Bjerrum defects as topological charges and the residual entropy of ices

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Abstract

The concept of the residual entropy of ice, i.e., the configurational entropy of proton disorder at zero temperature, was introduced by L. Pauling in order to explain the observed discrepancy between the calorimetric and spectroscopic values of the absolute entropy of water. The missing entropy term was calculated using three assumptions:
(i) all ice configurations satisfy the Bernal–Fowler ice rules (these rules state that each oxygen is covalently bonded to two hydrogens, each oxygen forms two hydrogen bonds to two other oxygens, and there exists exactly one hydrogen between a pair of neighboring oxygens);
(ii) all configurations have the same energy; and,
(iii) the positions of hydrogens in the oxygen–oxygen bonds are uncorrelated.

In this contribution the residual entropy of ices (Ih, Ic, III, V, VI) and clathrates (I, II, H) is calculated assuming (i) and (ii). The Metropolis Monte Carlo simulations in the range of temperatures from infinity to a size-dependent threshold are followed by the thermodynamic integration. In addition, the entropy of ice III exhibiting partial disorder is calculated as the function of occupation probabilities. Violation of assumption (ii) is discussed.

It sometimes happens that a route to results is more interesting than the results themselves. Thus, we studied the interaction of Bjerrum defects (topological charges) as the function of temperature at two levels of approximation: the ideal solution and the Debye–Hˊuckel theory. The finite-size effects in the residual entropy are then estimated as

$S(N) = S(\text{thermodynamic limit}) + a/N + b \ln N/N + c/N\hat{}1.5,$

where N is the number of molecules, a,b,c are constants and in 3D it holds c=0. This result enabled us to accurately extrapolate to the thermodynamic limit.

References:
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