

## FEDSM-ICNMM2010-30826

### VISCOSITY STUDIES OF AQUEOUS SOLUTIONS OF HAFNIUM OXIDE PARTICLES AND POLYSTYRENE NANOSPHERES

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#### ABSTRACT

Nanoparticle colloidal system rheology has long been researched, without many concrete conclusions. Literature has been devoted to the viscosity and shear properties of these systems since Einstein's PhD thesis. However, most models are based on molecular dynamics which are not necessarily applicable to real systems, and most real systems are modeled by empiricism. This report looks to unify these approaches through rheological testing and mathematical analysis in order to achieve several goals using a system composed of hafnium oxide particles suspended in water. The first goal is to have a viscosity model that fits not only empirical data, but also the relevant theory and first principles. By employing the modern techniques of a rheometer-on-a-chip to nano-scale particles, the limitations of traditional rheometry are bypassed. The molecular dynamics approaches are converted to zero-shear and infinite-shear viscosities which can be applied to traditional models. A modern model was then derived, applied to new data, and agreement was found to a satisfactory degree. No significant change in viscosity with shear rate was found experimentally or analytically. Traditional research is done with spherical particles, such as polystyrene nanospheres, as which we are approximating hafnium oxide (HfO<sub>x</sub>) to be. Polystyrene nanospheres are nominally spherical and commercially available at relatively inexpensive costs. Actual spherical data was required for appropriate comparison, and the findings show that the spherical particles have distinct properties.

#### INTRODUCTION

This work aims to fully characterize the rheology of hafnium oxide (HfO<sub>x</sub>) particles suspended in water by a unified approach

of rheological testing and mathematical analysis through viscosity measurements, surface tension measurements and dynamic contact angle studies in addition to first principles analysis. These fluids contain HfO<sub>x</sub> particles with proprietary surfactants, and were originally in 65 and 68% concentrations in water. Industrial applications exist for these fluids, such as use in the immersion lithography industry, so full characterization data is required. The hafnium oxide research assumed the particles to be able to be modeled as hard-spheres. Polystyrene nanospheres were then acquired to compare to the hafnium oxide particles, and to determine a standard reference set of data. Thus in conjunction, this work also aims to characterize aqueous solutions of polystyrene nanospheres. Polystyrene was chosen as the working material since it is available commercially on the nanoscale in aqueous solutions.

#### VISCOSITY

Much of the basis for colloidal rheology stems from the original work of Einstein in 1906 and 1911 on Brownian motion [1],[2]. Micro-sized particles can interact with each other in a fluid by various methods: Brownian motion, van der Waals forces and physical contact. Such particles could be any shape, but the simplest form to model is that of uniform rigid spheres. Krieger, Woods and colleagues continued to explore this matter, which they defined as dispersions of uniform colloidal spheres [3]-[5]. Between 1969 and 1977, Batchelor published many works on the dynamics of small spherical particles [6]-[9]. Woodcock, Beenakker, Russel and Gast continued these studies in the 1980's, along with significant contributions by van der Werff, de Kruif and colleagues [10]-[17]. In the early 1990's, John Brady started his computational analysis of Brownian motion, Stokesian dynamics, and particle interactions [18],[19].

By the late 1990's, many studies had been performed on various systems as detailed in Table 1.

Literature on nanofluids has greatly expanded in recent years. We define a nanofluid as a suspension of nano-scale particles in a continuous medium (fluid). Most of the available literature focuses on colloidal or hard-sphere dispersions consisting of a specific particle in a fluid matrix. These particles range in size from 7 to 640 nm, with most concentrations around 10% particles by volume or less. Some research has looked into concentrations of larger scale particles up to 50 and 60% by volume.

We chose to look at particles on the 1 to 2 nm scale, which has not been reported in literature yet. In addition, we chose to look into particle concentrations of at least 20 – 30% by volume range. The smallest particle that has been studied in this concentration is 28 nm. Particle-particle interactions at these moderate concentrations are assumed to be negligible. Testing was also done up to 65 and 68% concentrations, nearing the close-pack limit of spherical particles.

