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## Neutron scattering of molecular liquids over a broad range of densities

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**Abstract.** High-pressure neutron diffraction measurements on fluid hydrogen chloride, carbon dioxide, ammonia, sulphur hexafluoride and methane at different supercritical states are reported. Some aspects of the experiment and the data evaluation are mentioned. The measurements were performed to assess the usefulness of some pair potentials reported in the literature for statistical mechanical calculations, based on the extended reference interaction site model (RISM) in combination with the HNC closure. The density-dependent measurements proved to be useful for tests of the individual potentials.

### 1. Motivation

The fundamental idea of calculating the properties of liquids is to start from first principles; that means to start from an intermolecular potential and to compute the microscopic structure and the macroscopic thermodynamic properties from the given potential by applying methods such as statistical mechanical theories or computer simulations. In following this idea a lot of progress was made, especially by the rapid development of the computer simulation technique. One of the most important quantities for the description of the microscopic properties of a liquid is the atom pair correlation function  $g_{\alpha\beta}(r)$ , which gives the probability of finding an atom of type  $\beta$  at a distance  $r$  from an atom  $\alpha$ . In the case of monatomic liquids one diffraction experiment gives the atom pair correlation function directly; in the case of molecular liquids the sum of all atom pair correlation functions can be measured.

The experimentally determined atom pair correlation functions have often been used to test statistical mechanical theories and computer simulations. From a good agreement between experiment and theory it is concluded that the chosen statistical mechanical approximation or computer simulation is correct and, because all these calculations are based on an intermolecular potential, also that the applied intermolecular potential is exact.

Of course, a good agreement between experimental and theoretical data indicates the exactness of the potential used in the calculations. However, we have to bear in mind that the comparison between experiment and theory was made only for *one* thermodynamic state, so we cannot completely exclude that the agreement is rather fortuitous. A more severe test of the applied theories and potentials is provided by the comparison between experiment and theory for more than one thermodynamic state. A significant change in the thermodynamic state of a liquid can be exerted by variation of the density. Therefore we performed neutron scattering studies on supercritical liquids.

## 2. The high-pressure equipment, experimental technique and data evaluation

The high-pressure equipment has been described in [1, 2]. It consists of a pressure-generating system and a system containing the liquid. The two systems are separated by a metal bellows. The pressure is generated by a hand-operated screw press and transmitted by the bellows from the oil branch to the liquid branch. The cylindrical pressure cell consists of a Ti–Zr zero alloy and withstands pressures up to 2000 bar. The cell is heated at the top and the bottom and the temperature is controlled at both ends of the cells by thermocouples. Since we observed in the course of our first measurements that even temperature fluctuations of only 1 °C cause significant changes in the scattered intensity due to fluctuations in the density, we constructed the temperature and pressure regulation so that the fluctuations of both variables were constrained to be within 0.2%. An additional crucial point is that the effect of the density variation on the scattered intensity is small. Therefore any change in the experimental set-up, when the pressure is varied must be strictly excluded. Hence all valves and the other equipment are installed outside the bell-jar so that the pressure can be changed and the cell can be filled or evacuated without any change in the sample environment or the beam geometry.

The measurements were performed in the energy-dispersive mode on the instrument SANDALS at ISIS, Chilton, Oxon and in the angular dispersive mode on the instruments D4 and D20 at the ILL, Grenoble. In order to correct the data of the angular dispersive measurements for absorption and multiple scattering we evaluated a formalism for thick-walled cylindrical cells. The formalism is based on an optimized Monte Carlo technique and was tested by a neutron diffraction experiment which we performed on liquid deuterated benzene inside a thick-walled high-pressure cell. Additionally, the real scattering of the sample and an unusual real beam profile were taken into account [3]. For correction of inelastic effects we applied the dynamic monatomic gas approximation with the effective mass as fitting parameter.

