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Critical Parameters of a Square-Well Fluid

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Abstract : We report extensive molecular dynamics (MD) computational investigations into the thermodynamic description of supercritical properties for a model fluid that is the simplest realistic representation of atoms or molecules. The pair potential is a hard-sphere repulsion of diameter σ with a very short attraction of length λσ. When λ = 1.005 the range is so short that the model atoms are referred to as “adhesive spheres”. Molecular dimers, trimers …etc. up to large clusters, or droplets, of many adhesive-sphere atoms are unambiguously defined. This then defines percolation transitions at the molecular level that bound the existence of gas and liquid phases at supercritical temperatures, and which define the existence of a supercritical mesophase. Both liquid and gas phases are seen to terminate at the loci of percolation transitions, and below a second characteristic temperature (Tc2) are separated by the supercritical mesophase. An analysis of the distribution of clusters in gas, meso- and liquid phases confirms the colloidal nature of this mesophase. The general phase behaviour is compared with both experimental properties of the water-steam supercritical region and also with formally exact cluster theory of Mayer and Mayer. Both are found to be consistent with the present findings that in this system the supercritical mesophase narrows in density with increasing T > Tc and terminates at a higher Tc2 at a confluence of the primary percolation loci. The expended plot of the MD data points in the mesophase of 7 critical and supercritical isotherms in highlight this narrowing in density of the linear-slope region of the mesophase as temperature is increased above the critical. This linearity in the mesophase implies the existence of a linear combination rule between gas and liquid which is an extension of the Lever rule in the subcritical region, and can be used to obtain critical parameters without resorting to experimental data in the two-phase region. Using this combination rule, the calculated critical parameters Tc = 0.2007 and Pc = 0.0278 are found be agree with the values found by of Largo and coworkers. The properties of this supercritical mesophase are shown to be consistent with an alternative description of the phenomenon of critical opalescence seen in the supercritical region of both molecular and colloidal-protein supercritical fluids.

Keywords : critical opalescence, supercritical, square-well, percolation transition, critical parameters.
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