

SABBATICAL LEAVE REPORT
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During my 9-month sabbatical at the University of Alberta, I conducted a pioneering research on colloidal properties of nanoparticles and suspensions made of nanoparticles (often referred in the literature as nanofluids) using facilities and instrumentation available at the Department of Chemical and Materials Engineering. The research was motivated by recent experimental and theoretical findings, which strongly suggest that physical and surface properties (energy, catalytic activity, optical properties, etc.) of nanoparticles and their interactions in colloidal systems are significantly different from comparable properties for micro- and macro-sized particles, and that these properties vary strongly with particle diameter at nanometer length scales. The effects of particle size (and therefore surface curvature) are magnified in colloidal systems because of the very large specific interfacial areas in such finely dispersed systems. In these nanofluids, the thickness of the liquid interphase between individual particles may be on the order of the particle diameters themselves. Much of the "liquid phase" in such systems is located within a few molecular distances from the nanoparticle surfaces, and many of its properties may be very different from those of the corresponding bulk liquid. These effects lead to colloidal properties in nanofluids that can be very different from otherwise identical colloidal systems with larger micron sized particles. Unfortunately, the basis for the underlying particle size effects at the nanoscale is not well understood. The existing theoretical models describing interaction forces between micron-sized particles incorporate assumptions that are not even approximately applicable to systems with nanoparticles.

In the first phase of the program, colloidal forces between atomic force microscopy probes and flat substrates in nanoparticle suspensions were measured. Silicon nitride tips and glass spheres with a diameter of 5 to 15 μm were used as the probes whereas mica and silicon wafer were used as substrates. Aqueous suspensions were made of 5 to 80 nm alumina and 10 nm silica particles. Oscillatory force profiles (referred to as structural forces) were obtained using atomic force microscope. Two major research findings included: a) nanoparticles remain to be stratified in the intervening liquid films between the probe and substrate during the force measurements, and b) oscillation of the structural forces shows a periodicity close to the size of nanoparticles in the suspension (silica nanoparticles remain separated by no more than one to two layers of water in these structures). Such structural effects were only manifested for systems featuring attractive and weak repulsive interactions of nanoparticles with the probe and substrate.

Next, the atomic force microscope was used to measure surface forces between nano-sized silicon nitride tips and individual nanoparticles or their clusters deposited on substrates in electrolyte solutions. Silica nanoparticles (10 nm diameter) were deposited on an alumina substrate and alumina particles (5 nm to 80 nm diameter) were deposited on a mica substrate using aqueous suspensions. Ionic concentrations and pH were used to manage attractive substrate-particle electrostatic forces. The tip was located on deposited nanoparticles using an

operator controlled offset to achieve stepwise tip movements. Nanoparticles were found to have a negligible effect on long-range tip-substrate interactions, however, the forces between the tip and nanoparticle were detectable at separations of several nanometers and less. Exponentially increasing short-range repulsive forces, attributed to the hydration forces, were observed for silica nanoparticles. The effective range of hydration forces was found to be 2-3 nm with the decay length of 0.8-1.3 nm. These parameters are in a good agreement with the results reported for macroscopic surfaces of silica obtained using the surface force apparatus suggesting that hydration forces for the silica nanoparticles are similar to those for flat silica surfaces. Hydration forces were not observed for either alumina substrates or alumina nanoparticles. Instead, strong attractive forces between the silicon nitride tip and the alumina (nanoparticles and substrate) were observed. For nanoparticles forming clusters, oscillation of structural forces was recorded with a periodicity that is close to the size of nanoparticles used, similar effect as observed in measurements of tip-substrate interactions in suspensions of nanoparticles.

Results of this research were disseminated through journal publications and conference presentations. The following papers were published:

AFM Colloidal Forces Measured between Microscopic Probes and Flat Substrates in Nanoparticle Suspensions, J. Drelich, J. Long, Z. Xu, J. Masliyah, J. Nalaskowski, R. Beauchamp, Y. Liu, *Journal of Colloid and Interface Science*, 301(2) (2006) 511-522.