## Literature Review

After Einstein's initial work on particle-particle interactions in 1906 and 1911, research seemed to stop in the area until the 1950's [1], [2]. Over the years the approaches have varied and yet there is not clear consensus on many ideas of nanoparticle viscosity [3] - [27]. A summary chart of all the experimental studies is included as an appendix in Table 1 [5], [12], [28] - [39], and some of the theoretical highlights are presented here.

In a paper by de Kruif and colleagues [12], they define the dimensionless shear rate as the Peclet number and equilibrium constant as:

$$Pe \equiv ba^3 \eta \dot{\gamma} / kT \quad (1)$$

In a publication with van der Werff [14], de Kruif defines the Peclet number as

$$Pe_2 \equiv \frac{a^2 \dot{\gamma}}{D_0} = \frac{6\pi\eta_s a^3 \dot{\gamma}}{k_b T} \quad (2)$$

where  $D_0$  is the Stokes-Einstein diffusion coefficient,  $\eta_s$  is the viscosity of the solvent, and  $k_b T$  is the thermal energy. In this work they quote the classic Einstein work from 1906 and 1911 [1], [2]

$$\eta / \eta_s = 1 + (5/2)\phi \quad (3)$$

where  $\eta$  is the viscosity of the suspension,  $\eta_s$  is the viscosity of the matrix fluid and  $\phi$  is the volume fraction of the uniform round spheres. This can be rearranged to give us

$$\eta = \eta_s + (5/2)\phi\eta_s \quad (4)$$

We can calculate a shear rate by rearranging (2)

$$\dot{\gamma} = \frac{Pe \cdot k_b T}{6\pi\eta_s a^3} \quad (5)$$

In addition, we are looking for the shear rate that gives us shear thinning as a function of  $\phi$ . In this case we take equation (5) and substitute in (4) rearranged to solve for the volume fraction. If the shear rate is known, and so is the estimated final viscosity required, the volume fraction required can be found.

$$\dot{\gamma} = \frac{Pe \cdot k_b T}{6\pi \left( \frac{\eta}{1 + (5/2)\phi} \right) a^3} \quad (6)$$

This work does not take into account the dependence of viscosity on the shear rate. Thus it cannot be assumed to be a complete model. Cross [27] seems to be the only provide a model that can be altered to account for this interdependence. His work seems to be largely ignored until Mewis resurrected it in 1989 [24] to work out said interdependence. Cross did not include this in the original model, but it lent itself to change.

## Preliminary Calculations

For an example calculation take a particle of 2 nm diameter ( $d_p = 2$  nm), at a concentration of 40% ( $\phi = 0.4$ ). Assume that the gap between the wafer and the needle is 250 nm ( $h = 250$  nm). We assume a Peclet number of 1 ( $Pe = 1$ ) which gives us a condition of 50% advection. Taking solvent viscosity of water to be  $\eta_s = 8.90 \times 10^{-4} Pa \cdot s$  we get our dispersion viscosity to be  $\eta = 1.78 \times 10^{-3} Pa \cdot s$

## Setup of Test

The rheological properties of the fluids involved were tested using microrheometry techniques. Preliminary tests were done with deionized water from the University of Wisconsin – Madison's Nuclear Reactor Laboratory (UWNR). This water was used to test the parameters of the Rheosense VROC Rheometer-on-a-Chip setup. Results were found to agree with given values. There were two samples sent, and diluted. The originally 65% concentration was diluted to 65, 60, 50, 40, 30,

20, 10, 5 and 1 % by weight of the hafnium oxide dispersed in water. The originally 68% concentration was diluted to 68, 30, and 5 % by weight. These were diluted on the UW-Madison campus in the MVAL lab with the UWNDR deionized water and with deionized water sent with the hafnium oxide samples from Cornell University. Each concentration was tested at shear rates of 100, 500, 1,000, 5,000 and 10,000 [1/sec]. The spherical tests were run on 10% polystyrene nanospheres suspended in water. There were three nanosphere sizes tested: 3 nm, 10 nm, and 30 nm in diameter.

