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Editorial

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Nanoparticles in a Liquid: New State of Liquid?

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Atoms at a solid surface have different co-ordination numbers, bond lengths, and bond angles, with manifest differences in chemical and physical properties of surface atoms relative to their counterparts in the bulk material [1]. In materials where the fraction of atoms at or near the surface is relatively small (e.g. most bulk materials) the effects of surface atoms on macroscopic phenomena are often negligible. This is not true when materials are in the form of nanoparticles, where their highly subdivided state leads to a very high fraction of the total atoms residing at or near a surface. For nanoparticles, the differences between the bulk and surface properties of constituent atoms can often dominate the overall properties of the material. These effects manifest themselves as an increase in vapor pressure [1], a decrease in melting point [1], and/or an increase in surface tension/surface energy [2] when compared to their macroscopic counterparts. Nanoparticles also experience significant changes in optical and electronic properties due to quantum size effects and energetic effects initiated by the increasing contribution of the particle surface to the energy of particles [3,4].

For nanoparticles, the effects of disturbed co-ordination and high surface curvature can influence not only their physical properties, but also the character of their interaction with the environment. Such interactions are poorly studied, especially in liquids. Monolayer adsorption occurs more easily on nanoparticles than on flat surfaces [1], largely due to effects on surface energy and structure noted above. However, it is generally more difficult to form multilayers of physically adsorbed analytes on the highly curved surfaces of nanoparticles. The obstacle for multilayer adsorption on highly curved surfaces could result from changes in the steric relationships between successive adsorbed layers, but the nature of analyte interactions with nanoparticles is not well understood.

The surface of any condensed matter, solid or liquid, is distinguished from the bulk by different inter-atomic and inter-molecular distances and arrangements caused by the presence of unsaturated interactions for atoms and molecules located at the surface. This difference in atomic/molecular structure between bulk and surface regions is responsible for localized effects of the solid phase on the structure and properties of the liquid phase immediately adjacent to the solid. For example, liquid ordering near flat solid surfaces to the depth of 1-3 nm has been well documented experimentally and theoretically, but whether similar liquid ordering would occur on a highly curved surface has only been speculated [5]. There is almost no experimental data showing directly or indirectly the structuring of the liquid molecules on small crystalline or highly curved surfaces of nanoparticles. The measurements of colloidal forces for nanoparticles of silica and alumina using atomic force microscopy suggest that 10 nm silica particles are surrounded by about 1 nm hydration layer in electrolyte solutions [6] but this finding needs to be confirmed in other laboratories and for other nanoparticles. It is possible that the size dependence of interfacial energy in nanoparticles contributes to structuring of liquids immediately adjacent to nano-surfaces.

What could be the consequences of structured layers surrounding nanoparticles in suspensions? Let us consider how the volume fraction of a structurally modified liquid might vary with particle size as the particle size is reduced to the nanometer range. In figure 1, a close packed arrangement of spherical particles is shown with a shell of structurally modified liquid of thickness δ_o. In figure 2, the effect of particle size and δ_o are shown for a particle volume fraction of 5%. If we assume thicknesses of the liquid shell around each particle to be δ_o=1, 2, or 3 nm, it is clear that even modest values of δ_o lead to very significant volume fractions of structurally modified liquid. Furthermore, it is also evident that the volume fraction of the ordered liquid depends very strongly on particle size, and for the parameters used here, will become quite small for particle sizes much above a few tens of nanometers. In other words, the properties of liquids in highly concentrated suspensions could differ significantly from properties of similar liquid suspending microscopic or macroscopic particles. A fundamental question will need to be answered with

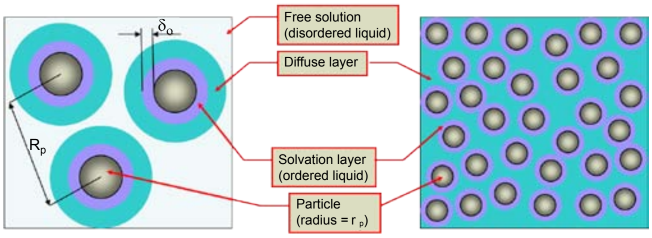

Figure 1: Schematic illustration of a nanoparticle suspension with diffuse layers and ordered liquid shells around nanoparticles.

