Introduction to Special Issue on Water and Associated Liquids

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In the past 40 years there has been major progress in developing a quantitative as well as qualitative understanding of the structural and thermodynamic properties of dense simple fluids and fluid mixtures both in bulk and at their liquid-vapor interfaces. Relatively simple theories are possible because in bulk systems the slowly varying attractive van der Waals forces on a given molecule tends to cancel and the liquid structure is dominated by the packing of the harshly repulsive molecular cores. At interfaces and in other nonuniform environments attractive forces no longer cancel but their averaged effects can be accurately treated by a simple mean field theory.

Associated liquids present new and more difficult problems that are the focus of much current research, as illustrated by work in this special issue. Here we imagine there exist a small set of very strong but directionally localized attractive interactions that can compete efficiently with the core packing forces, generally producing a smaller number of strongly bonded neighbors than are generated by core forces alone. Under appropriate conditions this can lead to fluids with fluctuating networks of nearest neighbor bonds. Workers in this area often use model potentials that incorporate this physics in the simplest possible way and try to arrive at a theoretical understanding of their consequences. Determining typical configurations even in bulk systems is highly nontrivial. Incorporating large solutes or forming an extended interface necessarily disrupts the bulk bond network and this introduces additional theoretical and practical challenges.

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Water is arguably the most important but most elusive of all liquids. Attempts to understand its hydrogen bond network inspired early work on associated liquids and many of its properties can be most naturally linked to the formation and/or disruption of hydrogen bonds. But many open questions remain about how to characterize precisely and understand even basic features of the “hydrogen bond network” generated by more realistic models of water. And certain characteristic thermodynamic anomalies of water such as the density maximum at 4 °C and a diffusion anomaly where diffusion increases with pressure can be captured in non-associated models which use spherically symmetric potentials with two characteristic length scales.

It seems clear that water presents a host of theoretical and experimental challenges that cannot be understood by solely focusing on network association, though this remains the most dramatic and characteristic structural feature of water. In particular, an understanding of water’s behavior as a solvent with general charged or polar solutes requires treating long-ranged electrostatic interactions and dielectric screening properties as well. Moreover a quantitative understanding of even the hydrogen bond network, particularly in ordered structures such as ice, likely involves quantum and charge transfer effects not treated in standard water models. Thus an outstanding problem in statistical physics is the development of a general theoretical and computational framework that can deal with these and other issues in more realistic models of water.

This special issue of the *Journal of Statistical Physics* presents seventeen papers that collectively give a snapshot of current work on water and simple models of associated liquids. Any such collection is necessarily incomplete but we believe it gives a good indication both of the wide range of current research ideas and of the many questions that remain open.