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### AN INVESTIGATION INTO THE NON-UNIFORMITY OF DENSITY IN NANOFLUIDS

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#### ABSTRACT

This study uses molecular dynamics simulations to investigate the affects of platinum nanoparticle lognormal size distribution and agglomeration on the local density of the surrounding xenon base fluid. Over the range of platinum nanoparticle diameters (25-150 nm), the radial distribution function showed an increase in the local fluid density. This increase in local density is shown to be caused by the formation of liquid layers that surround the nanoparticle. Liquid layer formation is found to be highly dependent on the cross-correlation between the platinum and xenon atoms. The local density is shown to increase with smaller nanoparticle diameter and aggregation reduces this change in density. Since aggregation is a dynamic phenomenon, the density becomes both spatially and temporally dependent. This space-time dependency of nanofluid density is compared to the linear mixing models normally applied to nanofluid systems.

#### INTRODUCTION

In an ideal homogeneous fluid, the distribution of atoms is relatively uniform throughout the entire system and the corresponding radial distribution function is an adequate description of the time-averaged local density structure at any given location. In contrast, when a nanoparticle is suspended in fluid, the local density distribution of the surrounding fluid is altered due to the strong solid-fluid interactions, creating a thin liquid layer (~1nm) around the nanoparticle. This altered time-averaged local density structure is often used as an explanation for thermal conductivity enhancement in nanofluids [1-3], even suggesting that an amorphous-like fluid structure is formed near the nanoparticle surface creating conduction paths for enhanced energy transfer[4]. This non-uniformity in the local density may be enhanced even more when nanoparticles cluster into either spherical or rod-like structures, which has already

been shown to possibly enhance thermal conductivity in nanofluids [5-7]. A snapshot of a nanoparticle-centered volume slice (picture not shown) supports the previously mentioned assertion that the density of the surrounding local fluid can become significantly non-uniform. This could impact how calculations of the thermophysical properties of nanofluids are determined and eventually analyzed. To quantify spatial and temporal fluctuations in local density of the surrounding fluid, principal component analysis that has been adapted by D'Abramo [8] to characterize local liquid density is used.

#### THEORY

In this analysis, the fluid surrounding the nanoparticle is separated into  $n$  spherical concentric layers (Figure 1) where their respective densities are described by distribution functions. To determine how the local density at each layer

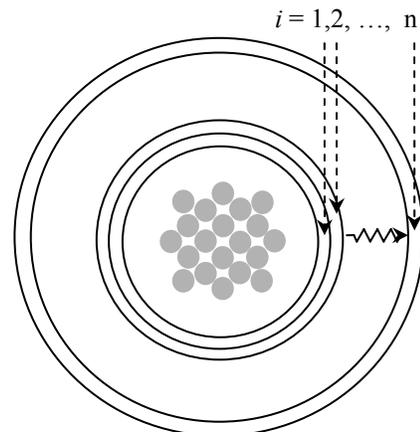


Figure 1: Surrounding fluid separated into  $n$  spherical concentric layers.

fluctuates relative to the time-averaged local density, a local density covariance matrix,  $\tilde{C}$ , is formed and is determined by

$$\tilde{C} = \langle (\rho - \langle \rho \rangle)(\rho - \langle \rho \rangle)^T \rangle \quad (1)$$

where  $\tilde{C}$  is a symmetric matrix,  $\rho$  is an  $m \times n$  matrix of  $m$  observations of  $n$  volume slices surrounding the nanoparticle describing the radial density distribution within the system, and  $\langle \rangle$  denotes time average. Next, the rotational matrix  $\tilde{O}$  composed of the eigenvectors of  $\tilde{C}$  is found such that it transforms  $\tilde{C}$  into the diagonal matrix of eigenvalues  $\tilde{\Lambda}$

$$\tilde{O}^T \tilde{C} \tilde{O} = \tilde{\Lambda} \quad (2)$$

These eigenvectors in  $\tilde{O}$  are the principle components of  $\tilde{C}$  and have been shown to describe the structural configuration in multidimensional space that maximize/minimize fluctuations in density. In general, the highest concentrations of fluctuations occur in the first three eigenvectors of  $\tilde{O}$ , which may account for as much as 95% of the variation. Using these eigenvectors, the configuration of density within the system can then be reconstructed to visualize these variations.