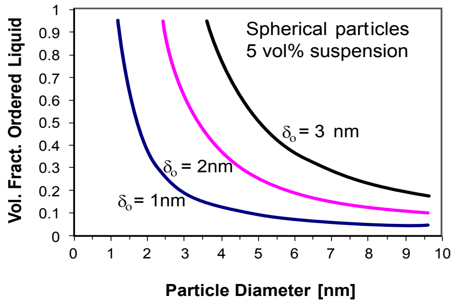

Figure 2: Effect of particle diameter (d_p=2r_p) and ordered layer thickness (δ_o) on the volume fraction of ordered liquid in a suspension containing 5 vol% nanoparticles.

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regards to whether such a suspension can remain stable for any type of nanoparticle. It is known that nanoparticles rapidly aggregate in water as the result of Electric Double Layer (EDL) compression [7].

We don't need to analyze the solvation layers to understand that nanoparticles can produce suspensions of unique liquid structure and characteristics [8]. If we consider the EDL adjacent to a solid surface (Figure 3), which is at least a few times thicker than any solvation layer, we immediately recognize that EDLs of nanoparticles could overlap in suspensions of very modest solid concentrations. The figure 1 schematic shows this scenario and figure 4 makes first-attempt predictions for a simple particle-to-particle arrangement such as in figure 1. Figure 4 shows two types of correlations. The broken lines represent the effect of particle size on the particle center-to-particle center distance for three different volume fractions of nanoparticles in suspension (V_p). The solid lines mark the largest particle center-particle center distance at which EDLs of two particles overlap, for three different electrolyte concentrations made of one valency ions. Any suspension made of nanoparticles with a size equal to or smaller than the diameter at the point of intersection between broken and solid lines will have no free solution. In other words, the entire electrolyte solution will be in a state of overlap between EDLs of the nanoparticles. As the result, for such suspensions the liquid structure surrounding nanoparticles will be different than what is typically predicted by classical colloid science.

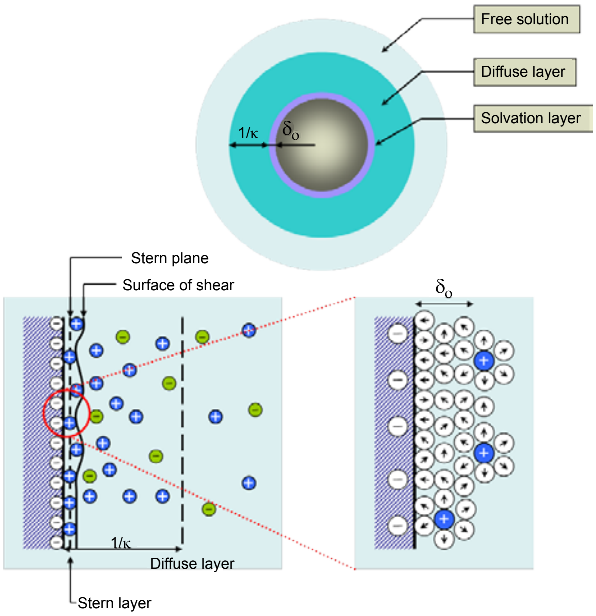

Figure 3: Structure of electrical double layer near a solid surface for a nanoparticle. Electrical double layer are discussed in details in every textbook of colloid science.

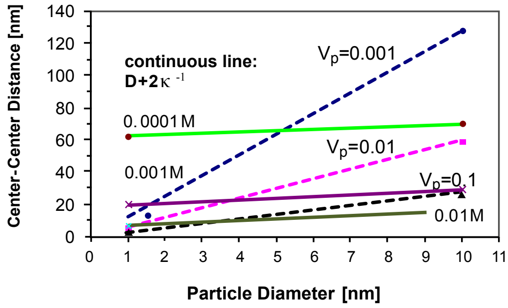

Figure 4: Effect of particle size on the particle center-to-particle center distance for three different volume fractions of nanoparticles in suspension (V_p), broken lines. The solid lines mark the largest particle center-particle center distance at which EDLs of two particles overlap.

Although the synthesis and characterization of nanoparticles has progressed at an incredible pace in the last couple of decades, many questions remain regarding the interactions of the nanoparticles with liquids and their effect on liquid state and its character. The details of liquid interaction with nanocrystals and nanoparticles are not well understood. Nevertheless, it is quite reasonable to hypothesize that the structure of liquids immediately adjacent to nanocrystals and nanoparticles can be rather different from the structure of the same liquids with larger macro-sized particles. These factors, coupled with the geometrical arguments briefly discussed above and the evidence for effects of closely spaced surfaces on the structure of intervening liquids [9], form the central hypotheses for the research needed in this area.

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