CHAPTER 1

Introduction
1.1 Advancement in Experimental Techniques

Condensed matter physics deals with a wide variety of topics, ranging from gas to liquids and solids, as well as plasma, where owing to the inter-play between the motions of a tremendous number of electrons and nuclei with rich varieties of physical phenomena [1]. In the modern time, materials which are of prime technological importance are being studied seriously theoretically as well as experimentally. Better understanding of structural and thereby other properties became possible after the discovery of X-rays. Fundamental properties of metals and their alloys are investigated precisely with the help of theoretical and experimental methods. This emerging field of science which includes the solid as well as liquid state of matter is known as condensed matter physics [2].

Liquid metals play a crucial role, as they exhibit pronounced inelastic features in the terahertz (THz) frequency region. For this main reason, in the last 30 years, many experimental investigations have been performed on these systems by means of inelastic neutron scattering (INS) technique, which was, up to few years ago, the only tool adequate to investigate the dynamics of condensed matter in mesoscopic wave vector region. The energy resolution problem involve for X-rays (IXS): here the energies of the incident photons are typically of order keV, i.e., $10^6$–$10^7$ times higher than those of the excitations we are interested in. In such a case, the resolution demand clearly becomes quite severe. This circumstance has in fact prevented for many years an efficient and widespread use of IXS. This situation started to improve in the late 1990s which saw a substantial progress in the development of powerful and directional X-ray sources. At present, the incident X-rays used in the scattering experiments are obtained from an easy-tunable, ‘white’ X-ray radiation produced by the so-called ‘third-generation’ synchrotron facilities. At present, in IXS it is possible to reach absolute energy resolutions of the order of 1
meV (very close to those of INS) with resolving powers higher than $10^7$ [3]. The first energy resolved observation of phonons with synchrotron radiation [4-6] became feasible by using a three-axis spectrometer with crystal optics operating close to backscattering geometry. This technique was developed further with second generation instruments at the European Synchrotron Radiation Facility (ESRF, France) and at the Advanced Photon Source (APS, USA) allowing routinely an energy resolution of 1–2 meV [7]. By the experimental point of view, the study of the dynamics of simple liquids in the mesoscopic wave-vector region is traditional prerogative of Inelastic Neutron Scattering (INS). Since the pioneers Copley and Rowe [8], a significant amount of work has been done in this field by many authors [9-18].

A very important advantage of inelastic X-ray scattering lies in the fact that it has almost no restrictions in the accessible energy-momentum space, since the coupling of the energy to the momentum transfer is negligible. Therefore, this method is extremely attractive for studying the coherent part of the dynamical structure factor of non-periodic structures like amorphous materials, glasses or liquids with high sound velocities. It opens up a new possibility to study in detail the dynamics of propagating and local modes in the whole range from the hydrodynamic limit to the many particle behavior.

The mechanisms of relaxation processes, connected with the collective excitations both in hydrodynamic and in microscopic areas about one to two inter-atomic distances, have been well established with the help of numerical simulation, and recently detailed information on the relaxation processes has been obtained by experimental IXS data. However, many aspects of the physical origin of the relaxation processes in microscopic areas of liquid metals still remain unclear [19].
On the numerical side, the access to the coherent dynamic structure factor is straightforward, once a realistic interaction potential has been found [19-25]. The only limitations are given by the finite computing power, as the spectral resolution of the dynamic structure factor is related to the temporal extension of the run, while the lowest accessible wave-vector decreases at increasing the particle number. Numerical techniques always allow an accurate determination of the dispersion curves, up to the extent that important effects, such as positive dispersion of sound have been unambiguously pointed out. The available experimental and numerical evidences, allowed the development of theoretical framework with the aim of giving a general description of the liquid phase dynamics.

A crucial point, in this context, is the understanding of the general properties of the memory function, such as the existence of well defined time-scales and their relation with the microscopic dynamics. A number of models have been developed, utilizing concept from mode coupling and kinetic theories [26-28]. Broadly speaking, within these models, the memory function is described in terms of a decaying function of time, characterized by two relevant time-scales. A faster one is thought to be related to the rattling motion of a particle within the cage of its nearest neighbors. This interaction is modeled as a markovian term, the so-called binary collision contribution. On the slower time-scale, the particle moves diffusing between cages, hence this process, highly temperature dependent, is intimately related to the glass transition physics.

