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FIRST REACTIONS

Nanoscale Self-Assembly: Seeing Is Understanding

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In this issue, Alivisatos et al. investigate nanorod dynamics by fluid state TEM; Kyle Bishop reflects on what this means for the field of nano assembly.

In the midst of the second world war, Derjaguin and Landau[1] in Russia and Verwey and Overbeek[2] in The Netherlands arrived independently at a theory to explain the kinetic stability of colloidal dispersions. The celebrated DLVO theory combined two types of forces—long-ranged electrostatic repulsion and short-ranged van der Waals attraction—to predict the rates at which nano- and microparticles aggregate irreversibly in time. Knowledge of these and other colloidal forces has since been applied to direct the spontaneous self-assembly of colloidal materials with emerging applications in optics, electronics, and catalysis. Despite their critical importance, measuring the interactions between colloidal objects *in situ* remains a challenging endeavor. One approach uses video microscopy[3] to collect particle configurations and/or dynamical trajectories from which to infer particle interactions with the help of statistical mechanical models. This approach was used to validate the DLVO theory for the electrostatic repulsion between charge microspheres;[4] however, its extension to nanoscale particles has been limited by the spatial resolution of optical microscopy. Now, with the advent of *in situ* liquid phase transmission electron microscopy (TEM), it is possible to apply similar techniques to quantify—for the first time—interaction potentials between nanoscale components. In this issue, Alivisatos and co-workers[5] demonstrate the power of this approach by measuring the interaction potential between pairs of charged nanorods. Their investigation reveals an interesting twist on the classic story of colloidal stability: anisotropic interactions between the rod-shaped particles lead them to aggregate selectively at their ends to form particle chains. The ability to watch this and other assembly processes in real time offers new insights into the forces and mechanisms underlying nanoscale self-assembly.

In the present study, gold nanorods (47 nm long by 14 nm wide) stabilized by cationic surfactants are flowed into a Si_3N_4-windowed microchannel and imaged via TEM at rates of about four frames per second. By tracking the relative positions of the rods' centers, the authors construct the radial distribution function $g(r)$, which measures the average particle density at a distance r from any given particle. Their analysis reveals a low density "halo" surrounding each particle indicating the presence of repulsive forces between neighboring rods. At equilibrium, these forces can be expressed as gradients of the potential, $u(r) = -k_BT \ln g(r)$, which quantifies the effective interaction between two particles. Calculating $u(r)$ in this manner, the authors find that nanorods interact through a repulsive potential that decays exponentially with distance, $u(r) \propto e^{-\kappa r}$, over a length $\kappa^{-1} = 16$ nm. This observation is consistent with the screened electrostatic interactions predicted by DLVO theory, in which κ^{-1} is identified as the Debye screening length. The measured value of κ^{-1} corresponds to a salt concentration of ca. 0.4 mM, which unfortunately cannot be independently controlled due the generation of charge carriers by the electron beam.

The authors show that neighboring rods tend to align parallel to one another before attaching irreversibly at their respective ends.

Despite repulsive electrostatic interactions, the charged nanorods are stable against aggregation only in a kinetic sense. Their Brownian motion can "kick" them over an energy barrier and into a deeper, thermodynamically favored potential well due to short-ranged attractive forces between the particle surfaces. Here, this classic view of colloidal stability takes an interesting twist. Owing to the anisotropic shape of the particles and their nanoscale dimensions comparable to the screening length, the energy barriers that inhibit colloidal aggregation are not spherically symmetric. As a result, it is more probable for charged rods to "collide" end-to-end than side-to-side, although the latter is favored

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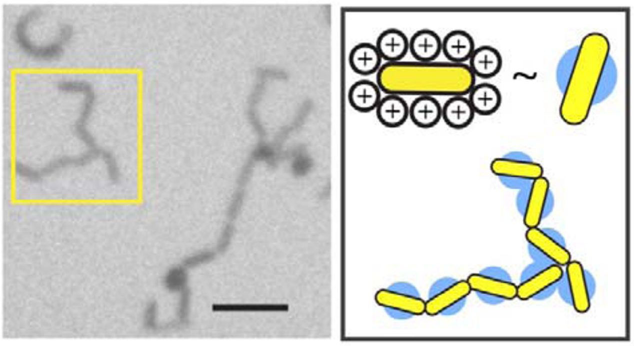

Figure 1. Alivisatos and colleagues show that gold nanorods assemble in an end-to-end fashion.[5] Reprinted with permission from ref 5. Copyright 2015 American Chemical Society.

thermodynamically due to the higher contact area. Alivisatos and co-workers capture the dynamics of such end-to-end attachments in real time to confirm this intuitive but unexpected assembly mechanism (Figure 1). The authors show that neighboring rods tend to align parallel to one another before attaching irreversibly at their respective ends. This simple kinetic mechanism is distinct from that of previous studies on linear nanorod assemblies, which rely on heterogeneous surface chemistries to encourgage end-to-end attachment.[6]

No longer must nanoscale colloids be viewed only as relics dried on the desert of a TEM grid or frozen in a tomb of amorphous ice.

Beyond this pioneering demonstration, *in situ* TEM promises to reveal a wealth of quantitative information on the forces acting between nanoscale objects as well as the dynamic processes by which they assemble. To this end, previous studies of micron-scale colloids by optical video microscopy over the past two decades can provide useful guidance in extracting such information. Of course, current capabilities of *in situ* TEM are not without limitations. Samples are confined to quasi-two-dimensional domains, which may lead to apparent particle—particle interactions that differ from those found in bulk dispersions.[7] Another challenge is controlling the beam-induced generation of charged species (e.g., solvated electrons), which can alter the ionic strength and/or surface charge thereby modifying electrostatic interactions *in situ*. As shown here, however, this effect can also be used as an external stimulus to induce the self-assembly of charge stabilized components. Finally, it is important to note that the diffusive dynamics of colloidal objects accelerates with decreasing size—a 10 nm particle diffuses one particle diameter in ~1 μs. Thus, it would be highly desirable to increase the temporal resolution of TEM imaging to better resolve the dynamics of nanoscale objects. Nevertheless, current limitations aside, the potential importance of this method is hard to overstate. No longer must nanoscale colloids be viewed only as relics dried on the desert of a TEM grid or frozen in a tomb of amorphous ice. We can now "see" these materials in their native state, and seeing is understanding.

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