The Origin of Local Density Enhancements in Compressible Supercritical Fluids

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In order to probe the nature of different solvents, solvatochromic experiments rely on the sensitivity of some property of the solute probe to the locally surrounding solvent environment. It is now well known that in compressible supercritical fluids the mean local density around solute probes may be either enhanced or depleted relative to the bulk density and that it is this altered local density which will determine the probe signal. Yet, the physical origins of this well-known local density enhancement/depletion phenomena have gone unexplained, such that we are unable to predict the dependence of these local densities on thermodynamic condition.

We have developed a series of theoretical tools for characterizing local solvent densities and applied them to a simple supercritical fluid at a series of compressible state points. This work, which focusses on the distribution of local densities supported by the fluid and on the correlation between the (short-range) local densities and (long-range) spatially-extended density inhomogeneities associated with nearby critical phenomena, uncovers the fundamental origin of mean local density enhancements in these fluids. We find that both a "potential-induced" mechanism, which becomes increasingly important at low densities, and an "inhomogeneity-induced" mechanism, which is maximally important in the critical region, contribute to the observed mean local densities, and that a competition between these effects controls the location of the maximum local density enhancement. We also examine the reorganization lifetime of the local solvent environments, a quantity important for predicting solvatochromic effects on dynamics solute processes, and show the connection between this short length-scale quantity and the long-length-scale phenomena of critical slowing down.

The effect of these local solvent environment properties on solute processes will be illustrated via a simulation study of solute vibrational relaxation.