

## **Large-scale Monte Carlo simulations for aggregation, self-assembly and phase equilibria**

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In this review article, we discuss the application of advanced Monte Carlo sampling techniques to particle-based simulations of complex chemical systems and processes. These simulations provide microscopic-level information and thermodynamic properties that are often difficult to obtain by experimental means. Large-scale Monte Carlo simulations using transferable (but empirical) force fields demonstrate that retention in reversed-phase liquid chromatography can neither be described by a bulk partitioning nor an interfacial adsorption mechanism, that the high-temperature, high-pressure solubility of helium in *n*-hexadecane is well reproduced by a force field that is fitted to the critical parameters without accounting for quantum effects, that entrainers can increase the solubility in supercritical carbon dioxide without specific aggregation, and that differences in size are sufficient to cause segregation of anions at the aqueous vapor–liquid interface. In addition, we describe first principles Monte Carlo simulations of the vapor–liquid phase equilibria of water employing Kohn-Sham density functional theory.