## 3. Investigated systems

First of all, we performed neutron diffraction measurements on deuterium chloride for seven different thermodynamic states [1]. The effect of the temperature variation on the structure is small despite the fact that hydrogen chloride forms hydrogen bonds. In contrast to this result, a significant effect of the density variation is detectable in the weighted sum of atom pair correlation functions  $G(r)$ . It is a general feature that the function  $G(r)$  becomes more structured when the density is reduced. We tested several interaction potentials of Lennard-Jones type with added partial point charges for hydrogen chloride and calculated the function  $G(r)$  using the RISM formalism with the PYA and HNC closure. By comparing the results of the RISM calculations for different thermodynamic states with the experimental results, we succeeded in determining a potential that describes the experimental curves better than does the potential determined from measurements for only one thermodynamic state. Additionally, we performed a Monte Carlo simulation with a potential calculated by quantum mechanical methods [5]. The Monte Carlo simulation shows the same trend as the experimentally determined curves.

In a similar way we investigated carbon dioxide at the supercritical temperature of 380 K and at three different densities [6]. We tested different closure relations in the statistical mechanics and some three-centre-pair potentials, reported in the literature. It turns out that none of the potentials given in the literature reproduces the experimental

results satisfactorily in the framework of the RISM theory, such indicating the deficiency either of the interaction potential or of the applied theory. In order to gain more insight into the structure of carbon dioxide we simulated the carbon dioxide system with the *ab initio* Monte Carlo technique [7]. The technique was used to investigate the effect of the density variation on the short-range order. In our simulation the model system contains 3000 carbon dioxide molecules and we checked very carefully that the resulting configuration was independent from the starting configuration. The analysis of the simulated system with respect to the orientation of neighbouring molecules revealed no preferred orientation between neighbouring molecules at low densities, whereas parallel orientations are more likely at higher densities.

Another system that we studied is ammonia. The measurements were performed at a temperature of 449 K at four densities in the range 0.318–0.700 g cm<sup>-3</sup>. In the orthorhombic solid phase the ammonia molecule forms six hydrogen bonds, three by its own hydrogen atoms and three with the hydrogen atoms of neighbouring molecules. However, in contrast to our measurements on hydrogen chloride, the hydrogen bond is not clearly detectable in the measurements of liquid ammonia. There is only a weakly pronounced shoulder which can be interpreted with some licence as a hydrogen bond. With increasing density, however, the intramolecular structure changes, since the covalent N–D bond becomes slightly longer and the D–N–D angle increases. The experimental  $G(r)$  functions were compared with theoretical results obtained from the RISM equation with the HNC closure. A series of potentials were tested and a potential was determined by fitting the parameters of a site–site Lennard-Jones potential to the experimental results. In the course of these calculations we were confronted with a new situation for us, in that the iterative solution of the RISM equation diverged for densities near the region of the gas–liquid coexistence curve.

All of the systems discussed up to now were liquids consisting of non-spherical molecules. Now we turn our interest to neutron measurements on liquids consisting of spherical molecules. We started our measurement on these systems with sulphur hexafluoride [8]. The density of this liquid was varied in the range 0.85–1.85 g cm<sup>-3</sup> at the supercritical temperature 398 K. These measurements were the first measurements that we performed in the energy-dispersive mode at the SANDALS instrument of ISIS. Because the sulphur hexafluoride molecule can be considered to be a spherical molecule, we expected no orientational correlation. The weighted sum of atom pair correlation functions, however, shows that the shortest intermolecular peak which can be assigned to an intermolecular F–F distance nearly vanishes with decreasing density. This behaviour is typical for a liquid that is close to crystal order at the highest density and whose order vanishes more and more when the density is reduced. Likewise the peak at  $r = 5.0$  Å becomes smaller with decreasing density and is shifted to larger  $r$  values. This peak is a superposition of intermolecular S–S, S–F and a second F–F distances. We performed RISM calculations on sulphur hexafluoride for the investigated thermodynamic states with the aim of deducing a potential that describes the experiments over the measured range of density. Starting from a Lennard-Jones seven-centre potential with parameters taken from the literature, we modified the values so that we achieved a good agreement between experiment and calculation. However, we were unable to reproduce the first peak, except for the highest density. Additionally, we performed *ab initio* Monte Carlo simulations on sulphur hexafluoride. Both these methods, which are independent from each other, give very consistent results and an excellent agreement between simulated or calculated  $G(r)$  functions and the experimental functions could be achieved. From the analysis of the angular distribution function of the simulated system it can be deduced that the sulphur hexafluoride molecules form an intermolecular structure at the highest density, similar to the structure of its solid phase. From these results we must

conclude that the interaction of sulphur hexafluoride is more anisotropic than had been expected.

