1 Prologue

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1.1 Prologue

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 19\textsuperscript{th} century, good progress had been made on the theory of the gaseous state. During the 20\textsuperscript{th} 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 [1.1-1.5].

Liquid metals are an outstanding example of systems combining great relevance in both industrial applications and basic science. On the one hand, they find broad technological application ranging from the production of industrial coatings (walls of refinery coker, drill pipe for oil search) to medical equipments (reconstructive devices, surgical blades) or high performance sporting goods. Most metallic materials, indeed, need to be refined in the molten state before being manufactured [1.6].

Liquid metals, in particular the monatomic ones, have been recognized since long ago to be the prototype of simple liquids, in the sense that they encompass most of the physical properties of real fluids without the complications which may be present in a particular system [1.7]. In addition to that, metallic fluids such as molten sodium, having similar density and viscosity to water, find application as coolant in nuclear reactors. For this reasons, current interest of work is focused on the non crystalline systems i.e. liquid metals.
In the gaseous state, the atoms are distributed randomly and their motion seems to be completely regular. 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 an 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 slowly [1.2].

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” [1.8].

Liquid metals can be described as mixtures of electrons and ions. Some of the electrons (the core electrons) remain very close nuclei 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 [1.9].
Until the 1960s the understanding of the physical properties of metals proceeded rather slowly. It was Ziman, indeed, who made the theory of liquid metals respectable for the first time [1.10], and the Faber-Ziman theory, developed in 1961–1963 and dealing with electronic and transport properties, is attractively introduced in Faber’s book [1.11], which is an excellent treatise of the physical properties of liquid metals [1.11]. The other text which can be considered a classic is March’s book [1.10], which provides a comprehensive overview over liquid metals. It is from these texts that a first clear definition of liquid metal can be outlined. At first glance, indeed, the words “liquid metal” is self explanatory: by definition any metal heated to its melting point can be cast in this category. Liquid metals, however, are implicitly understood to be less general than the above definition, and no literature clearly states an exact definition. Although no precise agreement has been made, there are certain characteristics shared by liquid metals, descending from a close interplay between ionic structure, electronic states, and transport properties. The book of Shimoji [1.13] deals with the fundamentals of liquid metals in an elementary way, covering the developments achieved after the book by March [1.12]. It does not address, however, the dynamical properties in great detail.

Addison’s book [1.14] is much like March’s general book [1.12], but is more focused on applications of alkali metals, especially on their use in organic chemistry. In addition, Addison discusses many methods for purifying and working with liquid alkali metals. March [1.12] is more theoretical whereas Addison [1.14] is practical, but both authors focus on a thermodynamic explanation of liquid metals [1.6].

There are, then, a number of books which are more general and more specific at the same time, in the sense that they deal with the wider class of simple liquids (including noble fluids, hard-sphere fluids, etc.), but they are mainly concerned with structural and dynamical properties only [1.3, 1.4, 1.15-1.17]. They are practically
ineludible for those aiming at a rigorous approach to the statistical mechanics description of the liquid state.

It can be difficult to find an exhaustive updated database of the physical properties of liquid metals, especially as far as dynamics is concerned. But the handbooks of Iida and Guthrie [1.18] and Ohse [1.19] are remarkable exceptions, with the second one specifically addressing liquid alkali metals.

The dynamics of liquid metals has been extensively investigated by inelastic neutron scattering (INS) and computer simulations with the main purpose of ascertaining the role of the mechanisms underlying both collective and single-particle motions at the microscopic level. In the special case of collective density fluctuations, after the seminal inelastic neutron scattering study by Copley and Rowe (1974) [1.20] and the famous molecular-dynamics simulation of Rahman (1974) [1.21] in liquid rubidium, the interest in performing more and more accurate experiments is continuously renewed: it was soon realized, indeed, that well-defined oscillatory modes could be supported even outside the strict hydrodynamic region. In molten alkali metals, moreover, this feature is found to persist down to wavelengths of one or two inter particle distances, making these systems excellent candidates to test the various theoretical approaches developed so far for the microdynamics of the liquid state. Up to ten years ago the only experimental probe appropriate to access the atomic dynamics over the interparticle distance region were thermal neutrons, and using this probe fundamental results have been gained [1.6]. There are, however, certain limitations of this technique which can restrict its applicability; first, the presence of an incoherent contribution to the total neutron scattering cross section. The second reason is dictated by the need of satisfying both the energy and momentum conservation laws which define the (Q-E) region accessible to the probe [1.7].
Paralleling the development of INS facilities, new ideas arose on both theoretical and numerical fields from 1975 and in intervening decades, driven by kinetic theory applied to Enskog’s fluid [1.22-1.26], allowing one to describe the hydrodynamic region in terms of the three-pole approximation, or to reproduce the dynamic structure factor at wavelengths comparable to the inverse mean particle distance in terms of extended heat mode [1.27]. Kinetic approaches were eventually complemented by memory function formalism and by mode coupling theory [1.28-1.35].

