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Nuclear magnetic resonance-based study of ordered layering on the surface of alumina nanoparticles in water

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Layering of water molecules on the surface of alumina nanoparticles in an alumina/water nanofluid is studied using nuclear magnetic resonance (NMR). The data suggest that a thin ordered layer (~ 1.4 nm) of water molecules surrounds each nanoparticle. This ordered layer increases the nanoparticle effective volumetric fraction; however, the nanofluid thermal conductivity appears to be unaffected by this layer, and in good agreement with Maxwell's effective medium theory. Furthermore, the NMR data suggest that the nanoparticles do not enhance, but rather stifle micromixing in the base fluid. © 2009 American Institute of Physics. [doi:10.1063/1.3276551]

It is well known that short-range forces in colloidal systems can create an ordered layer of fluid molecules around the solid particles.¹⁻³ According to Yan *et al.*⁴ the thickness of this layer can be estimated as $h = 1/\sqrt{3}(4M_f/\rho_f N_a)^{1/3}$, where M_f and ρ_f are the molecular weight and density of the fluid, respectively, and N_a is the Avogadro's number; for water, $h \sim 0.28$ nm. This layer, whose effect on the colloid's effective transport properties (viscosity and thermal conductivity) can be safely neglected for large (micro-) particles, could become important in nanocolloids, also known as nanofluids, due to the small size and high surface-to-volume ratio of the nanoparticles. In fact, heat transfer in nanofluids has been linked to the high thermal conductivity of this ordered layering on the surface of the nanoparticles.⁵⁻⁹ Therefore, it is of interest to measure the thickness of the ordered layer for a simple, well-characterized, nanofluid, and assess its expected impact on the nanofluid thermal conductivity.

The nanofluid used in this work was purchased from Nyacol (AL20) and was made of alumina nanoparticles in aqueous solution of nitric acid (pH=4) for particle stabilization. TEM images of the samples show a "granular" shape of the nanoparticles, with aspect ratio near unity. The hydrodynamic particle diameter for this nanofluid, as measured with dynamic light scattering, was 42.6 ± 2.5 nm. The Brunauer-Emmett-Teller (BET) surface area was $S_A \sim 185$ m²/g, corresponding to an effective diameter $d_{BET} \sim 8.3$ nm. The discrepancy between these two diameters indicates that either some particle agglomeration is present in the nanofluid, or the particles are porous. The as-received particle concentration was 20 wt % (~ 6 vol %), which was independently confirmed using neutron activation analysis and thermogravimetric analysis. The viscosity (measured with a capillary viscometer) was found to be $\mu = \mu_f \exp[4.91\phi/(0.2092 - \phi)]$, where μ_f is the viscosity of water. Details of the measurements performed to characterize the nanofluid can be found in Ref. 10.

The thickness of the ordered water-molecule layer around the alumina nanoparticles can be estimated from measurements of the self-diffusion coefficient of water in the nanofluid samples, which were performed using nuclear

magnetic resonance (NMR). For the NMR measurements the samples were diluted with pure (99.9%) heavy water (D₂O) to avoid radiation damping effects; the differences in line-shape, diffusion coefficient, density, and viscosity between D₂O and H₂O are negligible in this context. We used a 300 MHz Bruker Spectrometer with a maximum z-gradient strength of 28.35 G/cm. The experiments were performed at 25 °C. The diffusion coefficient was measured using a pulsed gradient stimulated echo sequence with bipolar gradients, also known as the Cotts 13-interval pulse sequence.¹¹ The Cotts 13-interval pulse sequence was slightly modified in this work to include DEPTH pulses,¹² to select the central homogeneous region of the sample. A crusher pulse of duration 10 ms and 20% strength was applied during the diffusion time, Δ . The total attenuation of the acquired signal when compared to the same pulse sequence with $g=0$ for the Cotts 13-interval pulse sequence is given by¹¹

$$E = \frac{S}{S_{g=0}} = e^{-Db} \quad \text{with} \quad b = q^2 \left(4\Delta + 6\tau - \frac{2}{3}\delta \right), \quad (1)$$

where g , τ , and δ are the magnitude of the magnetic field gradient, wait period between rf pulses, and the gradient time, respectively. The wavenumber, q , is defined as $q = \gamma g \delta$, with γ being the gyromagnetic ratio of the proton. The self-diffusion coefficient of the water molecules in the sample, D , is determined by taking the slope of the E versus b curve (in semilog scale), as shown in Fig. 1. Details of the NMR measurements and data processing can be found in Ref. 13.