In continuation of our study of liquids consisting of spherical molecules, we investigated the methane system [9]. The methane molecule has a tetrahedral symmetry and therefore can be considered spherical. We performed the neutron experiments at three densities at the supercritical temperature 370 K. The variation in the density has only a weak effect on the intermolecular correlation functions. Statistical mechanical calculations according to the RISM formalism with different closures were performed, and an intermolecular potential of a (12-6) Lennard-Jones type with partial charges on the atoms was deduced that reproduces the experimentally determined functions for all investigated thermodynamic states. Additionally, the corresponding structure factor of statistically orientated methane molecules was calculated. Since the agreement between experiment and theory is very good, it can be concluded that no orientational correlation exists in liquid methane.

#### 4. Conclusions

Summarizing our results, we can conclude that neutron scattering studies of liquids over a broad range of thermodynamic states provide a good check of the usefulness of intermolecular potentials. By comparison of experimental data and several theoretical models, reliable individual atom pair correlation functions and from these, by means of statistical mechanical theories, realistic intermolecular potentials can be deduced that describe the intermolecular structure in the investigated thermodynamic range in a satisfying manner.

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#### References

- [1] Bausenwein T, Bertagnolli H, Tödheide K and Chieux P 1991 Determination of the structure of fluid deuterium chloride by neutron diffraction at high pressure *Ber. Bunsenges. Phys. Chem.* **95** 577
- [2] Bausenwein T, Bertagnolli H, David A, Goller K, Zweier H, Tödheide K and Chieux P 1994 Structure and intermolecular interactions in fluid ammonia: an investigation by neutron diffraction at high pressure, statistical-mechanical calculations and computer simulations *J. Chem. Phys.* **101** 672
- [3] Bausenwein T, Bertagnolli H, Tödheide K and Chieux P 1991 Multiple scattering and self-absorption correction for high-pressure neutron diffraction with cylindrical cells *Nucl. Instrum. Methods B* **61** 527
- [4] Gutwerk D, Bausenwein T and Bertagnolli H 1994 The determination of Lennard-Jones potential parameters of fluid hydrogen chloride by RISM calculations over a broad range of densities *Ber. Bunsenges. Phys. Chem.* **98** 920
- [5] Steinhäuser O, Borešch S and Bertagnolli H 1990 The effect of density variation on the structure of liquid hydrogen chloride. A Monte Carlo study *J. Chem. Phys.* **93** 2357
- [6] Bausenwein T, Bertagnolli H, Gutwerk D, Tödheide K and Chieux P 1992 The structure of fluid carbon dioxide by neutron diffraction at high pressure and by RISM calculations *Mol. Phys.* **76** 127
- [7] Bertagnolli H, Glania C, Zweier H and David A 1993 Structure modelling of fluid carbon dioxide using *ab initio* Monte Carlo-simulation *Ber. Bunsenges. Phys. Chem.* **97** 1130
- [8] Strauss G, Zweier H, Bertagnolli H, Bausenwein T, Tödheide K and Chieux P 1994 High-pressure neutron diffraction on liquid sulphur hexafluoride and interpretation by statistical-mechanical theories and computer simulations *J. Chem. Phys.* **101** 662
- [9] Strauß G, Bassen A, Zweier H, Bertagnolli H, Tödheide K, Soper A K and Turner J 1996 High-pressure neutron diffraction on fluid methane *Phys. Rev. E* **53** 3505