Molecular properties and spectroscopy along the phase diagram

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INTRODUCTION

The combination of quantum mechanics with molecular modeling is a powerful tool for studies of simple and complex liquids. In addition, it may also be used to study the spectroscopic and reactivity of molecules in solution, a situation that is germane in chemical laboratories. The understanding of the solvent effects is thus a major concern in the rationalization of experimental results.

METHODS

In the last two decades theoretical treatments have been developed to incorporate solvent effects. An important direction of research uses some sort of computer simulation to perform hybrid calculations. This is generally called QM/MM method, because both classical and quantum methodologies are employed. Conventional QM/MM methodology can be so costly that normally only a small fraction of the system is indeed treated by quantum mechanics. A systematic procedure based on a sequential Monte Carlo (or Molecular Dynamics) quantum mechanics (S-QM/MM) methodology has been developed in our group [1] that treats the solvent as an explicit liquid system. Different applications [2] have been made including absorption and emission spectra, NMR parameters, vibrational circular dichroism, chemical reactivity, etc. As long as the thermodynamic condition can be imposed this opens a large avenue for applications in other parts of the phase diagram. Hence, we have also addressed the technologically and environmental friendly condition of supercritical fluids.

RESULTS AND DISCUSSION

Several applications will be shown indicating the accuracy of the calculated results. In particular we discuss the structural aspects of supercritical CO_2 and its role on the spectrum of para-nitroaniline as obtained from Born-Oppenheimer Molecular Dynamics[3].

More recently we have pointed our focus to the vicinities of the critical point. Theoretical studies of the critical behavior of fluids have been conducted mostly by universal scaling functions and renormalization theories. We have given the first explicitly calculated values of the dielectric constant in the close vicinity of the critical point ($T > T_c$). Thus, the behavior of the dielectric constant, only slightly above the critical point, is determined using first-principle quantum mechanical calculations for the first time. Our multiscale results[4] obtained by combining statistical mechanics and first-principle quantum mechanics indicate that the dielectric constant of Ar only 2K above T_c and around the critical isochoric (0.531 g/cm^3) becomes density-independent (Fig. 1).
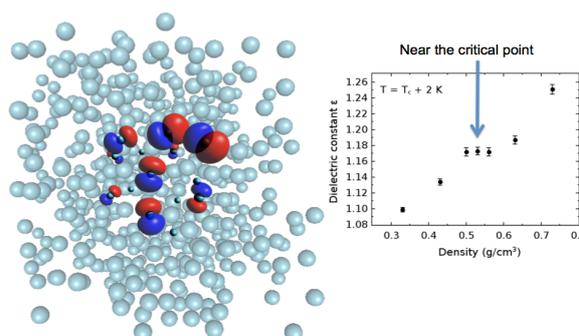

Figure 1. Change of the dielectric constant of Ar.

ACKNOWLEDGMENTS

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