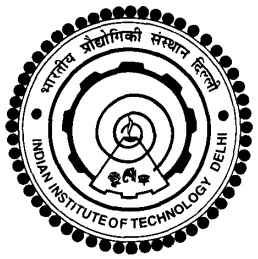
# COMPUTER SIMULATIONS OF TETRAHEDRAL LIQUIDS AND NANOPARTICLE DISPERSIONS

B. SHADRACK JABES




DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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# COMPUTER SIMULATIONS OF TETRAHEDRAL LIQUIDS AND NANOPARTICLE DISPERSIONS

**by**

**B. SHADRACK JABES**

**DEPARTMENT OF CHEMISTRY**

*Submitted*

*in fulfillment of the requirements of the degree of*

**Doctor of Philosophy**

**to the**


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# Certificate

This is to certify that the thesis titled **"COMPUTER SIMULATIONS OF TETRAHEDRAL LIQUIDS AND NANOPARTICLE DISPERSIONS"** is being submitted by **Mr. B. Shadrack Jabes** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy**. This thesis is a record of bona-fide research work carried out by him under my guidance and supervision. In my opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree.

The results contained in this thesis have not been submitted to any other university or institute for the award of any degree or diploma.

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B. Shadrack Jabes Date

# Abstract

This thesis presents molecular dynamics studies of two types of complex fluids: tetrahedral atomic liquids and nanoparticle dispersions. In the case of tetrahedral fluids, relationships between structural order, thermodynamics and transport properties are characterized, using as examples: (a) water, (b) single-component ionic melts ($GeO_2$, $SiO_2$, $BeF_2$), (c) liquid phases of Group IV elements (C, Si, Ge, and Sn) (d) binary ionic melts (LiF-$BeF_2$). Simulations of $GeO_2$ demonstrate structural, pair entropy and diffusional anomalies but no density anomaly, consistent with low degree of tetrahedrality predicted by the radius ratio rules. The transition from simple to tetrahedral liquid behavior is illustrated by the Stillinger-Weber (SW) potential, applicable to group IV elements and water. The density anomaly is observed only at intermediate tetrahedralities, while the heat capacity anomaly exists for all SW systems with a tetrahedral, crystalline ground state. Different tetrahedral liquids are compared with respect to order maps, nesting of anomalous regimes and the relationship between structural order and onset of the density anomaly. Systems with similar order maps in terms of the degree of correlation between tetrahedral and translational order also show similar tetrahedral order distributions at the onset temperature for the density anomaly. The degree of tetrahedrality is controlled by composition in the case of a binary fluid (e.g LiF-$BeF_2$). There is a clear correlation between pair entropy and local tetrahedral order as the fluoroberyllate network forms. Network formation is accompanied by qualitative changes in transport properties, such as breakdown of Rosenfeld-scaling between diffusivity and pair entropy as well as the Nernst-Einstein and Stokes-Einstein relationships. The second category of complex liquids studied here are nanoparticle dispersions of alkyl-thiolated gold clusters in ethane solvent. The pair potential of mean force is shown to have a significant degree of anisotropy due to ligand shell fluctuations that can cause deviations from simple liquid behaviour.

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