### Handling Considerations

There were several concerns that arose during the handling of the fluids. All surfaces were cleaned with alcohol and rinsed with DI water ahead of usage, so the contact angle of the fluid on the glass would be zero. This would create a thin film of the fluid with particles. Once the fluid evaporated, a thin film of plated out particles would be left on all surfaces. This coating ended up on the rheometer surface, the syringe pump surface, the syringe, and the table. Cleanup was done by first wiping away the visible coating with dry paper toweling, then wiping down the surfaces with deionized water, followed by methanol alcohol. Surgical quality nitrile gloves were worn, along with particle masks with the highest grade of filtration short of respirators. These considerations apply to both the  $HfO_x$  and polystyrene particles, as they were treated the same in all of the testing. The  $HfO_x$  particles seemed to flake out of solution and dry out more quickly and easily than the polystyrene particles, but this observation was not quantified.

### Preliminary Results

There are two types of hafnium oxide samples sent from Cornell University, differing in original concentration and proprietary formulations of the hafnium oxide particles. The first sample was originally 65% hafnium oxide particles by weight, and the second fluid was originally 68% hafnium oxide particles by weight. Each sample was diluted down to several different concentrations. The results are reported both as the given shear rate and viscosity, and a corrected “true” shear rate and viscosity. This correction is obtained through the Weissenberg-Rabinowitsch-Mooney analysis inherent within the software package, which was a proprietary LABVIEW based program from RheoSense.

### DATA ANALYSIS

The data from the original studies are presented in Figures 1 and 2. If a larger size channel is used in the rheometer (which would require an internal chip change) even larger shear rates could be examined. The two different fluids showed the same

patterns. Figure 3 describes the change in viscosity with concentration in terms of weight percentage.

