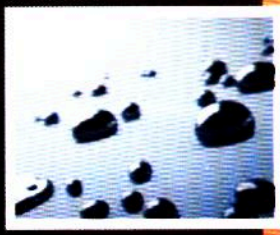

" LIQUID METALS: SEARCHING FOR PROPERTIES AT ELEVATED TEMPERATURES"

30th Inaugural Lecture

of the Federal University of Technology,
Owerri (FUTO), Imo State.

Delivered On
Wednesday, 19th October 2016

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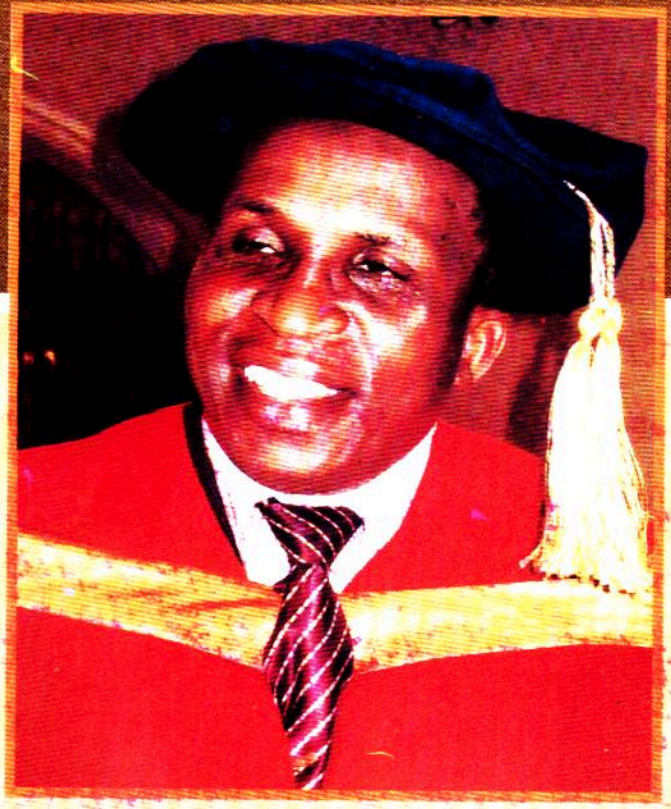

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LIQUID METALS: SEARCHING FOR PROPERTIES AT ELEVATED TEMPERATURES

"In the beginning, God created the heavens and the earth. The earth was formless and empty, and darkness covered the deep waters. And the Spirit of God was hovering over the surface of the waters". Genesis 1:1-2 (NLT)

1.0 INTRODUCTION

Physics is a subject that causes great respect mixed with some kind of fear in many people. It must be noted that Physics is all around us. We can see Physics from the simple home appliances such as the kitchen knife to the space shuttle. All advances in the world today including many destructions are possible due to advances in Physics.

Physics therefore is the scientific subject that studies matter and energy and how they interact with each other. Matter is anything that has weight and occupies space. It ranges from sub atomic particles (i.e. the particles that make up the atom and the particles that make up these particles), to stars and galaxies. On the other hand, energy is the ability of a system to do work or cause an activity. Energy can take the form of motion, light, electricity, radiation, gravity, etc.

Physics can be viewed (without any form of contradiction) as the most fundamental or 'father' of the natural sciences and engineering. For instance, chemistry studies interaction of energy and matter in chemical systems while biology could be seen as application of chemical properties in living things. Today the

principles and laws of Physics are applied in homes, computers, medicines, agriculture, industries and regrettably in wars and for destructive purposes.

1.1 HISTORY OF PHYSICS

The word Physics was taken from the Greek word 'physis' meaning "nature". It is a branch of science developed out of philosophy. It was originally referred to as 'natural philosophy'. It was a term used to describe a field of study concerned with the 'workings of nature'.

The study of physics dates back to Antiquity with the Babylonians and with Hellenistic writers such as Archimedes and Ptolemy. Other examples include the Pre Socratic Philosophers in Greece (650 – 480 BC). Thales (around 580 BC) who was dubbed "the father of Science" for refusing to accept various supernatural, religious or mythological explanations for natural phenomena but proclaimed that every event had a natural cause. He suggested that water is the basic element of matter and experimented with attractions to rubbed amber. Heraclitus (around 500 BC) proposed that the only basic law governing the universe was the principle of change and that nothing remains in the same state indefinitely. This made him one of the scholars in ancient physics to address the role of time in the universe. Also Leucippus and his student Democritus (5th century BC) were the first to develop the theory of atomism.

Aristotle (384 – 322 BC) a student of Plato, promoted the concept that observation of physical phenomena could ultimately lead to the discovery of the natural laws governing them. Aristotle founded the system known as Aristotelian Physics. He attempted to explain ideas such as motion and gravity with the 'theory of four elements'. Aristotle believed that all matter was made of aether or some

combination of four elements namely earth, water, air and fire. According to Aristotle, these four terrestrial elements are capable of inter-transformation into their natural state. Aristotelian physics remained the mainstream scientific paradigm in Europe until the time of Galileo Galilei and Isaac Newton.

Isaac Newton born in England in the year of Galileo's death carried to full fruition the ideas of Galileo and others who preceded him. In 1686, he presented his three laws of motion in his Philosophiae Naturalis Principia Mathematica, popularly called the Principia. Newtonian physics held sway from the 17th century AD and mechanical models became evident. The interpretation of macroscopic phenomena was adequately done using Newton's laws.

Next were efforts made in the interpretation of the nature of light. Prominent in this exercise were Newton's corpuscular theory of light, Huygen's wave theory of light and Thomas Young's experiment (1801). These theories attempted to extrapolate the idea of waves (sound to light) propagating in some elastic medium which is also present in vacuum called the aether. In 1887, the famous Michelson – Morley experiment conclusively demonstrated that the aether does not exist. This result led Albert Einstein (1905) to formulate his postulates and the special theory of relativity.

The era of Modern Physics was kicked off by Max Planck (1900), when in his attempt to solve the problem of the interpretation of black body radiation introduced the idea of energy quantization, which was the forerunner of Quantum Mechanics. Quantum Mechanics along with Relativity Theory form the foundation of Modern Physics.

Time will fail us to mention in details the early discoveries in physics, like the discovery of electron by J. J. Thompson (1897), x-ray by Roentgen (1895), radioactivity by Henri Becquerel (1896), the development of electromagnetic theory and the detection of electromagnetic waves by Hertz (1889). The above discoveries led to revolution in power, as electric power was substituted for fossil fuels and human muscle power. Radio and television were developed and today we have telecommunication.

To conclude this history, we give below a brief table of timeline discoveries in physics. This table shows the advances in the knowledge of the laws of nature consisting either of experimental discoveries or theoretical proposals that were confirmed experimentally.

Table 1 Timeline advances in physics as adapted from (http://en.wikipedia.org/wiki/Timeline_of_fundamental_physics_discoveries)

Advances in the knowledge of the laws of nature consisting either of experimental discoveries or theoretical proposals that were confirmed experimentally.	
250 BC	Archimedes principle: Archimedes
1514	Heliocentrism: Nicholas Copernicus
1589	Galileo's Leaning Tower of Pisa experiment: Galileo Galilei
1600	Earth's magnetic field discovered : William Gilbert
1613	Inertia: Galileo Galilei
1621	Snell's law: WillebrordSnellius
1660	Pascal's Principle: Blaise Pascal
1660	Hooke's law: Robert Hooke
1687	Laws of motion and law of gravity: Newton
1782	Conservation of matter: Lavoisier
1785	Inverse square law for electric charges confirmed: Coulomb
1801	Wave theory of light: Young
1803	Atomic theory of matter: Dalton

1806	Kinetic energy: Young
1814	Wave theory of light, interference: Fresnel
1820	Evidence for electromagnetic interactions: Ampère, Biot, Savart
1824	Ideal gas cycle analysis, internal combustion engine: Sadi Carnot
1827	Electrical resistance,.: Ohm
1838	Lines of force, fields: Michael Faraday
1838	Earth's magnetic field: Weber
1842–3	Conservation of energy: Mayer, Kelvin
1842	Doppler effect: Kelvin
1845	Faraday rotation (light and electromagnetic): Faraday
1847	Conservation of energy 2: Joule, Helmholtz
1850–1	Second law of thermodynamics: Clausius, Kelvin
1857-9	Kinetic theory: Clausius, Maxwell
1861	Black body: Kirchhoff
1863	Entropy: Clausius
1864	Dynamical theory of the electromagnetic field: Maxwell
1867	Dynamic theory of gases, Maxwell
1871–89	Statistical mechanics: Boltzmann, Gibbs
1884	Boltzmann derives Stefan radiation law
1887	Electromagnetic waves: Hertz
1893	Radiation law: Wien
1895	X-rays: Röntgen
1896	Radioactivity: Becquerel
1897	Electron: Thompson
1900	Formula for Black body radiation: Planck
1905	Special relativity: Einstein Photoelectric effect: Einstein Brownian motion: Einstein

1905	Photoelectric effect: Einstein
	Brownian motion: Einstein
	Equivalence principle
1911	Discovery of the Atomic nucleus: Rutherford
	Superconductivity: KamerlinghOnnes
1913	Bohr model of the atom: Bohr
1916	General relativity: Einstein
	Stern–Gerlach experiment
1923	Matter waves
	Galaxies
	Particle nature of photons confirmed
1925–7	Quantum mechanics
1925	Stellar structure understood
1927	Big Bang: Lemaître
1928	Antimatter predicted: Dirac
1929	Expansion of universe confirmed: Hubble
1932	Antimatter discovered: Anderson
	Neutron discovered: Chadwick
1933	Invention of the electron microscope: Ernst Ruska
1937	Muon discovered: Anderson&Neddermeyer
1938	Superfluidity discovered
	Energy production in stars understood
1939	Uranium fission discovered
1944	Theory of magnetism in 2D: Ising model
1947	Pion discovered
1948	Quantum electrodynamics

1948	Invention of the Maser and Laser - Charles Townes
1956	Electron neutrino discovered
1956–7	Parity found violated
1957	Superconductivity explained
1959–60	Role of topology in quantum physics, predicted and confirmed
1962	SU(3) theory of strong interactions Muon neutrino found
1963	Quarks predicted = Murray Gell-Mann and George Zweig
1967	Unification of weak and electromagnetic interactions Solar neutrino problem found Pulsars (neutron stars) discovered
1968	Experimental evidence for quarks found
1968	Dark Matter theories - Vera Rubin
1970–3	Standard model of elementary particles invented
1971	Helium 3superfluidity
1974	Black hole radiation predicted Renormalization group Charmed quark found
1975	Tau lepton found
1977	Bottom quark found
1980	Quantum Hall effect
1981	Theory of cosmic inflation proposed
1982	Fractional quantum Hall effect
1995	Bose–Einstein condensate found : Wolfgang Ketterle
1995	Top quark found
1998	Accelerating expansion of universe found
1999	Slow light experimentally demonstrated : LeneVestergaardHau
2000	Tau neutrino found
2003	WMAP observations of Cosmic microwave background
2012	Higgs Boson found
2014	Gravitational waves detected from Cosmic microwave background

1.2 STUDY OF PHYSICS

The study of physics can be done as theoretical, experimental or computational. Theoretical physics employs mathematical models and abstraction of physical objects and systems to rationalize, explain and predict natural phenomena. Theoretical physics produces physical theories. A physical theory is a model of physical events. It is judged by the extent to which its predictions agree with empirical observations. The quality of a physical theory is also judged by its ability to make new predictions which can be verified by new observations.

Theoretical physics can be approached in one of different ways. "Phenomenologists" for example employ semi-empirical formulas to agree with experimental results, often without deep physical understanding. "Modelers" (also called "model builders") try to model speculative theories that have certain desirable features or apply the technique of mathematical modeling to physics problems. Some other theorists attempt to create approximate theories, while others try to unify, formalize, reinterpret or generalize extant theories or create completely new ones altogether. In general, theoretical physicists use mathematics to describe certain aspects of nature.

Experimental physics consists of disciplines and sub-disciplines in the field of physics that are concerned with the observation of physical phenomena and experiments. Experimental physics is concerned with data acquisition, data acquisition methods and the detailed conceptualization and realization of laboratory experiments. This is in contrast with theoretical physics, which is more concerned with predicting and explaining the physical

behavior of nature.

Experimental physics uses two main methods of experimental research which are controlled experiments and natural experiments. Controlled experiments involve often the use of laboratories as laboratories can offer a controlled environment, while natural experiments are used, for example, in astrophysics when observing celestial objects where control of the variables in effect is impossible.

Computational physics is the study and implementation of numerical methods to solve problems in physics for which a quantitative theory already exists. Computational physics does not create theories, rather it makes use of existing theories to produce results which can be compared with experiments.

Computational physics is sometimes regarded as a sub-discipline (or offshoot) of theoretical physics. However, it is also viewed as an intermediate branch between theoretical and experimental physics. It is also considered a third way that supplements theory and experiment. It is well known that in physics, many theories that are usually based on mathematical models are used to predict precisely how systems behave. Unfortunately, it is often difficult and sometimes impossible to solve these mathematical models for a particular system to produce useful predictions. In situations like these, numerical approximations are used.

