

# Nano-structure and phase transitions in the liquid phase of metallic and non-metallic elements

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## ABSTRACT

The generally accepted model of the liquid phase is that of a single "homogeneous" phase, with a structure which is more or less homogeneous throughout the pressure-temperature field in which it is the stable phase. Herein we present data in the liquid state to argue that the liquid of any composition exists in several differently structured nano-phases. The local configurational variations that specify what can broadly be called a "phase" in the liquid include local coordination number, bond angle, coordination sphere and bond length. The elements that are studied herein include: Hg, Bi, Sn, S, Se, Te. The understanding of nano-phases in the liquid state can be a precursor to quenching persistently metastable solid phases which may have promise for applications in biotechnology.

*Keywords:* nanostructure, liquid phase, short range order.

## 1. Introduction

Herein is presented a coherent model and description of the behavior of the liquid state of elemental metals, and covalently-bonded non-metallic elements and binary molecules such as water. The data and interpretations specifically focus on metals, bismuth, tin, and mercury, and on group VI A elements, sulfur, selenium, and tellurium, with some reference to water. The interpretation given herein of over 30 years of data [1-7] proposes that the liquid state is composed of non-homogeneous local configurations with very short range nano-order (broadly referred to as 'phases') which undergo transitions from one to another, depending upon the thermodynamic environment. Thus the liquid state cannot be modeled as the conventionally /historically described disordered *random network* of atoms or molecules, but as a mixture of nano-heterogeneous regions in pressure-temperature-composition space (p-T-X) that are characterized by bond angle, bond strength, coordination number, coordination sphere, density, and chemical potential. Recent

work on the polymorphic structures of ice and the local transitions in water [8] has reinforced the requirement and demand in modern phase equilibrium and the emergent field of nano-science that an overall model/theory of the liquid state must be forthcoming based on individual local structures that are favored at specific domains and ranges in a *p-T field*. The other thermodynamic variables in the equation of state that define the Gibbs function, electric and magnetic field, will also necessarily influence the nano configurations of liquid state species.

## 2. The Liquid State of Elemental Metals

We have conducted detailed studies of the elemental metals bismuth [1], tin [2], mercury [3], and lead [4], and interface studies with copper and platinum, using a wide variety of hydrostatic and quasi-hydrostatic equipment including argon pressure vessels, the Bridgman opposed anvil system, a diamond cell apparatus, and a hexahedral press. We measured *in-situ* optical, electrical conductance or resistance, specific volume, heat of formation, and magnetic properties over the course of 35 years of research. We also conducted detailed x-ray diffraction studies of solidified products quenched from p-T regions where the charge was held for various periods of time. All of these studies have consistently revealed second-order type transitions in the liquid state indicating that the liquid is *not* homogeneous and that liquids do *not* change structure monotonically as a function of pressure and temperature. *In situ* x-ray diffraction techniques, including angular dispersion analysis and energy dispersion analysis [5-7], also yielded a characteristic scattering pattern corresponding to a preferred probabilistic short-range liquid nano structure. The nano structure of the liquid state of metals is suggestive of non homogeneity in the liquid state of semi-conductive materials and the liquid state of non metals because of the covalent bond vulnerability to the effects of changing pressure and temperature. These research findings give rise to a better understanding of nano-

configurations in materials that have been either rapidly quenched, or slow-cooled from the liquid state, whether the resulting solid is non-crystalline such as glasses or whether polycrystalline or even single crystal materials (and defects therein). This implication is in keeping with the conclusions that the various “phases” and nano configurations of the liquid state are consistent with the character of the p-T melting curve (such as maxima and cusps) of the associated solid [1,2,9,10]. Implications from the research referenced and interpreted herein, are pertinent to precipitated phases and hence draw attention to biomedical applications related to blood flow through arteries, and to matter built up in the brain such as associated with brain diseases as Alzheimer’s. Knowledge of the structure of precipitated and disproportionated phase will in due course lead to improved treatment of disorders that relate to material and chemical phenomena. For a comprehensive review of the specifics of the p-T-X characteristics of liquid-state nano-configurations, the reader is urged to study the original references [1-10] and the most recent review and interpretation given in Ref.11.