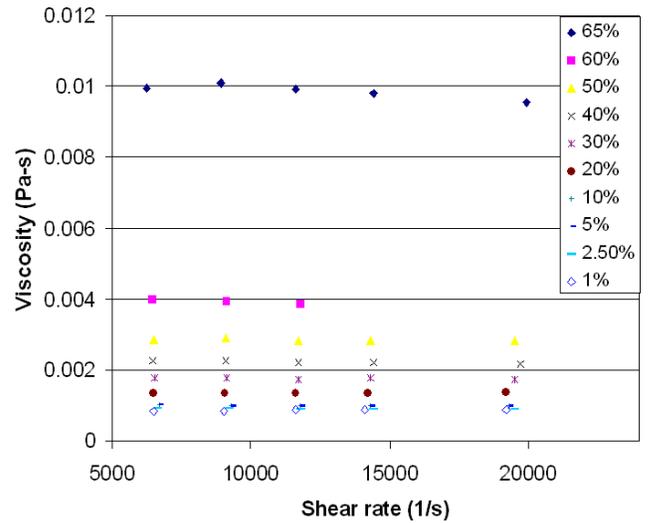


Figure 1. Originally 65% by Weight

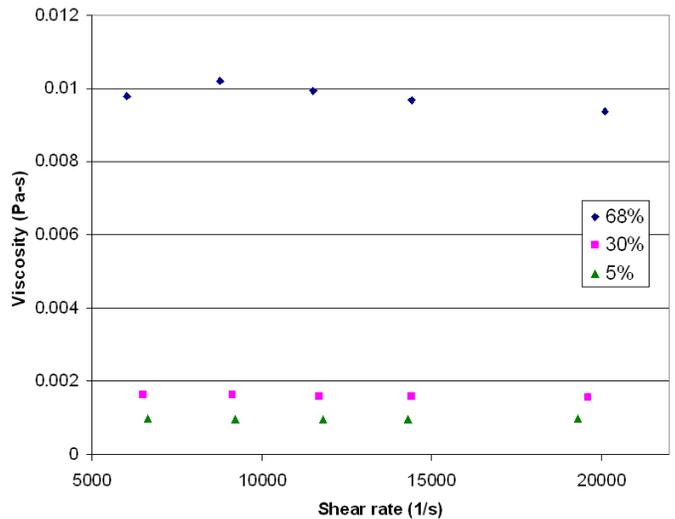
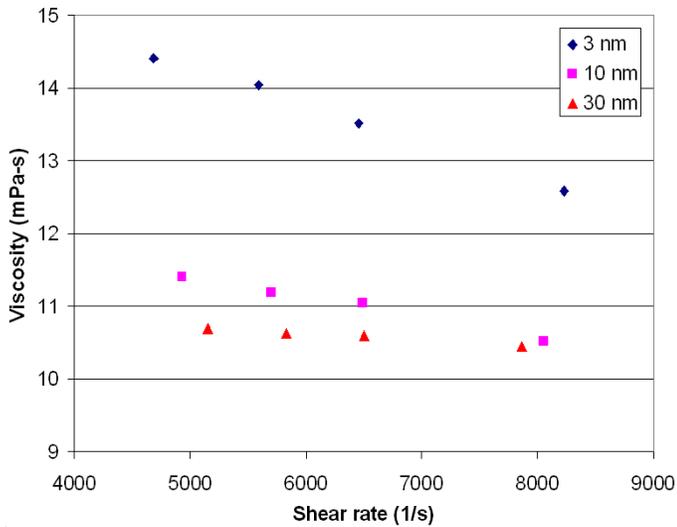
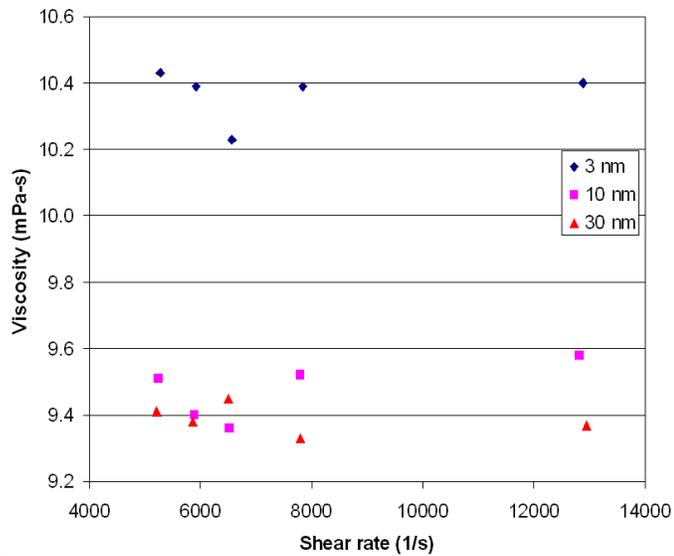