Turning attention to numerical advances in the liquid metals field, the major achievements are probably related to the introduction of the pseudopotential concept [1.36-1.40] which, besides offering a deeper comprehension of physical properties such as electrical resistivity, provided a clue for realistic numerical simulations.

In molecular dynamics, indeed, the choice of a realistic interatomic potential—i.e., a potential model able to reproduce structural properties—is crucial to allow the determination of the dynamics of the system via the integration of the classical Newton equations. Exploiting the pseudopotential theory, it has been possible to express the atomic interaction as a sum of pairwise interactions, ruled by an effective density-dependent interaction [1.6].

In this respect, one of the most successful expressions is the effective potential proposed for liquid metals [1.41]. The numerical simulation framework is particularly useful since the single-particle and the collective dynamics can easily be investigated within technical restrictions due to the finite box size (defining the minimum accessible wave vector) and computation time (related to the statistical quality and to the energy resolution of the calculated spectra). Broadly speaking, the features of the atomic collective motion, i.e., the details of the $S(Q,\omega)$ line shape, turns out to be less noisy and more straightforward than the corresponding INS
results: no absolute normalization is required, no mixing between coherent and
incoherent dynamics occurs, and, above all, basically no resolution corrections are
needed [1.6].

Among the new insights into liquid metal physics which began to emerge in
the 1960s was the realization that several stands of theory were converging. Simple
non-metallic liquids like argon have become well understood through steady progress
in liquid state theory. This theory was ready for use for liquid metals if their
interatomic forces resembled. Striking developments in the physics of crystalline
metals were showing that this was indeed conceivable, so a fusion of metal and liquid
state theories began, and continues still. In other words, liquid metals can be seen as
one class of structurally disordered or non-crystalline state which also includes all
other liquids and glasses and amorphous semiconductors. It is also a disordered array
of ions immersed in a gas electron [1.5, 1.11, 1.13].

The general character of metals results from the dense fluid of free electrons
that permeates them. Indeed pure liquid metals can be mixture of (i) a fluid of
positively charged ions and (ii) a gas of negative electrons containing one electron per
ion in sodium, two in calcium, and so on according to valency. There will, therefore,
be about $10^{28}$ electrons/m$^3$, and these are loosely called “free electrons” because they
can move through the entire system. The free electron gas conducts electricity well
and is also responsible for thermal conduction, metallic reflectivity, and all the other
typically metallic properties. To understand a liquid metals we must tackle three
problems which are not really separate. They concern the forces between the ions and
the electrons, the forces between one ion and another, and the way electrons behave in
a disordered environment [1.5, 1.11, 1.13].

The ions contains tightly bound to nuclei. The free electrons flow through the
ions under the control of two major influences: (a) the electrostatic attraction of the
positive ions and (b) a complicated response to those electrons bound to the nuclei. A powerful development of the modern wave mechanical theory of solids made it possible to treat influence (b) mathematically as if it were and electrostatics influence like (a) except that it is a repulsion, which partially cancels the attraction (a). The net effect of the two is quite small and is called a weak pseudopotential. An electron passing through an ion may therefore be thought of as deviated by the appropriate pseudopotential. However, the ions do not suddenly exert its influence as the electron crosses a well-defined ionic boundary. The ions are positively charged and the electron gas is mobile, and therefore the ions exert a long range influence on the gas by attracting electrons to them. Meanwhile the free electrons are also repelling each other, and a complex balance of forces sets in whose ultimate effects is to envelop each ion in an electron cloud. This cloud, being negative, neutralizes the effects of the positive ion rather completely at large distances and less completely at smaller distance. The cloud of electrons piled up near an ion is called the ion screening cloud and the total effect on an approaching electron of the pseudopotential and the screening cloud is called the screened pseudopotential. We may therefore say that from the point of view of one electron passing through a liquid metal it encounters the screened potential of the ions (the nearest ones being felt more strongly) and is scattered by them. The total effect of all the ions acting through their weak screened pseudopotential on all the electrons is to produce the very electrons clouds that screen the ions. This idea underlies most current thinking about liquid metal physics. Pseudopotential can be calculated from first principles, i.e., from the known nature of the ions, and they enable a good account to be given the conductivity and other electronic properties [1.5, 1.11, 1.13].