Computational physics is the subject that deals with these numerical approximations. These approximation of solutions are written as finite (and typically large) number of simple mathematical operations or algorithms, and a computer is used to

perform these operations and compute an approximated solution and expected error.

Some examples of areas that lie within the scope of computational physics include;

- Large scale quantum mechanical calculations in nuclear, atomic, molecular and condensed matter physics
- Large scale calculation in such fields as hydrodynamics, astrophysics, plasma physics, meteorology and geophysics
- Simulation and modeling of complex physical systems such as those that occur in condensed matter physics, medical physics and industrial applications
- Experimental data processing and image processing
- Computer algebra, development and applications

It is worthy to note that advances in microelectronics, numerical analysis and computer science, have all impacted positively on computational physics. Computer graphics and visualization now play an important role in the scientific process as they can provide a greater understanding of physical processes. The huge increase in the power of computers in recent years has made an impact on the role of computational physics. In some cases,an entire problemcan now be solved computationally without the need for any experimental input.

2.0 MATTER

We have earlier described Physics as a scientific subject that studies MATTER and ENERGY and the interaction between them. Matter as we know is anything that has weight and occupies space. Matter is classified into four states which are solids, liquids, gas and plasma. A brief description of each state is given below.

2.1 SOLID

Solid is a state of matter that is characterized by structural rigidity and resistance to changes in shape and volume. The atoms in a solid are tightly bound to each other, either in a regular geometric lattice or irregularly. Solids can be classified as metals, minerals, ceramics, organic solids such as wood and polymers, composite materials, semiconductors, nanomaterials and biomaterials. These classes of solids can be categorized structurally as crystalline or amorphous.

Crystalline solids are those solids whose constituents are arranged in a regular pattern. In some cases, the regular ordering can continue unbroken over a large scale (Fig. 1).

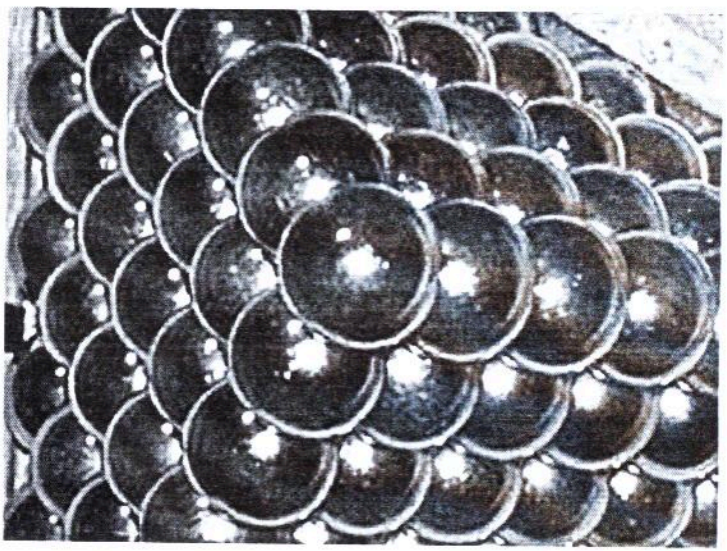

Fig 1: Closely packed atom in a crystalline solid.

(http://en.wikipedia.org/wiki/file:Fcc_lattice_4.jpg)

Examples of crystalline solids are metals, diamonds and most ceramics. Amorphous solids do not exhibit a long range order in the position of the atoms. Examples of amorphous solids include polystyrene and glass.

2.2 GAS

In terms of atomic or molecular arrangement and in contrast to the solid state, the atoms or molecules in the gaseous state are vastly separated and distributed randomly and their motions seem to be completely irregular as they can freely translate throughout the whole volume in which they are contained. A gas may be made up of individual atoms like in the case of visible gas or elemental molecules made from one type of atom like oxygen or compound molecules made from a variety of atoms like carbon dioxide.

2.3 PLASMA

Plasma can be loosely described as an electrically neutral medium of positive and negative particles. The overall charge of a plasma is roughly zero. Even though the particles are unbound, these particles are not 'free'. When the charges move, they generate electrical currents with magnetic fields and as a result, they are affected by each other's fields. This governs their collective behavior with many degrees of freedom. Plasma consists of charged particles. Heating a gas may ionize its molecules or atoms. This will either increase or reduce the number of electrons in them thus turning it into plasma. Ionization can be induced by other means such as a strong electromagnetic field applied with a laser or microwave generator. Plasma can also be created by the application of an electric field on a gas.

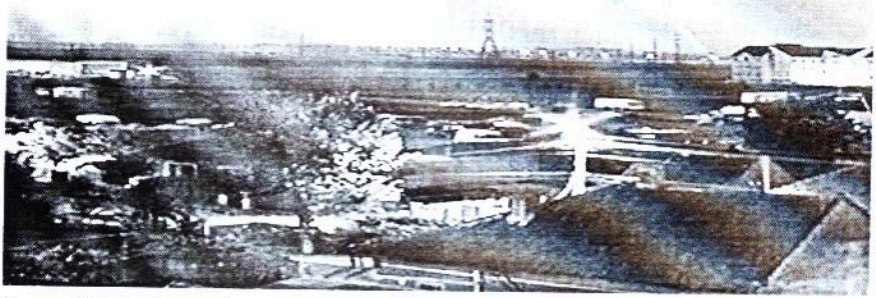

Fig 2:Lightning is an example of plasma present at Earth's surface.(http://en.wikipedia.org/wiki/file:Lightning_over_Oradea_Romania_3.jpg)

2.4 LIQUID

The liquid state of matter is made up of tiny vibrating particles of matter, such as atoms and molecules. They are held together by intermolecular bonds. Like gas, a liquid is able to flow and take the shape of the container but unlike gas, a liquid does not disperse to fill every space of a container. Liquid particles unlike solids, are bound firmly but not rigidly. They are able to move around one another freely, resulting in a limited degree of particle mobility. In a liquid, atoms do not form a crystalline lattice as in solids and do not move far apart from each other as in gases. They do not show any form of long range order. This is evidently shown with the absence of Bragg peaks in x-rays and neutron diffraction studies.

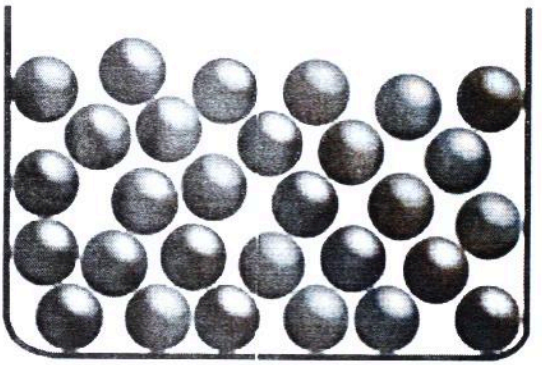

Fig 3:Structure of a classical monatomic liquid. Atoms have many nearest neighbors in contact, yet no long-range order is present. (http://en.wikipedia.org/wiki/file:teilchenmodell_fluessigkeit.sog)

3.0 STUDY OF LIQUIDS

3.1 SIMPLE LIQUIDS

From my personal point of view, I consider the liquid state as the first state of matter that existed at creation. I buttress this with the statement of the Bible in Genesis chapter 1 verses 1 and 2. I will therefore wish to arrange the states of matter in order of existence as liquid, plasma, gas and solid. The solid was the last state of matter to come into existence.

It is therefore not surprising that the study of the liquid state of matter was not as direct as that of solid and gaseous states. By the early 19th century man has perfected the theories of the ideal crystalline solids and the ideal gas. However it was difficult to derive a model of an 'ideal liquid'. This may not be unconnected with the fact that at creation, the liquid state was part of the earth that was declared "formless".

The concept of idealized models is very useful in studying the

properties of matter. An ideal model of matter can be defined as a hypothetical substance which has the characteristic features of real matter. One advantage of these ideal models is that they are simple to treat mathematically and their concepts are usually clear.

For the solid state, the ideal model is an ideal solid or a perfect crystal. In this model, the atoms are regularly arranged at the lattice points. This regular arrangement of atoms is long ranged, three-dimensional and undisturbed by thermal agitation. On the other hand, the idealized model for the gaseous state is the ideal gas. In this model, each atom can freely translate throughout the volume in which it is contained. These simple results lead to useful results for real solids and gases. Such results include, Einstein's formula for specific heat, the Brillion zone, the Boyle-Charles law, etc. Extensions and corrections of these idealized models for describing real substances can provide close agreement with experimental data.

Unfortunately, it is very difficult to provide an ideal model for the liquid, hence it is considerably more difficult to explain the behavior of a liquid. The atom in the liquid state can easily migrate through fluctuations in density arising from the thermal motion of surrounding atoms. An atom in the liquid state will be interacting with the atoms which surround it, vibrating as though it were an atom in the solid state. At the next moment it may behave as an atom in the gaseous state and move freely about the surrounding. Here, atomic distances and time scales are needed for a good understanding of the structure and properties of liquids.

Liquids can be classified into simple and complex liquids. Simple liquids consist of liquids with one component atom. Examples include metallic liquids. However, as the number of components or atom types in a liquid increases, the liquid complexity increases. Even though common in nature, water is classified as a complex

liquid.

3.2 LIQUID METALS

Liquids from pure metals provide us with the simplest form of a liquid. This is because they are mono-component and may possess only one form of interaction among the atoms. The study of the properties of liquid metals has been of considerable interest to researchers. This is probably because apart from being the simplest form of the liquid state, it has been considered as a possible source of information on the interactions within their solid counterparts. For instance, Ashcroft and Lekner(1966) reported that the average band gap for metals was deduced from the knowledge of their resistance in the liquid state. It is also now well known that liquid metals offer unique properties as high temperature working fluid. Hensel and Edwards (1996) wrote on the use of liquid sodium in fast-breeder nuclear reactors, particularly given sodium's reactive nature.

Today, there is a new class of metallic alloys called 'Liquidmetals' or 'Vitreloy'. They are a class of amorphous metal alloys. They are called 'liquidmetals' because they retain their amorphous liquid structure on cooling from melt. They were developed by California Institute of Technology research team. The amorphous structure of this category of alloys was achieved by relatively slow cooling rates. This 'liquidmetal' solid alloy was introduced for commercial use in 2003.'Liquidmetal' alloys combine a number of desirable material features, including high tensile strength, excellent corrosion resistance, very high coefficient of restitution and excellent anti-wearing characteristics. For example, 'liquidmetal' alloy is stronger than high-strength titanium, with a yield strength of 1640 MPa. High-strength titanium (Ti-6Al-4V) has a yield strength of 830 Mpa and an ultimate tensile strength of only 900 Mpa. Like most glasses, the yield strength of 'liquidmetal' alloy is nearly identical to its

ultimate tensile strength, meaning that when the material is stressed to its yield limit, rather than plastically deforming, it will break, and is therefore technically considered brittle, even though it is highly elastic.

In addition, on July 25, 2013, the US Patent & Trademark Office published a patent application from Apple that reveals methods for forming three-dimensional structures which may be configured to provide desirable characteristics with respect to light, sound, and fluid travel. Hidden within Apple's patent is the fact that it relates to liquid metal applications. (http://www.patentlyapple.com/patently-apple/2013/07/apple-invents-methods-of-forming-3d-structure-with-liquid-metal.html)

Since the unveiling of these technological applications of liquid metals and the thrilling connection between liquids and their solid counterparts, the study of liquid metals has passed from being mere laboratory curiosities to inroads to information for engineering, technological and scientific applications.

Presently, there is an increasing need to understand the various properties of oxides and salts in the liquid state due to their important role in metallurgical processes such as slag-metal reactions.

Emerging and technological applications often require the use of metallic alloys. This is as a result of their improved properties of strength, electrical conductivities, corrosion resistance and refractory tendencies. This improved quality of engineering materials obtained through alloying makes metallic alloys of high scientific interest. Their structures and properties in the molten state are also believed to be pointers to certain interactions in the solid state and in themselves are used for far reaching technological applications.

3.3 COMPUTATIONAL APPROACH IN THE STUDY OF LIQUID METALS

The liquid state of matter has been studied over a long period of time from both the theoretical and experimental stand points. Experimental observations on liquids can be traced down to the observation of Brownian motion and presently to recent experiments on neutron scattering. Experimental works which include direct and indirect measurements have improved the understanding of the structure and particle dynamics that characterize liquids.

Theoreticians on the other hand have tried to construct simple models which explain how liquids behave. A large number of metals become liquid at very high temperatures. At these elevated temperatures, some experimental measurements of the properties of such metals or alloys are very difficult, yet knowledge of the properties and dynamics at such temperatures may be relevant in the understanding of their applications. The need therefore arises on how to determine the properties at elevated temperatures beyond the experimental limit. Under the present circumstance, computational methods become inevitable.

In this section I briefly introduce the major computational approaches to the study of liquid metals. These approaches include methods of model calculations, integral equation approach and computer simulation methods.