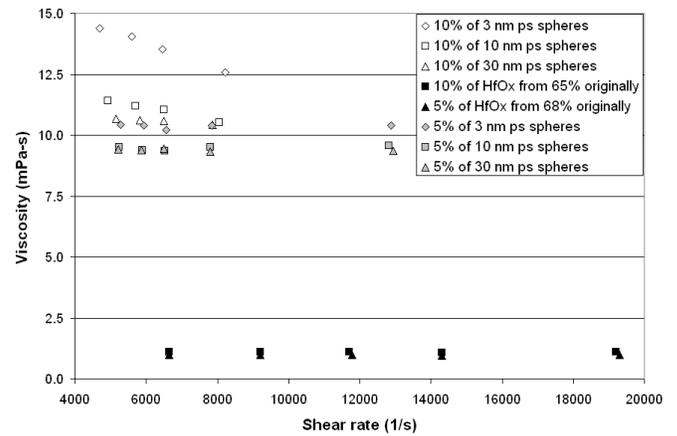
Figure 2. Originally 68% by Weight



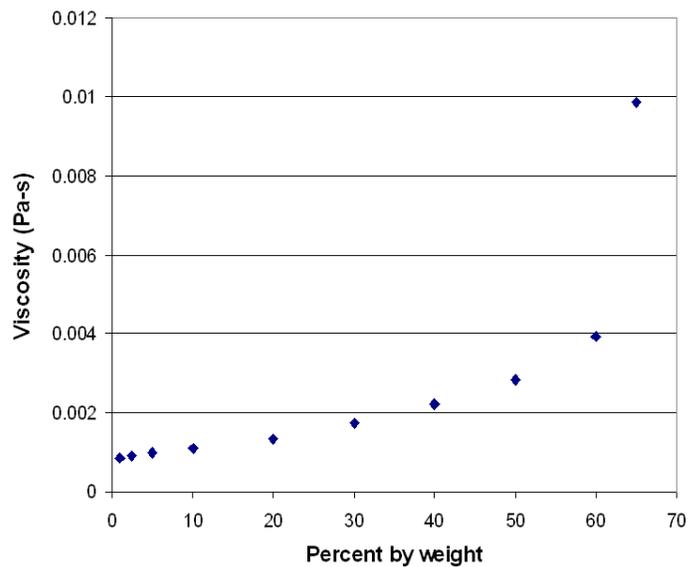
**Figure 3. Shear rate vs. viscosity for aqueous 10% polystyrene nanosphere solutions**



**Figure 4. Shear rate vs. viscosity for aqueous 5% polystyrene nanosphere solutions**



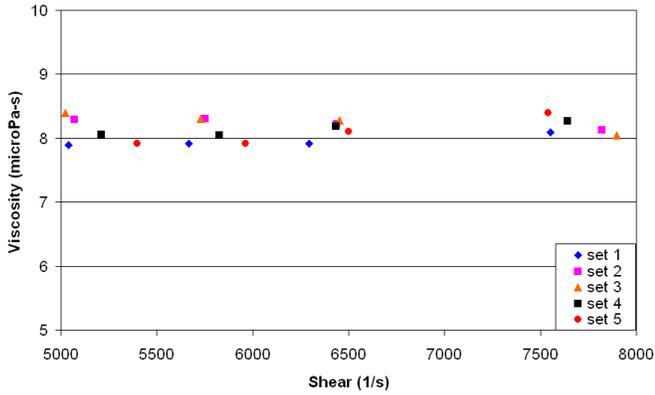
**Figure 5. Shear rate vs. viscosity for aqueous polystyrene nanosphere and hafnium oxide solutions**



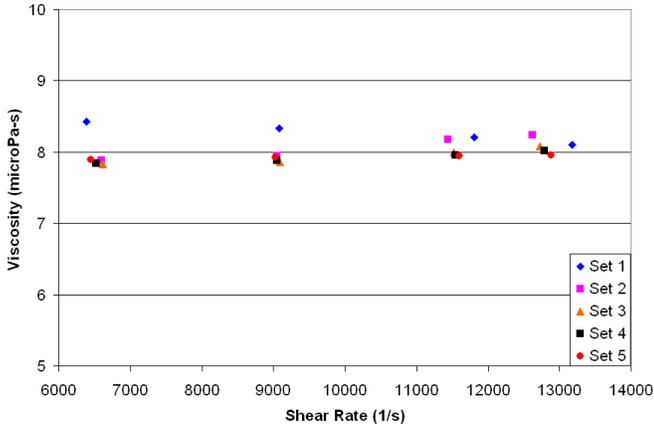
**Figure 6. Viscosity as a Function of Weight Percentage**

### Repeatability studies

An initial repeatability study was done with deionized water and some HfO<sub>x</sub> concentrations. These samples were reused in the same test as before, but run identically for 5 times to see if the results deviated. The temperature bath was again run through the jacket surrounding the VROC chip. Results are shown below. The results of all 5 runs only have a standard deviation of 0.169 cP from 8.314 cP for DI water, and 0.172 cP from 8.55 cP for the 1% concentration sample. Figures 7 and 8 show the data from these studies and agreement is found in both cases.



