Multiscale Simulation of Nanoparticle Aggregation for Scale Up of High-Rate Synthesis Methods

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Iowa State University, the University of Minnesota, and Kansas State University have joined forces in an interdisciplinary team specializing in multiscale simulation and experiments ranging from the atomic scale to nanoparticle processing scales to attack the important problem of controlling nanoparticle aggregation in high-rate synthesis methods. The project integrates theoretical simulations and experimental validation (see Fig. 1 below) of phenomena starting from surface forces at the atomic scale, to particle aggregation at the nanoscale, to shear-induced restructuring of nanoparticle clusters at the micron scale, up to cluster dynamics in turbulent reacting flow at the process scale. The multiscale simulation techniques developed in this project will be applicable to the scale up of a wide range of nanoparticle synthesis methods to industrial production, and will allow for the *a priori* design and optimization of commercial processes for producing nanoparticles. This research will ultimately benefit the chemical and pharmaceutical industries in their efforts to prevent nanoparticles from aggregating into larger clusters, which can alter the fundamental characteristics of their products.

In addition to the PIs, three Senior Investigators at Iowa State (B. Narasimhan, S. Subramaniam, and R. D. Vigil) are participating in the project, and the investigators have international collaborations with ETH Zurich (Morbidelli and Pratsinis) and Turin Polytechnic (Marchisio). Industrial partners include BASF, The Dow Chemical Company, DuPont, and Merck.

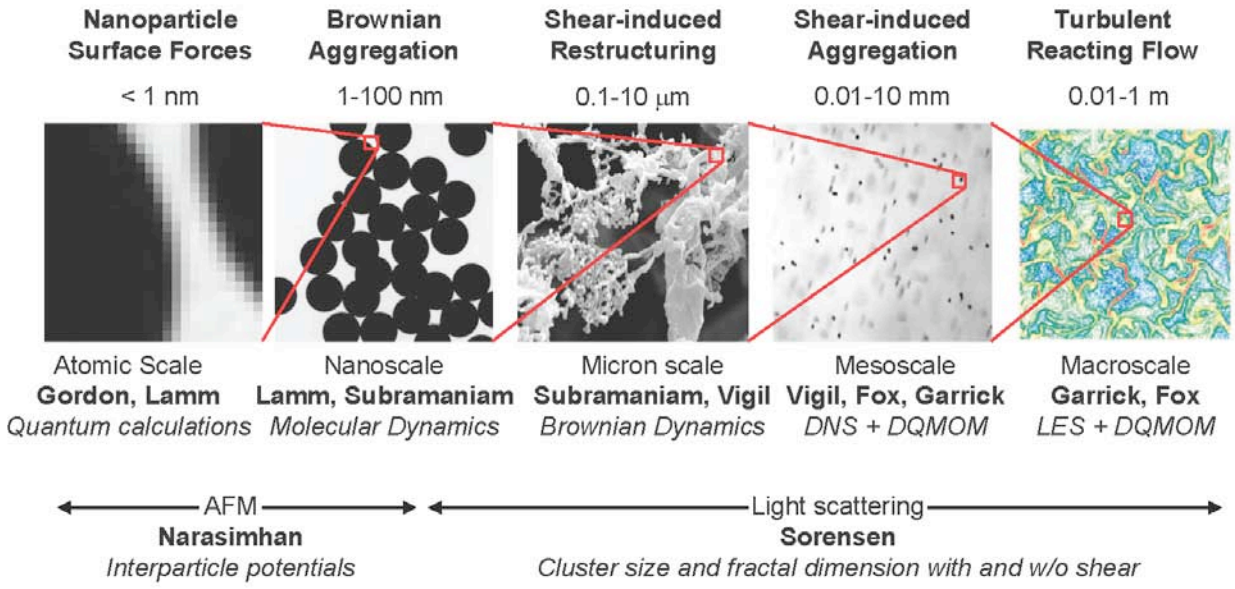
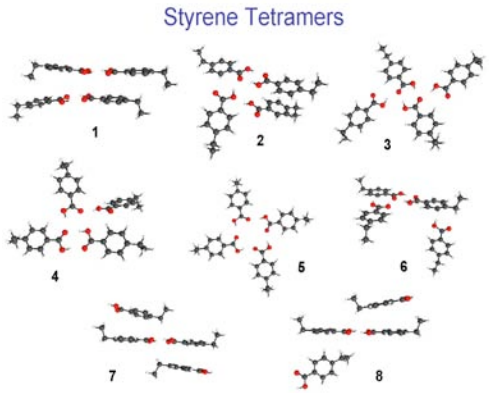
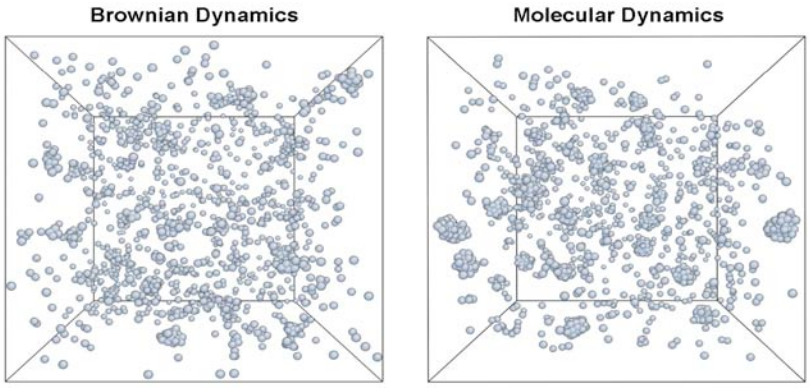


