# CHAPTER 1

**IMPORTANCE OF PHYSICS OF SMALL PARTICLES**

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1.1 Introduction

Scientists have been dealing with particles of diameters in the range 1-100 nm in dispersed systems, which are referred to as colloidal particles, since the founding of the colloid chemistry in the 1860s. However, it is only in the last 25 years we have been able to study individual particles of this size. Presently these particles are also referred to as small particles, nanoparticles, ultrafine particles, microcrystals and microclusters. Much effort has been put by many scientists to investigate the properties of these particles. The result has been the discovery that these particles have properties not displayed by larger or smaller collection of atoms or molecules, properties that suggest many scientific and technological applications (1). The growing interest in the physics of small particles is due to the expectation that investigation on such systems may lead to extremely valuable information at the microscopic level. Atoms in a cluster have, in general, a different surrounding with respect to those in the bulk state (2-4). Many quantities such as temperature, surface tension, surface area and even the volume that are used in the description of macroscopic systems become ill-defined as the cluster size decreases (3,4). Therefore, many difficulties are encountered in calculating the properties of small particles from classical thermodynamic
considerations (2,3). Numerous experimental and theoretical studies have been made to investigate the various properties of microclusters. These studies have opened new horizons in the field of physics of microclusters.

1.2 Importance of Small Particle Research

The evolution of the structural, chemical, vibrational and other properties as atoms form progressively larger clusters leading to a macroscopic solid has long been a problem for solid state and theoretical physicists. Many questions are to be answered about the properties of these clusters (5). Over what size range does the transition between molecular and bulk properties occur?. Is the transition abrupt or gradual, monotonic or oscillatory?. Do all properties make the transition in the same cluster size range?. The answers to these and other questions are being increasingly pursued both experimentally and theoretically. Presently, the science of fine particles has acquired technological importance also because of the view that it may be possible to produce macroscopic systems with given properties from submicroscopic particles by properly choosing their composition, size and other characteristics (6). The current activity in cluster research is expected to make it possible to understand and predict not only the immediate cluster properties but also to obtain a
clarification of the relationship between molecules and condensed matter (7). Studies on clusters have brought about many unexpected but interesting results (8) but it is believed that continued research in this field may unravel many more of the exquisite properties of these novel micro-materials.

1.3 Existing Knowledge

Detailed configurational analyses of clusters have been made by many scientists using techniques such as EXAFS and XANES along with high resolution electron microscopy and electron diffraction (9-13). Experimental investigations indicate that small clusters assume different geometrical structures as the clusters grow by the addition of atoms, molecules or even small aggregates of atoms (5). This reconstruction due to the attachment of atoms or aggregates of atoms will continue until the cluster attains a final lattice structure (5) and the resulting structure may not be the same as that of the material in the bulk state. Even if the structure of the cluster happens to be identical with that of the bulk, the lattice parameters may vary. This variation may either be due to a contraction (9) or an expansion of the lattice (7,12). Montano et al (7) through EXAFS studies showed that for microclusters of Ag, Fe and Ge there was a 3% lattice contraction. For clusters of smaller
size they observed a lattice expansion. Lee and Stein studied the structural variations of argon clusters (8). Thus the investigation of the structure of microclusters yield important information regarding the structural changes a cluster undergoes as it grows, the surface stress and the resultant lattice contraction experienced by clusters and also the lattice expansion in small clusters (9).

Chemical reaction studies will provide a useful probe into the structural makeup of clusters and directly investigate the approach of the chemical behaviour of clusters to that of the bulk surface (13). The earliest reaction studies of iron, cobalt and niobium clusters reacting with N₂ and D₂ have shown sharp variations in reactivity as a function of cluster size (14-20). Following these early reaction studies considerable theoretical (21-26) and experimental (27-34) investigations have been done to study the effect of size on various properties of clusters.

Theoretical and experimental study of lattice vibrations have now well established that real crystals when their dimensions are relatively small show transverse and longitudinal bulk modes as well as surface modes which have intermediate frequencies; when dimensions become extremely small only surface modes persist (35,36). Raman scattering studies on microcrystals have also shown that the Raman
lines varied in frequency and intensity with the size of the crystallites and also with the nature of the surrounding medium (37,38). Laser Raman spectroscopy (LRS) has been efficiently used to investigate the peculiar vibrational properties of small particles (37-40).

Much attention has been paid in recent years to the photophysical and electrochemical properties of small particles (41). The changes in band gap energies and electrical properties of small particles have been examined in detail (42). Ionisation potentials (27-29), electron affinities (30,31) and magnetic properties (32,33) of microclusters have been found to depend on the cluster size.

The study of various physical properties of clusters remains one of the most important tasks of cluster research. Kinetic aggregation has historically been one of the most widely studied subject within colloid science. The random tenuous clusters that are produced when clusters aggregate have a well defined symmetry as their structure is invariant under a change in length scale. This is called dilation symmetry, and objects that possess it are called fractals (40). All of our knowledge of these structures has come from computer simulations (43-46). Much of the current interest in this field was stimulated by Witten and Saunder (43,44) who considered a growing cluster to which new
particles were added one at a time by random diffusion. But more realistic models are cluster-cluster aggregation models which can represent the actual experimental situations (44). TEM imaging has been efficiently used to analyse the structure of the aggregates of the clusters.

A lot of information is available presently about the properties of small particles but a number of problems related to them remain to be settled. No exact knowledge is available from which cluster size on the structure resembles bulk structure and on atomic disorder inside and within the surface atomic shell. The various physical and chemical properties of well characterized clusters remain one of the most important tasks of cluster research. The important problem of magnetism in clusters did not received much attention. Another problem of great concern is how the metallic properties change as the cluster size decreases. Experimentally more knowledge can be expected from techniques such as laser Raman spectroscopy, EXAFS, LEED and photoemission and traditional optical measurements. Experimental and theoretical studies solved many problems related to small particles, but many new ones have emerged.

1.4 Work Undertaken in the Present Study

In this work the author has made an attempt to study some of the important properties of microclusters of
certain materials. The particles for this study have been prepared as fine suspensions by electrical disintegration and by chemical methods. The size of the particles range from 8 to 48 nm. The crystal structures and lattice contraction of small particles of silver, silver iodide, mercuric iodide and arsenious trisulphide have been investigated using electron diffraction. Electron diffraction along with TEM imaging has been used to study the phenomenon of cluster aggregation observed in suspensions of sulphur, silver, silver iodide and mercuric iodide. The peculiar vibrational properties of small particles of sulphur, silver iodide and mercuric iodide have been investigated using laser Raman spectroscopy. The interaction between clusters of silver and arsenious trisulphide and the interaction between silver iodide and mercuric iodide have been studied using techniques such as electron microscopy, EDAX, X-ray analyses and laser Raman spectroscopy (LRS). The pattern formation exhibited by the product of interaction when clusters of silver and arsenious trisulphide are allowed to interact through a diffusion controlled process, and the growth of the composite clusters, when clusters of silver iodide and mercuric iodide are allowed to interact have been studied. The velocity of ultrasonic waves in suspensions of small particles of sulphur and in suspensions of small particles
of silver iodide for different concentrations were determined. From this data the compressibility of the suspension and that of the suspended particles have been estimated. The investigation of ultrasonic attenuation in suspensions of small particles of silver iodide have also been carried out.
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