3.3.1 MODEL CALCULATION METHODS

This involves the use of analytical solutions of liquid state equations which are based on some model approximations. These methods can be used to study structural, transport, surface and thermodynamic properties of liquid metals and alloys. The analytical solutions are obtained based on simple potentials

associated with a given model. These models are expected to mimic sufficiently well, the basic features of the real metal and in particular its liquid structure. Some of the model fluids include the following:

i) The Neutral Hard Sphere (NHS) Model: This model assumes that the interacting atoms in a liquid metal are like neutral (uncharged) hard sphere of radius σ/2, where interacting potential is given by

$$V(r) = \begin{cases} \infty, & r < \sigma \\ 0, & r > \sigma \end{cases} \qquad (3.1)$$

ii) One-Compound Plasma (OCP) Model: The One-Compound Plasma consists of point particles carrying a charge Ze and embedded in a homogeneous neutralizing background with a potential

$$V(r) = \frac{\Gamma}{r} \qquad (3.2)$$

Where Γ is the plasma parameter defined as the ratio of the electrostatic energy E_s to the thermal energy E_t.

where $E_s = \frac{Z^2 e^2}{R_s}$

and $E_t = K_B T$

R_s is the ion sphere radius, Z is the valence of the metal, e is the electronic charge, K_s is the Boltzmann constant and T is absolute temperature.

iii) The Charged Hard Sphere (CHS) Model: In this model, each charge Ze is enclosed in a hard sphere of radius σ/2, embedded in a uniform neutralizing background. Hence, it is characterized by two disposable parameters, the charge Ze and the hard sphere diameter σ. The particles interact with each other via the potential

$$V(r) = \begin{cases} \infty, & r < \sigma \\ \frac{(Ze)^2}{r}, & r > \sigma \end{cases} \qquad (3.3)$$

iv) The Soft Sphere (SS) Model: Thismodel is also known as the inverse power potential because it uses the 12th-power as a reference system. The properties of this reference system are expressed in terms of hard sphere packing fraction , by using a modified form of the hard-sphere variational theory. Hence the hard-sphere packing fraction is used as the scaling parameter. The potential of the soft sphere is a modification of the hard sphere and is given as;

$$V(r) = \begin{cases} \infty, & r < \sigma \\ \epsilon\left(\frac{(r^*)^n}{r}\right), & r > \sigma \end{cases} \quad (3.4)$$

Where σ is the sphere diameter, ϵ is a constant, $r^* = 1$ and n = 12.

v) The Quasi-Chemical Approximation (QCA): This model is a statistical and thermodynamic model used mostly for binary liquid alloys. This model assumes that a binary alloy consists of a mixture of A atoms, B atoms and a number of complexes AB. It also assumes that the energy of AB, BB and AA bonds depends on the bond being part of the complex or not. The grand petition function for this model is given as;

$$\Xi^2 = \xi_A^2 \phi_A^{2(2-1)} \ell_{AA} + \xi_B^2 \phi_B^{2(2-1)} \ell_{BB} + 2\xi_A \xi_B \phi_A^{2-1} \phi_B^{2-1} \ell_{AB} \quad (3.5)$$

where $\xi_i = q_i(T) exp\left(\frac{\mu_i}{K_B T}\right)$

and $q_i(T)$ are the partition functions associated with inner and translational degrees of freedom of atom i. $\mu_i s$ are the chemical potentials.

$$\ell_{ij} = exp\left(\frac{-(\epsilon_{ij} + P_{ij} \cdot \Delta\epsilon_{ij})}{K_B T}\right) \quad (3.6)$$

ϵ_{ij} denotes the energy of the free ij bond and $\Delta\epsilon_{ij}$ is the change in the energy if the ij bond is in the complex $A_\omega B_\omega$. P_{ij} denotes the probability that the bond in the cluster is part of the complex. ω_i are constants.

Using the above model, the excess free energy of mixing for the alloy is given by the expression

$$\frac{G^{xs}m}{NK_BT} = \int_0^c \ln\gamma dc \qquad (3.7)$$

Where is the ratio of activity coefficients of the constituted species of the alloy and c is the concentration of the A specie.. The free energy of mixing is very strategic in the determination of an important parameter 'the concentration-concentration fluctuation at the long wavelength limit ($S_{cc}(0)$) given as

$$Scc(0) = \frac{NK_BT}{(\delta^2 Gm/\delta c^2)TPN} \qquad (3.8)$$

where c is the concentration of the A species of the alloy.

The quantity $S_{cc}(0)$ is a very important parameter in studying order in the liquid binary alloy. The measure on whether an alloy has tendency to homocoordination and heterocoordination is determined from the departure of $S_{cc}(0)$ from its ideal values. Basically, if $S_{cc}(0)$ is less than ideal values, it is an indication of heterocoordination (preference of unlike atoms to pair as nearest neighbours) while if $S_{cc}(0)$ is greater than ideal values, it implies the alloy has tendency to homocoordination (preference of like atoms to pair as nearest neighbours). If $S_{cc}(0)$ is equal to ideal values, the alloy manifests ideal mixing behaviour. The $S_{cc}(0)$ is also used to determine the ratio of the mutual and self-diffusivities of the alloy species.

$$\frac{Dm}{Ds} = \frac{c(1-c)}{Scc(0)} \qquad (3.9)$$

where D_m is the mutual diffusivity and D_s the self-diffusivity. This parameter is of physical significance because of its possible application in technology and corrosion phenomena.

The statistical models are of great importance in the study of surface properties of liquid metals and alloys at elevated temperatures. Studies of surface have become essential from the point of view of understanding in a fundamental way, such surface related phenomena as heterogeneous catalysis, epitaxial growth and corrosion as well as mechanical behavior and kinetics of phase transformation.

Works of many researchers such as Moran-Lopez and Falicov (1978), Urias and Moran-Lopez (1981), Georges and Egry (1995) show that the surface composition of the alloy differs from that in the bulk. This phenomenon known as surface segregation is believed to have strong influence on many surface interactions. Some of the properties determined under surface studies include surface tension, surface concentration of alloy species and surface concentration-concentration fluctuation at longwavelength limit used in deducing the extent of order on the surface of the liquid alloy.

Transport properties such as viscosities and diffusivities of liquid alloys at elevated temperatures and throughout the concentration range are most times difficult to determine experimentally.This atomic diffusion phenomenon control mass transport and hence affect the distribution of solute in a solid or liquid solution. Model calculation and simulations provide alternative means of determining these properties at elevated temperatures where experimental determination is difficult or very costly.

3whereD_m is the mutual diffusivity and $D_s$the self-diffusivity. This parameter is of physical significance because of its possible application in technology and corrosion phenomena.

The statistical models are of great importance in the study of surface properties of liquid metals and alloys at elevated temperatures. Studies of surface have become essential from the

.point of view of understanding in a fundamental way, such surface related phenomena as heterogeneous catalysis, epitaxial growth and corrosion as well as mechanical behavior and kinetics of phase transformation.

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3.3.2 INTEGRAL EQUATION APPROACH

The integral equation methods are among the techniques used in the study of the structure and thermodynamic properties of the liquid systems. The integral equation methods are defined by the Oinstein-Zernike (OZ) relation which reads for N-component case as

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Oinstein-Zernike (OZ) relation which reads for N-component case as

$$h_{ij}(r) = C_{ij}(r) + \sum_k C_k n \int h_{ik}(r^1)\, C_{kj}(|r - r^1|)dr \qquad (3.10)$$

wherei, j, k = 1, . . ., N together with a nonlinear closure relation, relating the potential and structure functions in a fundamental way. The use of integral equations is enabled due to the technical advancement made in the development of two very efficient algorithms for solving non-linear integral equations thereby forcing quick convergence of iterations. The principal disadvantage of integral equation approach is that to achieve thermodynamic self-consistency, the method becomes computationally time consuming.

3.3.3 COMPUTER SIMULATIONS

Two methods normally employed in computer simulation are the Molecular Dynamics and Monte Carlo Simulation methods.

In Molecular Dynamics (MD) simulation method, the Newtonian equations of motion are numerically solved for a given system, i.e. the positions and velocities of the atoms at subsequent time intervals are computed and stored. Molecular dynamics simulation method uses the derivative of the pair potential in the computational process. It can be used to study equilibrium properties and time dependent phenomena evaluated at averaged times. The molecular dynamics simulations have successfully been applied with impressive results.

The Monte-Carlo Method (MC) determines the equilibrium properties of a system using particle position by applying a random sampling technique which is generated by the computer. The

Monte-Carlo method uses the pair potential and is restricted only to the study of the configurational thermodynamics properties.

4.0 MY CALCULATIONS

My Vice Chancellor Sir, in a few subsections, I want to make a brief review of my calculations and contributions in the study of liquid alloys. As it is obvious, the only liquid metal at room temperature is mercury (Hg), for this liquid metal, the experimental determination of its properties poses no serious difficulty. However, for some other metals and elements, they become liquid at elevated temperature. At such elevated temperatures, determination of some properties is either difficult or too costly to carry out. My works over these years have bothered on determination of properties of liquid metals especially the alloys at high temperatures. Some of these determined properties have in a number of ways helped to elucidate or throw more light on behaviours of these metals or alloys. Under this section, I will present my works under five subheadings which are structural studies, thermodynamic studies, transport properties, surface properties and molecular dynamics studies.

4.1 STRUCTURAL STUDIES

The structural studies focused on some moltensilicides such as Cu-Si and Ni-Si. These are a simple family of materials which combine metals with silicon. In the solid state, they have potential usefulness in the manufacture of new generation of microchips (Reader, 1992; Maex, 1993)

In experimental studies of structures of liquid metals and their alloys, one determines the pair distribution function g(r). This is carried out through the use of x-ray, neutron, or electron diffraction

techniques. The pair distribution function is then obtained from measured intensities by using the formula.

$$g(r) = 1 + \frac{1}{2\pi^2 n_0 r}\int_0^\infty q\left(\frac{I}{Nf^2} - 1\right) Sin\,(qr)\,dq \qquad (4.1)$$

where $q = \frac{4\pi Sin\,\theta}{\lambda}$

2θ is the scattering angle (of x-rays), is the wavelength of the incident beam, fis the atomic scattering factor and I is the intensity of reflected beams from the liquid. The pair distribution function g(r) is proportional to the probability of finding a given atom at a distance r from a reference atom. The relative intensity (I/Nf^2) is defined as the liquid structure factor S(q). The calculation of other properties such as electrical resistivity, thermopower, knight shifts, diffusion coefficients, orderingetc of the liquid alloy depends on the ability to obtain the partial structure factors $S_{ij}(q)$ from the total structure factor S(q). Obtaining these partial structure factors $S_{AA}(q)$,$S_{BB}(q)$ and $S_{AB}(q)$ (for a A – B binary alloy) from experiment is difficult since it will require at least three independent measurements for evaluating these. Model calculations offer a simpler way of determining the structure factors. Here the Lebowitz solution of the Percus-Yevick equation for binary mixtures with a square well attractive tail as a perturbation (Gopala and Satpaty, 1990; Gopala Rao and Murty, 1975) was applied to study structural properties in Ni-Si, Cu-Si and Pb-Bi binary alloys. This calculation first yielded the Ashcroft-Langreth partial structure factors. The Bhatia and Thornton partial structure factors (Bhatia and Thornton, 1970) were obtained from the Ashcroft-Langrethpartial structure factors. The Bhatia-Thornton partial structure factors relates structural properties of a liquid

metallic alloy to its thermodynamic properties through th concentration-concentration fluctuation at the long wavelengt Scc(0).

The results of the calculations showed that the model did better fo the Pb-Bi, Cu-Si than the Ni-Si. Structurally Si, has more influence o Ni than Cu. The results are shown in Figs 4 – 6.

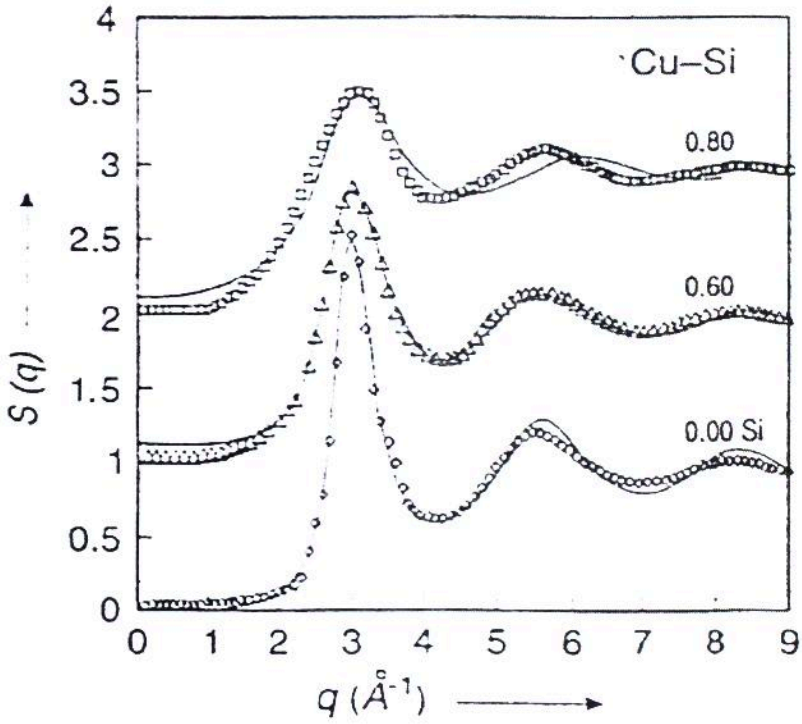

Fig 4: Total structure factor of Cu-Si liquid alloy at temperatures above 1300K. Points represent experimental values while lines represent calculated values.