**Figure 7. Viscosity vs Shear Rate - DI water, temp bath on sensor**



**Figure 8. Viscosity vs Shear Rate 1% (from 65%)**

## Models from Literature Review

The literature review shows the evolution of the available models. An easier approach to get viscosity as a function of shear rate is to rearrange Equation (6) to

$$\eta = \frac{6\pi a^3 \dot{\gamma}}{Pe \cdot k_b \cdot T (1 + 5/2)\phi} \quad (7)$$

If the equation for  $Pe$  is plotted in both limits (from reference [12]) they cross at  $Pe=1$ . The limits on the plot where the curves level off are  $Pe=10^{-2}$  and  $Pe=10^2$ . These three cases are examined for both 65% and 68%, assuming the diameter ( $a$ ) of the particles is on average 4 nm, the temperature is at 300K, and  $k_b$  is the Boltzmann constant.

This viscosity definition is not much use to us as it is purely theoretical, and does not have any shear dependence on the viscosity. If shear dependence on viscosity exists, it must be accounted for. The work of Kreiger and Dougherty [3] uses this model and also makes use of the average distance between particles to define the shear rate. As these values are not known for real fluids, this model does not tend to be useful for laboratory data.

Mewis [24] suggests a model originally brought forth by Cross [27] that is for colloidal suspensions. This model and others rely on knowing the zero-shear viscosity. The authors acknowledge that the zero-shear viscosity and the high shear limits are not always known. These values must be determined experimentally when given a new fluid.

Mewis gives Cross' model as

$$\eta_r = \eta_{r\infty} + \frac{\eta_{r0} - \eta_{r\infty}}{1 + (b\sigma_r)^m} \quad (8)$$

This is a power law model, which is frequently used as a model for the viscosity of non-Newtonian fluids. Here  $b$  is some constant, not defined well by Mewis. Also, Mewis defines the reduced shear stress

$$\sigma_r = \frac{\eta \dot{\gamma} a^3}{kT} \quad (9)$$

Since Mewis acknowledges that viscosity can change with shear rate, he defines a reduced shear rate as

$$\dot{\gamma}_r = \frac{\eta_0 \dot{\gamma} a^3}{kT} \quad (10)$$

and then the reduced shear rate and reduced shear stress are substituted into Equation(8) to give

$$\eta_r = \eta_{r\infty} + \frac{\eta_{r0} - \eta_{r\infty}}{1 + (b \dot{\gamma}_r)^m} \quad (11)$$

Unfortunately, Mewis does not define how values for  $b$  or  $b'$  are obtained except to say that it is the inverse of the relative shear stress. All that is known is that  $b$  is a constant. A common assumption is that it is a constant of only order 1. De Kruif [12] gives the same  $O(1)$  constant  $b$ , but places it in the definition of Peclet number instead of the viscosity (it follows through that this is the same constant). De Kruif assumes also that it is  $O(1)$  and thus not a large multiplier. Mewis claims an advantage

over Krieger by including the shear dependence of viscosity. De Kruif defines a similar equation as Mewis, but non-dimensionalizes it by the Peclet number.

### Curve Fit of Preliminary Data

Each line in the HfO<sub>x</sub> plots can be shown to fit a polynomial. For instance the 65% sample can be modeled by

$$\eta = -3 \times 10^{-12} \dot{\gamma}^2 + 5 \times 10^{-08} \dot{\gamma} + 0.0098 \quad (12)$$

The 68% sample can be modeled by

$$\eta = -6 \times 10^{-12} \dot{\gamma}^2 + 1 \times 10^{-07} \dot{\gamma} + 0.0095 \quad (13)$$

These equations are closely related to each other, and the values of viscosity are close as shown in Figure 6 when they are on the same axis.