All these concepts, developed on simple liquids for the sake of simplicity, can be extended to more complex systems, taking care of the presence of additional phenomena. On the other side, although this description successfully applies to the liquid-state dynamics, a further extension to the complex liquid systems has not been probed
yet. An overview of this approach, applied to the specific case of liquid polyvalent.

This thesis is devoted to the understanding of some of those fundamental aspects that characterize the microscopic and macroscopic dynamics of disordered systems.

1.2 Pseudopotential and Liquid Metals

The liquid state of matter is intuitively perceived as being intermediate in nature between a gas and a solid. Considerable effort has been made over the last couple of decades to understand the physical properties of matter in either liquid state or solid state. In the gaseous state, the atoms are distributed randomly and their motion seems to be completely irregular. On the other hand, the atoms in the crystals show only a slight vibration about a definite point in the regular three dimensional lattices. These extremes in the atomic distribution contribute to the construction of simple models for the structure of these two states. The 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 on ordering in near neighbor regions. This ambiguous situation hinders the construction of a model or the structure of the liquid state, and thus the liquid state theory has progressed rather slowly [29].

Liquid metals can be described as mixtures of electrons and ions. Some of the electrons (the core electrons) remain very close to nuclei as in the case of solid state and are negligibly affected by the atomic motion. The remaining electrons (valence electrons) are mobile through the assembly of ions and are responsible for the transport as well as cohesive properties of the liquid metals [30]. The attractive electrostatic interaction between the negatively charged electrons and
the positively charged nucleus (ions) is mainly responsible for the formation of the solids or liquids. The valence electrons referred to as the outer most electrons, are responsible for virtually all kind of physical as well as chemical properties of materials. To study such properties various techniques are developed. The pseudopotential method [2] is one of the simplest tools to study various physical and chemical properties of materials.

The concept of pseudopotential [31-35] has been developed within the ‘one electron model’, appears at first sight artificial and inconsistent. In the one electron model “each electron is considered separately as moving in the average field of nuclei and all the other electrons”. The interaction potential between an ion and an electron may be replaced with a weak potential. Such a potential is known as the pseudopotential.

Pseudism is a system of ideas stemming from the fact that a short range “compensatory” term may be added to the electron-ion interaction potential which will model the combined action of the nucleus and the core electrons while leaving unchanged the long range part (Columbian tail) of the potential. An original potential may be modified by adding a more or less arbitrary potential, but from the scattering theory point of view it will remain the same and it does not change the eigen values of the Schrödinger equation. Generally, the pseudopotential is set up in a model form in which the bare ion potential is consisting of certain parameters. This is developed within certain closed region such that the exact form of the true potential is replaced by it. Today the pseudopotential theory is widely used for studying the static, dynamic, electronic, magnetic, thermodynamics and molecular dynamics of bulk metals, liquid metals, alloys, metallic glasses and other disordered phases of materials.
Our understanding of the liquid (or molten) state of metals has progressed far within the past decades. Thanks to the advances in both x-ray and neutron scattering sources, it is now possible to measure the dynamics on a microscopic scale with very good statistical accuracy. The interest in understanding liquid metals on a microscopic scale is easy to comprehend; liquid metals have all the complexities of simple fluids like Argon, and in addition the sea of conduction electrons interacts with itself and with the positively charged ions. For this reasons, current interest of work is focused on the non-crystalline systems, i.e., liquid metals.

