PBM modelling of Pickering emulsions for Janus particles synthesis

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PBM MODELLING OF PICKERING EMULSIONS FOR JANUS PARTICLES SYNTHESIS

Graziano Frungieri [1] – Heiko Briesen[1]

[1] Lehrstuhl für Systemverfahrenstechnik, TUM School of Life Sciences, Technische Universität München, Gregor-Mendel-Straße 4, 85354 Freising, Germany

Janus particles are colloidal particles that like god Janus who has two faces, have two sides, with different surface properties. Similarly to molecular surfactants, Janus particles can be used to build supra-colloidal structures in a variety of configurations, including micelles, vesicles, helices, bilayer, and have found application as sensors, nanomotors, e-ink in electronic devices, drug delivery carriers, or as responsive materials (Zhang et al. 2017) [1]. However, the lack of an established synthesis route for a high-yield, predictable and scalable production of Janus particles still hinders their full exploitation.
A common route for the synthesis of Janus particles relies on the selective surface modification of an originally homogeneous solid particle. The most promising technique to obtain such a modification relies on the use of an oil-in-water Pickering emulsion. In this kind of emulsion, solid particles, partially wettable by both phases, adsorb tightly at the liquid-liquid interface between the continuous phase and the oil droplets, thus allowing one to carry a topologically selective functionalization of the surface of the particles exposed to the water medium (Figure 1). Compared to a planar masking, the use of Pickering emulsions is attractive because it is scalable, it allows for the modification of particles as small as tens of nanometers, it offers a large specific interfacial area for particle immobilization and, consequently, large yields.

In this work we present a numerical model able to capture the fundamental physics underlying the emulsification and particle adsorption steps occurring in a Pickering emulsion under shear flow. The model uses a Monte Carlo algorithm to stochastically solve a bivariate Population Balance Equation, which accounts for the time evolution of the droplet size and surface coverage by the solid particles. The model takes into account both coalescence and breakup dynamics (Lee and Matsoukas 2000 [2], Frungieri and Vanni 2021 [3]) and assumes the solid particles to arrange according to an hexagonal packing on the droplet surface. A collision efficiency model is introduced to take into account the lowering of the coalescence probability, as droplets get covered and stabilized by solid particles (Pawar et al. 2011 [4]).

The code has been tested to simulate the evolution of a population of droplets initially monodisperse in size and bidisperse in surface coverage. Figure 2a) reports the temporal evolution of the droplet surface coverage for differently composed emulsions, where the fraction $x_{0,0}$ indicates the fraction of droplets with zero surface coverage at the initial time (with the other part of the population having initially a surface coverage equal to 0.5). It can be seen that for the emulsion in which $x_{0,0}$=0.95 (i.e., a population initially largely composed by free-surface droplets), the surface coverage is constant in the first stage of the process, it increases quite abruptly, and eventually reaches an asymptotic value of about 0.6. This behaviour has to be ascribed to the fact that initially the dynamics of the process is governed by the coalescence between free-surface droplets. As soon as coalescence events between partially covered droplets starts to affect the dynamics, the average surface coverage rapidly increases, as a consequence of the interfacial area reduction due to coalescence. In Figure 2a), it can be seen that such a behaviour, however, changes as the initial population composition is modified. For low values of $x_{0,0}$, a more prompt rise of the average coverage, which approaches more rapidly a larger asymptotic value, occurs. The evolution of the Sauter diameter (Figure 2b) suggests that in all emulsions the asymptotic state is the result of the onset of a size stabilization phenomenon. However, the reason for it depends on the initial population composition. The size stabilization is a result of an equilibrium between coalescence and breakup in the system with $x_{0,0}$=0.95, where droplets grew up to the point to become vulnerable to breakup, it is instead due to a reduction of the coalescence efficiency, as a consequence of the large surface coverage of the droplets, in the case of $x_{0,0}$=0.10.
Finally, the model is expected to be able to shed light on the complex balance between droplet coverage, coalescence and breakup, and to provide useful guidance in the choice of experimental setups and in the interpretation of experimental results.

References

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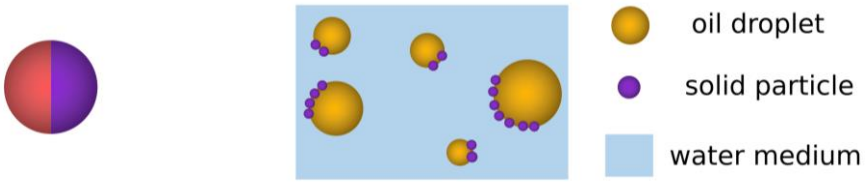

Figure 1: left) Janus particle, right) Pickering emulsion.

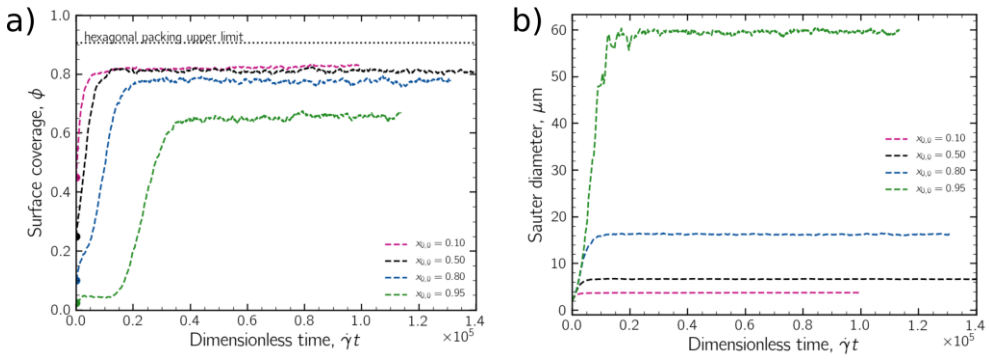

Figure 2: a) Temporal evolution of the droplet average surface coverage, b) Sauter diameter of the oil droplet population. A shear-coalescence kernel is used to model coalescence rates. Breakup rates are assumed to scale linearly with the droplet size. The droplet volume fraction is 10^{-3}, the applied shear rate is 10 s^{-1}.