Metastable water

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Introduction

Metastable forms of water occur in various areas of science and technology. Supercooled water is important in cryobiology and for cloud formation. Water under tension appears in plant capillaries, in mineral inclusions and ultrasound fields. Superheating is a well known phenomenon. Metastable amorphous ice is considered in cometary physics.

Around 1980 Angell directed the attention of the water community to the supercooled state in two review articles. Below the melting temperature the well known anomalies of water increase dramatically. Volume and entropy fluctuations seem to diverge, dynamic properties show strong deviations from the Arrhenius behaviour which can be described by a power law dependence. Besides the well known polymorphism, which manifests in various crystal structures of ice, a polyamorphism with sharp transitions between two distinct forms of amorphous ice was established by the experiments of Mishima.

To explain this behaviour, two major scenarios are discussed which are of fundamental importance for the understanding of disordered materials. The presently most intensely discussed model emerged from computer simulation studies of Stanley *et al.* It postulates the existence of a second critical point as the end point of an equilibrium line between two differently structured metastable liquid phases, whose extension to lower temperatures describes the transition between the two amorphous ice phases. The figure on the front cover illustrates this scenario, which is described in detail in the contribution on page 1551.

A second, so called singularity free scenario explains the strong increase of the thermodynamic response functions by a (p,V,T)-surface with strong curvatures but no phase separation. Percolation and lattice models belong in this category. The cover picture also illustrates the difficulties arising in the experiments: the white area between the homogeneous nucleation temperature T_H of the supercooled liquid and the temperature T_X, where on warming up the amorphous ice crystallisation sets in inevitably, marks a region, where (at present) non-crystalline condensed forms of water can not exist long enough to be studied experimentally.

The scientific program

In his opening lecture Stanley reviewed the present knowledge of the supercooled and glassy state of water and presented various indications from experiment, simulation and theory for the existence of the second critical point. Debenedetti introduced his model of an associated liquid, which comprises a continuous transition between the two described scenarios, depending on the strength and geometry of the hydrogen bonds. He emphasized possible difficulties in distinguishing experimentally between the two situations.

Angell widened and generalized the spectrum of observations by considering other materials with local tetrahedral order and showed that such liquids constitute a distinct group within the glass formers. Mishima presented results of his sophisticated experiments on ice suspensions which allowed one to trace the free energy surface of the metastable liquid. The dynamics and kinetics in supercooled water and amorphous ice were investigated experimentally as well as by computer simulations (Koza, Sciortino). A broad discussion was provoked by the results presented by Kay. His experiments on nanostructured amorphous ice layers yield indications for the existence of highly viscous supercooled water at 160 K and give estimates of the corresponding diffusion coefficients. However, contrary conclusions were drawn from Cowin's ion deposition experiments.

Computer simulations of the structure and thermodynamics of supercooled water and amorphous ice were discussed by Poole and Pusztai; simplified models with waterlike behaviour were described by Speedy and Robledo. The range of existence and the coexistence of various metastable ice polymorphs, the resulting experimental problems in preparation and identification, as well as the thermodynamic consequences were illuminated by Johari, Finney, Hallbrucker and Kuhs. Experiments on nucleation phenomena in the supersaturated vapour, in single levitated droplets, in aerosols and on the role of nucleation for the formation of stratospheric ice clouds were reported by Strey, Baumgärtel and Koop.

The influence of dissolved particles on the temperature dependence of the anomalies and the demixing behaviour at low temperatures were discussed by Holz and Sorensen. In several talks the behaviour of supercooled water at interfaces and in confined geometries was treated (Bellissent-Funel, Dore, Forstmann, Gallo, Behrens and Bergmann). Unfortunately the list of interesting talks and poster contributions can not be given completely here.

Future prospects

The meeting showed impressively that even after many decades of intense research, surprising new facets of water have been discovered, whose importance for biological systems can only be speculated upon. Further development can be expected in the following directions: exploration of the experimentally not yet accessible region of non-crystalline states by an interplay of extensive simulations and elaborate experiments, increased investigation of mixed and non-uniform aqueous systems (solutions, supercooled water in pores, at interfaces and in biological systems) as well as the investigation of structurally related materials.

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