1.1 INTRODUCTION

The states of matter, primarily, be divided into three classes i.e. solid, liquid and gas. Also there is one special state, which is called "amorphous or glassy". This state is generally obtained by rapid quenching from melts, and has an atomic distribution very close to that of the liquid state. By the end of the 19th century, good progress had been made on the theory of the gaseous state. During the 20th century, great advances have been obtained in the theory of the solid state. In contrast to these two states, the theory of the liquid state seems to have made slow progress. But there is an increasing need for understanding of the various properties of metals in the liquid state, because of their important role in metallurgical processes such as slag-metal reactions. Therefore the present work is focused on the liquid state of some simple metals and some simple binary alloys.

In the crystal state, all atomic positions are fixed. But there are fluctuations in the atomic distribution of liquids and gases in near-neighbour regions. Also such fluctuation disappears at greater distances. The fluctuation in the atomic distribution in near-neighbour regions for liquids is larger than that of gases. This is also supported by the X-ray diffraction experiment that the atomic distribution function of liquid is, in general, very close to that of gaseous state near the critical point of the material. This shows the similarity between the atomic distribution of liquid and gas.

It is also found that solids are rigid and give sharp Bragg reflection in a diffraction experiments, demonstrating an ordered arrangement of
atoms or molecules. Liquids and gases are fluids; they do not give sharp Bragg reflection, but diffuse rings, showing that there is an ordered arrangement of molecules. Thus there is a clear distinction between solids and fluids (though this is somewhat blurred by the existences of glass and amorphous solids). On the other hand, there is no such quantitative distinction between liquid and gas, as Van der Waals pointed out explicitly. The continuity of liquids and gaseous states at temperature below the critical temperature, two fluids phases can coexists in equilibrium, the denser phase is called liquid and the less denser phase is called gas. Above the critical temperature, the co-existence of fluid phase is not observed. The difference between liquid and gas is essentially "the difference in density" [1.1].

Using the data for density and specific heat, we can easily find a similarity between the liquid and crystal states. The latent heat of fusion which corresponds to the difference between crystal and liquid is smaller than the latent heat of vaporization corresponding to the difference between liquid and gas. This implies that the energetic properties in the liquid state are rather similar to those in the crystal state. Thus we can't give a definite comment on the similarity of the liquid state to either the gaseous state or the crystal state. Therefore, an alternative approach to express the characterized structure of non-crystalline systems is required [1.2].

In the gaseous state, the atoms are distributed randomly and their motion seems to be completely irregular. While in the crystals the atoms show only a slight vibration about a definite point in the regular three dimensional lattice. These extremes in the atomic distribution contribute to the construction of simple models for the structure of these two states. The

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atomic distribution in the liquid state is rather irregular compared with that of the solid state and, in contrast to that of the gaseous state shows an ordering in near neighbour regions. This ambiguous situation hinders the contribution of a model for the structure of the liquid state, and thus the liquid state theory has progressed slowly [1.2].

Usually, matter exists either as a dense solid or as a dilute vapour at low pressures. For each of these states there is an ideal model which is a good approximation to reality and forms the basis for theoretical discussion. These are the ideal crystal lattice and the ideal gas models, respectively. In the ideal crystal, emphasis is on structural order, modified slightly by the thermal motion of the atoms; whereas in the ideal gas, emphasis is on the random atomic positions, and the motions are modified slightly by the fact that atoms cannot overlap each other.

At higher pressures a third state of matter appears i.e. the liquid state. This state occurs over a temperature range that separates the regions occupied by the solid and vapour states. Initially there was no mathematically tractable model which gives an accurate approximation to the liquid state. Such a model in contrast to the crystal and gas models needs to cover structural and thermal properties with equal emphasis. There are many conceptual models; for example, it is argued frequently that a liquid is similar to a dense fluid of hard spheres in thermal equilibrium with its container. If this or any other simple approximation applies, it should be expected that liquid properties would show systematic trends and relationships. The diagram of state that describes the relationships between pressure, volume and temperature plays vital role to specify a liquid. For a dense liquid the volume change on melting is small.
compared with the volume change on evaporation. The temperatures at which most elements are liquid are high enough that the system may be discussed from a classical point of view [1.3].