The study of liquid structure and its properties is important for scientific and technological reasons. For instance, many crystals are grown or refined from the
molten state, and a better knowledge of the dynamics of impurities can improve crystal quality. However, our knowledge of the liquid structure is much less than our knowledge of the crystalline structure of matter. This is due to the fewer techniques available to study liquids, as well as intrinsic difficulties in formulating models for them [1.2, 1.12, 1.13]. Liquid metals can be considered as an ensemble of ions and electrons in a disordered configuration with good electrical and thermal conductivity. In contrast to a solid metal, there is no long- or medium range order. Short-range order is evidenced by a strong peak in the pair correlation function as determined by x-ray or neutron diffraction experiments [1.2]. Herein lies the basic difficulty in formulating a model for a liquid: the theory must include the potentials between all pairs of ions. Simplifications that might be included in the model reflecting a periodic arrangement of atoms (as in a crystalline solid) or to a completely disordered structure (as in a gas) are not applicable to a liquid [1.42].

Recent progress in the structural analysis of non-crystalline materials [1.42-1.50] reveals many interesting microscopic features for their structures. In principle, various properties of non-crystalline materials can be estimated from the structural data (like structure factor; \( S(q) \) and pair distribution function; \( g(r) \)) when coupled with an appropriate theory. Because of its importance to physics, chemistry, metallurgy, industry, engineering and materials science, there are many theoretical treatments on the relation between microscopic structure and macroscopic properties for non-crystalline materials [1.1-1.126]. In all these treatments, considerable interest has been focused to investigate the better reference system to calculate the static structure factor of liquid metals using pseudopotential approach. 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 calculations can be expressed possibly in an analytic form.

Hence the literature survey [1.1-1.126] suggests that it is highly desirable to search a better reference system which gives good explanation of various physical 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 requirements in explaining various physical properties of liquid metals.

In all these studies [1.1-1.126] very few attempts have been made on transition liquid metals. One of the most interesting points in the field of liquid state physics is whether the liquid structure of transition metals having the incomplete d shells differs from that of simple metals [1.2]. The elements in the d block of the periodic table are known as transition metals. Many interesting properties of the transition liquid metals as a group are due to the results of their partly filled d sub shell. In general their properties are dependent on the electronic configuration of the electrons in the outer shell and in the penultimate outer shell. The transition metals have different oxidation states which makes them useful as catalysts. Ions in higher oxidation states tend to make them good oxidizing agents whereas elements in low oxidation states become reducing agents. They form coloured compounds, complex ion and also form alloys with themselves and with other elements. The presence of the unpaired and paired electrons in the d sub orbital become them paramagnetism and diamagnetism respectively.

The various properties 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 [1.1-1.126]. Although a lot of work has been done on it, 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 pair-wise potentials. 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. Also it is found in the literature survey [1.1-1.126] that some ab-initio pseudopotentials suitable for perturbation theory of the ionic interactions were generated. In general, the pseudopotentials like Fiolhais et al model [1.51-1.53], Ashcroft empty core model (AS) [1.54, 1.55], Heine-Abarenkov model (HA) [1.55, 1.58, 1.59], Harmonic model potential (HMP) [1.55, 1.58, 1.59], Krasko-Gursky (KG) model [1.60, 1.61], Animalu Heine (AH) model [1.60], Generalized nonlocal model potential (GNMP) [1.62-1.64], energy independent nonlocal model potential (EINMP) [1.65, 1.66] etc. have been applied to study the various properties of liquids. To describe the structural information researchers have used different reference systems like Percus-Yevick Hard Sphere (PYHS) [1.56-1.59, 1.67-1.85], One Component Plasma (OCP) [1.61, 1.77, 1.86-1.101], Charged Hard Sphere (CHS) [1.77, 1.102-1.117], Hard Sphere Yukawa (HSY) [1.118, 1.119], Soft Sphere (SS) [1.120-1.122], and Optimized Random Phase Approximation (ORPA) [1.123-1.126]. We believe that only a combined analysis of structure and structural based various properties 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.

Looking to this situation, we thought it worthwhile to study the static, dynamic, vibrational and electronic properties of some liquid transition metals using our own model potential [1.67-1.70, 1.72, 1.86] by applying different reference systems to incorporate the structural information of liquid.

Thus the aim and perspective of the present thesis is to project “Study of Static, Dynamic, Vibrational And Electronic Properties of Some d Shell Liquid Metals Using Pseudopotential Theory” based on established physical and computational approach.
1.2 Summary of chapters

The entire thesis is divided into eight chapters as per following descriptions.

Chapter 1 deals with a survey of the previous investigations in the field and the motivation for the present work. It also describes the introductory part and an overview of the entire thesis.

