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General scheme of the research work

The microscopic structure and dynamics of alcohol-water liquid mixtures has been studied experimentally by diffraction methods, and by the follow-up computer simulations (molecular dynamics, MD, and Reverse Monte Carlo, RMC), as a function of composition and temperature. As complementary research, we have also considered the atomic level structure of amorphous solid systems (covalent and metallic glasses) via diffraction and EXAFS methods, and RMC modeling. Particle configurations (sets of 3D Cartesian coordinates) provided by MD and RMC have been subjected to further (mostly geometrical) analyses analyses. As a result, detailed descriptions of the local structure, in terms of neighbour- and angular distributions, hydrogen bond statistics, etc…, are obtained.

Results concerning molecular liquids

(1) The evolution of the structure of liquid water-methanol mixtures as a function of temperature has been studied by molecular dynamics simulations, with a focus on hydrogen bonding. The combination of the OPLS-AA (all atom) potential model of methanol and the widely used SPC/E water model has provided excellent agreement with measured X-ray diffraction data over the temperature range between 298 and 213 K, for mixtures with methanol molar fractions of 0.2, 0.3 and 0.4. Hydrogen bonds have been identified via a combined geometric/energetic, as well as via a purely geometric definition. The number of recognizable hydrogen bonded ring structures in some cases doubles while lowering the temperature from 298 to 213 K; the number of sixfold rings increases most significantly. An evolution towards the structure of hexagonal ice, that contains only sixfold hydrogen bonded rings, has thus been detected on cooling water-methanol mixtures.

(2) Results of systematic molecular dynamics studies of ethanol-water mixtures, over the entire concentration range, were reported previously that agree with experimental X-ray diffraction data. These simulated systems are analyzed in this work to examine cluster formation and percolation, using four different hydrogen bond definitions. Percolation analyses revealed that each mixture (even the one containing 80 mol% ethanol) is above the 3D percolation threshold, with fractal dimensions between 2.6 and 2.9, depending on concentration. Monotype water cluster formation was also studied in the mixtures: 3D water percolation can be found in systems with less than 40 mol% ethanol, with fractal dimensions between 2.53 and 2.84. These observations can be put in parallel with experimental data on some thermodynamic quantities, such as the excess partial molar enthalpy and entropy.

(3) Following preliminary studies on a few interaction potentials and at most two sets of diffraction data of liquid water, here an extended collection of water potentials is considered, along with four experimental total scattering structure factors. The basis of comparing interatomic potentials was the compatibility with results of neutron and X-ray diffraction experiments on pure water, using the

scheme applied by Pusztai et al. (2008). The scheme combines experimental total scattering structure factors (TSSF) and partial radial distribution functions (PRDF) from molecular dynamics simulations in a single structural model. Goodness-of-fit values to the O-O, O-H and H-H simulated PRDF-s and to the experimental neutron and X-ray TSSF provided a measure that can characterize the level of consistency between interaction potentials and diffraction experiments. As an addition to classical water potentials, PRDF-s from one 'ab initio' molecular dynamics simulation have also been investigated. Out of the sets of partial RDF-s investigated here, the ones corresponding to the BK3 polarizable, and—somewhat surprisingly—to the simple 3-site TIP3P potentials have proven to be the most consistent with various combinations of diffraction results taken for the present study.

(4) In connection with the study mentioned just above, neutron- and x-ray weighted total structure factors of liquid water have been calculated on the basis of the intermolecular parts of partial radial distribution functions resulting from various computer simulations. The approach includes reverse Monte Carlo (RMC) modelling of these partials, using realistic flexible molecules, and the calculation of experimental diffraction data, including the intramolecular contributions, from the RMC particle configurations. The procedure has been applied to ten sets of intermolecular partial radial distribution functions obtained from various computer simulations, including one set from an ab initio molecular dynamics, of water. It is found that modern polarizable water potentials, such as SWM4-DP and BK3 are the most successful in reproducing measured diffraction data.

(5) Reverse Monte Carlo (RMC) modeling of liquid water, based on one neutron and one X-ray diffraction data set, applying also the most popular interatomic potential for water, extended simple point charge (SPC/E), has been performed. The strictly rigid geometry of SPC/E water molecules had to be loosened somewhat, in order to be able to produce a good fit to both sets of experimental data. In the final particle configurations, regularly shaped water molecules and straight hydrogen bonding angles were found to be consistent with diffraction results.

