

Modeling and Simulation of Nanoparticle Aggregation in Liquid Suspensions

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Abstract

Aggregation of nanoparticles in liquid suspension is a phenomenon that affects the design and scale-up of process equipment for nanoparticle synthesis. The growth of nanoparticle clusters and their interaction with macroscale shear is a fundamental multiscale problem that is very challenging from a modeling and simulation perspective. This is due to the wide range of scales with significant two-way interactions. At intermediate scales involving tens to thousands of nanoparticles (each 10-100 nm in size), molecular dynamics and Brownian dynamics simulations are employed. One important link in this bridging of scales is the accurate modeling and simulation of nanoparticle aggregation using Brownian dynamics.

In this talk I motivate the need for simulation techniques such as Brownian dynamics by showing that the size separation between nanoparticles and solvent molecules makes MD simulations of large aggregating systems prohibitively expensive. Simple physical arguments are then used to deduce that the radial distribution function which results from the relative dispersion of nanoparticle pairs, is the essential feature of multiparticle dynamics that must be captured by BD simulations in order to accurately simulate the structure of nanoparticle aggregates.

Taking MD simulations of a model aggregating system as a benchmark, I explore the possibility of improving the specification of the potential of mean force in BD. Invoking the concept of stochastic equivalence between the MD and BD systems, it is possible to derive constraints on the BD model (in terms of friction coefficient and potential of mean force) that must be satisfied in order for accurate simulation of the structure of aggregates. The second-order statistics of particle systems are described by the second-order density $\rho^{(2)}$, which when rescaled yields the radial distribution (or pair correlation) function. The evolution equation of this second-order density is derived, and the terms describing its transport in relative-velocity and relative-acceleration space are identified. The conditional relative acceleration of nanoparticles in a solvent bath interacting through Lennard-Jones potentials is computed from static configurations, as well as from MD. A possible route to deriving the optimal potential of mean force for Brownian dynamics from an MD pair-potential specification is described. Extension of these ideas to a general second-order transport theory to describe clustering in particle systems is briefly outlined.