Chapter 2 describes the historical background and theory of pseudopotential. The detailed construction of the newly proposed pseudopotential [1.67-1.70, 1.72, 1.86] and its applicability to some d shell liquid metals viz. 3d (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn), 4d (Zr, Pd, Ag and Cd) and 5d (Pt, Au and Hg) are also discussed in this chapter. The role of screening and different form of the local field correction functions is also explained. To see the influence of exchange and correlation effect, Hartree (H) [1.1], Hubbard–Sham (HS) [1.127, 1.128], Vashishta–Singwi (VS) [1.129], Sarkar et al (S) [1.130], Taylor (T) [1.131], Ichimaru–Utsumi (IU) [1.132] and Farid et al (F) [1.133] local field correction function are used in entire thesis.

Chapter 3 deals with the structural properties [1.86] of liquid transition metals viz. 3d (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn), 4d (Zr, Pd, Ag and Cd) and 5d (Pt, Au and Hg). The structural properties like structure factor $S(q)$, pair distribution function $g(r)$, interatomic distance $r_1$, long wave length limit of structure factor $S(0)$ and first coordination number $n_1$ are computed using Percus-Yevick Hard Sphere (PYHS) [1.56-1.59, 1.67-1.85], One Component Plasma (OCP) [1.61, 1.77, 1.86-1.101] and Charged Hard Sphere (CHS) [1.77, 1.102-1.117] reference systems. The first and second peak positions and related magnitudes are also tabulated. All the results are compared with experimental data [1.2], wherever exist.

In chapter 4, the electronic transport properties [1.72] like electrical resistivity ($\rho$), thermoelectric power ($Q$) and thermal conductivity ($\sigma$) of liquid 3d (Sc, Ti, V, Cr,
Mn, Fe, Co, Ni, Cu and Zn), 4d (Zr, Pd, Ag and Cd) and 5d (Pt, Au and Hg) transition metals are calculated for different oxidation states (valencies). To calculate electronic transport properties, Ziman’s formula is applied along with Percus-Yevick Hard Sphere (PYHS) [1.56-1.59, 1.67-1.85], One Component Plasma (OCP) [1.61, 1.77, 1.86-1.101] and Charged Hard Sphere (CHS) [1.77, 1.102-1.117] reference systems. The calculated results are compared with available experimental data [1.11, 1.134-1.38] as well as other theoretical data [1.75].

A pseudopotential perturbation scheme based on Gibbs-Bogoliubov (GB) variational technique is considered to study the thermodynamical properties of liquid transition metals in Chapter 5. In this chapter, the thermodynamical properties like internal energy ($E$), entropy ($S$), Helmholtz free energy ($F$), isothermal compressibility ($\chi_T$) and specific heat ($C_V$) of 3d, 4d and 5d liquid transition metals are calculated. The structure factor $S(q)$ are also generated using obtained variational parameter ($\eta$) from various reference systems like Percus-Yevick Hard Sphere (PYHS) [1.56-1.59, 1.67-1.85], One Component Plasma (OCP) [1.61, 1.77, 1.86-1.101] and Charged Hard Sphere (CHS) [1.77, 1.102-1.117]. The detailed comparison of presently generated data is made with the available experimental [1.2, 1.139-1.142] and others such theoretical data [1.64, 1.76, 1.90, 1.93, 1.94, 1.120, 1.123, 1.143-1.147].

Atomic transport properties like shear viscosity coefficient ($\eta$) and self-diffusion coefficient ($D$) of 3d, 4d and 5d liquid transition metals are investigated in Chapter 6. The present results are compared with available experimental [1.13, 1.148-1.152] and others theoretical data [1.153-1.161].

In Chapter 7, vibrational properties of 3d, 4d and 5d liquid metals are investigated. Here the electron dispersion and phonon dispersion relations for liquid transition metals are generated. From these relations we have obtained longitudinal...
and transverse sound velocities, bulk modulus ($B$), modulus of rigidity ($G$) and Young’s modulus ($Y$) of liquid transition metals. The present results are compared with available experimental data [1.162, 1.163].

The final and concluding Chapter 8 summarizes the entire work of the present study along with the important general conclusions. The applicability and advantage of the present pseudopotential are also mentioned in this chapter. The future scope of further investigations of the work is also pointed out at the end. The necessary results, discussions and conclusions are made at the appropriate point in every chapter.

During the course of this work, the presently constructed model potential [1.67-1.70, 1.72, 1.86] is applied to study the electronic transport properties of liquid lanthanides using PYHS [1.56-1.59, 1.67-1.85] reference system. The results are presented as Appendix A 1 to the thesis. The study is also extended to compute surface properties (like surface tension ($\gamma$) and surface entropy ($S_V$)) of Fe, Co, Ni liquid metals and atomic transport properties of $3d$ liquid transition metals using PYHS [1.56-1.59, 1.67-1.85] reference systems. These results are discussed in the Appendices A 2 and A 3 respectively.
Chapter 1

References:


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Chapter 1