Despite the improvement in thermal inelastic neutron scattering (INX) and high energy X-ray inelastic scattering (IXS) techniques for investigating dynamic structures of liquids, due to the smaller incoherent scattering length than the coherent scattering length in many liquid metals; determination of single particle correlation functions is difficult [36-38]. In this scenario, one mostly resorts either on computer simulation experiments like molecular dynamics or on the theoretical modeling, both with appropriate inter-atomic interaction potential for the system under consideration. However, one of the basic problems in any theoretical evaluation of liquid-state dynamic properties is the non-availability of reliable inter-atomic potentials [39-43]. Especially, the problem is sever at low-density (or equivalently at high temperature), where liquid starts losing short-range order, and exhibits gas-like unstructured behaviour [39,44]. It is to be mentioned, however, that for inert gases situation is much more favourable as compared to liquid metals. Even simple nearly–free–electron (NFE) alkali metals due to their wide liquid temperature range show verities of features at elevated temperatures [40,41,45]. Attempts are therefore made in the past [40-43,46] to improve effective ion-ion interaction potentials for liquid alkali metals: there appear mainly two approaches to tackle this task. (i) To fit the potential parameters to some known thermo-physical properties [46]
at different higher temperatures, and (ii) using the phenomenological factor in the expression of inter-atomic potential [40,41] to treat the low-density behavior (i.e., characteristic Friedel oscillations observed at normal metallic density gets suppressed at low-densities, to be more explicit). Another important issue pertaining to the understanding of the structure of simple liquids is related to the n-body distribution functions $g^{(n)}(\vec{r})$; measuring the probability density for two, three and more particles at given positions. For pair-wise inter-atomic potential $V(\vec{r})$, although all thermodynamic and dynamical properties can be calculated through the knowledge of pair-correlation function $g^{(2)}(\vec{r}) = g(\vec{r})$ and its derivatives with respect to state parameters like density ($\rho$) and temperature ($T$); $\frac{\partial g(\vec{r})}{\partial \rho}$ and $\frac{\partial g(\vec{r})}{\partial T}$; needed in such studies depend on triplet correlation function $g^{(3)}(\vec{r})$.

Unfortunately, however, it is still not possible to calculate the desired higher order correlation functions readily using the microscopic theory, even though our broad understanding about the features of the time correlation functions [47], and one may adopt realistic approximations to estimate them.

The mass transport coefficients such as diffusion and viscosity coefficients of liquids are important quantities both from scientific and technological point of view. For example, knowledge of the liquid state diffusion coefficient is required to understand material processing techniques such as binary solidification and glass formation. Also, many of industrially important reactions are controlled by the diffusion of reactant species. Information on the physical and thermodynamic properties of liquid metals is important in technological applications. Liquid metals are important in modern industries/areas such as metallurgy, welding, casting, glass forming, and as coolant in the nuclear industry. In addition, how the physical
properties and structures change with temperature, concentration and pressure is also of general interest to researchers in physics.

In conventional approach, the most calculations of liquid free energy were based on the computation of pair-wise weak potential energy in addition to the ideal gas kinetic energy \( \frac{3}{2} k_B T \). Further, the entropy and other structural information are included from appropriate reference system consistent with the gas-like phase [48,49]. This approach depends on the knowledge of the interatomic interactions as well as correlation functions. Alternatively, in his series of papers [50-53], Wallace has proposed a technique and notion to compute thermodynamic properties of the elemental liquid and solid metals. In one such approach [51], the author proposes a high temperature expansion of the ion-motional quasiharmonic free energy for evaluating the vibrational free energy from the knowledge of the phonon frequency moments. While in his subsequent paper [52], he develops a liquid state theory to construct the Hamiltonian for monoatomic liquid metals within the adiabatic approximation. Result for entropy of liquid mercury and other simple metals are compared with experimental findings up to the temperature three times higher than the normal melting temperature. Recently, Trachenko and his co-workers [44,54,55], have proposed a similar solid-like approach for calculating internal energy and constant volume specific heat \( (C_V) \). They attributed decrease in liquid specific heat with temperature to the increasing loss of low frequency transverse modes. Further, by incorporating anharmonicity through thermal expansion, they were able to reproduce experimental specific heats for 21 different kinds of liquids. Nevertheless, it is to be mentioned that the theory relates \( C_V \) to the viscosity and liquid relaxation time stipulates the knowledge of thermal expansion a \textit{priory}. 
Therefore we choose rubidium and other polyvalent liquid metals for the following reasons. Rb is the heavy alkali metal for which extensive experimental data is available over wide temperature range. Its electronic structure remains almost unaltered on melting so that it can be described by the nearly-free-electron (NFE) model. Due to these reasons, it is possible to test and validates the computational scheme proposed in the present thesis. On the other hand, though the other polyvalent metal do not fall strictly in this category, the concept of local pseudopotential is still valid [56]. Secondly, for example, tin is one of the exceptional metals having widest liquid temperature range, while Ga show highly complex structure. This provides the stringent test for the validity of any theoretical model. In the present thesis, the numerical proposals apply to simple liquid metal Rb and then extended to some non-simple liquid polyvalent metals (in present case liquid Sn, Pb, Al, Ga and In).

