73f A General Orientational Order Parameter and Its Applications to Pure Water and Ion-Water Systems

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Quantification of local order provides an important tool in helping one understand the relationship between the macroscopic properties of a system and its underlying molecular structure. We present a new orientational order parameter that is based on the angular distribution of a molecule's near neighbors. The position of each molecule in a nearest neighbor shell is calculated through the use of a local coordinate system centered at the position of the central molecule [1]. The azimuthal and zenith angles of each neighbor are recorded in a two-dimensional histogram and a quantitative measure of the orientational order is obtained from an analysis of this distribution. The approach can be used to produce a measure of the general or configuration specific (e.g. tetrahedral or octahedral) orientational order found in a system. Application to the Lennard-Jones system produced similar findings to those obtained in earlier work [2] where the bond-orientational order parameters of Steinhardt et al. [3] were used. Using these ideas to probe the structure of water has generated interesting results. A series of NVT molecular dynamics simulations was used to collect structural information over a range of densities and temperatures. Consistent with earlier work [4], we find that along an isotherm the fluid reaches a maximum in tetrahedral order at a density of 0.90 to 0.95 g/cm3. We also observe a significant reorganization in the structure of the fluid at densities around 1.15 g/cm3, which corresponds to the conditions where one finds a minimum in the translational order of the system [4]. Finally, we have recently initiated an investigation aimed at better understanding the orientational organization of water molecules around ions. We hope that this study will help us to better understand the complicated nature of ion solvation, for example, the relationship between orientational order and ion solvation entropy.

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