Figure 1. Overview of nanoparticle aggregation phenomena and relevant length scales under investigation in this project. The simulation and experimental techniques at each length scale are indicated below each scale.

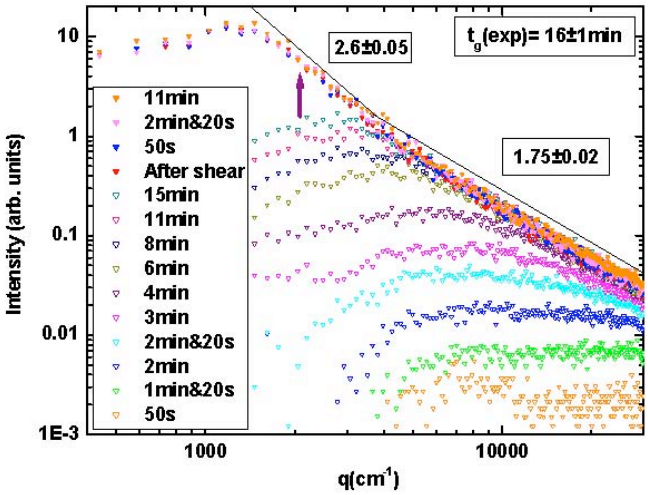
At the atomic level, we have developed accurate model potentials for styrene monomers using the general effective fragment potential (EFP2) method [2]. The advantages of this approach are (1) the low cost relative to *ab initio* calculations, (2) the absence of fitted parameters, (3) an accuracy comparable to second-order perturbation theory (e.g., MP2), and (4) identifiable physical interactions that can be mapped onto coarse-grained model potentials used in molecular dynamics. Because polymer-polymer interactions are beyond the scope of model potentials like EFP2, we have begun by investigating styrene-styrene interactions for molecular systems up to styrene tetramers [3] such as the eight configurations shown on the left. A systematic analysis of interaction potentials predicted by EFP2 as compared to MP2 has shown that EFP2 is fundamentally sound, but an improved screening procedure will be required to refine our interaction potential predictions. In future work, anionic styrene monomers that more closely match the nanoparticles used on our experiments will be investigated. In addition, larger styrene subunits will be employed, and a coarse-graining method will be implemented to map the EFP2 potential onto molecular dynamics. These predictions will be compared to atomic-force microscopy (AFM) experiments done in our labs.



