

Editorial for Special Issue on *Engineering Self-Assembly*

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Self-assembly can be loosely defined as the emergence of order in an initially disordered system by virtue of intrinsic interactions between the different components of the system, as opposed to being induced by external action. It is a phenomenon that is ubiquitous in the natural world and crucial in a myriad of practical applications. Some of the best known examples in nature are the formation of cell membranes, hierarchical DNA or protein assemblies, and the porous skeletons of invertebrate species like diatoms and sponges. Giant trees, that grow to 100 metres in height, demonstrate impressively that self-assembly is not confined to small scales. Industrial applications range from the traditional uses of amphiphilic surfactants in detergency to the synthesis of porous, functional and stimuli responsive nanomaterials. This diversity of existing applications and the prospect of many new ones have rendered self-assembly a rather wide-ranging research topic. The key challenge lies in the complexity of the systems, which makes discovery and understanding of the underlying assembly mechanisms very difficult for both experimentalists and theoreticians. The last few decades have seen a progressive shift in self-assembly research from a mainly experimental field to one in which theory and simulation play a key role. This arose from the realisation that only through detailed understanding of the molecular-level mechanisms of self-assembly can one hope to design and control such systems in practical applications. It is the contribution of molecular simulation to the goal of engineering self-assembling systems that is the focus of this special issue.

The contributions to this issue reflect, first of all, the diversity of self-assembly applications described above. For example, Patti and Cuetos [1] explore the phase behaviour of colloidal suspensions of cuboidal particles with potential relevance for liquid crystal displays, whereas Rozhkov et al. [2] present a detailed study of magnetic colloids that can be used to develop new responsive soft materials. The interactions between nanoparticles and surfactant micelles, and their effect on the rheology of suspensions, is the focus of the paper by Sambasivam et al. [3]. Schoch and Genzer [4], on the other hand, show how the structure of a solid substrate can be manipulated to control the adsorption of nanoparticles, which is relevant in several engineering problems, including fouling. A number of papers focus on self-assembly as the structure determining step in the formation of hierarchical porous materials. Their contribution ranges from studies of surfactant template aggregation in solution [5], to exploration of the complex free energy landscape in zeolite synthesis [6], to examination of the role played by peptide molecules in biomineralisation processes [7]. The paper by Jorge et al. [8] presents a detailed review of modelling efforts to understand how the different processing steps lead to the final structure of silica-based mesoporous materials. Finally, Bernardes et al. [9] demonstrate how atomistic simulations can be used to help interpret experimental data, clarifying the role of molecular correlations in the emergence of ordered domains in ionic liquids.

The simulation of self-assembly is technically challenging. The initiation of the assembly process always relies on the presence of a large number of interacting species – it ultimately is a very-many-body effect. The relevant time scales vary greatly, ranging from milliseconds for micelle formation to many years for the growth of bones and trees. The challenge here is that the time scale

of the self-assembly process is always much larger than the inherent time scales of the constituting species. To tackle these problems the model systems usually focus on the key aspects. Here, with one exception [9], all papers apply some form of coarse-graining in their simulations. It is common to represent colloids [1, 2] and nanoparticles [3, 4] as single interaction sites instead of describing them in atomistic detail, whereas surfactants [5, 8] and biomolecules [7] are usually modelled as a collection of beads, thus preserving some of their structure and flexibility. Although this reduction of the number of interaction sites may sometimes appear quite drastic, it is often a direct consequence of the need to sample large time and length scales in order to probe the self-assembly mechanism. The paper by Garcia Daza and Mackie [5] shows an interesting example where an aggregation process, that in reality may take minutes to complete, is accessed through a two-level approach where the inter-molecular interactions are highly coarse-grained by a mean-field approach, whereas the intra-molecular interactions are preserved. The drawback of intense coarse-graining is, of course, the loss of chemical detail, i.e. the loss of the subtle interplay between structure and interaction strength that, for example, is the key to the specific interactions in molecular biology. In some cases, this poses severe difficulties in relating simulation predictions to the real systems.

An interesting approach to overcome this difficulty is the application of multi-scale modelling. Although many flavours have been developed and promoted in recent years, they all share the same general concept of using models with higher level of detail (e.g., atomistic) to calibrate the parameters of more simplified models (e.g., bead-spring), thus allowing the latter to maintain at least some level of chemical specificity. This type of approach has led to much recent progress, for example, in our understanding of porous-material formation [8]. Another perspective of the challenge is the complexity of the free energy landscape of self-assembling systems. This viewpoint offers the opportunity to employ another class of techniques such as replica exchange Monte Carlo for adequate sampling. Examples of the application of these techniques are provided in the work of Bores et al. [6] and Rutter et al. [7].

Undoubtedly, the dramatic increase in available computational power at low cost has been fundamental to the recent success of molecular simulations in self-assembly research. In combination with the development of new simulation algorithms, it has allowed increasingly complex systems to be investigated, with many recent studies including more than a single self-assembling component [3, 4, 8]. These trends will continue in the future. Better models and algorithms supported by more computational resources will, through better understanding of the abstract principles of self-assembly and the symbiosis between experiment, theory and simulation, enable us to engineer self-assembly.

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