### Modeling

Using Equation (11) as a starting point, a newer model can be defined. Mewis varies the value of  $m$  from 1 to 3.53 and  $m'$  from 0.726 to 1.15 [24]. The first step is to define the reduced shear rate. In the case of a nano-particle,  $a$  (the diameter) is on the order of 1 nm. Substituting in the Boltzmann constant,  $a$ , and a steady-state temperature of 300K:

$$\dot{\gamma}_r = \frac{\eta_0 \dot{\gamma} a^3}{kT} = \frac{\eta_0 \dot{\gamma} (1E-9m)^3}{(1.381E-23J/K)(300K)} = \eta_0 \dot{\gamma} 2.414E-7 [m^3 / J] \quad (14)$$

Substituting Equation (14) into Equation (11) gives

$$\eta_r = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (b' \dot{\gamma}_r)^m} = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (b' \eta_0 \dot{\gamma} 2.414E-7 [m^3 / J])^m} \quad (15)$$

Equation (15) can then be used to find the viscosity at a given shear rate for the nano-particle solution, assuming the zero shear rate and infinite shear limit are known. These two values depend on the concentration as seen in the data analysis section. The concentration (weight percentage in the plot) drastically changes the viscosity. For the purposes of comparison,  $b'$  is taken to be unity. Results comparing the advanced model and the curve fit are shown below.

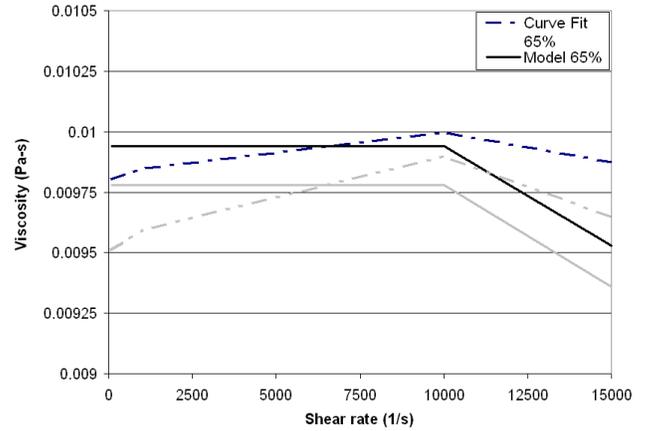


Figure 9. Model vs Curve Fit

Results show that the viscosity is relatively constant. Changing the value of  $m'$  from 0.5 to 2 did not change the results. The plot is shown for  $m' = 1$ , which would indicate a Newtonian fluid in the power-law model. Agreement seems best at moderate shear rates of 10,000 [1/s].

### DISCUSSION

By applying the new method of rheometry-on-a-chip the viscosity of nano-particle colloidal solutions was accurately measured with good repeatability. These results were then fit to an empirical curve. Traditional molecular dynamics models were altered to account for the shear rate dependence of the viscosity, and then compared with the empirical curves to satisfactory agreement. No significant change in viscosity with shear rate was found experimentally or analytically. The viscosity for the spherical particles was found to vary with shear rate, is visible in Figure 3. The shear-rate dependence seems to be greater for smaller sized particles, as the difference in slopes between the three data sets indicates. A comparison to the hafnium oxide data is shown in Figure 5. Hafnium oxide solutions had a lower viscosity by up to a factor of 10. The 5% solution results are not as stable as the 10% solution results, where as for hafnium the reverse seemed apparent.

Much of the molecular dynamic models are based on pure rigid spheres instead of real particles. The traditional research in Table 1 is also only accounting for particles that can be estimated as rigid spheres. Since Hafnium oxide is not necessarily spherical, testing rigid spheres in the same manner was necessary for full comparison and a more robust proof-of-concept. The comparison in Figure 5 shows that HfO<sub>x</sub> are at best only approximated by a spherical model.

