

Open Ph.D. thesis at Institut de Chimie Séparative de Marcoule (ICSM), Bagnols-sur-Cèze, France Ecole doctorale 459 Sciences Chimiques Balard (University of Montpellier)

Stability of colloidal organic dispersions predicted by multi-scale modelling

Starting date: October 2023

The objective of the proposed Ph.D. thesis is to quantify, using theoretical approaches, the phenomena at the origin of the **instability of colloidal organic dispersions** in order to be able to predict the **thermodynamic macroscopic properties** of dispersions encountered in a large number of fields: in separation chemistry first of all, for example for the recycling of strategic metals, but also in the field of formulation by micro-emulsification used in the pharmaceutical industry for the preparation of drugs or in cosmetics. The last few years have seen the development of new molecular modelling methods, allowing the description of these com-



plex systems at nanometric sizes. The structure is thus better and better characterized. Nevertheless, **modelling their thermodynamic properties** remains a difficult task due to the various phenomena involved: complexation, solvation, electrostatic interactions, polarization forces, etc., as highlighted in a recent article¹. The aim of this thesis project is thus to model these thermodynamic properties by an **original multi-scale approach based on a molecular description**. Such a program is necessary because the phenomena occur at various time and distance scales.

In **separation chemistry** and more precisely for Winsor II type systems (corresponding to an organic colloidal dispersion in equilibrium with an aqueous phase), recent experiments and simulations have highlighted the **presence of supramolecular aggregates**, similar to reverse micelles, whose characteristic size of several nanometers suggests a complex extraction process based on the selective formation of these compounds. In each aggregate, a polar core is surrounded by a more or less stretched curved interface consisting of amphiphilic extractant molecules. Modelling the stability of such solutions will thus require the calculation of the various interactions between aggregates. An important term will be the **interaction energy between carbon chains** (aggregates – aggregates, and aggregates – diluent) which spontaneously select a certain curvature and stretching, but whose intensity and role are still very poorly known.

We will therefore focus on the **influence of aggregation on the stability of such solutions**, from the spontaneous formation of aggregates in solution to their interactions. To do so, we will implement multi-scale approaches coupling molecular-scale simulations, typically by molecular dynamics, to mesoscopic-scale "coarse-grained" simulations.

Two approaches will be proposed during the Ph.D. thesis to better understand these phenomena:

- A first approach will consist of studying the effect of the concentration of the compounds present in solution on the stability of these solutions using **molecular dynamics simulations**. We will thus be able to verify whether this simulation method allows us to spontaneously observe the formation of phase separation, which will then allow us to calculate the limits of **spinodal** stability of the phase diagrams.
- 2. A second approach will consist of calculating the **interaction potential** between aggregates directly by means of **biased molecular dynamics simulations** (of the umbrella-sampling type). This potential will then be used as an input parameter for modelling on a mesoscopic "coarse-

¹ H. Zhang et al. Nature 542, 328–331 (2017). DOI: <u>http://doi.org/10.1038/nature21041</u>



grained" scale, such as **Monte Carlo** simulations, as this method provides direct access to the **activity in the organic phase**.

In the context of the **valorization of strategic metals** and in connection with the research activities developed these last years in the Laboratory of Mesoscopic Modelling and Theoretical Chemistry of the Marcoule Institute for Separation Chemistry², the subject of the Ph.D. thesis will focus on organic colloidal suspensions whose aggregates will be composed of lanthanide salts in the presence of extracting molecules of diamide type.

The **theoretical and numerical methods** developed during the Ph.D. thesis can be **adapted and transferred to other industrial applications involving colloidal suspensions**. During the thesis, the Ph.D. student will be led to disseminate his/her scientific results through publications in scientific journals and communications at national and international conferences.

Profile: We are looking for a highly motivated candidate with solid theoretical knowledge in physical chemistry. You have a Master's degree in chemistry, physical chemistry, chemical physics, theoretical chemistry or physics, or equivalent. You have an interest in programming and computer science, and ideally, you already have a basic knowledge of code (e.g., Python, Fortran, ... languages, Linux environment, Shell scripts ...). You also have good written and oral communication skills. You have the ability to work in a team while having the necessary autonomy to carry out your own research topic.

<u>Secured funding:</u> The Ph.D. thesis is funded by the French Alternative Energies and Atomic Energy Commission (CEA, Fundamental Research Division).

Net salary: ~1650 € / month (Gross salary: ~2100 € / month)

Further information: The successful candidate will join the LMCT group of ICSM and will be enrolled at the doctoral school ED459 Sciences Chimiques Balard of the University of Montpellier (France).

<u>Contact:</u> To apply, please send a cover letter, a detailed CV, and references to Dr. Magali Duvail (<u>magali.duvail@cea.fr</u>) and Pr. Jean-François Dufrêche (<u>jean-francois.dufreche@icsm.fr</u>) before April 26, 2023. Mesoscopic Modelling and Theoretical Chemistry Group (LMCT) ICSM UMR 5257 – BP 17171 Site de Marcoule F-30207 Bagnols sur Cèze, France

http://www.icsm.fr/icsm_engl/Imct_en.html

² M. Špadina et al. Langmuir 37, 10637–10656 (2021). DOI: <u>http://doi.org/10.1021/acs.langmuir.1c00673</u>