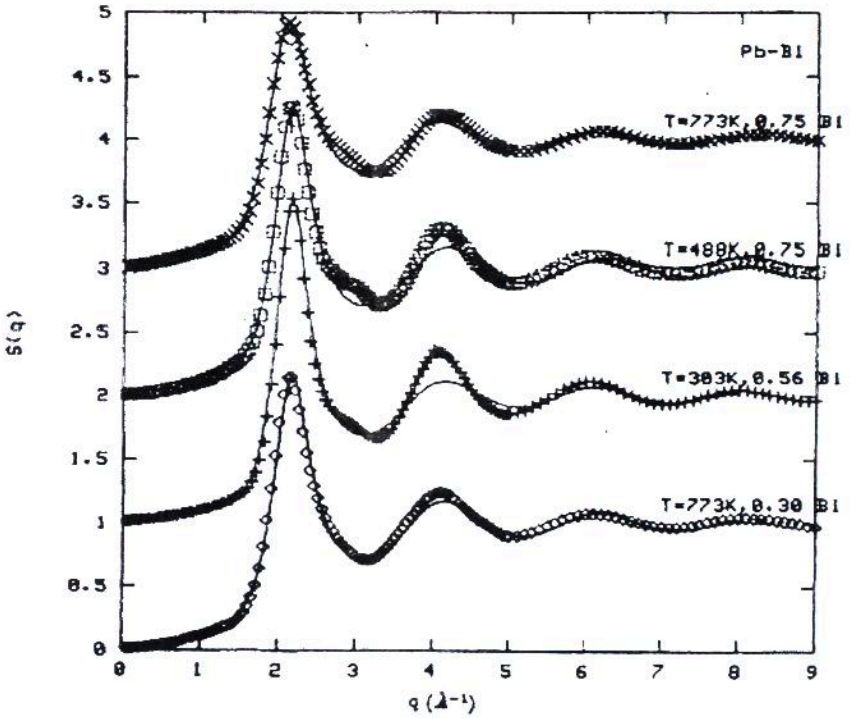

Fig 5: Total structure factor of Pb-Bi liquid alloy at temperatures up to 773K. Points represent experimental values while lines represent calculated values.

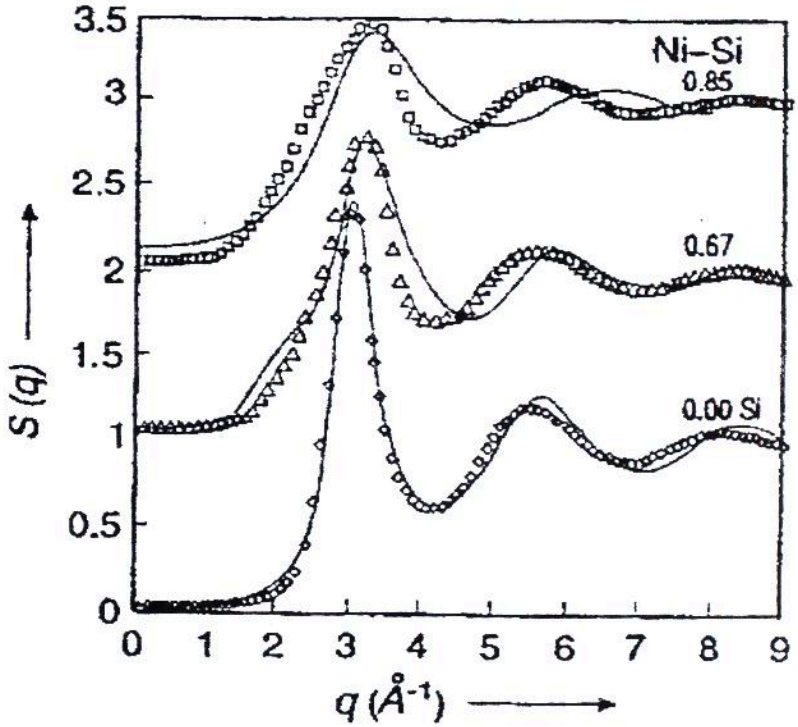

Fig 6: Total structure factor of Ni-Si liquid alloy at temperatures above 1400K. Points represent experimental values while lines represent calculated values.

The study of the $S_{cc}(0)$ suggests that all three alloys form compounds in their liquid state where Cu-Si exhibits the highest tendency among the three alloys studied. This is also a pointer to possible glass forming tendencies of these alloys. The detail of this work was published by Taylor and Francis in Physics and Chemistry of liquid (Anusionwu et al., 1997) and also in Zeitchrift fur Metalkunde

(Akinlade et al., 1998)..

Of more interest is the study of the Pb-Bi mollen alloy. Pb-Bi liquid alloy on its part has aroused research interests. Previous studies (Bhatia and Hagroove, 1974; Bhatia and Singh, 1984; Anusionwuet al., 1997) indicate that Pb-Bi liquid alloy is 'anomalous', partly because it manifests a small positive departure from linearity in the concentration dependence of liquid alloy volume and further a change in the total coordination number at high Bi concentration was observed. To understand further the observed change in the coordination number of the Pb-Bi liquid alloy, our study determined in detail using calculations to obtain the partial coordination numbers of liquid alloy and to observe its trend with variation in Bi concentration. To actualize this, the partial pair distribution functions were obtained from the Ashcroft-Langreth partial structure factors using the relation.

$$g_{ij}(r) = 1 + (2\pi^2 n_0 \gamma)^{-1} \int_0^\infty q\left(S_{ij}(q) - \delta ij\right) Sin(qr)dq \qquad (4.2)$$

The partial coordination numbers are then obtained using the expression ·

$$Z_{ij} = 2\int_{\gamma_0}^{\gamma_m} 4\pi\gamma^2 n_0 g_{ij}(r)dv \qquad (4.3)$$

Where γ_0 denotes the position for the beginning value of the pair distribution function and γ_m is the position of the peak value, the calculated partial pair distribution functions for Pb-Bi are shown below in figs 7 – 9.

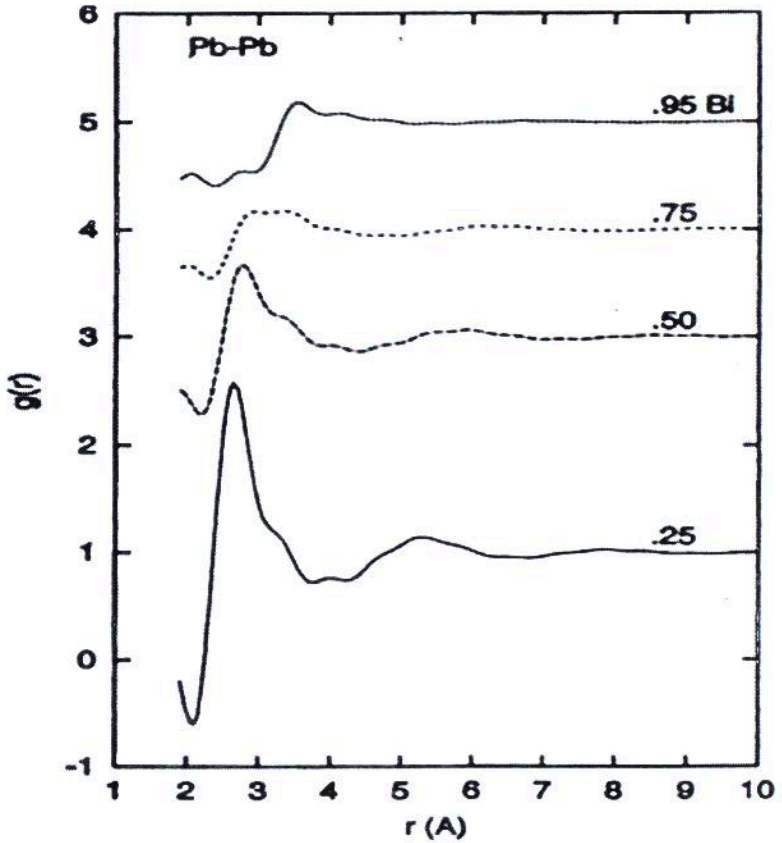

Fig 7: Partial Pair Distribution Function g_{ij} (r) of the Pb-Bi liquid alloy at 773K for the Pb-Pb pair

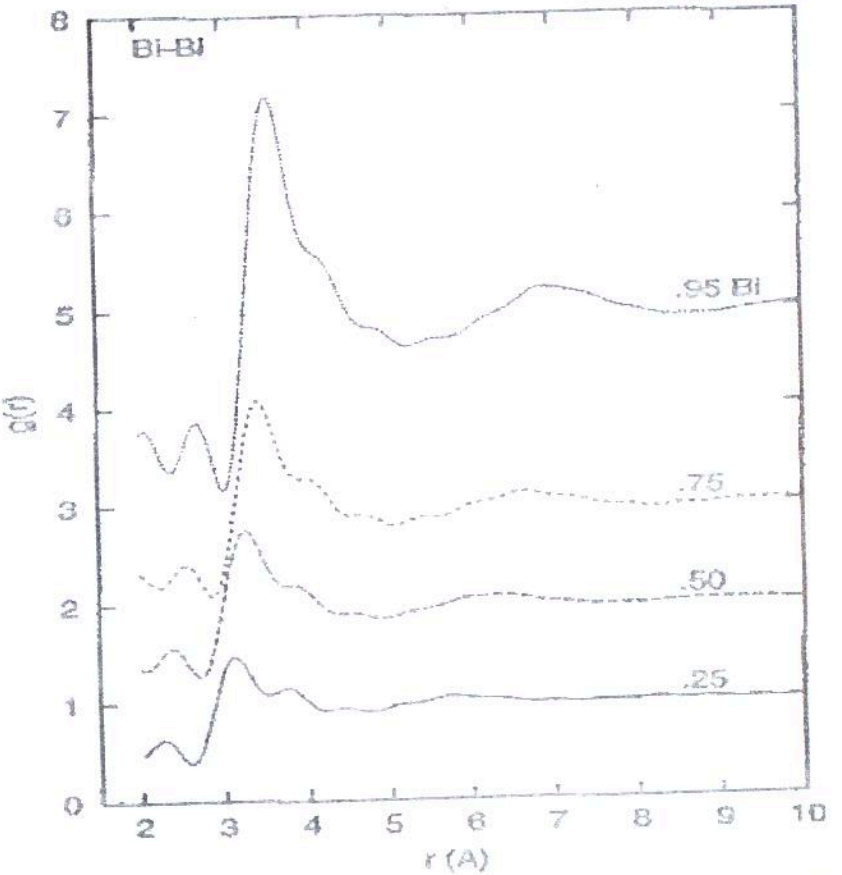

Fig 8: Partial Pair Distribution Function $g_{ij}(r)$ of the Pb-Bi liquid alloy at 773K for the Bi-Bi pair

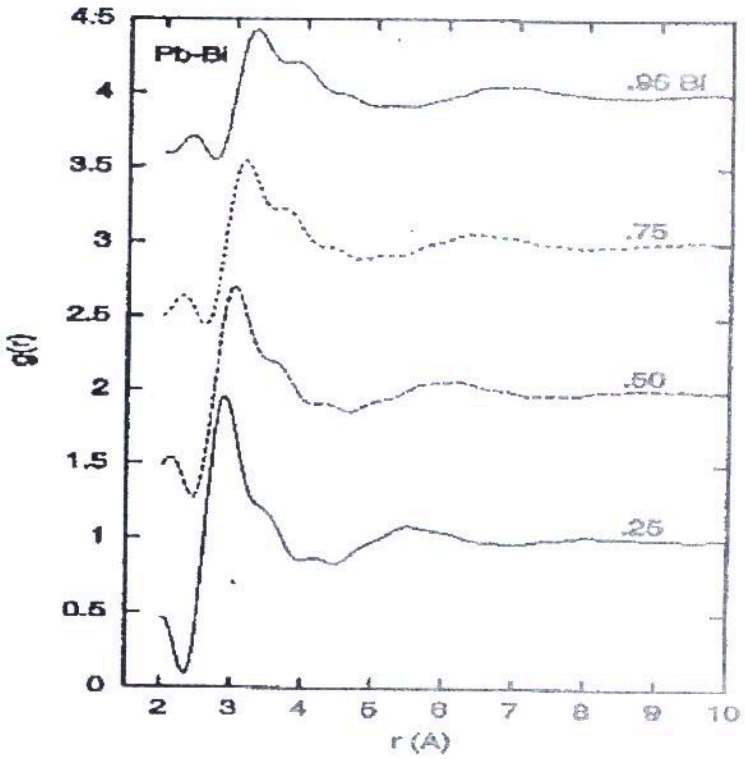

Fig 9:. Partial Pair Distribution Function $g_{ij}(r)$ of the Pb-Bi liquid alloy at 773K for the Pb-Bi pair

The results for the calculated partial coordination numbers are shown below in fig. 10.