The aim of "Physics of Liquid" is to understand why particular phases are stable in particular ranges of temperature, density, atoms, ions, with structural and dynamical properties of fluids phases to the size and shape of molecules, and the nature of forces between them. A century of efforts since the pioneering work of Van der Waals has led to the fairly complete basic understanding of the static and dynamical physiochemical properties of liquids. The advanced in statistical mechanics (the fundamental formulation of Gibbs and Boltzmann, integral equations and perturbation theories, computer simulation), in knowledge of intermolecular forces and in experimental techniques, have all contributed to this.

According to the types of interatomic forces, liquid may be classified as [1.3]:

(1) Spherical molecules (e.g. Ar and Kr): Interacting with Van der Waals forces and having 'steep' overlap effects.
(2) Homonuclear diatomic molecules (e.g. H2 and N2): The effects of electrical quadrupole moments and of molecular shape must be included.
(3) Metals (e.g. Na and Hg): Long range coulomb forces, and 'softer' overlap effects; electrical screening effects are important.
(4) Polar liquids (e.g. HBr): Simple molecules with an electric dipole moment as the most important multipolar moment.
(5) Molten salts (e.g. NaCl): Ionic systems but electrically neutral on a local scale; long range coulomb forces – electrical screening effects are important.

(6) Associated liquids or hydrogen bonded liquids (e.g. water and glycerol): Strong angular correlation effects.

(7) Liquids composed of large molecules or compounds that have important internal modes of motion (e.g. paraffins).

Existence of liquid seemed little mysterious at the beginning of 20th century, but today one can make fairly precise predictions of the solid-liquid gas phase diagram and of the microscopic and macroscopic static and dynamical properties of liquids [1.4, 1.5].

It was pointed out initially that liquids are similar to gases in their structure that means they are structureless. According to this point of view liquids are simply considered as a very dense gas. However experiments showed that this is not true. When the X-rays were passed through a liquid, the scattered X-ray radiations are not as ordered as solids but are also not as random as in gas. In their internal structure, liquids occupy an intermediate place between gases and solids. Therefore, structure of liquid is required for the investigation of various properties, is directly observed in X-ray and neutron diffraction experiments [1.6-1.9] or computed on the basis of various theories.

Liquid metals differ from the other classes of liquids considered so far primarily through the presence of the conduction electrons. Although, the theory of liquid metals has much in common with that of the other ionic liquids. The problem is complicated by the fact that the electronic
component requires a quantum mechanical treatment. Many elements show metallic behaviour in the liquid state, but their electronic band structures can differ widely. The present discussion is restricted to the so-called "simple" metals. The class of simple metals comprises those in which the electronic valence states are well separated in energy from the tightly-bound core states; their properties are reasonably well described by the nearly-free-electron model. Metals that are classified as simple in this sense include Li, Na, K, Rb, Cs, Mg, Zn, Hg, Ga and Al. Other liquid metals i.e. noble, transition, alkaline earths, lanthanides and actinides have more complicated electronic structures, and the theory of such systems is correspondingly less well advanced [1.10].

A liquid metal is also a disordered array of ions immersed in a gas of electrons. As we know in solid state physics, when the electron gas is derived from the outer s and p electrons, as in Na or Al, and when the mean free path for electron-ion collisions is several nearest-neighbour distances or more, the metal is regarded as simple and the electron as nearly free. Then a characteristic in metal physics is to regard the effect of the ions on the electrons as a perturbation on the motion of a free-electron gas or, in other words, to calculate 'corrections' to the motion of free electrons caused by the presence of ions. This is a treatment partly depends whether the electrons can be clearly divided between the ion cores and the gas and also on how strong the forces are between the electrons and ions [1.11].