Probing Colloidal Forces between a Si₃N₄ AFM Tip and Single Nanoparticles of Silica and Alumina, J. Drelich, J. Long, Z. Xu, J. Masliyah, and C.L. White, *Journal of Colloid and Interface Science*, 303(2) (2006) 627-638.

Structural Effects Recorded for AFM Tips Interacting with Individual Nanoparticles and Their Clusters Deposited on Substrates, J. Drelich, Z. Xu, and J. Masliyah, *Langmuir*, 22(21) (2006) 8850-8859.

Measurements of Colloidal Forces between Microscopic Probes and Substrates in Suspensions of Nanoparticles, J. Drelich, J. Nalaskowski, J. Long, Z. Xu, and J. Masliyah, in *Functional Fillers and Nanoscale Minerals: New Markets/New Horizons*, J.J. Kellar (Ed), SME, Littleton, CO 2006, pp. 217-229.

Measurements of Colloidal Forces between an AFM Probe and Nanoparticle Deposited on a Substrate, J. Drelich, Z. Xu, and J. Masliyah, In *Interfacial Phenomena in Fine Particle Technology*, Z. Xu and Q. Liu (eds), Proceedings of the 6th UBC-McGill-UA International Symposium on Fundamentals of Mineral Processing in Honor of Professor J. Laskowski, MetSoc, Montreal, Canada, pp. 61-72.

Additionally during my sabbatical at the University of Alberta, I interacted with graduate students and postdoctoral fellows from this institution and contributed to the research program on recovery of bitumen from oil sands. This program is funded by the Alberta's oil sands industry and Canadian government. The following publications resulted from this contribution:

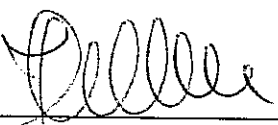
A Novel Method of Measuring Electrophoretic Mobility of Gas Bubbles, A.S. Najafi, J. Drelich, A. Yeung, Z. Xu, and J. Masliyah, *Journal of Colloid and Interface Science*, 308(2)(2007)344-350.

Determining Surface Potential of the Bitumen-Water Interface at Nanoscale Resolution using Atomic Force Microscopy, J. Drelich, J. Long, and A. Yeung, *The Canadian Journal of Chemical Engineering*, in press.

Effect of Operating Temperature on Water-Based Oil Sands Processing, J. Long, J. Drelich, Z. Xu, and J.H. Masliyah, *The Canadian Journal of Chemical Engineering*, in press.

I continue my close collaboration with researchers from the University of Alberta in Canada in the area of surface properties of nanoparticles and interfacial properties in nanoparticle colloidal systems. A collateral outcome will be to build strong, long term professional collaborations between the students, faculty, and institutions. Proficiencies gained through such interactions will stimulate new and more comprehensive approaches to the study of the nanoparticle-based systems. Our collaborative effort will largely concentrate on studying electric double layer, hydrophobic, and hydration forces. Experimental measurement of colloidal forces in liquids will be used to modify existing theoretical models of colloidal forces in nanoparticle colloidal systems. The newly developed theoretical models of nanoparticle properties and their colloidal interactions are needed to establish a solid foundation for engineering colloidal systems and self-assembly of colloidal building blocks into complex and controllable structures.

The broader impact of the collaboration draws from the current industrial and scientific thrusts to develop nanoparticle based films, coatings and solids with unique optical, electronic, and mechanical properties. Nanofluids and nanoparticle assemblies have the potential for use in applications as varied as heat transfer systems, catalysis, drug delivery, and microelectronics. In all of these applications, it is important to understand how individual nanoparticles assemble into large collections of nanoparticles and how the nanoparticles interact at a fundamental level. Important variables include the effects of particle size and shape and the character of the medium in which the nanoparticles are dispersed.


Signature _____ May 1, 2007