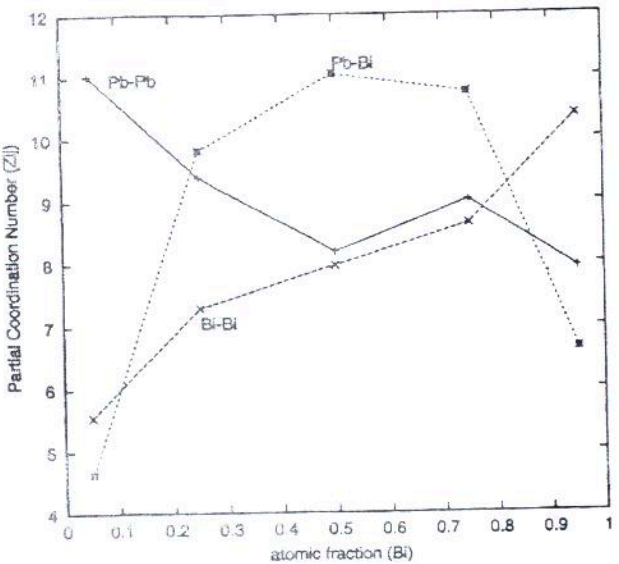

Fig 10: Variation of partial coordination numbers (Z_{ij}) with increase in Bi concentration at 773K.

From the figure above, the trend of the partial coordination numbers appeared as expected except at 0.75 atomic fraction of Bi, where the partial coordination number for the Pb-Pb pairs showed increase in value instead of a decreased value. This study therefore suggested that at that high Bi concentration, the Pb-atoms showed some tendencies to segregation. This also offered explanation for the earlier observed change in total coordination number for the Pb-Bi liquid alloy at high Bi concentration. This result was published in Taylor and Francis, Physics and Chemistry of liquids (Anusionwu, 2003)..

4.2 THERMODYNAMIC STUDIES

Model calculations have been found very handy in the study of thermodynamics and ordering in binary liquid alloys. The work of Bhatia and Hargrove (1974), which was later extended by Bhatia and Singh (1984), had been helpful in the search for the thermodynamic properties of liquid alloys at elevated temperatures. They developed a model under the framework of the Quasi Chemical Approximation (QCA). The fundamental idea about the quasi chemical model is that the properties of a compound forming A-B alloy can be explained by treating the alloy as a pseudo ternary mixture of A atoms, B atoms and AB_x complexes. This model using appropriate energetics can predict to a very reasonable extent the chemical activity of the alloy components, the free energy of mixing (G_m), the heat of mixing (H_m) and the entropy of mixing of the alloy(S_m).

In addition, parameters like the concentration fluctuation at the long wavelength limit $S_{cc}(0)$ and the Warren-Cowley short range order parameter can be determined (Warren, 1969; Cowley, 1950). These thermodynamic studies have revealed two classes of molten alloys which are those with compound forming tendencies and those with phase separatingtendencies. Our studies did not only classify the alloys studies into these two categories but also identify the probable intermetallic compounds formed in the molten alloy.

Presently, much of these theoretical calculations of thermodynamic properties and the study of ordering phenomenon have been applied to binary melts while applications to ternary alloys have to our knowledge not extensively pursued. In our work, we suggested that the thermodynamic properties of some class of ternary alloys could be easily explained by applying the Bhatia and Hagrove (1984) model with its extension. Here, we introduced what we termed a Pseudo Binary Approximation (PBA) (Anusionwuet al., 1997). With

this approximation a ternary alloy is considered pseudo-binary in configuration. This type of approximation could be possible for a class of molten ternary alloys consisting of pure metal and a compound of the form M-R_xS_y, where M denotes the pure metal while R_xS_y is the compound with x and y as numbers.

The calculation using the Pseudo Binary Approximation was made possible with the availability of an EMF data of Tanaka et al., (1994) on the liquid chalcagenide semiconductor alloys Bi-As_2Te_3 and Tl-As_2Te_3. The results of the calculations showed that, the approximation produced good agreement with experimental values of chemical activity and free energy of mixing for both alloys. However for Tl-As_2Te_3 the agreement was only qualitative at higher concentrations of Tl. (See figures below).

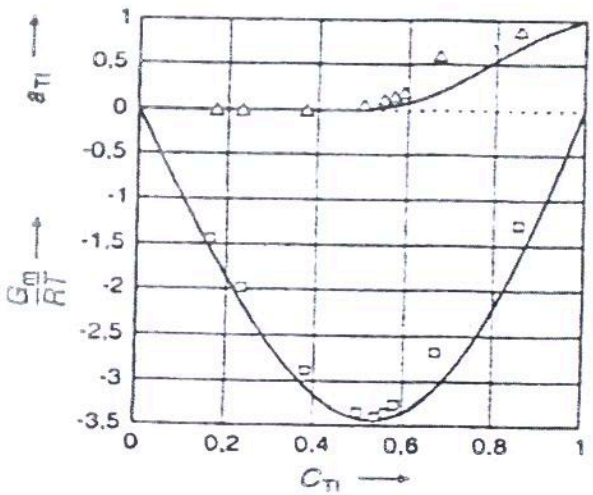

Fig 11: Free energy of mixing (G_m/RT) and activity values of Tl (a_{Tl}) for liquid Tl-As_2Te_3 alloy. Lines represent calculated values while points represent experimental values.

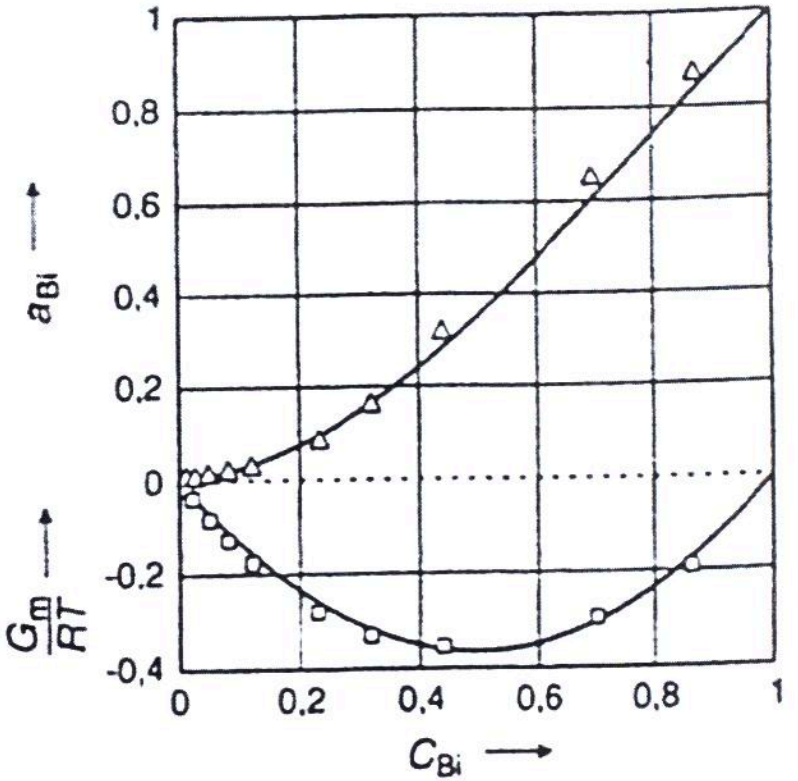

Fig 12. Free energy of mixing (G_m/RT) and activity values of Bi (a_{Bi}) for liquid Bi-As_2Te_3 alloy. Lines represent calculated values while points represent experimental values.

The calculations showed that a possible compound of composition $Tl_6As_2Te_3$ was formed at the molten state of the alloy and this could be more prominent above 0.5 Tl concentration as indicated in the figure for the $S_{cc}(0)$. HoweverBi-As_2Te_3 manifested features of ideal mixture with no tendencies of compound formation in the alloy.

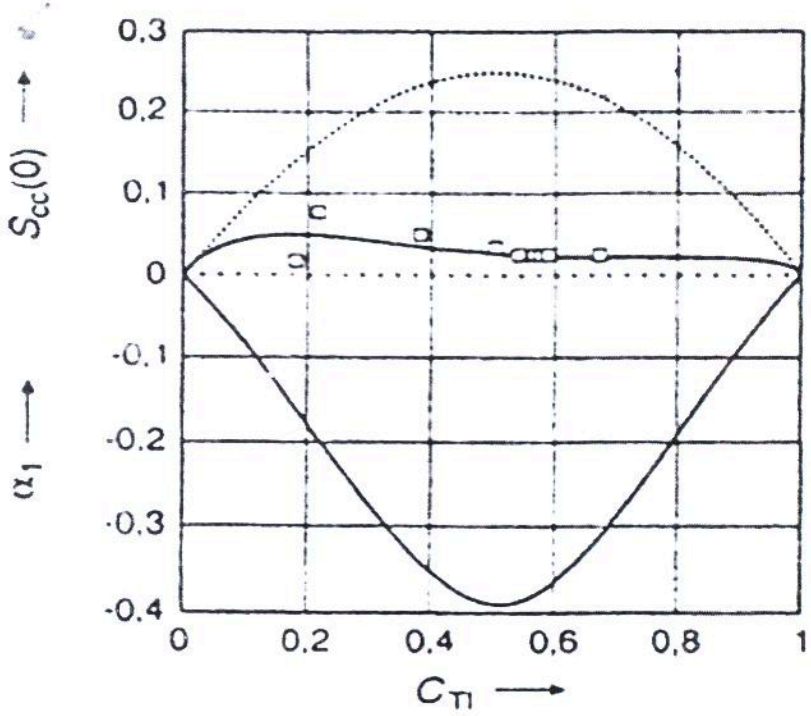

Fig 13: $S_{cc}(0)$ and Warren-Cowley short range order parameter values for liquid Tl-As_2Te_3 alloy. Lines represent calculated values, while Points represent experimental values.

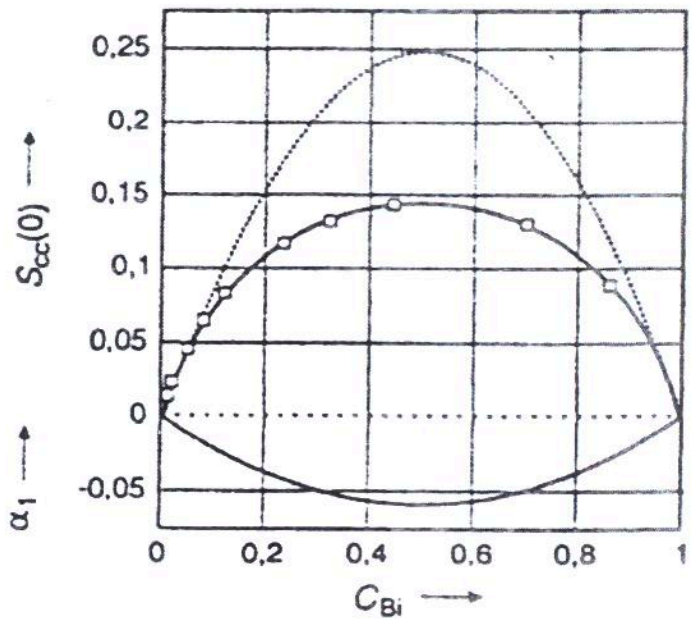

Fig 14: $S_{cc}(0)$ and Warren-Cowley short range order parameter values for liquid Bi-As_2Te_3 alloy. Lines represent calculated values, while Points represent experimental values.

The result of this work was published in Zeitshrift fur Metalkunde (Anusionwuet al, 1997). We also extended our calculations of thermodynamic properties beyond metal-metal alloys to nonmetal-nonmetal alloys and metal-nonmetal alloys. An example of this study is the Si-P alloy. In applying the quasi chemical model to this alloy, we sought to determine the possible complexes or compounds which exist in the liquid phase. The study of the nature and strength of complexes existing in an alloy melt is gaining increasing importance due to the fact that chemical complexes have been associated with the formation of glassy materials in binary

alloys (Ramachandra Rao et al., 1984)..

The calculations revealed that two complexes are present in the liquid Si-P liquid alloys. These complexes are $Si_2P$and Si_3P_2. Si_2P is one of the stable compounds formed in the solid state of Si-P alloy, with other compounds SiP and SiP_2 (Ugai et al., 1973). We therefore suggested that with increase in temperatures, only the compound Si_2P persisted into the liquid phase and a new complex Si_3P_2 is formed and coexisted with Si_2P in the liquid state.

The experimental data available for the thermodynamic properties of Si-P liquid alloy is for only up to 0.3 atomic fraction of P.Our calculations provided thermodynamic data for all the concentration range published in Indian Journal of Physics (Anusionwu et al., 2003)..