An electron passing through an ion will be deflected by the electron-ion potential. The ions are positive and the electron gas mobile, therefore the ions exert a long-range influence on the gas by attracting electrons to themselves. Meanwhile the electrons are also repelling each other and a
complex balance of forces sets in whose ultimate effect is to envelop each ion in an electron cloud. This cloud, being negative, neutralizes the electrostatic effect of the ion rather completely at large distances (several atomic diameters) and less completely at small distances. Liquid metals are different from the others by long range Coulomb forces, short range order, softer overlap effects with electrical screening effects [1.11].

The cloud of electrons is the screening charge and the total effect on an approaching electron of the ion and its screen is the screened potential. We may say that from the point of view of one electron passing through a liquid metal that it encounters the screened potentials of one ion after another and is scattered by them. The scattering alters the motion from what would otherwise have been free electron motion and perturbs the free electron gas, e.g. it causes corrections to the density of states. The summed effects of all the electrons undergoing this scattering are to produce the very electron clouds which screen the ions, so the process and its descriptive mathematics should be self-consistent [1.11].

During the last two decades, the structure and thermodynamics of liquid metals have been extensively studied with increasing sophistication in the modeling of the inter-ionic forces and in the classical statistical mechanics treatment of ionic correlations [1.1-1.3, 1.10-1.11]. Although a lot of work has been done on both the structure and thermodynamics, still some questions await a definite answer. The limitations of linear-response-theory based interactions are well known. It is also possible to consider the interactions based on second order perturbation theory as effective pairwise potentials [1.12-1.15]. In all these attempts the use of pseudopotential approach is found a remarkable success. But many existing studies have
been limited to local model potentials with empirically determined parameters [1.16-1.18]. Also it is found in our literature survey that some ab-initio pseudopotentials suitable for perturbation theory of the ionic interactions were generated. In general, the pseudopotentials like Ashcroft empty core model (AS) [1.19], Heine-Abarenkov model (HA) [1.20], Harmonic model potential (HMP) [1.21], Generalized nonlocal model potential (GNMP) [1.22], energy independent nonlocal model potential (EINMP) [1.23, 1.24] etc. have been applied to study the structure and thermodynamics of liquids. We believe that only a combined analysis of structural and thermodynamic data should be able to assess the quality of any model for the inter-ionic forces. However, only a few studies have been made addressing simultaneously these two problems.

The study of structural and thermodynamical properties of liquid metals has drawn much theoretical attention both for their intrinsic interest and for the relevance to an understanding of electronic properties. When focusing on trends of thermodynamic quantities, approximate but reliable theories aimed at modeling the free energy are still very useful tools. The simplest of such method is Gibbs-Bogoliubov (GB) approach [1.25, 1.26].

The general idea underlying the GB inequality is that the true Helmholtz free energy of a liquid metal is bounded from above by the free energy of a suitably chosen reference system plus the difference in average potential energy between the actual and the reference system, calculated using the distribution functions of the reference systems. Thus the choice of the reference system is clearly very important. Ideally the basis for choosing the best reference system is that one expects it to give the lowest free energy and the expressions required for the thermodynamic and
structure can be expressed possibly in an analytic form. People have applied popular reference system like

1. Percus-Yevick Hard Sphere (PYHS) [1.13, 1.24, 1.27-1.38]
2. One Component Plasma (OCP) [1.16, 1.39-1.47]
3. Charged Hard Sphere (CHS) [1.47-1.64]
4. Hard Sphere Yukawa (HSY) [1.65, 1.66]
5. Soft Sphere (SS) [1.67-1.69]
6. Optimized Random Phase Approximation (ORPA) [1.70-1.73]

Hence our literature survey suggested that it is highly desirable to search a better reference system which gives good explanation of various properties when it is used with a particular model potential. Thus proper combination of a model potential and a reference system is one of the basic requirement in explaining various structure and thermodynamics of liquid metals.

Looking to this situation, we thought it worthwhile to study the structure and thermodynamical properties of some liquid metals and binary alloys using our own model potential [1.33-1.35, 1.47, 1.59-1.64, 1.74-1.78] by applying reference systems to incorporate the structural information of liquid.