The diffusion coefficient data results are shown in Fig. 2, which reports the ratio of the diffusion coefficient in the nanofluid to that in pure D₂O, as a function of the alumina nanoparticle concentration. The diffusion coefficient decreases with increasing nanoparticle concentration, due to two effects: first, the tortuosity of the diffusion path of the water molecules is increased when solid particles stand in their way; second, the water molecules in the ordered layer on the surface of the particles are "bound" to and move with the particles, which have a lower diffusion coefficient than the free molecules. A simple model capturing both effects is as follows:

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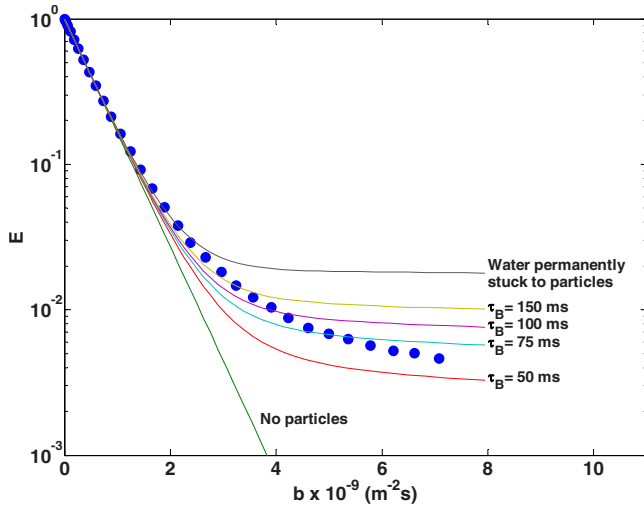


FIG. 1. (Color online) Attenuation plot for ~ 1 vol % alumina/water nanofluid. The linear low- b region is used to calculate the water molecule diffusion coefficient, D . The nonlinear high- b region is used to estimate the exchange time constant, τ_B .

$$D = (1 - P_{\text{bound}})D_{\text{free}} + P_{\text{bound}}D_{\text{bound}}, \quad (2)$$

where P_{bound} is the fraction of water molecules in the ordered layer. The diffusion coefficient for the free molecules, including the effect of tortuosity, is¹⁴ $D_{\text{free}} = D_0 / (1 + \phi/2)$, while the diffusion coefficient for the water molecules bound to the nanoparticles is equal to the diffusion coefficient of the nanoparticles, which is given by the well-known Einstein–Stokes’s relation $D_{\text{bound}} = k_B T / 3\pi\mu d$, where μ is the nanofluid viscosity reported above, and d is the nanoparticle hydrodynamic diameter. In Fig. 2 the diffusion coefficient D predicted by Eq. (2) is plotted for various values of ordered layer thickness, corresponding to different values of P_{bound} . It can be seen that the best fit with the experimental data is for a layer thickness of about 1.4 nm, or five water molecules, assuming a water-molecule diameter of about 2.8 Å.¹⁵ This value is much higher than estimated at the beginning of the letter using Yan *et al.*’s⁴ model, but is consistent with the work of other researchers. Yu *et al.*¹⁶ found an ordered layer that was approximately three liquid molecules thick on flat silicon surfaces, using nonpolar mol-

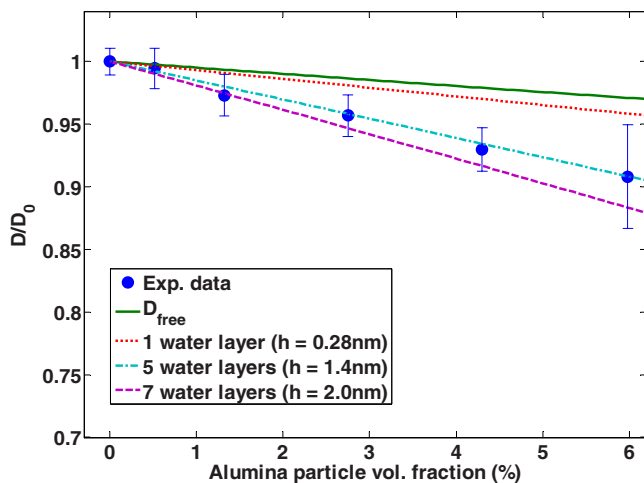


FIG. 2. (Color online) Self-diffusion coefficient of water molecules in nanofluid with alumina nanoparticles (●). Error bars are 95% confidence intervals.

ecules of tetrakis(2-ethylhexoxy)silane. Turanov and Tolmachev,¹⁷ who also used an NMR approach, estimated that there was an ordered layer six water molecules thick on silica nanoparticles. A key underlying assumption in Eq. (2) is that the water molecules in the ordered layer are “stuck” to the particle. It is possible to use the high- b (nonexponential) tail of the diffusion attenuation plots (Fig. 1), to crudely estimate a time constant for water molecule exchange from and to the layer. Kärger¹⁸ and Andrasko¹⁹ developed a two-site exchange (2SX) model to describe the nonexponential decay found in a two-zone system. The Kärger–Andrasko 2SX model contains the parameter τ_B , which is the mean lifetime the nuclear spins spend bound to the nanoparticles. The model was applied to our data and the best fit was found for values of τ_B of 50–100 ms. The details are in Ref. 13. Since the relaxation time for Brownian diffusion of the nanoparticles is $\sim \text{ps} \ll \tau_B$, the “sticky” layer assumption is accurate.

