of the droplet [8] so that a thermal gradient will also be established, while the overall mass (and size) of the droplet decreases. The multi-physics model must incorporate all of these processes.

We note that buoyancy forces have been neglected in this illustration, since if the droplet undergoes a tumbling motion these will be unimportant. Experimental images of the dried porous particles will be used to determine whether this is appropriate, and buoyancy effects will be included if required.

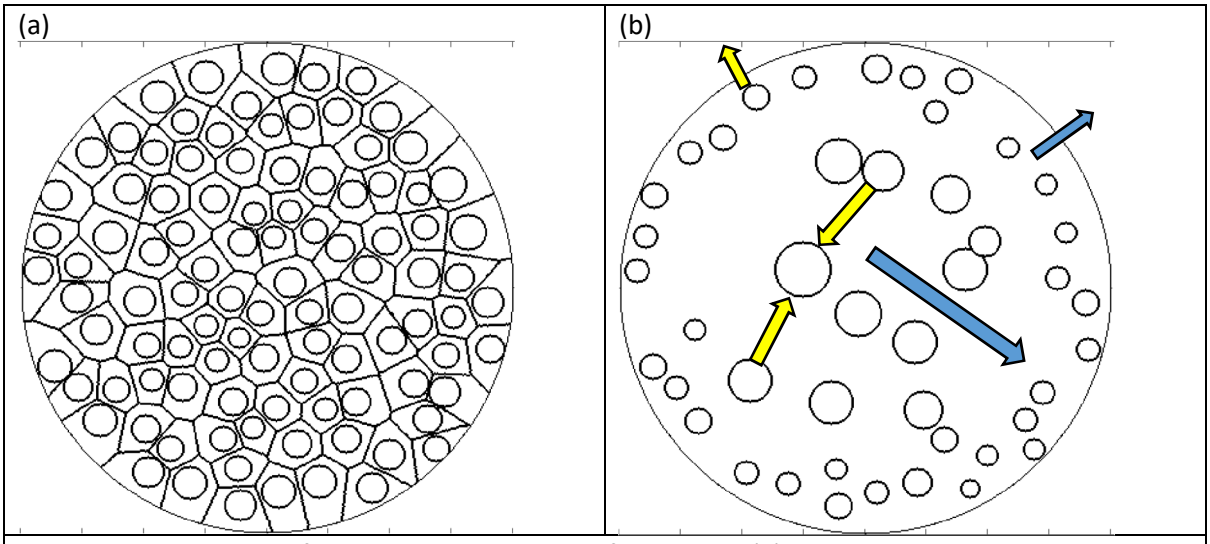

Figure 2. Illustration of mesoscale modelling of particles. (a) The initial bubble arrangement, showing the Voronoi cells used to estimate the initial bubble sizes. (b) At a later time, the bubbles have coarsened. The material transport process to be modelled are indicated by the arrows (blue for solvent, yellow for gas, see text for explanation).

Workplan

The PhD studentship can be divided into three major work packages and deliverables as follows:

Months 1-15: Development of the Mesoscale Model

The model illustrated in Figure 2 will be developed using a lattice-based (finite difference) approach. The gas density $g(\boldsymbol{r},t)$ within the solvent at position/time $(\boldsymbol{r},t)$ will be modelled using the diffusion equation:

$$\frac{\partial g(\boldsymbol{r},t)}{\partial t} = \nabla \cdot \big(D(\boldsymbol{r},t)\nabla g(\boldsymbol{r},t)\big) \qquad (1)$$

Here we explicitly show the dependence of the diffusion coefficient on position, since it will be influenced by the local concentration of the solute material in the solution and by the local temperature. Equation (1) will be computed using finite difference methods, with boundary conditions for the gas concentration at the bubble walls determined by the Gibbs-Thompson relation. In this way, the transport of gas between bubbles can be calculated, yielding the growth/shrink rates of individual bubbles. The model will be evolved over time using separation of timescales, since the bubble wall motion is slow compared to the diffusive transport.

Similar to equation (1), we model the solvent content throughout the droplet, with the boundary condition for evaporative processes at the outer particle wall. This in turn is influenced by the temperature. Since thermal conduction process are more rapid than material diffusion, we can model the isotropic droplet temperature evolution, balancing the evaporative loss of latent heat and the thermal conduction through contact with the drying gas outside the droplet. This allows the separation of timescales for the overall droplet shrinkage.

The multi-physics model thus yields porosity distributions parameterised by the diffusive motion of the solvent and gas through the continuous solution phase. A range of possible structures will be produced to compare with experimental images, to ensure that the model correctly embodies the various physical processes. Of particular interest is the effect of solubility of the gas in the solvent, which in turn influences the number density and size of the bubbles. A low solubility gas (e.g. N_2 in water) will yield well separated bubbles as illustrated in Figure 2, whereas high solubility (e.g. CO_2 in

water) might yield a more foam-like structure where the bubble walls have a curvature determined by the difference in pressure across the wall (we have previous experience of modelling foam-like microstructural evolution [9]). Nevertheless, the fundamental processes of gas diffusion between bubbles, solvent diffusion through the continuous phase, evaporation and thermal effects remain the same.

Deliverables: Reports on the model behaviour presented to the IFPRI annual meetings; manuscripts prepared for conference presentations and publication in leading internationally refereed journals.