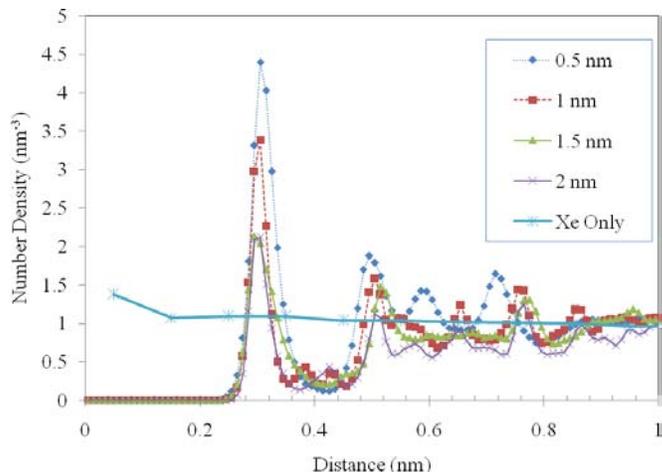
## METHODOLOGY

The base fluid was composed of 426 xenon atoms to maintain a density of approximately  $3 \text{ kg/m}^3$ , which corresponds to conditions of experimentally acquired data. [9] Each nanoparticle, suspended in the base fluid, was made by removing spheres of diameters 1, 1.5, and 2 nm from an fcc lattice structure of platinum atoms. All interatomic interactions in the system were assumed to be of the Lennard-Jones form with parameters defined in Table 1 below.

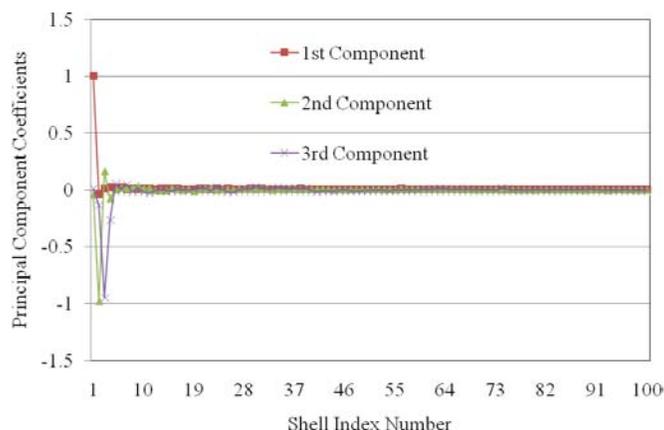
**Table 1. Interatomic interactions for platinum-xenon nanofluid.**

	Xe-Xe	Xe-Pt	Pt-Pt
$\sigma$ (kJ/mol)	1.99	24.05	65.77
$\varepsilon$ (Å)	3.95	2.73	2.54

The simulations were performed using the DL Poly molecular dynamics software. An NVT ensemble was defined for all simulations by a periodic cube with a volume of  $9 \text{ nm}^3$  at a temperature of 200K and pressure of 0 atms, using the Berendsen barostat and velocity rescaling. Each simulation (performed with a 2 fs timestep) was first equilibrated with 100,000 steps and then run for an additional 100,000 steps for an analysis time of 200 ps. The instantaneous density distribution profiles were created using DL Poly's van Hove distinct time correlation function over  $n = 100$  volume slices and 10,000 configurations samples. The principle component analysis was performed using Matlab.



