493g Monte Carlo Simulations of the Influence of Nanoscale Confinement on Surfactant Mesophases

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Over the past several years, there have been many examples of using confinement in 1D (in films), 2D (in channels / wires), and 3D (in particles) to produce well-defined nanoscale objects and hierarchical structures. Various unusual morphologies have been produced based on lyotropic mesophases, including oriented mesoporous ceramic films, nanotubes, helical wires, vesicles, hollow particles, concentric spheres, and spheres with radially oriented pores. Here, we present the results of coarse-grained lattice Monte Carlo simulations of surfactant solutions that illustrate how confinement and interfacial interactions gives rise to some of these structures. The simulations are detailed enough to model lyotropic liquid crystals that form in concentrated surfactant solutions, but coarse enough to permit them to spontaneously assemble during a simulations of reasonable length. We simulate model lyotropic mesophases confined in one or more dimensions. The confining surface is either rigid (walls) or flexible (an incompatible fluid). In general, we find that the interactions between surfactants and the interface can be manipulated to orient micelles parallel or perpendicular to the interface. However, the dimensions and curvature of the confining space also play an important role in determining how the liquid crystal phase is deformed. Integer numbers of layers of micellar aggregates are usually formed, even if the micelles must be deformed slightly. When an integer number of micelles cannot fit well into the confining space, defects are more likely to be encountered. The interplay between these effects helps to explain why the micellar aggregates in these confined structures sometimes re-orient (for example, in spherical particles with radially oriented mesopores) and sometimes change shape entirely (for instance in concentric spheres or tubes prepared under conditions where the bulk phase is hexagonal).