Molecular Dynamics Study of the Penetrable-Cohesive-Sphere Model Fluid

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The penetrable cohesive sphere (PCS) fluid is the simplest model Hamiltonian to exhibit two-phase gas-liquid coexistence. Potential energy (U-3NkT/2)) is defined as an average attractive energy proportional to the volume complement of overlapping clusters i.e. e ($\langle V_E/v_0 \rangle - N$); V_E is the excluded volume to an additional sphere in an ideal gas, of a configuration of N penetrable spheres; vo is the volume of a sphere. The PCS fluid exhibits thermodynamic properties of an ideal gas in both low-density and high-density limits. Equilibrium PCS thermodynamic properties transcribe analytically, and vice versa, to the Widom-Rowlinson model liquid mixture, i.e. the binary non-additive hard-sphere model in the limit of zero additivity. We describe fast algorithms for the determination of percolation transitions from MD simulation. Pressures at which clusters of excluded volume (V_E) and pockets of available volume (V_A), for a spherical molecule diameter σ , percolate the whole volume ($V = V_E + V_A$) of the ideal gas are calculated. We report reduced pressure-temperature ratios for the percolation transitions p^*_{PE} = 0.667+0.01 and $p_{PA}=0.91+0.01$ of the ideal gas. Further MD computations of PE and PA loci for the binary (A=B) fluid at finite concentrations of A in B, and B in A, establish a connection between the ideal-gas percolation transitions and the first-order phase-separation transition. When two percolation transitions intersect in the p-T plane, a critical dividing line is defined and computed on the composition (X_B) surface. At temperatures above T_c, there is a supercritical mesophase bounded by percolation loci. The PCS fluid percolation loci are obtained by transcription, and extend from a critical coexistence of gas plus liquid, to the dilute gas. Real fluids, exemplified by argon, have a phase diagram that resembles some aspects of the PCS model fluid, with a supercritical mesophase extending to low densities.