**Figure 2. Time averaged density profile for various analyzed fluids.**



**Figure 3. First three principal components of pure Xe fluid.**

## RESULTS

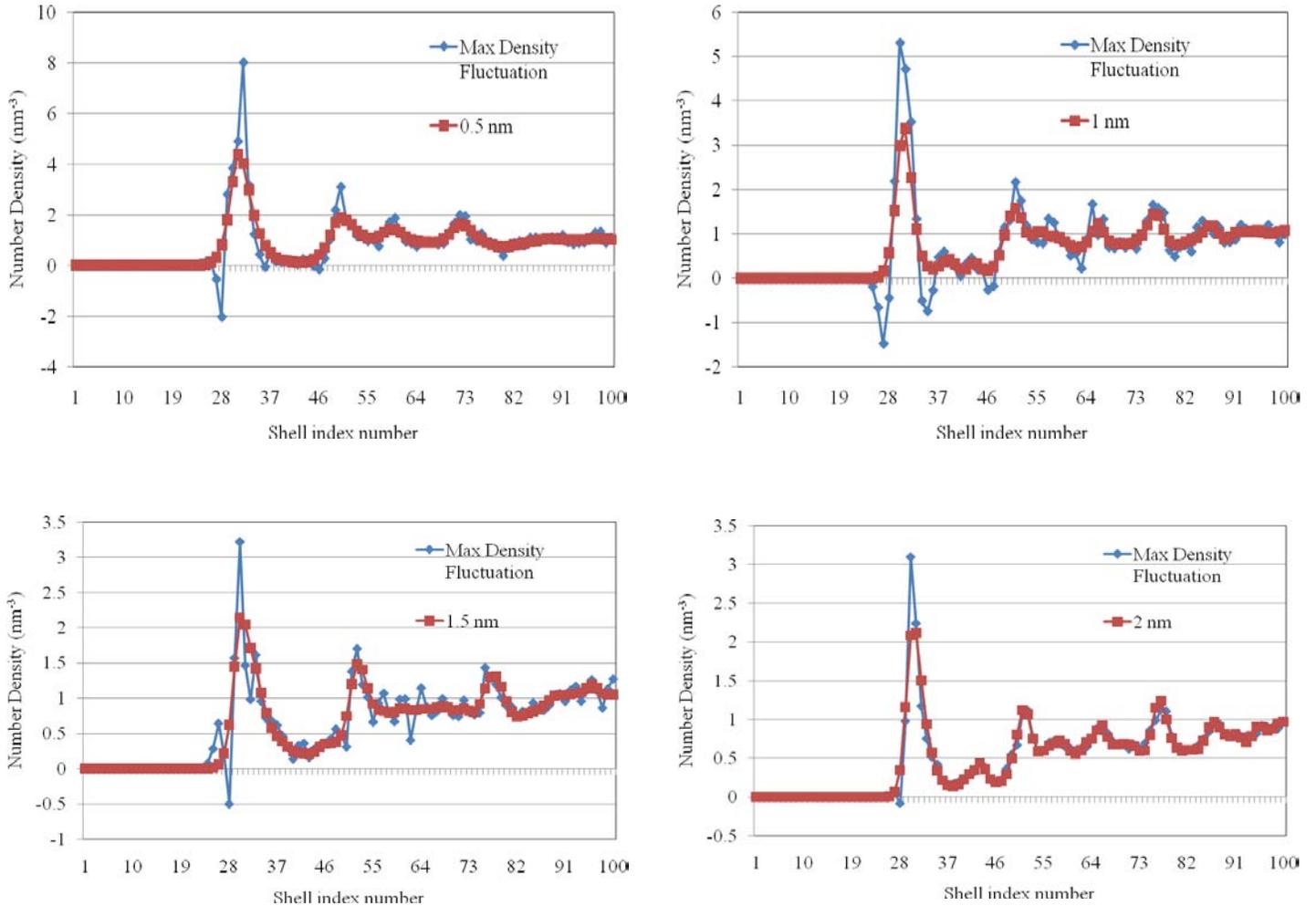
In Figure 2, the time-averaged density for each concentric layer is shown for xenon fluid only and for xenon with a single platinum nanoparticle having diameters of 0.5, 1, 1.5, and 2 nm. As with previous findings, it can be seen that liquid atoms form as many as five layers near the surface of the nanoparticle due to the strong interatomic interactions. Also, it is noticed that density is dependent on the diameter of the nanoparticle, with the number of ordered layers increasing from four (0.5 nm) to almost six (2 nm). The 1.5 nm diameter nanoparticle seems to lose an ordered layer that intuitively would appear  $\sim 0.61 \text{ nm}$  from the surface. This loss could be the result of a shift of xenon atoms from this location to a previous concentric volume which increased, due to nanoparticle size change.

**Table 2. Total variation and percentage of total variation for each principal component.**

	Total Variance	Percent of total variance in...		
		1 <sup>st</sup> PC	2 <sup>nd</sup> PC	3 <sup>rd</sup> PC
Pure Xenon	0.0814	81.7396	8.4986	3.1265
0.5 nm	2.1936	95.3605	3.6244	0.3727
1.0 nm	1.3595	96.6589	2.9298	0.2431
1.5 nm	0.2831	94.2973	4.9689	0.2883
2.0 nm	0.1283	97.8051	1.3198	0.4040

The fluctuations in the density of the 100 concentric shells of the pure xenon fluid over time are shown in Figure 3 by the first three components of the local density covariance matrix which composed 93% of the total variation. The general density pattern remained the same and most of the total variation ( $0.0814 \text{ nm}^{-6}$ ) occurs within the first five concentric shells and was predominantly temporal. For the 0.5 nm

nanoparticle, the total variation increased to  $2.1936 \text{ nm}^{-6}$  and then decreased to approximately the variance of the pure Xe fluid with a value of  $0.1283 \text{ nm}^{-6}$ . A comparison of the mean density distributions with the maximum fluctuations over the time period analyzed (Figure 4), shows that this fluctuation occurs in the local density within the fixed liquid layers and not in the radial direction. The total variance for each of the nanofluids (Table 2) decreases with increasing nanoparticle diameter, and the first principal component increasingly describes the total variance. The maximum fluctuation also corresponds to an instantaneous local density structure where the thermophysical properties differ from the time-averaged values. With a higher local density at specific spherical shell locations distributed around the nanoparticle, the dynamic energy transfer characteristics of the base fluid changes, favoring the amorphous-like structure described earlier.



**Figure 4. Maximum density fluctuation compared to the mean density distribution in fluid for nanoparticles of differing diameters.**

The principal component analysis described in Table 2 also shows that a higher percentage of simulation time is spent in a structure significantly different from the time-averaged structure described by the radial distribution function. Although many thermophysical characterizations of nanofluids are averaged over long time periods ( $>1$ ns), heat transfer characteristics are dynamic and these instantaneous density structures should be taken into account in future calculations.

## CONCLUSIONS

Fluctuations in the density distributions near the surface of a nanoparticle are significant when compared to the time-averaged distribution used in thermophysical characterization of nanofluids. The principal components of the local density covariance matrix showed that over the time period analyzed, greater than 95% of the time is spent in the fluctuated states. The change in the fluid structure, due to these instantaneous fluctuations in density, can be shown to enhance calculated dynamic properties such as thermal conductivity and viscosity.

## ACKNOWLEDGEMENTS

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