It has been suggested that ordered, solidlike layering around the particles can augment the effective volumetric fraction of the particles and thus increase the thermal conductivity of the nanofluid.^{5–9} To estimate the impact of the ordered layer on the thermal conductivity of the nanofluid, we have used the effective medium model developed by Maxwell over 100 years ago²⁰

$$\frac{k}{k_f} = \frac{1 + 2\beta\phi}{1 - \beta\phi}, \quad (3)$$

where k and k_f are the thermal conductivities of the nanofluid and base fluid, respectively; $\beta = (k_p - k_f) / (k_p + 2k_f)$, k_p is the particle thermal conductivity and ϕ is the particle volumetric fraction. If a finite temperature discontinuity exists at the nanoparticle–fluid interface, Eq. (3) would still apply provided one makes the substitution $k_f \rightarrow k_f + \alpha k_p$ (on the right-hand side), where $\alpha = 2R_b k_f / d$, R_b is the interfacial resistance and d is the particle diameter.

Let us assume that, due to the presence of the layer, the effective volumetric fraction of the nanoparticles becomes $\phi' = \phi[1 + hS_A \rho_p]$, where h is the thickness of the ordered layer, S_A is the BET surface area and $\rho_p \sim 3.9 \text{ g/cm}^3$ is the density of the alumina nanoparticles. We can regard the layer as a surface resistance of value $R_b = h/k_{\text{ice}}$, where $k_{\text{ice}} \sim 2.2 \text{ W/mK}$ is the thermal conductivity of ordered water, also known as ice. Using R_b and ϕ' (versus ϕ) in Eq. (3), it is possible to estimate the thermal conductivity enhancement caused by the ordered layer. The results are shown in Fig. 3 along with the predictions of the plain Maxwell’s model ($h = 0, R_b = 0$) and the actual thermal conductivity of the nanofluid, as measured by a custom-made transient hot wire apparatus.²¹ The plots in this figure suggest that the ordered layer should increase the nanofluid thermal conductivity somewhat; however, the experimental data display no enhancement beyond the plain Maxwell’s model, suggesting that the presence of an ordered layer does not affect thermal conductivity in the alumina–water system studied here. While the possibility of cancelling effects (an increase due to layering countered by a decrease due to surface resistance) cannot be ruled out, the results in Fig. 3 clearly show that the magnitude of the effect of layering in this particular nanofluid is at most $\sim 15\%$ (at 6 vol %), and lower at lower concentrations.

It has also been suggested that Brownian motion of the nanoparticles agitates the fluid, thus creating a micro-

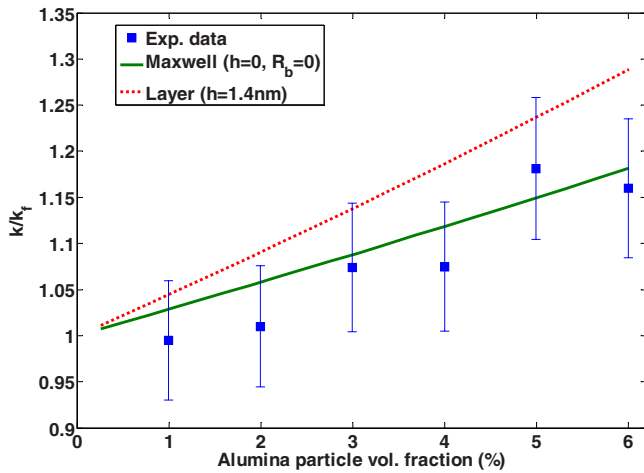


FIG. 3. (Color online) Thermal conductivity ratio of water-based nanofluids with alumina nanoparticles. Error bars represent propagated instrumentation uncertainty. For the Maxwell and layer models it was assumed $k_p = 35$ W/mK, $k_f = 0.6$ W/mK in the calculations.

agitation or micro-convection effect that increases energy transport.^{22–26} We shall note here that, if this hypothesis were correct, an enhancement of the water molecule diffusion coefficient with increasing particle concentration would be expected from increased fluid agitation, whereas in fact the data in Fig. 2 show the opposite trend, over a time scale of Δ . This corroborates the doubts raised by other researchers^{27–29} about the physical correctness of the micro-convection hypothesis.

In summary, the structure of a water-based nanofluid with alumina nanoparticles was probed through NMR measurements of the fluid self-diffusion. A thin layer of water molecules (approximately five molecules thick) was found to surround each nanoparticle with a correlation time >50 ms. It was shown that the increase in the nanoparticle effective volumetric fraction due to this water layer should increase the nanofluid thermal conductivity, while the measured thermal conductivity in fact shows no measurable deviation from the Maxwell's model for the alumina-water system tested in this study. Also, the so-called microconvection mechanism is in conflict with our experimental data.

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