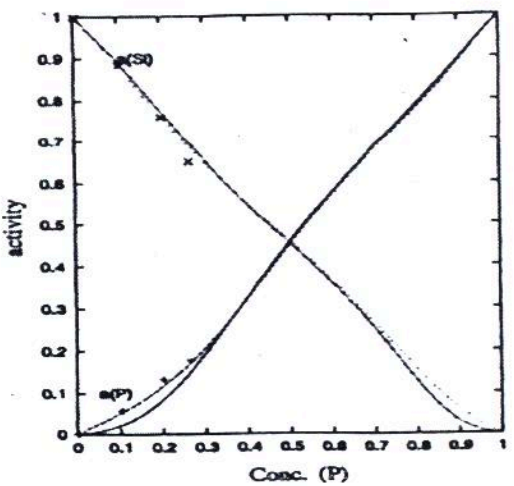

Fig 15: Activities of Si and P in Si-P liquid alloy at 1750K. Lines represent calculated values while points represent experimental values.

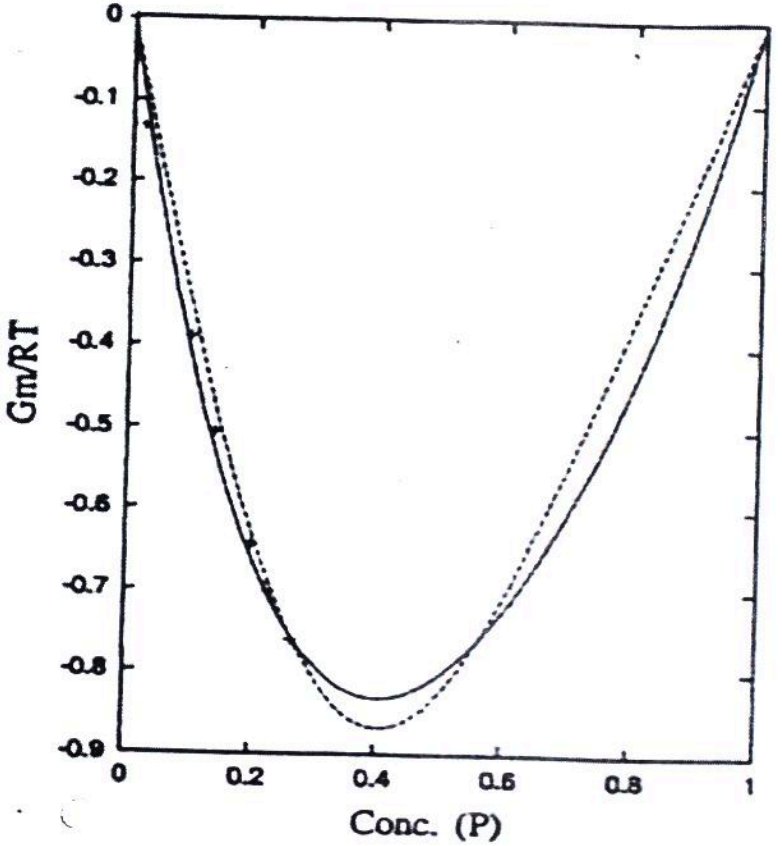

Fig 16: Free energy of mixing (G_m/RT) values for liquid Si-P alloy at 1750K. Lines represent calculated values while points represent experimental values.

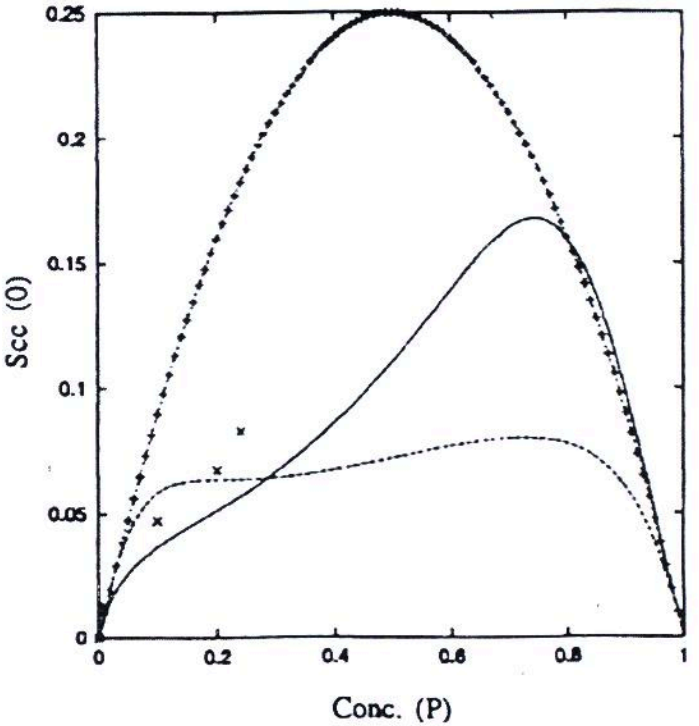

Fig 17: $S_{cc}(0)$ values for liquid Si-P alloy at 1750K. Lines represent calculated values while points represent experimental values.

I present below a table of a few liquid alloys, with the predicted complexes present and the nature of ordering in the liquid alloy.

Table 1. Liquid binary alloys and predicted complexes formed

Alloy	Temp (K)	Complexes Formed	Nature of Ordering	References
In-Pb	873	In_2Pb_3	CF	Anusionwu & Adebayo (2010)*Elsevier*
In-Mg	900	$InMg_2$, $InMg_3$,In_2Mg_3	CF	Anusionwu & Adebayo (2010)*Elsevier*
Li-Mg	889	Li_3Mg_2	CF	Anusionwu (2002)*Elsevier*
Cu-Zr	1499	Cu_3Zr_2	CF	Anusionwu & Adebayo (2001)*Elsevier*
Cu-Si	1599	Cu_5Si, Cu_3Si_2	CF	Anusionwu & Adebayo (2001)*Elsevier*
Zn-Au	1175	Zn_4Au_3, Zn_4Au_6	CF	Anusionwu (2000)*Taylor & Francis*
Cu-Hf	1873	$CuHf_2$, Cu_4Hf, Cu_8Hf	CF	Anusionwu*et al.* (2003)*Springer*
Ge-Ga	1273	No complexes	NM	Anusionwu (2004)*Taylor & Francis*
Ge-Sb	1273	Ge_2Sb	CF	Anusionwu (2004)*Taylor & Francis*
Li-Pb	878	Li_4Pb, Li_3Pb	CF	Anusionwu*et al.* (2005)*Taylor & Francis*
Sb-Sn	770	$SbSn_2$	CF	Anusionwu (2006)*Springer*
In-Sn	770	No complexes	NM	Anusionwu (2006)*Springer*
Rb-Pb	878	Rb_5Pb_3	CF	Anusionwu& Adebayo (2006)*Elsevier*
Na-Cs	373	No complexes	PS	Anusionwu (2003)*Elsevier*
Na-Bi	873	Na_3Bi	CF/PS	Anusionwu (2003)*Elsevier*
Na-Sn	873	Na_8Sn	CF	Anusionwu (2003)*Elsevier*
Al-Ga	1100	No complexes	PS	Anusionwu*et al* (2009)*Springer*
K-Pb	879	K_3Pb_2, K_4Pb_4	CF	Anusionwu (2005)*Springer*
Al-Ge	1220	Al_2Ge_3	CF	Anusionwu*et al* (2009)*Springer*

CF – compound forming; NM – Normal Mixing, PS – Phase Segregating

4.3 SURFACE PROPERTIES OF LIQUID ALLOYS

Another area of interest in my studies is the surface properties of liquid alloys. The general outcome of investigations in the neighbour hood of alloy surfaces (Urias and Moran-Lopez, 1981; Sakuari et al., 1985) indicates that the surface composition of an alloy differs from that in the bulk. The study of surfaces and interfaces is of interest as they are essential to understanding in a fundamental way surface related phenomena such as heterogenous catalysis, epitaxial growth, corrosion, as well as

mechanical behaviour and kinetics of phase transformation. In addition, for such studies seeking for the development of lead-free soldiers, candidate alloys must show acceptable surface related properties such as wettability, pasting range, interfacial adhesion and surface tension. Interfacial adhesion and surface tension of a liquid binary alloy can be dependent on the surface composition of the alloy. You will agree with me that at elevated temperatures where most metals become liquids, it will be difficult to measure these surface related properties experimentally.

My work on some liquid alloys was to use available statistical formulation (Prasad and Singh, 1991; Prasad et al., 1994) based on the concept of a layered structure near the interface to perform calculations to obtain surface composition as a function of the bulk composition of the alloy and the surface tension as a function of the bulk composition of the alloy.

In one of my studies, in addition to determining the surface tension and surface composition of the alloy throughout the concentration range, the assessment of the effect of size ratio between the alloying elements on the surface properties was carried out. Five liquid binary alloys exhibiting variations in size and characteristics were studied. They are Na-Cs, Sn-Ga, Cu-Ni, Na-Te and Li-Ba. Our choice of these alloys was based on the nature and size ratio of the alloy compounds. While Na-Cs, Sn-Ga and Cu-Ni manifest phase separating tendencies in the bulk and with size ratios (ratio of the larger to the smaller atom) of 2.99, 1.49 and 1.06 respectively, Li-Ba and Na-Te are compound formers with size ratios of 3.09 and 1.13 respectively.

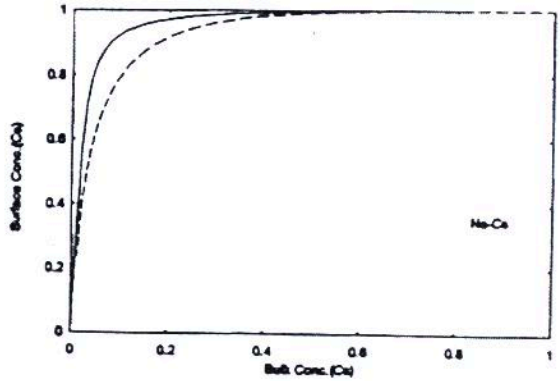

Fig 18: Surface concentration of Cs Vs Bulk concentration of Cs in a Na-Cs liquid alloy at 383K. Solid line are values without size ratio considerations while broken lines are values when size ratio effects were considered.

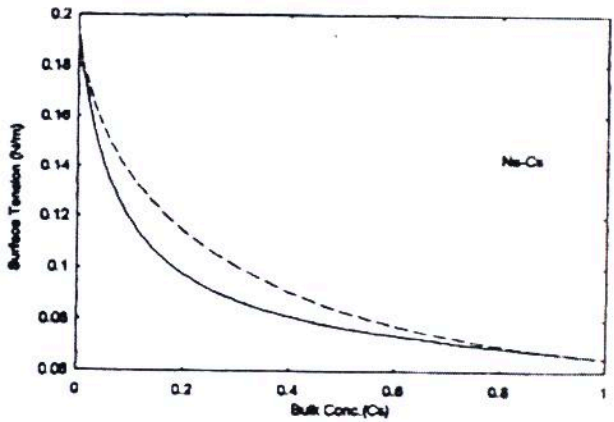

Fig 19. Surface tension values Vs Bulk concentration of Cs for the Na-Cs liquid alloy at 383K.Solid lines are values without size ratio considerations while broken lines are values when size ratio effects were considered

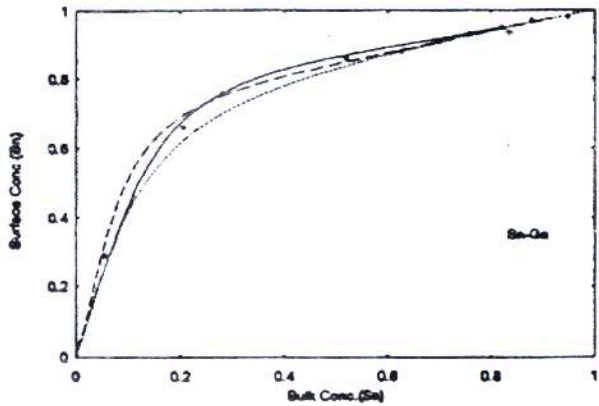

Fig 20: Surface concentration of Sn Vs Bulk concentration of Sn in a Sn-Ga liquid alloy at 773K. Solid lines are values without size ratio considerations while broken lines are values when size ratio effects were considered. Points are experimental values due to Singh et al., (1990)

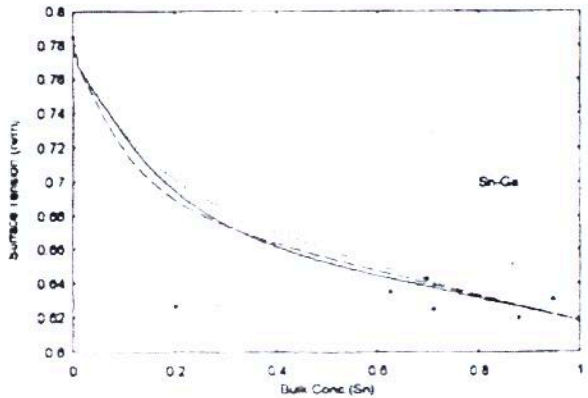

Fig 21: Surface tension values Vs Bulk concentration of Sn for the Sn-Ga liquid alloy at 773K.Solid lines are values without size ratio considerations while broken lines are values when size ratio effects were considered. Points are experimental values due to Singh et al., (1990)

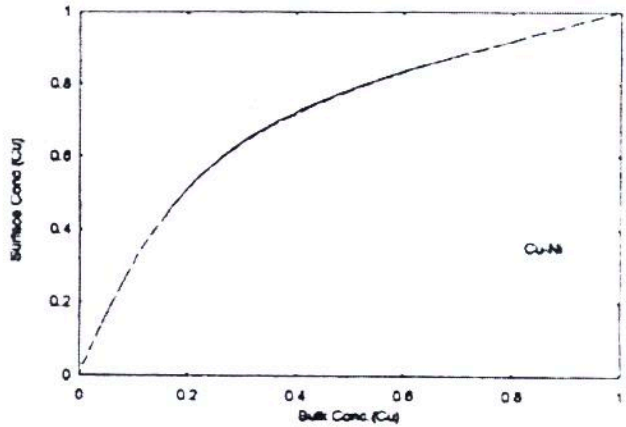

Fig 22: Surface concentration of Cu Vs Bulk concentration of Cu in a Cu-Ni liquid alloy at 1823K. Solid lines are values without size ratio considerations while broken lines are values when size ratio effects were considered.