## CONCLUSIONS

Many nanofluids are currently being researched for industrial applications. Much of the background theory being used for comparison is based on the hard-sphere model. This work gives concrete results of a fluid that is actually composed of hard spheres, and can be used as a benchmark for other fluids to see how closely they follow realistic hard-sphere particle interactions. In addition, several conclusions about hafnium oxide particles suspended in water can be drawn from the studies shown here. In terms of the viscosity, we found no significant change in viscosity with shear rate experimentally or analytically for the  $\text{HfO}_x$ , while the polystyrene spheres had a rate dependant viscosity. As far as the surface tension is concerned, there were two main findings for the  $\text{HfO}_x$ : First, as expected, surface tension decreases with increased particle concentration. Second, at higher concentrations the drop seems to shrink up or contract in a noticeable manner. The findings for polystyrene were interestingly different: the surface tension increased with particle size greatly but didn't seem to change with concentration except at the largest size of 30 nm particles. The dynamic contact angle testing provided insight into several interesting phenomena. First of all, droplets of the fluid show a density gradient at all concentrations. Within the droplets, clumps of particles formed, and at higher concentrations the droplets left a trail of particles on the quartz surface. These phenomena could severely impact these fluids in an industrial application. Since the trail is left with higher concentrations, it's not difficult to imagine that a nano-scale trail is left at the lower concentrations that are not visible to the naked eye. This means that in an industrial application any surface would be contaminated. The density gradient meanwhile simply implies non uniformity. If uniformity is a required in the application, than either of these fluids at any concentration are not ideal. Actual hard spheres are even less ideal since they deposited a film at any speed or concentration.

## ACKNOWLEDGMENTS

The authors would like to thank Sematech, International for funding this research and Cornell University for providing the  $\text{HfO}_x$  nanoparticle solutions.

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## ANNEX A

### TABLE 1. PREVIOUS STUDIES

Reference	Year	Particle	Fluid	Part. Size	Concen.	Viscosity	Surface Tension	Shear	$\dot{\gamma}$
Woods, Krieger [5]	1970	PS, PVT	hydroxyethyl cellulose	70-112 nm	0-0.50 vol. frac.	X		X	10-10,000
de Kruif, van Iersel, Vrij [12]	1985	Silica	cyclohexane	78 nm	0-0.619 vol. frac.	X		X	45-807
Van der Werff, de Kruif, Blom, Mellema [15]	1989	Silica	cyclohexane	28-76 nm	0.10-0.60 vol. fract.	X		X	Not given
Phan, et al.[28]	1996	PMMA-PHSA	decalin, traclin	518, 640 nm	0.505+ vol. frac	X		X	0-50
Meeker, Poon, Pusey [29]	1997	PMMA	cis-decalin	301 nm	0.430-0.494	X		X	0-0.4
Lee, Yang [30]	1998	Silica (coated w/ silane)	alkoxide TEOS	200.5 nm	0.35-0.45 vol. fract.	X		X	0.01-1,000
Das, Purta, Roetzel [31]	2002	Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	38 nm	1-6% vol concen.	X		X	10-1,000
Tseng, Lin [32]	2003	TiO <sub>2</sub>	H <sub>2</sub> O	7-20 nm	0.05-0.12 vol. fract.	X		X	0-1,000
Namburu, Kulkarni, Dandekar, Das [33]	2007	SiO <sub>2</sub>	60:40 ethylene glycol, H <sub>2</sub> O	20, 50, 100 nm	0-10% part. vol.	X		X	0-275
Papir, Krieger [34]	1970	PS	benzyl alcohol, m-cresol	115-455 nm	0-50% part. vol.	X			-
Mewis, Frith, Strivens, Russel [24]	1989	PMMA	decalin, Excol D200/240	84, 475, 1220 nm	0-0.80 vol. frac.	X			-
Segrè, Meeker, Pusey, Poon [35]	1995	PMMA	cis-declan	178-301 nm	0-0.494 vol. frac.	X			-
Studart, Amstad, Gauckler [36]	2006	Al <sub>2</sub> O <sub>3</sub> Gallol-PEG	H <sub>2</sub> O	65 nm	30% vol.	X			-
Nguyen, Desgranges, Roy, Galanis, Mare, Boucher, Mintsa [37]	2007	Al <sub>2</sub> O <sub>3</sub> CuO	H <sub>2</sub> O	36, 47 29 nm	1, 4.5 & 9.1%	X			-
Kamibayashi, Ogura, Otsubo [38]	2008	Silica	PEO, H <sub>2</sub> O	8-46 nm	12% part. vol	X			-
Murshed, Tan, Nguyen [39]	2008	TiO <sub>2</sub>	H <sub>2</sub> O	15 nm	0.1% part. vol	X	X		-