Our work at the nanoscale has focused on the development of molecular dynamics (MD) and Brownian dynamics (BD) simulation tools for aggregating nanoparticles. While both MD and BD are separately well documented in the literature, our goal is to use them at overlapping length scales with the interaction potentials developed from EFP2. We therefore began our investigation with a systematic comparison of the two methods for the same system of nanoparticles. As can be seen in the two images on the left taken at the same time instant, the MD simulation (which is two orders of magnitude more expensive to compute) has a slightly higher probability of producing large clusters. Nevertheless, the BD simulation produces realistic cluster mass distributions and can be "tuned" to match the MD results. In future work we will extend the BD simulations to much larger systems, and add fluid shear to study cluster restructuring and shear-induced aggregation. These results will be directly compared to our small angle light-scattering experiments under non-sheared and shear-flow conditions.

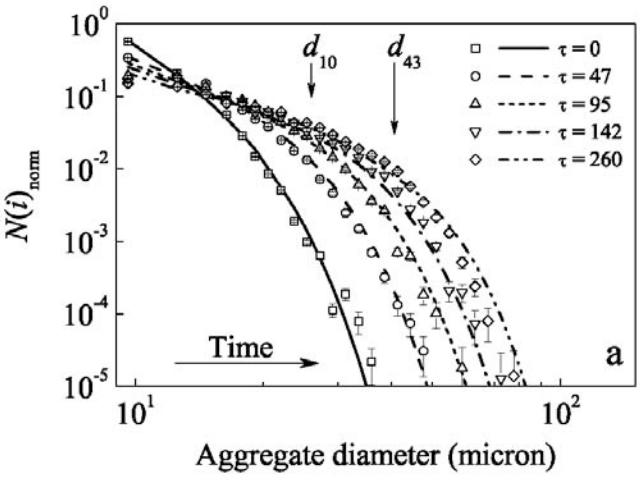


As clearly observed in our light-scattering experiments, the effect of shearing on colloidal nanoparticle gels is complex and dependent on the characteristic size of the nanoparticle clusters. In the graph below, the measured scattering intensity is plotted against the inverse cluster size (q)



as a function of time. The evolution of the experimental curves stops when a gel is formed at around 16 min after introducing the 20-nm particles into the flow cell. The resulting aggregated gel has a "double structure" as indicated by the change in slope from 2.6 to 1.75 at approximately q equal to 3000 1/cm, corresponding to 3 microns. At length scales smaller than 3 microns, the structure of the gel is characteristic of non-sheared Brownian aggregation, while at larger length scales the structure is more compact, as observed in shear-induced aggregation [4]. In the coming year, we will use BD simulations under shear-flow conditions to attempt to reproduce the experimental curves. Once successful, the BD simulations can be employed to investigate the effect of nanoparticle size, shear history and surface forces on the structure of nanoparticle gels.

The simulation and experimental tools described above will be used to develop "first principles" aggregation and breakage kernels for predicting the cluster mass distribution (CMD) in sheared nanoparticle suspensions. The extension to turbulent flow, which is typical of industrial processes, will use direct numerical simulation (DNS) and large-eddy simulations (LES) to generate realistic shear fields. The figure at the left shows a comparison of predicted vs. experimental CMDs for 10-micron latex particles under turbulent flow conditions using semi-empirical kernels [5]. Our ultimate goal is to extend these kernels to nanoparticles using the multiscale simulation tools developed in this research project. Models based on the direct quadrature method of moments (DQMOM) will then be implemented in our macroscale simulation codes for use by industry for scale up of high-rate synthesis methods for large-scale nanoparticle production.



References

[1] For further information about this project email **rofox@iastate.edu**
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