### 1.3 Outline of Thesis

The thesis comprises of five chapters as outlined below.

Chapter 1 begins with the introduction to recent advances in both x-ray and neutron scattering sources, making possible to measure refined structure and the dynamics on a microscopic scale with very good statistical accuracy. The different experimental and theoretical methods for measuring and calculating different physical properties of liquid metals are also discussed. The relatively narrow area of condensed matter physics that we will be studying is also described. The importance of the liquid metals study in various fields of science and technology is highlighted.

Chapter 2 explains the theoretical methods employed for the present work. The theory and formalism of pseudopotential, screening
and local field correction function is discussed in the present chapter. Also, the modified empty-core potential due to Hasegawa et al. [57] is discussed in details. We present a literature survey of the existing information about liquid metals and its various physical properties. This helps us in identifying a specific research problem. At the end of the chapter 2, we formulate our problem for the present study. A general scheme of determining potential parameter and thereby various physical properties is also outlined at the end of the chapter.

In Chapter 3, the theoretical background of all the computed physical properties along with the necessary formulae is presented.

In Chapter 4, we present the results of different physical properties of above mentioned liquid polyvalent metals using pseudopotential approach and discussions are also made. Temperature dependence of structure factor and pair correlation function is calculated. To compute the phonon frequencies of liquid metals, the quasi-crystalline approximation technique with interatomic pair potential developed by Takeno and Goda (TG) is used. A simple analytical model for atomic motion is used to obtain velocity autocorrelation function (VACF) for liquid metals. The coherent behavior of liquid metals in terms of the dynamic structure factor employing viscoelastic theory has also been studied. The predicted results for VACF, cosine power spectrum, mean square displacement, diffusion and viscosity coefficients have been compared with recent available molecular-dynamics data and experimental data, and a good agreement has been achieved. Here, we propose a simple approach for liquid metals based on second order perturbation theory and contribution of anharmonicity, derive the necessary equations, and perform the numerical tests comparing results of our present approach with the other approaches. In this work, we propose how to include the anharmonic effects in the approach to liquids from the solid-like state. The Gibbs-Bogoliubov (GB) variational method is
applied to investigate the thermodynamic properties (thermal expansion, Helmholtz free energy, entropy etc.) of some liquid polyvalent metals. The calculation of electrical resistivity, thermoelectric power and thermal conductivity based on the self-consistent approximation as suggested by Ferraz and March is presented in the same chapter. The outcome of the present study is discussed in light of other such results and with predictions of Wiedemann and Franz law. This confirms the applicability of the present scheme up to very high temperature.

In chapter 5, conclusions and future prospects of the present work has been discussed. Important discussions regarding the applicability, advantage of presently formulated pseudopotential and scheme of determining potential parameter are also addressed. The scope of further investigations of the work is also pointed out at the end.

The thesis ends with appendix where the distinct physical and vibrational properties of high-temperature LaS, through current state-of-the-art first principles computations are investigated. Self-consistent plane-wave basis set and ultrasoft pseudopotential for electron–ion interaction have been used to obtain ground state properties for lanthanum monosulfide. Phonon dispersions and phonon density of states at ambient as well as at high temperature conditions are also derived using the density functional perturbation theory. For high-T thermo-physical properties, quasiharmonic GIBBS code was used with necessary inputs provided by the present ab initio calculations. The present study show good agreement for cohesive and certain finite temperature thermodynamic properties including entropy, specific heats ($C_V$ and $C_P$), equation of state and structural phase transition (B1 to B2) at high pressure and high temperature. The present study raises subtle question regarding the microscopic understanding of the phase stability which is discussed in length in
appendix. Further, based on the Lindemann’s melting law, P-T diagram is constructed.

Important and useful references are listed at the end of each chapter for making it reader friendly and we have used the atomic unit system throughout the calculations.

In the present work, in numerical calculations, we have adopted atomic unit system: Mass of the electron $m = 0.5$; Charge of the electron $e^2 = 2.0$; Reduced Planck constant $\hbar^2 = 1.0$ and Energy is in Rydberg.
References

44. D. Bolmatov, V. V. Brazhkin and K. Trachenko, Scientific Reports 2, 421 (2012).