(6) By making use of literature X-ray diffraction data, extensive molecular dynamics computer simulations have been conducted for ethanol-water liquid mixtures in the water-rich side of the composition range, with 10, 20 and 30 mol % of the alcohol, at temperatures between room temperature and the experimental freezing point of the given mixture. All-atom type (OPLS) interatomic potentials have been assumed for ethanol, in combination with two kinds of rigid water models (SPC/E and TIP4P/2005). Both combinations have provided excellent reproductions of the experimental X-ray total structure factors at each temperature; this provided a strong basis for further structural analyses. Beyond partial radial distribution functions, various descriptors of hydrogen bonded assemblies, as well as of the hydrogen bonded network have been determined from the simulated particle configurations. A clear tendency was observed towards that an increasing proportion of water molecules participate in hydrogen bonding with exactly 2 donor- and 2 acceptor sites as temperature decreases. Concerning larger assemblies held together by hydrogen bonding, the main focus was put on the properties of cyclic entities: it was found that, similarly to methanol-water mixtures, the number of hydrogen bonded rings has increased with lowering temperature. However, for ethanol-water mixtures the dominance of not the six-, but of the five-fold rings could be observed.

(7) Starting from the molecular dynamics simulations mentioned above, we took a closer look at the time-dependent behavior of molecules. Temperature dependent hydrogen bond energetics and dynamical features, such as the diffusion coefficient and re-orientational times, have been determined for ethanol-water mixtures with 10, 20 and 30 mol % of ethanol. Concerning pairwise interaction

energies between molecules, it was found that water-water interactions become stronger, while ethanol-ethanol ones become significantly weaker in the mixtures, than the corresponding values characteristic to the pure substances. Concerning the diffusion processes, for all concentrations the activation barrier of water and ethanol molecule become very similar to each other. Re-orientational motions of water and ethanol become slower as ethanol concentration is increasing. Characteristic re-orientational times of water in the mixtures are substantially longer than these values in the pure substance. Re-orientational motions of water (especially the ones related to the H-bonded interaction) become very similar for those of ethanol in the mixtures.

(8) Synchrotron X-ray diffraction experiments and molecular dynamics simulations have been performed on simple aliphatic aldehydes, from propanal to nonanal. The performance of the OPLS all-atom interaction potential model for aldehydes has been assessed via direct comparison of simulated and experimental total scattering structure factors. In general, MD results reproduce the experimental data at least semi-quantitatively. However, a slight mismatch can be observed between the two datasets in terms of the position of the main diffraction maxima. Partial radial distribution functions (PRDF) have also been calculated from the simulation results. Clear differences could be detected between the various O-H partial radial distribution functions, depending on whether the H atom is attached to the carbon atom that is doubly bonded to the oxygen atom of the aldehyde group or not. Based on the 3 different O-H PRDF-s, as well as on the various H-H PRDF-s, it may be suggested that neighboring molecules turn toward each other (somewhat) preferentially by their aldehyde ends. From gOO(r) and gC'C'(r), and from intermolecular angular correlations presented, it may be discerned that no (or at most, extremely weak) orientational correlations are present between neighboring aldehyde groups.

(9) As a follow-up of the above series of experiments, the total scattering structure factors of pure liquid n-pentanol, pentanal, and 5 of their mixtures have been determined by high energy synchrotron X-ray diffraction experiments. For the interpretation of measured data, molecular dynamics computer simulations were performed, utilizing 'all-atom' type force fields. The diffraction signals in general resemble each other over most of the monitored scattering variable, Q, range above 1 Å-1, but the absolute values of the intensities of the small-angle scattering maximum ('pre-peak', 'first sharp diffraction peak'), around 0.6 Å-1, change in an unexpected fashion, non-linearly with the composition. MD simulations are not able to reproduce this low-Q behavior; on the other hand, they do reproduce the experimental diffraction data above 1 Å-1 rather accurately. Partial radial distribution functions are calculated based on the atomic coordinates in the simulated configurations. Inspection of the various O-O and O-H partial radial distribution functions clearly shows that both the alcoholic and the aldehydic oxygens form hydrogen bonds with the hydrogen atoms of the alcoholic OH-group.

