

**DIFFRACTION AND COMPUTER SIMULATION
STUDIES OF MOLECULAR LIQUIDS**

PhD Thesis

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Background

Liquids, mostly in the form of solvents and solutions, are an integral part of our life. Understanding the structure of these, sometimes even biologically interesting systems, is an important challenge of our times. The physical, chemical and biological behaviour of these materials is determined by the arrangement of particles, namely, by their atomic and molecular structure.

Understanding the behaviour of simple liquids is a pre-requisite for revealing the structure of complex systems mentioned above, like that of the physiologically important aqueous solutions. As a first step, researchers of Neutron Physics Department of the RISSPO have (among others) started the systematic study of the structure of molecular liquids. The most elementary systems, simple liquids – liquid noble gases (helium, argon); diatomic homonuclear (N_2 , O_2) and heteronuclear (CO, NO) molecular liquids – have been followed by polyatomic molecular liquids.

Goals

Joining this effort, I have started to study molecular liquids containing tetrahedral molecules; first came the XY_4 liquid family (carbon-, silicon-, germanium-, vanadium-, titan- and tin-tetrachloride and tin-tetraiodide), whose liquids consist of perfect tetrahedral molecules. Next, liquids whose molecules resulted from the gradual distortion of perfect tetrahedral molecular symmetry (chloroform, bromoform, methyl-iodide, methylene-chloride, methylene-bromide, methylene-iodide) have followed.

I have applied diffraction methods (neutron-and X-ray diffraction) and interpreted the results by model systems (Reverse Monte Carlo models and reference systems). This complex approach makes detailed structural analyses possible for these systems at an unprecedented level and quality.

My primary aim was to reveal the orientational correlations, since this piece of information denotes the most complete understanding of the structure. Additional fundamental questions concerning these systems are the effects of size and symmetry differences between molecules on the intra- and intermolecular behaviour.

New scientific results

1. It has been confirmed that for liquids containing molecules with perfect tetrahedral symmetry one diffraction measurement is sufficient for detailed structural analyses. The reasons for this are:
 - a) both measurements are sensitive especially to chlorine (or iodine) atoms and these ligands define the position of central atoms,
 - b) these molecules are highly symmetric.

On the other hand, for the studied liquids with distorted tetrahedral molecules both measurements are necessary for the adequate description of the structure [S1,S4].

2. The behaviour of molecular centres in each member of all the three studied liquid families is closely related with that of monatomic simple liquids. The central atoms (with ligands) behave, within a very good approximation, as in close-packed systems. The mutual arrangements of molecules are governed by basic properties such as the density and the packing fraction [S1,S2,S4].
3. The most frequent arrangement of molecules is the 2:2 (edge-to-edge) orientation. For liquids with two types of ligands the specific features observed are reflected in the characteristic of maxima of centre-ligand partial radial distribution functions [S1, S2, S3].
4. The alternating nature of 1:2 and 2:3 correlation functions is a common characteristics and at the same time, distinctive sign of liquids with tetrahedral molecules studied here. Effects of different molecular sizes arising from varying the central atom – as well as varying ligands, see tin-tetraiodide – and effects of different molecular shape due to the gradual distortion of tetrahedra result in the diminution of intensities of oscillations [S1,S2,S3].
5. Slight distortion of tetrahedral molecules gave rise to changes in terms of orientational correlations similar to those originating to slight variations of the size of central atoms of perfect tetrahedral molecules [S1].
6. The strongest intermolecular correlations, both at the two-particle and three particle levels, can be observed for CCl_4 . TiCl_4 and VCl_4 liquids stand for the other extreme, whose liquid structures are nearly identical to those of the corresponding hard sphere systems [S1,S2].

7. Effects due to varying the molecular structure are reflected particularly in terms of the short range behaviour (between neighbouring molecules), while the longer range features denote uniform 'class characteristics' [S1,S2,S3,S4].

Publications related to the dissertation:

[S1] Sz. Pothoczki, L. Temleitner, P. Jóvári, S. Kohara, L. Pusztai; Nanometer range correlations between molecular orientations in liquids of molecules with perfect tetrahedral shape: CCl₄, SiCl₄, GeCl₄ and SnCl₄

J. Chem. Phys.; **130**, 064503 (2009)

Independent citations: 1

[S2] Sz. Pothoczki, L. Pusztai; Molecular liquid TiCl₄ and VCl₄: Two substances, one structure?

J. Mol. Liq.; **145**, 38 (2009)

Independent citations: 1

[S3] L. Pusztai, Sz. Pothoczki, S. Kohara; Orientational correlations in molecular liquid SnI₄

J. Chem. Phys.; **129**, 064509 (2008)

Independent citations: 2

[S4] Sz. Pothoczki, L. Pusztai, S. Kohara; The structure of liquid iodomethane, CH₃I/CD₃I

J. Phys.: Condens. Matter; **19**, 335204 (2007)

Independent citations: 1