Months 16-30: Molecular simulation of an exemplar system

In order to parameterise the model and obtain deep understanding of the key transport processes, an exemplar system will be examined in detail. Following initial discussions with IFPRI partners, we anticipate using lactose-water droplets with N_2 or CO_2 gas as the exemplar, although this is open to further discussions with partners.

Molecular dynamics (MD) simulations of lactose in water can be performed using open source tools [10-11]. Literature shows that the GLYCAM06 force field [12] performs well for lactose solutions [13]. Mulheran's group has a long track record of building and analysing MD simulations, as illustrated in Figure 3 for a study of glycine in water at oil and air interfaces [4]. The latter is particularly interesting for this project since it demonstrates how the surface regions can be different from bulk, with consequences for the surface tension of the interface.

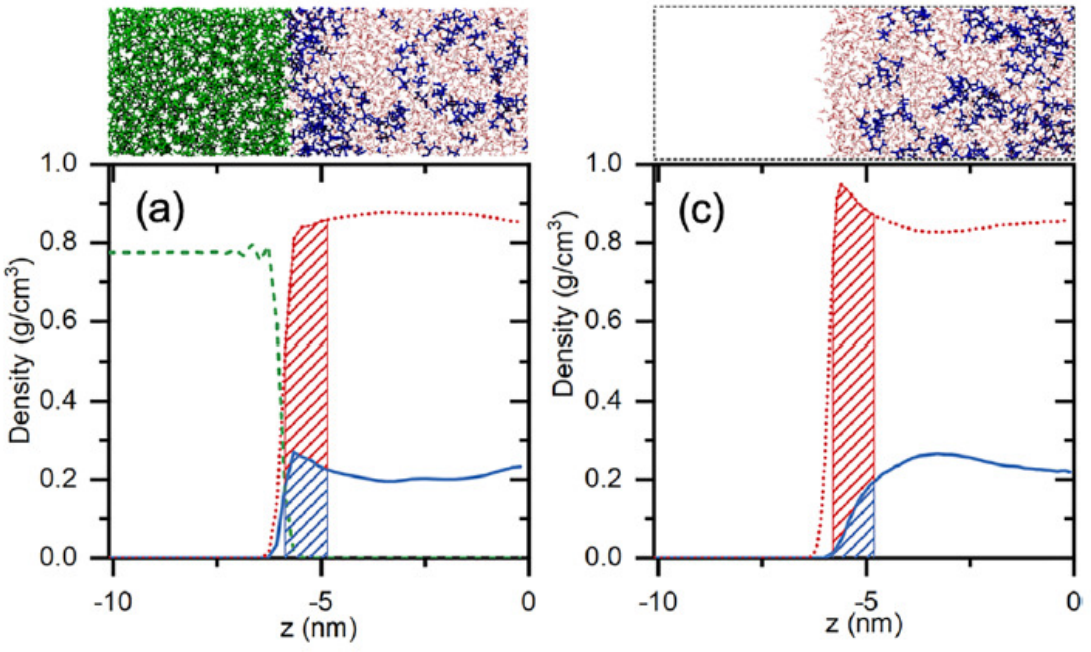

Figure 3. MD simulations of glycine solutions at (a) an oil/water interface; and (b) a water/gas interface. The oil (tridecane) is green, water red and glycine is blue. The density profiles are averaged across the interface region [4].

In this work we will use investigate how the water diffusivity varies with lactose concentration and temperature, which is necessary for the complete description of solute transport described above. Similarly, we will explore the diffusivity of dissolved N_2 and CO_2 molecules through the lactose solution at various lactose concentrations and temperatures. Furthermore, the impact of the lactose concentration on the gas interface surface tension will be determined. Taken together, the results will

help refine the mesoscale model and ensure that the modelling addresses physically meaningful regions of the mesoscale parameter space.

Deliverables: Reports on the model behaviour presented to the IFPRI annual meetings; manuscripts prepared for conference presentations and publication in leading internationally refereed journals.

Months 31-36: Consolidation and planning of future opportunities

The success of the approach to combine molecular and mesoscale models will be assessed by confrontation with experiments performed at different starting lactose concentrations, N_2 and CO_2 pressure drops, and drying gas temperature. Final adjustments to the modelling approaches will be made as required.

The work package will conclude with consideration of other material systems that could be described by the models, including the addition of surfactants to stabilise the bubbles. Adaptations required to model alternative drying configurations will be assessed, and recommendations for future work made.

Deliverables: Report to the IFPRI annual meeting to include recommendations for future work; manuscripts prepared for conference presentations and publication in leading internationally refereed journals.

Thesis and paper write-up: Following these work packages, the student will have six month's funding remaining to write their thesis and finalise outputs.

Budget Request

Item	**Cost/£**	**Cost/USD^**
Fees and stipend for 42 month studentship at the University of Strathclyde	£90,000*	$108,000
Travel budget to attend IFPRI meetings, workshops and conferences	£5,000**	$6,000
Consumables (laptop, access fees to the ARCHIE-WeSt supercomputer)	£5,000	$6,000
Total	**£100,000**	**$120,000**

^ At time of writing, the exchange rate is $1.20/£1.00

* This is based on the currently published University of Strathclyde studentship rates for 2023-2026

** The travel budget can be modified if there are variations in the above. Alternative funds for travel and subsistence, such as through University and learned society groups, will be sought if required.

References

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