Thus the aim and perspective of the present study is to project "STRUCTURE AND THERMODYNAMICS OF SOME SIMPLE LIQUID METALS AND BINARY ALLOYS BY PSEUDOPOTENTIAL APPROACH" based on established physical and computational approach.
The content of the thesis is organized in six chapters as per the following description.

The present Chapter 1 deals with the introductory part and also gives an overview of the whole thesis. A survey of the previous investigations in the field and the motivation for the present work are also described in it.

Chapter 2 of the thesis describes the historical aspects of the development of the pseudopotential theory and its capabilities as a tool for calculating and understanding various properties of matter. The detailed construction and characterization of the pseudopotential form factor is presented here. The parameter of the potential is determined by employing values of the wave vector, $q_0$, where the form factor takes first zero value, i.e. $W(q) = 0$ for $q = q_0$ [1.35, 1.47, 1.61-1.63, 1.76-1.78]. The role of the screening and various forms of the local field correction functions is also discussed. In present study, the most fascinating and advanced form of the local field correction function due to Sarkar et al [1.79] is applied to see the screening influence with respect to more commonly used dielectric functions of Hartree [1.80] and Taylor [1.81].

It is a basic problem in the Physics of metals and liquids to study the structural properties of liquid metals. In Chapter 3, the structures of some monovalent, divalent, trivalent and polyvalent liquid metals viz; Li, Na, K, Rb, Cs, Mg, Zn, Cd, Al, In, Tl and Pb are investigated [1.47, 1.60, 1.61]. Here we use Percus-Yevick Hard Sphere (PYHS), One Component Plasma (OCP) and Charged Hard Sphere (CHS) as reference systems to generate the structure factor $S(q)$. Applying these structure factors $S(q)$, the pair
distribution functions \( g(r) \) are generated. The temperature dependency of \( S(q) \) and \( g(r) \) is also included in the study. The long wavelength limit of \( S(q) \), inter atomic distance \( r_i \), and coordination number \( n_i \) are also calculated. The first and second peak position and related magnitudes of \( S(q) \) and \( g(r) \) are investigated on the basis of present computation. All the results are compared with the experimental data, wherever exist.

Many metallic materials are manufactured after they have been refined sufficiently in the molten state. Therefore, it is a central problem in metallurgical chemistry to study the properties of liquid metals and alloys, in particular their thermodynamic and kinetic properties. A pseudopotential perturbation scheme based on Gibbs-Bogoliubov (GB) variational technique is considered to study the thermodynamical properties of some simple liquid metals in Chapter 4. The internal energy, entropy, Helmholtz free energy, isothermal compressibility and Bulk modulus of some simple liquid metals [1.33-1.35, 1.62, 1.63] are investigated in this chapter. The detailed comparison of presently generated data is made with the available experimental and other such theoretical data. The conclusions emerging from these comparisons are also pointed out.

The computed internal energy, entropy, Helmholtz free energy, Heat of mixing and excess entropy of mixing of alkali-alkali binary alloys are presented in Chapter 5 on the basis of Gibbs-Bogoliubov (GB) variational approach [1.74].

The final and concluding Chapter 6 summarizes the entire work of the present study alongwith the important general conclusions. Important
discussions regarding the applicability and advantage of the present pseudopotential are also mentioned in this chapter. The scope of further investigations of the work is also pointed out at the end. The necessary results and discussions are made at the appropriate point in every chapter.

During the course of this work, the model potential [1.33-1.35, 1.47, 1.59-1.64, 1.74-1.78] is also applied in the structural study of liquid rare earth metals (Nd, Dy, Ho, Er and Lu) [1.59] and 3d transition metals (Ti, V, Cr, Mn, Fe, Co, Ni and Cu) [1.64] by treating CHS reference fluid. The results are presented as Appendices A 1 and A 2, respectively, to the thesis.

The study is also extended to compute the electron and phonon dispersions of monovalent (Na), divalent (Mg), trivalent (Al) and tetravalent (Pb) liquid metals. The results are discussed in the Appendix A 3.
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