Ligand-mediated nanoparticle interactions at fluid-fluid interfaces

V Garbin[1], I Jenkins[2], T Sinno[2], J C Crocker[2] and K J Stebe[2]

[1]Department of Chemical Engineering, Imperial College London, UK, [2]Department of Chemical and Biomolecular Engineering, University of Pennsylvania, USA

Nanoparticle self-assembly at fluid-fluid interfaces is exploited in several emerging technologies including 2D functional nanomaterials with tunable properties [1]. In spite of their importance in determining the interfacial microstructure, our understanding of the pair interactions of nanoparticles at interfaces is still limited. Significant differences with nanoparticle interactions in the bulk arise due to the discontinuity in solvent properties at the interface. This discontinuity causes the grafted ligand layer on the particles to rearrange in asymmetric configurations that depend on ligand length and grafting density.

To gain insights in ligand-mediated nanoparticle interactions at interfaces, we measured the two-dimensional osmotic pressure (surface pressure) of a self-assembled nanoparticle monolayer in experiment [2]. The measurements were compared with the results of Brownian Dynamics simulations, which allow the calculation of the pressure due to entropy and interparticle interactions in the monolayer.

Computed pressure-density curves with a pair potential that accounts for ligand-mediated steric repulsion agree with experiment for a fitted value of the range of interaction that is in keeping with the contour length of the ligand used in experiment. This indirect measurement of the pair potential between ligand-capped nanoparticles at interfaces will be helpful in constraining future molecular dynamics simulations of nanoparticle systems.

This work provides insight into the pivotal role played by grafted ligands in the energetics and mechanics of nanoparticle-laden interfaces.

[1] V. Garbin, Physics Today 66(10), 68-69 (2013)
[2] V. Garbin, J. C. Crocker, K. J. Stebe, Langmuir 28, 1663–1667 (2012)