Multiple Critical Points for Square-wells with Repulsive Shoulders: Renormalization Calculations Compared with Simulations

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For artificial fluids composed of hard spheres that interact via attractive square-well potentials with repulsive shoulders, the pressure, temperature, and density at the first, low density, critical point found in published molecular dynamic simulations are predicted reasonably accurately by a simple, approximate renormalization group theory, as well as by several alternative theories that have been reported in the literature. The previously reported predictions, in particular of the density, at the second, high density, critical point have been less satisfactory. For spheres with reasonably high repulsive shoulders, agreement with simulations is found for the low density critical point for renormalization calculations that employ a radial distribution function (rdf) for the repulsive interactions which is not greatly different from that for hard spheres of large diameters, extending to nearly the full width of the repulsive shoulders. A low density critical point, though not at the correct location, is found even when the oscillations in the rdf for the repulsive interactions are omitted, i.e. when that rdf is replaced simply by a constant. But a second, high density, critical point appears only when there are substantial oscillations of the rdf, with the location (pressure, temperature, and density) of that critical point quite sensitive to the magnitude and location of the oscillations, which for these "squeezable" spheres differ substantially from those expected for large spheres with diameters extending out nearly to the outer edge of the repulsive shoulders. With use of the correct, quite different, rdf renormalization calculations, proceeding in the same manner as for the low density critical point, are now found to give results in good agreement with simulations for the second critical point. Possible usefulness and limitations of renormalization calculations for other multiple critical point predictions will be discussed.