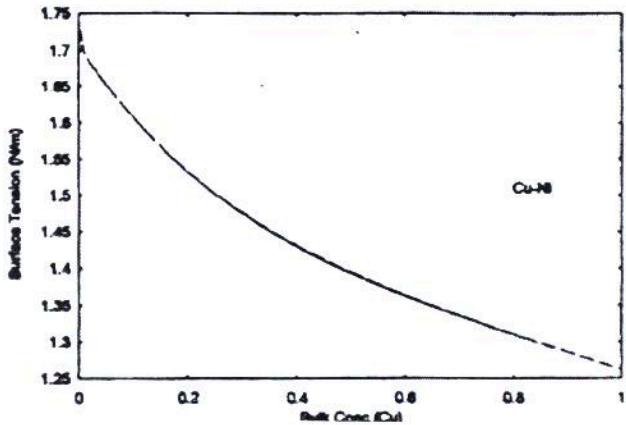

Fig. 23. Surface tension values Vs Bulk concentration of Cu for the Cu-Ni liquid alloy at 1823K.Solid lines are values without size ratio considerations while broken lines are values when size ratio effects were considered

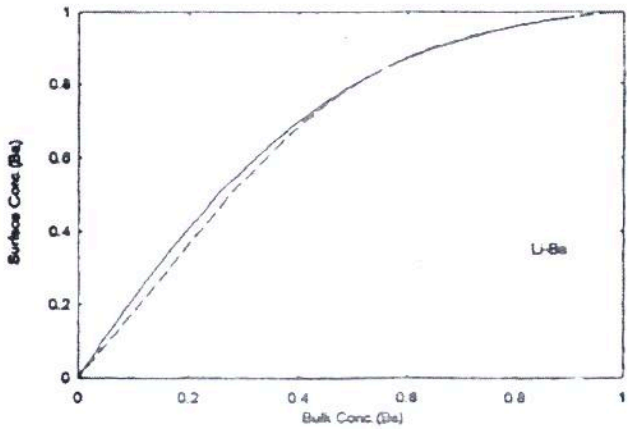

Fig 24:. Surface concentration of Ba Vs Bulk concentration of Ba in a Li-Ba liquid alloy at 773K. Solid lines are values without size ratio considerations while broken lines are values when size ratio effects were considered.

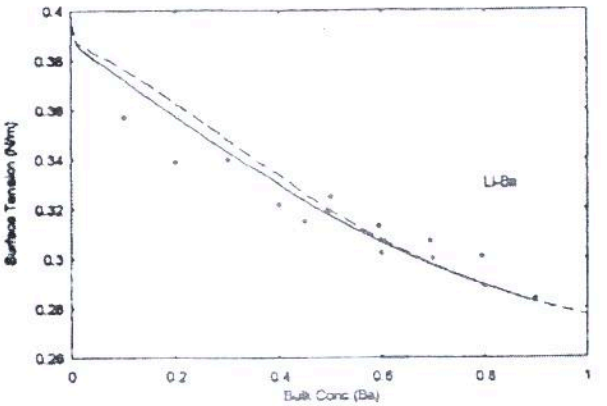

Fig. 25. Surface tension values Vs Bulk concentration of Ba for the Li-Ba liquid alloy at 773K.Solid lines are values without size ratio considerations while broken lines are values when size ratio effects were considered. Points are experimental values due to Petric et al., (1989)

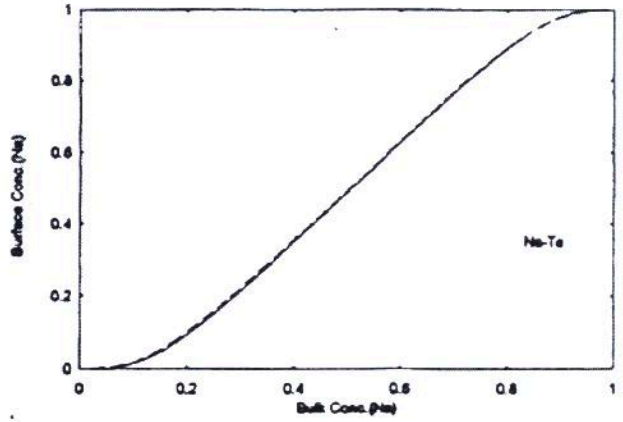

Fig.26. Surface concentration of Na Vs Bulk concentration of Na in a Na-Te liquid alloy at 753K. Solid lines are values without size ratio considerations while broken lines are values when size ratio effects were considered.

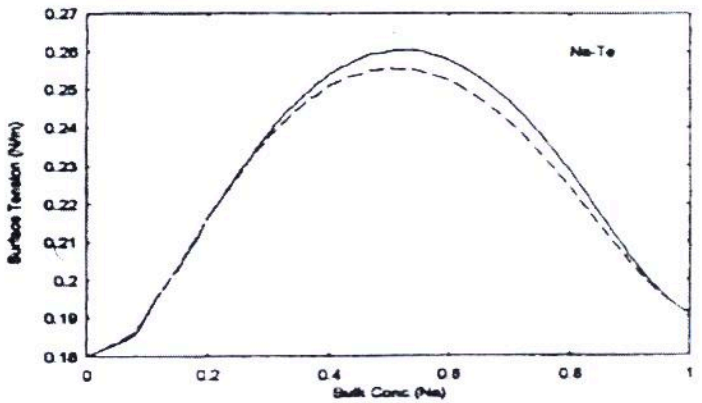

Fig 27. Surface tension values Vs Bulk concentration of Na for the Na-Te liquid alloy at 753K.Solid lines are values without size ratio considerations while broken lines are values when size ratio effects were considered

The graphs in figure 18 - 27 show the results of our calculations. First, the calculations of Sn-Ga for surface composition and surface tension had good agreement with experimental values (Singh et al., 1990; Anusionwu et al., 1998). In addition the calculated surface tension values for Li-Ba was also in agreement with experiment (Petric et al., 1989; Anusionwu et al., 1998). This gave us strong confidence that calculated values obtained for other alloys where experimental data are not available can be relied upon. Secondly, the calculation showed that in the Na-Cs liquid alloy, the Cs atoms prefer to segregate to the surface leaving more of the Na atoms in the bulk. For Sn-Ga, both atoms are at the surface with more of the Sn atoms present at the surface. The situation is same for Cu-Ni and Li-Ba. However for Na-Te, our calculations showed that the surface composition of the alloy is equivalent to the bulk composition (Anusionwu et al., 1998).

Effects of size ratio of alloying components appear prominent for phase segregation systems (Na-Cs, Sn-Ga and Cu-Ni) and the effect reduces with reduction in the size ratio. For the compound forming systems, (Li-Ba and Na-Te), size ratio has no significant effect on their surface properties. Many other alloys were studied to determine the nature of their surface composition and predicted surface tension values throughout the concentration range. I list below a few of the alloys studied, the predicted dominant alloy component at the surface and the bulk composition range in which they are prevalent.

Table 2: Alloys and their surface compositions

Alloy	Temp (K)	Dominant atom at surface	Bulk concentration range of Dominant atom	Predicted % of Dominant atom at Equiatomic Bulk composition.	References
In-Zn		In	0.0 – 1 (In)	95.2	Anusionwu and Ilo -Okeke (2005a)*Taylor & Francis*
Li-Pb	878	Li	0.5 – 1 (Li)	50	Anusionwu et al. (2005) *Taylor & Francis*
In-Sn	770	Nil	0.0 – 1 (Sn)	50	Anusionwu (2006)*Springer*
Sb-Sn	770	Sb	0.2 – 1 (Sb)	83	Anusionwu (2006)*Springer*
Rb-Pb	878	Rb	0.2 – 1 (Rb)	97	Anusionwu and Adebayo (2006)*Elsevier*
Na-Sn	873	Na	0.4 – 1 (Na)	96	Anusionwu (2003)*Elsevier*
Na-Bi	873	Na	0.4 – 1 (Na)	66	Anusionwu (2003)*Elsevier*
Na-Cs	373	Cs	- -	100	Anusionwu (2003)*Elsevier*
Al-Ga	1100	Ga	0.1 – 1 (Ga)	76	Anusionwu et al. (2009)*Springer*
Al-Ge	1220	Ge	0.3 – 1 (Ge)	59	Anusionwu and Adebayo (2001)*Elsevier*
Ge-Ga	1273	Nil	0.0 – 1 (Ge)	50	Anusionwu (2003)*Taylor & Francis*
Ge-Sb	1273	Sb	0.0 – 1 (Sb)	78	Anusionwu (2003)*Taylor & Francis*
Sn-Zn	1123	Sn	0.0 – 1 (Sn)	94	Anusionwu and Ilo -Okeke (2005b)*Elsevier*
K-Pb	879	K	0.2 – 1 (K)	92	Anusionwu (2005)*Springer*
Ag-In	1273	In	0.1 – 1 (In)	81	Anusionwu and Echendu (2010)*Taylor & Francis*
Ag-Sb	1073	Sb	0.1 – 1 (Sb)	98	Anusionwu and Echendu (2010)*Taylor & Francis*

4.4 STUDY OF TRANSPORT PROPERTIES

The development of new materials sometimes requires the knowledge of thermodynamic and thermophysical data which due to experimental difficulties have not been measured (Novakovic et al., 2005). Some of these properties whose data for alloys are scanty due to difficulties in measurement at high temperatures include transport properties such as viscosities and mutual diffusivities (Iida and Guthrie, 1988).

The viscosity of liquid metals and alloys is an important physical

property that influences the activities of refining, casting and solidification as well as the general behaviour of liquids (Hirai, 1993). The need for the study of viscosity of liquid metals and alloys stems from the importance of viscosity in both the technology and theory of liquid metal behaviour. For example, a liquid metal's viscosity is a main factor dominating the rise of small gas bubbles and non-metallic inclusions through it. Also, useful information on the rate of transfer of impurity elements from metal to slag can be obtained by continuously monitoring the slag's viscosity during reaction and subsequent composition changes (Iida and Guthrie, 1988).On the other hand, the distribution of solute in a solid or liquid solution is dependent on mass transport which is controlled by atomic diffusion phenomena.

For these properties, we use theoretical models, in some cases modify and apply them to predict the values of these properties for some liquid metallic binary alloys. Here, we combined the Darken's thermodynamic equation for diffusion (Darken, 1948) and the model of Protopapers et al. (1973) to compute the mutual diffusivities for some liquid binary alloys such as Cd-Ga, Ag-In and Ag-Sb (Anusionwu et al., 2009; Anusionwu and Echendu, 2010). The figures for the calculated mutual diffusivities are shown below.

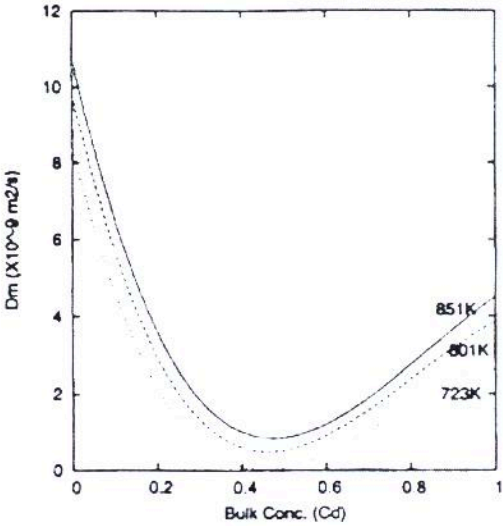

Fig 28: Diffusivities of Cd-Ga liquid alloys at 723, 801 and 851K.

