





Laboratory: Centre Interdisciplinaire de Nanoscience de Marseille (CINaM) Aix Marseille Université - CNRS UMR 7325

Department: Sources et Sondes Ponctuelles Supervisors: Romain GROSSIER (grossier@cinam.univ-mrs.fr / +33(0)6 62 92 28 79) Stéphane VEESLER (veesler@cinam.univ-mrs.fr / +33(0)6 62 92 28 66)

<u>Subject</u>: Induction time measurements in crystal nucleation confining picoliter to femtoliter contracting droplets.

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Fig 1 : time-lapse images of contracting salted droplets until crystal nucleation

If snowflakes, Champaign bubbles, clouds or salt crystals appear to have nothing in common, physics of nucleation do make a link: they all "appear", nucleate, the same way. In fact, physics of nucleation rules all first order phase transitions, where matter make transition from a phase (gas, liquid, solid) to another, a physic on which rely numerous industrial and natural processes. To operate this transition, a population of clusters, precursors of the new phase, try to grow through successive attachments/detachments of individual atoms or molecules. For clusters where attachments had been statistically favored over detachment processes, they reach a critical size: this is the end of nucleation, and the newly formed phase can grow. This gives nucleation an inherently stochastic nature: exact prediction of the number, the time and the localization of such successful clusters is impossible. Also, clusters are small (some nanometers) and sparse: using highly resolved (in both space and time) experimental techniques to directly observe such fleeting clusters is like looking for a needle in a haystack.

Such experimentation context imposes both a statistical and indirect approach of the phenomena and rely on repeated measurements of the induction time: the time it takes clusters to reach critical size. Such measurements would give the nucleation probability density function, from which information on the nucleation process can be extracted. Such measurement, if conceptually simple, generally impose hypothesis to be fulfilled. First, the critical cluster has to grow before being detected: this time adds to the induction time and is dependent of the chosen detection system. Second, during this time, we must postulate there is no cluster population effects: each nucleated cluster will finally reach detectable size.

The proposed PhD focuses on studying nucleation through induction time measurements of crystals in picoliter to femtoliter contracting (evaporating) droplets. The dedicated in-house developed experimental bench is based on microfluidics and ensure statistical validity: hundreds of identical droplets [1] can be simultaneously characterized [2] with optical microscopy. The size of the droplets assures nucleation confinement [3] to occur: a unique and single critical cluster is allowed to nucleate per droplet, avoiding population effects.

Also, in such a confinement context, critical cluster is immediately detectable: pure induction time is measured. All these aspects make this experimentation framework a promising route to study nucleation and its control [4].

Desired PhD student, with experimentalist profile and physics / physical-chemistry background, will have interest in:

-designing experiments

-developing the experimental bench

-using statistics, to interpret data

-image processing software/techniques (ImageJ software and PYTHON language coding) -collaborate with industrial partners

For non-French speakers, we provide French courses.

References:

[1] Generating nanoliter to femtoliter microdroplets with ease

R. Grossier, Z. Hammadi, R. Morin, A. Magnaldo, S. Veesler, *Applied Physics Letters* 98 9 091916-3 (2011)

[2] Localizing and inducing primary nucleation

Z. Hammadi, R. Grossier, A. Ikni, N. Candoni, R. Morin, S. Veesler, Faraday Discussions 179 489-501 (2015)

[3] Reaching one single and stable critical cluster through finite sized systems

R. Grossier, S. Veesler, *Crystal Growth and Design* 9 4 1917-1922 (2009)

[4] Predictive nucleation of Crystals in Small Volumes and Its Consequences

R. Grossier, Z. Hammadi, R. Morin, S. Veesler, *Physical Review Letters* 107 2 025504 (2011)