(10) The structure factors of pure 1-propanol, 2-propanol and mixtures of 1-propanol/water and 2-propanol/water, as a function of composition, have been determined experimentally, by synchrotron X-ray scattering, and by molecular dynamics simulations. The primary aim was to find interatomic potentials that reproduce measured structural data at the highest possible level. For this reason, various alcohol potential models have been employed, including united atom (UA) and all atom (AA) types, in combination with a TIP4P-based model for water. In order to improve agreement with experimental values of the dielectric constant and mass density, a new UA force field for the alcohols has also been constructed. It has been shown that the X-ray weighted structure factors may be represented by the UA force field (both the original and the new UA) satisfactorily for the pure alcohols; agreement for the aqueous mixtures may be termed 'qualitative' in the best cases. That is,

for calculating structural properties, the UA-type potentials are not applicable for 1-propanol/water and 2-propanol/water mixtures. On the other hand, the OPLS/AA force field has proven to be consistently better in comparison with the X-ray diffraction data; also, for the reproduction of neutron diffraction data, only the all atom type potential is applicable.

(11) Highly concentrated aqueous lithium chloride solutions were investigated by classical molecular dynamics (MD) and reverse Monte Carlo (RMC) simulations. At first MD calculations were carried out applying twenty-nine combinations of ion-water interaction models at four salt concentrations. The structural predictions of the different models were compared, the contributions of different structural motifs to the partial pair correlation functions (PPCF) were determined. Particle configurations obtained from MD simulations were further refined using the RMC method to get better agreement with experimental X-ray and neutron diffraction data. The PPCFs calculated from MD simulations were fitted together with the experimental structure factors to construct structural models that are as consistent as possible with both the experimental results and the results of the MD simulations. The MD models were validated according to the quality of the fits. Although none of the tested MD models can describe the structure perfectly at the highest investigated concentration, their comparison made it possible to determine the main structural properties of that solution as well. It was found that four nearest neighbors (oxygen atoms and chloride ions together) are around a lithium ion at each concentration, while in the surroundings of the chloride ion hydrogen atom pairs are replaced by one lithium ion as the concentration increases. While in pure liquid water four water molecules can be found around a central water molecule, near the solubility limit nearly all water molecules are connected to two chloride ions (via their hydrogen atoms) and one lithium ion (by their oxygen atoms).

(12) Series of molecular dynamics simulations for 2-propanol-water mixtures, as a function of temperature (between freezing and room temperature) and composition (x_{ip}= 0, 0.5, 0.1 and 0.2) have been performed for temperatures reported in the only available experimental structure study. It is shown that when the all-atom OPLS-AA interatomic potentials for the alcohol are combined with the TIP4P/2005 water model then near-quantitative agreement with measured X-ray data, in the reciprocal space, can be achieved. Such an agreement justifies detailed investigations of structural, energetic and dynamic properties on the basis of the simulation trajectories. Here we focus on characteristics related to hydrogen bonds (HB): cluster-, and in particular, ring formation, energy distributions and lifetimes of HB-s have been scrutinized for the entire system, as well as for the water and isopropanol subsystems. It is demonstrated that, similarly to ethanol-water mixtures, the occurrence of 5-membered hydrogen bonded rings is significant, particularly at higher alcohol concentrations. Concerning HB energetics, an intriguing double maximum appears on the alcohol-alcohol HB energy distribution function. HB lifetimes have been found significantly longer in the mixtures than they are in the pure liquids.

(13) *Hypothesis:* The structural details, viscosity trends and dynamic phenomena in *t*-butanol/water solutions are closely related on the molecular scales across the entire composition range. Utilizing the experimental small- and wide-angle x-ray scattering (SWAXS) method, molecular dynamics (MD) simulations and the 'complemented-system approach' method developed in our group it is possible to comprehensively describe the structure-viscosity-dynamics relationship in such structurally versatile hydrogen-bonded molecular liquids, as well as in similar, self-assembling systems with pronounced molecular and supramolecular structures at the intra-, inter-, and supra-molecular scales. *Experiments:* The SWAXS and x-ray diffraction experiments and MD simulations were performed for aqueous *t*-butanol solutions at 25 °C. Literature viscosity and self-

diffusion data were also used. *Findings:* The interpretive power of the proposed scheme was demonstrated by the extensive and diverse results obtained for aqueous *t*-butanol solutions across the whole concentration range. Four composition ranges with qualitatively different structures and viscosity trends were revealed. The experimental and calculated zero-shear viscosities and molecular self-diffusion coefficients were successfully related to the corresponding structural details. The hydrogen bonds that were, along with hydrophobic effects, recognized as the most important driving force for the formation of *t*-butanol aggregates, show intriguing lifetime trends and thermodynamic properties of their formation.