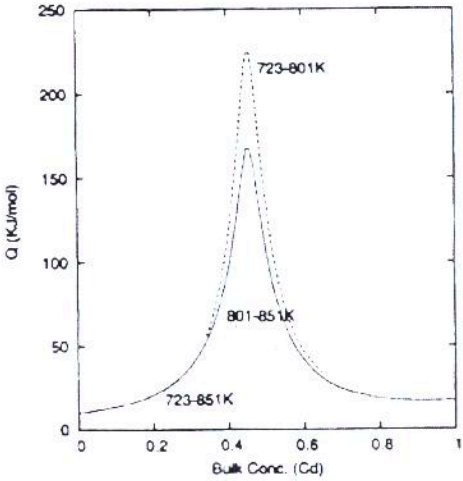

Fig 29: Calculated activation energy of Diffusion for Cd-Ga liquid alloys

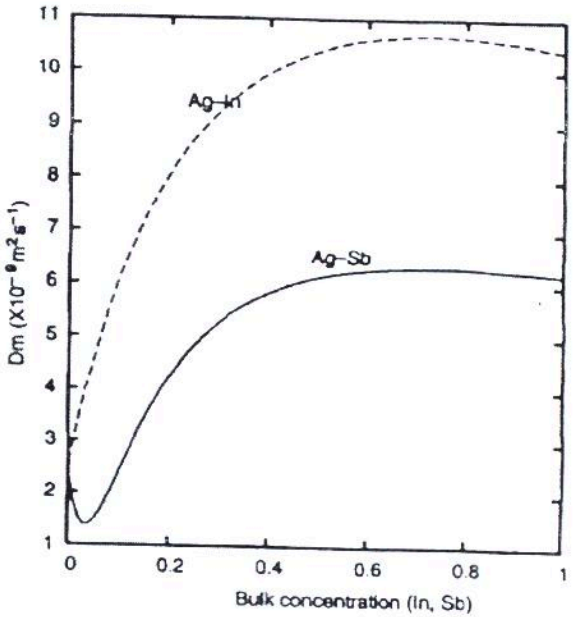

Fig 30: Calculated Diffusivities of Ag-In and Ag-Sb liquid alloys at 1273K and 1073K respectively.

Mutual diffusivities for Cd-Ga at 723K approached zero between 0.4 and 0.5 atomic fraction of Cd. This is an indication that Cd and Ga species are immiscible within the mentioned concentration range and temperature. Our calculations showed that mutual diffusivities decrease with increasing segregation tendencies. In Ag-Sb liquid alloy, segregation among alloy species is expected below 0.1 atomic fraction of Sb. Within this concentration range Ag-Sb manifested very low values of mutual diffusivities. In addition, our calculations for Cd-Ga revealed that with the presence of an immiscibility gap, the mutual diffusivities do not vary with temperature according to the Arhenius law over the region of immiscibility. The calculated activation energy for diffusion reached a high peak of 220 J/mol within the region of immiscibility.

The viscosities of liquid metallic alloys were approached with two models. First the modified model of Morioka et al.(2002) which employs both kinetic and rate theories to describe the viscosity of liquid metals. While the model of Kucharsky (1986) relates the viscosity of a liquid binary alloy to the activity coefficients of the liquid alloy compounds. Using the modified model of Morioka et al. (2002), the viscosities of liquid metallic alloys such as Ag-Cu, Hg-Na, Ag-Sb and Bi-Su were computed (Echenduet al., 2010). Some of the results are shown in the figures below. Our calculations in many cases showed a qualitative trend with experimental results, indicating the need for further modification of the model.

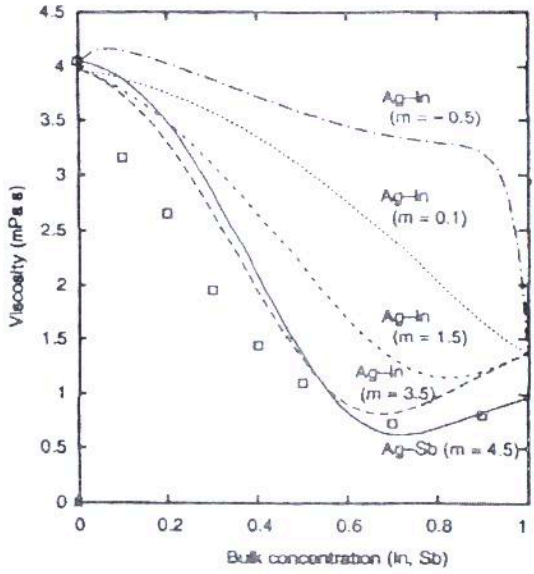

Fig 31: Calculated viscosity values for Ag-In and Ag-Sb liquid alloys at 1273K and 1073K respectively. Lines are calculated values for different values of the parameter m while points are experimental values of Ag-Sb at 1273Kdue to Iida and Guthrie (1988).

Calculations based on the models of Kucharsky (1986) also yielded a qualitiative trend for Ag-Sb and made predictions of trend for Ag-In liquid alloy (Anusionwu and Echendu, 2010)..

4.5 MOLECULAR DYNAMICS STUDIES

Molecular Dynamics simulation methods form another approach in my search for the properties of liquid alloys at elevated temperatures. One advantage of this method is that studies can be extended to multicomponent alloys and other compounds. The method of Molecular Dynamics simulation is a technique at the atomic level, where it is possible to predict all the physical properties of a crystalline material. The procedure consists of solving numerical equations of atomic motion using Newton's second law of motion. Initial coordinates of positions and velocities are assumed with boundary conditions specified. This boundary condition is usually periodic and particles are enclosed in a box and this box is replicated in space by rigid translation in three criterion coordinates. The implication of this is that, a particle that leaves a computational box on one side will be replaced by another identical particle from the opposite box. The simulation box is formed from a cube of side L with L x L x L as unit cell volume in which N number of particles are enclosed.

Using the Molecular Dynamics simulation, we have calculated some properties of some metallic alloys. In the study of the Fe-Mg binary alloy (Adebayo and Anusionwu, 2007) we used the Lennard-Jones potential, and properties such as diffusion coefficients and viscosity were calculated for different temperatures. Table 3 gives some results of the calculations.

Table 3 Values of diffusion coefficient (D) and viscosity () for Fe-Mg alloy at various temperatures.

T(K)	$D(10^{-9}m^2s^{-1})$	η(mpa) x 10
1273	0.5759	93.0346
1373	0.6411	92.6909
1473	0.6689	92.3961
1573	0.7237	92.1402

Another study on Ag-Cu binary alloy using Lennard-Jones potential, 710 atoms of Ag and 290 atoms of Cu also yielded interesting results for surface tension, coordination numbers,diffusion coefficients and viscosities for 29% Cu at different temperatures (Adebayo and Anusionwu, 2006).
Some extracted values are given in the Table below. The graphs for other quantities can be fully accessed in the paper published in the European Physical Journal (Adebayo and Anusionwu, 2006).

Table 4. Values of calculated coordination number (Z), diffusion coefficients (D) and collision frequency () for Ag-Cu alloys at various temperatures.

T(K)	Z	Inv	$D(10^{-9}m^2s^{-1})$
1153	8.9359	2.8566	0.4460
1163	8.5363	2.8631	0.4491
1173	8.5111	2.8651	0.4557
1183	8.5721	2.8665	0.4581
1193	8.6008	2.8697	0.4609

5.0 RANDOM THOUGHTS

My Vice Chancellor Sir, permit me to think aloud on few issues that relate to my work, Physics in FUTO and the Nigerian Universities academic programme.

5.1 THE LIMITATIONS

Computational work today is very important and cannot be neglected in the present scientific and technological dispensation. Computational research work helps scientists to go beyond the experimental limit and the theoretician to visualize his ideas. Computational physics moves ahead of experiment especially in areas where experimentation is very difficult or costly. Computational physics provides the possible answers before the experimental results. This is an area of scientific research which would have thrived greatly in our nation where sophisticated experimental equipment are not sufficient. However, certain factors such as lack of constant power supply, unavailability of required workstations and internet access have limited the scope of computation which a scientist in this part of the world can do. Certain calculations run for several hours and some for days before convergence or equilibrium is attained. Availability of power supply continuously for such lengths of times in our environment is not usually possible. This will make such computations almost impossible. I want to call on Government to transform places like the National Mathematical Centre Abuja to cater for the needs of the computational and mathematical research scientists in this nation.

5.2 PHYSICS IN FUTO

My Vice Chancellor Sir, I am proud to say that I am a graduate of this highly revered institution of Technology, Federal University of Technology, Owerri. I am of the class of '88' being part of the third sets of graduates from the Industrial Physics programme. The FUTO Physics programme was designed to be a combination of Physics and Engineering which will ultimately yield a product called

technology and what is termed today as interdisciplinary. Therefore a FUTO Physics student does all courses in physics and majority of the courses in related engineering discipline. This is different from the conventional physics programmes in other universities. Reports from employers and personal experience reveal the edge FUTO physics graduates have over their counterparts from conventional universities and in many occasions the engineers in related disciplines. Our graduates could continue as physicists, do higher degrees as engineers(when they do so, they excel) or be self-employed in relevant areas.

Being a product of the five year physics programme in FUTO, I support this five year programme in the Department of Physics. Its advantages outweighs the disadvantages. The present Physics curriculum in FUTO cannot be achieved under a four year programme.

5.3 THE NUC BLOCK MOULD MODEL

Before I conclude, I wish to make a few comments on the Nigerian Universities Commission Benchmark Minimum Academic Standards (BMAS) for universities academic programmes. I see theNUC BMAS programme like a block mould which will produce exactly the same shape of blocks. The NUC BMAS provides all courses to be done in a programme, including the electives and the course contents.The BMAS is not the required minimum, it is the expected maximum requirement. If the BMAS programme is implemented as desired by NUC,

i) All students of the same programme from all universities will do exactly the same courses
ii) The curriculum of an overriding university present in the development of the BMAS is forced downon other

universities irrespective of what is their vision.

iii) The duties of the University senates are taken away.
iv) The BMAS in a way erodes the Universities autonomy.
v) The independence and supremacy of each university's senate on academic matters are eroded
vi) There is the possibility of NUC setting and conducting common examinations for the universities which may be called Unified Universities Degree Examination(UUDE).

Nature abhors a block mould idea. Physics programme in FUTO must not be a replica of Physics programme at University of Nigeria, Nsukka or University of Ibadan. Their cores may be similar but their tilting may not be identical. Individual universities should be allowed to put in flavours to their programmes which make them unique.

I am advocating that the NUC BMAS for programmes in Nigerian Universities be modified as follows:

i) The BMAS should only indicate about nine units of compulsory courses for each semester. These courses can be called NUC courses. The remaining units should be filled up at the dictates of individual universities' senates.
ii) Universities should be allowed to run programmes in line with their vision and mandate.

5.4 CONCLUSION AND ACKNOWLEDGEMENTS

In my presentation this afternoon, I have shown my efforts and contributions in determining properties of liquid metals at high temperatures using computational methods. I believe you learnt something.

I want to thank the All Mighty God for the grace and privilege to deliver this lecture today. I also want to thank the Vice Chancellor for approving today's lecture and providing all necessary resources that made it possible. My gratitude goes to my parents Late Mr Cyril U. Anusionwu and Mrs Martina E. Anusionwu for their parental care and personally funding my education to the postgraduate level.

Mr.& Mrs. K. Kuruvilla are remembered for giving me good foundation in Mathematics and Physics at the secondary school level. During my undergraduate days, the contributions of Prof. Amagh Nduka and Late Prof B. N. Onwuagba cannot be overlooked. I also wish to acknowledge Dr. A. J. Ogbonna of the MME Department, FUTO. I want to thank Prof L. A. Hussain, former Vice Chancellor of LASU and Prof O. Akinladewho were my supervisors during my PhD programme.

I thank the Director, Abdus Salam International Center for Theoretical Physics, Trieste, Italy for making me an Associate of the Centre. My gratitude also goes to the Swedish International Development Cooperation Agency (SIDA) for travel and financial support for many of my research works. I also thank Prof E. Burkel of University of Rostock, Germany for supporting my full participation in the Euro School on Synchrotron Studies of New Materials which held at Rostock, Germany. I acknowledge in a special way the Management of the Federal University of Technology, Owerri for the study fellowship given to me to do my PhD programme.

My special gratitude goes to Prof F. C. Eze the 7th substantive Vice Chancellor of FUTO, for being a mentor. I also wish to acknowledge the useful thoughts shared together with my respected colleagues

Prof. C. E. Akujor, Prof. I. M. Mejeha, Prof I. C. Ndukwe and Dr. C. E. Orji. I will not forget the spiritual covering, encouragements and support of my pastor, Arch Jarlath Onuegbu. and Pastor Bonaventure Onyenakazi

Finally, I acknowledge my lovely wife Dr (Mrs) Njideka Bede and my children, Favour, Nchedo, Utochukwu and Goodgift for their love and support. May God bless you all in Jesus Name, Amen.

Thank you.

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S/No	LECTURE	TOPIC	DATE
1	Prof. C.O G Obah	'Communication in the service of a nation'	Dec. 12, 1986
2	Prof. E.O.I Banigo	" Food Processing and Preservation. Paths to self sufficiency ".	Jan. 18, 1989
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4	Prof. S.C.O. Ugbolue	" In the throes of polymer and Textiles"	Dec. 11, 1996
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