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

Leslie Woodcock C.S
Dept. of Physics, University of Algarve, Faro, Algarve, Portugal
lvwoodcock@ualg.pt

The penetrable cohesive sphere (PCS) fluid is the simplest model Hamiltonian to exhibit two-phase gas-liquid coexistence. Potential energy \( U - \frac{3NkT}{2} \) is defined as an average attractive energy proportional to the volume complement of overlapping clusters i.e. \( e \left( < V_E/v_0 > - N \right) \); \( V_E \) is the excluded volume to an additional sphere in an ideal gas, of a configuration of \( N \) penetrable spheres; \( v_0 \) 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 \textit{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 \( \sigma \), 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 \( p^*_PE = 0.667 \pm 0.01 \) and \( p^*_PA = 0.91 \pm 0.01 \) 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.