### 3. The Liquid State of Covalently-Bonded Non-Metals and Molecular Materials

Using the techniques described in the previous section detailed studies have been conducted on the Group VI A elements, sulfur, selenium, and tellurium in the liquid state at atmospheric and the high pressure. Transitions between different liquid configurations, due to changes in pressure and temperature, were in general of a much larger magnitude than those associated with the low-melting metals, and were often more persistently metastable especially in molten sulfur. This is because crystalline sulfur is based on an octameric puckered ring structure that upon melting transforms to an equilibrium mixture of rings, broken rings (ring scission), and polymeric chains, with the chain structure being favored above moderate pressures (in the tens of kbar range). The rather strong secondary bonding between neighboring chains (due in part to van der Waals interactions) favors and fosters persistently metastable phases that are insoluble in water and often insoluble in carbon disulfide as well [10]. The polymerization of liquid sulfur at 1 atm at 159C, is a key liquid  $\rightarrow$  liquid transition, and above about 0.8 kbar molten

sulfur melts *directly* to polymer [10]. Liquid sulfur undergoes chain scission and an accompanying decrease in viscosity at 1 atm at about 188C, yet with increasing temperature the polymer concentration of the liquid continues to increase as the average chain length decreases from about  $\sim 10^6$  atoms at maximum viscosity.

The research has shown that sulfur in the crystalline and in the liquid state is an archetype material, and with increasing pressure and temperature shows a progression from an insulating ring structure, through a modestly semi-conductive chain structure, to the metallic state. In the liquid phases, the ring, the chain, and metallic species are associated with unique nanostructures rather than with a homogeneous liquid [10].

Selenium and tellurium, in their crystalline form at atmospheric pressure, are based on a helicoidal

A8 zigzag chain structure. At 1 atm selenium melts to a mixture of short chains and eight-membered rings. Liquid tellurium at atmospheric and at high pressure suffers a number of transitions based on changes in local coordination number and changes in bonding. Since group VI A elements are characterized by an  $s^2p^4$  valence shell, the tendency toward forming closed rings (typically 8-membered or 6-membered, but sometimes other variations) and long chains is favored with the typical primary coordination number (c.n) of 2, at least at 1 atm to the kbar range. The two available p-states to achieve a closed valence shell allow the liquid states to be very susceptible to structural transitions on a nano level caused by changes in pressure and temperature. It should be pointed out and emphasized that in the liquid state, the term “phase” is utilized in a loose or broad form, not in the sense of a true equilibrium phase in the crystalline form such as the diamond phase of carbon. Instead, the disordered character of the liquid state gives rise to a statistical property associated with the various local structural configurations, generally with a Maxwell Boltzmann distribution giving the probability of breaking chemical bonds. Therefore, only locally in short-range or in very short range (nano) scales, or neighborhoods, does a reconstructive-like or displacive-like “phase” transition in species configuration occur, depending upon p-T. Therefore in the liquid state a specific configuration or “phase” is favored thermodynamically within a domain of p-T-X,

rather than being a sole unique equilibrium form as in the crystalline state.

Water with its two covalent bonds and obtuse bond angle, and two lone pairs, and strong polar character has thus properties that render the molecule highly susceptible to structural changes caused by p-T. This delicate vulnerability to p-T can have profound biological implications in the immune system, and in genetics because of water molecules sheathing the DNA double helix.

#### 4. Summary, Conclusion, and Inferences

In the liquid state of group VI elements, sulfur, selenium, and tellurium, and for the low-melting-point metals, bismuth, mercury, and tin, there is detailed reproducible evidence for non-homogeneity and unique nano-configurations at specific p-T (regions in p-T space or the projection of the Gibbs surface on the pressure-temperature plane). It is inferred that many other liquids behave in a similar manner, and possibly all liquids at appropriate values of p-T. It is concluded that the liquid state is well modeled by postulating a non-homogeneous mixture of nano-clusters as the general structural archetype for the liquid state of matter.

It is also proposed /inferred that unique liquid configurations can be useful in their quenched persistently metastable forms for specific applications potentially in a wide spectrum of areas such as electronics, optoelectronics and medical science/technology (to include diffusion barriers and thin film technology, particulate solvents in blood chemistry and in pancreatic and intestinal functions, and in catalysis such as in enzymatic action). Exploring for such possible applications is still in the area of very basic research, but the mechanistic phenomenology that is cornerstone to such feasible applications is the uniqueness of local short range order nanostructure regarding fundamental structure and chemical bonding properties. It should also be realized that useful properties of liquid nano-“phases” may be achieved by variations of applied electrical or magnetic fields, and even though modifying these variables (at relatively low to moderate magnitude) may not necessarily affect the strong covalent primary bonding or the electron delocalization associated with metallic bonding, the intervention of electromagnetic driving force may affect secondary bonding and non-satisfied valence states. The forced dielectric

breakdown of a nanophase, for example, can create a short or an electron (carrier) path that is needed for an alternate neuron communication pathway in the central or peripheral nervous system. Optical excitation of a liquid nanophase can also effectuate a property change that could be biochemically useful. Pressure-temperature induced influences on the water molecule can have very profound effects in living systems.

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