Local Structure of Supercritical Fluids Near the Widom Line

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Supercritical fluids (SCFs) are widely used [1] in many chemical industries, including pharmacy, materials science and more. Main advantages of SCFs include their environmental friendliness, unique combination of liquid density and gas diffusivity, as well as, perhaps most notably, their structural/dynamical fluctuations.

It has been long known, that within supercritical region exists a line, so-called Widom Line, that extends the vapor-liquid coexistence curve. Upon crossing this line, in either isobaric or isochoric conditions, many thermodynamical properties of the SCF have large fluctuations or even discontinuities. It is, therefore, possible, to optimize many of the processes utilizing SCFs by precisely picking the operating temperature and pressure. For this, a precise mapping of the Widom Line onto the phase-space is required. Traditional experimental methods may include [2] investigations of heat capacity, compressibility, thermal expansion coefficients and so on.

Previous theoretical investigations of the Widom Line also have focused on the changes in thermodynamically properties, such as isobaric/isochoric heat capacities. In contrast, we have proposed functions of local structural order as an indicator of Widom Line crossings. In this work, we have performed molecular dynamics (MD) simulations of TIP4P/2005 water from 175 bar to 375 bar between 300K and 1100K and Cygan et al. [3] carbon dioxide from 70 bar to 100 bar between 250K and 600K. We have analyzed the systems with such functionals as nearest-neighbor radial distribution functions, Voronoi space-tesselation analysis and DBSCAN. We show that certain extrema in the average values, fluctuations or rates of change of average values of respective local parameters can define purely local Widom Lines that are in decent agreement with experiments.

References

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