

## Liquid Phase Electron Microscopy of Soft Matter

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Soft matter systems include polymers, colloids, gels, surfactants, liquid crystals and biological materials. Such systems are important in a wide variety of fields including food science, separation science, medicine and energy conversion and storage. Inherent to soft materials is their easy of manipulation with changing environmental conditions, due to their molecular kinetic energy being close to  $k_B T$ . This feature is frequently exploited to control the structure and properties of soft matter, for example, by the self-assembly of building blocks into higher order systems. [1]

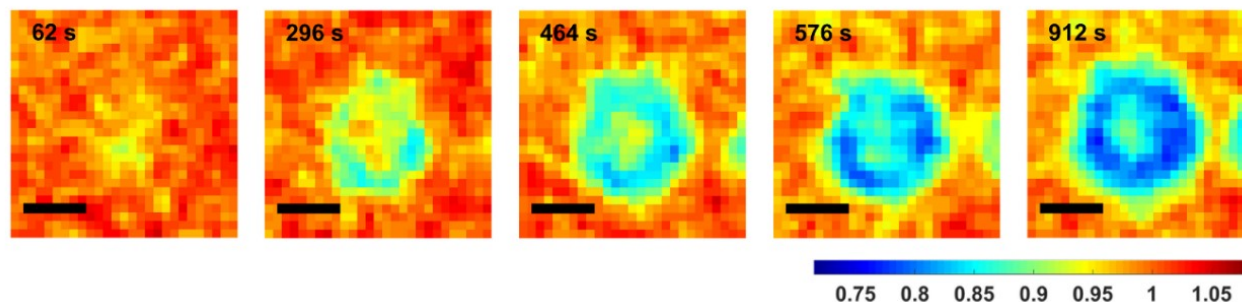
To understand the soft matter self-assembly it is essential to obtain direct, real-time, high-resolution information at the single particle level. [2] To this end liquid phase electron microscopy (LPEM) provides a unique opportunity due to the high combination of temporal and spatial resolution. [3] In LPEM experiments it is essential to consider the effects of beam-sample interactions and confinement. For soft matter, this is even more essential due to their inherent susceptibility to changing environmental conditions. Another inherent consideration for imaging soft matter (typically comprised on low  $Z$  elements) is the low contrast produced by the objects under inspection. For the acquisition of dynamic data, this low contrast will inherently limit the spatial or resolution obtainable in comparison to high contrast materials.

In this paper we discuss our recent efforts to image soft material systems by LPEM. We discuss philosophies and strategies related to soft matter beam-sample interactions in liquid phase EM, including the use of ex-situ or control experiments. We show how automated data processing and computational simulations can be used to obtain molecular level insights from low contrast, low resolution data. We also discuss the effects of confinement in the liquid cell environment. We focus primarily on block copolymer assemblies in water, which find applications in, for example, biomedicine, templated synthesis and catalysis. These systems are ideal to study as one of the key challenges in this field is understanding the complex thermodynamic and kinetic pathways which govern their formation. We show that liquid phase EM can provide unique insights into the self-assembly process allowing us to propose a new design strategy for controlling their formation.

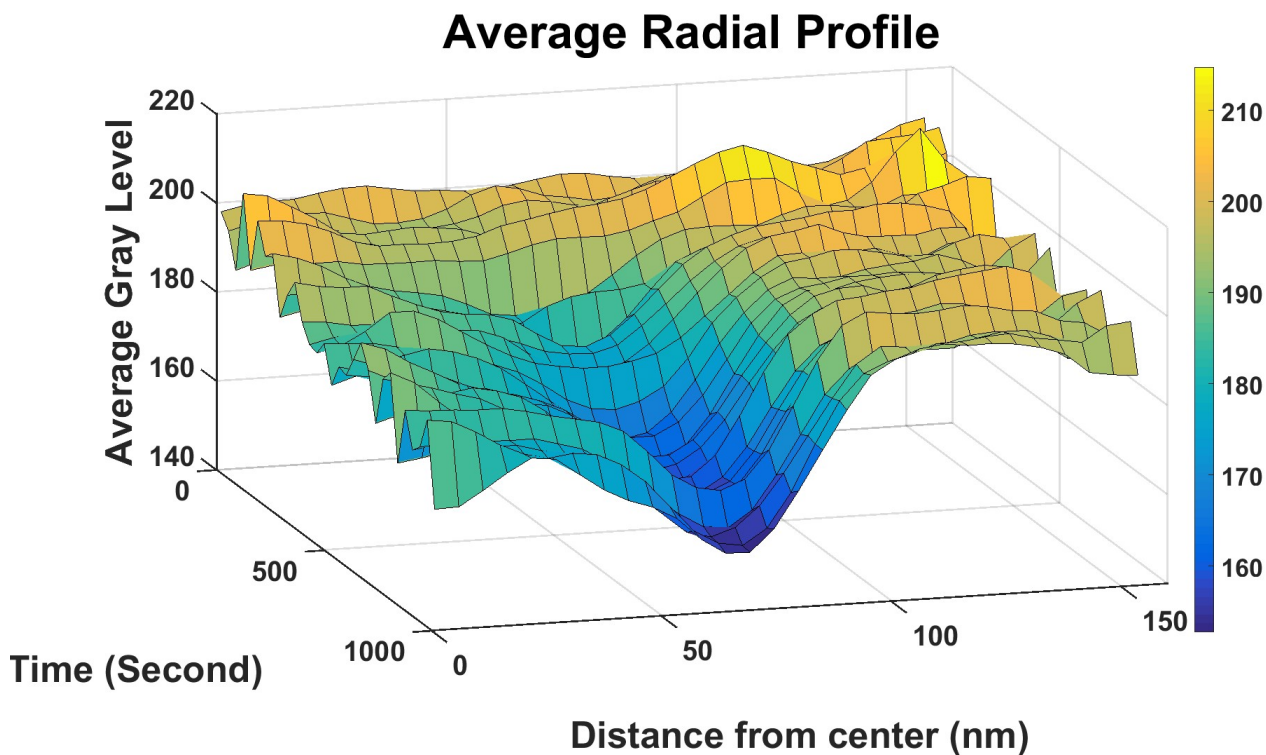
Figure 1 shows snapshots from a LPEM experiment to observe the formation of block copolymer vesicles. TEM imaging was performed on a FEI Technai 20 (type Sphera) operated at 200 kV equipped with a LaB6 filament and a  $1k \times 1k$  Gatan CCD camera. The self-assembly was conducted inside the microscope by diffusing water into a solution of the amphiphilic block copolymer dissolved in acetone. The increase in water concentration initiates the assembly of the polymers to minimize the interactions of the hydrophobic block with water. Figure 2 shows the radial profile evolution of a single vesicle. The evolution of the vesicle membrane can be used to quantitatively analyze the self-assembly process.

## References:

- [1] IW Hamley, Introduction to soft matter: synthetic and biological self-assembling materials. (John Wiley & Sons, Chichester).  
 [2] LR Parent *et al*, *J. Am. Chem. Soc.*, **139** (2017), p.17140.  
 [3] JJ De Yoreo and NAJM Sommerdijk, *Nature Reviews Materials* **1** (2016), p.16035.



**Figure 1.** LPEM time series showing the formation of a polymer vesicle. Scale bar = 50 nm



**Figure 2.** Radial profile showing the evolution of the vesicle membrane (indicated by the blue color) as a function of time