Results concerning amorphous solids

(1) The structure of glassy $Cu_{47.5}Zr_{47.5}Ag_5$ has been investigated by neutron diffraction with isotopic substitution, X-ray diffraction as well as by using Cu and Ag K-edge extended X-ray absorption spectroscopy (EXAFS). Experimental datasets have been fitted simultaneously with the reverse Monte Carlo simulation technique. Nearest neighbor distances and coordination numbers have been determined and compared with those of glassy $Cu_{50}Zr_{50}$ and $Cu_{47.5}Zr_{47.5}Al_5$. It has been found that the Cu-Cu coordination number drops upon adding Al or Ag to $Cu_{50}Zr_{50}$. Both Ag and Al prefer Zr to Cu. The total coordination number of Ag is 13.9 ± 0.6 while that of Al is 10.2 ± 1.0 suggesting that in spite of their similar molar volumes the effective sizes of Ag and Al in the CuZr matrix are quite different.

(2) The short range order in $Ge_{30}Ga_5Sb_{10}Se_{55}$ and $Ge_{21}Ga_5Sb_{10}Se_{64}$ glasses was investigated by X-ray (XRD) and neutron diffraction (ND) as well as extended X-ray absorption fine structure (EXAFS) measurements at the Ge, Ga, Sb and Se K-edges. Large scale structural models were obtained by fitting simultaneously the experimental data sets by reverse Monte Carlo (RMC) simulation technique. It was found that Ge, Sb and Se atoms follow the Mott-rule and have 4, 3 and 2 nearest neighbors, respectively. The average coordination number of the Ga atoms was around 4. The structure of these glasses can be described by the chemically ordered network model: the Ge–Se, Ga–Se and Sb–Se bonds are the most prominent while Ge–Ge and Ge–Sb bonds are formed only in Se-poor compositions. Models generated by RMC contained some long distances (0.3–0.4 Å higher than the usual covalent bond lengths) between Ge–Se and/or Ge–Ge pairs. Dedicated simulation runs confirm the existence of these bonds.

(3) Short range order in $As_{40-x}Cu_xTe_{60}$ (x = 0, 10, 20, 25, 30) glasses was studied by neutron- and X-ray diffraction, combined with extended X-ray absorption fine structure (EXAFS) measurements at the K-edges of all components. Large-scale structural models were generated by fitting the experimental datasets simultaneously in the framework of the reverse Monte Carlo simulation technique. These simulations revealed that As and Te atoms bind to about 3 and 2 As/Te neighbors, respectively, both of which possess Cu neighbors. The Cu Te bond length is 2.57 ± 0.02 Å while the Cu As distance is as high as 2.86 ± 0.04 Å. The results further showed that besides As and Te, Cu atoms also bind to Cu. The total coordination number of Cu is significantly higher than 4 for the compositions x = 25 and 30.

(4) The structure of $Ge_{20}Sb_{10}S_{70}$, $Ge_{23}Sb_{12}S_{65}$ and $Ge_{26}Sb_{13}S_{61}$ glasses was investigated by neutron diffraction (ND), X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS) measurements at the Ge and Sb K-edges as well as Raman scattering. For each composition, large scale structural models were obtained by fitting simultaneously diffraction and EXAFS data sets in

the framework of the reverse Monte Carlo (RMC) simulation technique. Ge and S atoms have 4 and 2 nearest neighbors, respectively. The structure of these glasses can be described by the chemically ordered network model: Ge-S and Sb-S bonds are always preferred. These two bond types adequately describe the structure of the stoichiometric glass while S-S bonds can also be found in the S-rich composition. Raman scattering data show the presence of Ge-Ge, Ge-Sb and Sb-Sb bonds in the S-deficient glass but only Ge-Sb bonds are needed to fit diffraction and EXAFS datasets. A significant part of the Sb-S pairs has 0.3–0.4 Å longer bond distance than the usually accepted covalent bond length (~2.45 Å). From this observation it was inferred that a part of Sb atoms have more than 3 S neighbors.

(5) The structure of Ge_xTe_{100-x} (x = 14.5, 18.7, 23.6) glasses prepared by twin roller quenching technique was investigated by neutron diffraction, X-ray diffraction and Ge-K-edge X-ray absorption spectroscopy measurements. Large scale structural models were obtained for each composition by fitting the experimental datasets in the framework of the reverse Monte Carlo technique. It was found that the majority of Ge and Te atoms satisfy the 8-N rule. Simulation results indicate that Ge-Ge bonding is not significant for $x = 14.5$ and 18.7. The shape and position of the first peak of the Ge-Ge partial pair correlation function evidence the presence of corner sharing tetrahedra already in compositions ($x = 14.5$ and 18.7) where ’sharing’ of a Te atom by two Ge atoms could be avoided due to the low concentration of Ge.

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