Thermodynamic Description of Liquids and Glasses

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A state of random close packing of spheres (RCP) is found to have a thermodynamic status and a central role in the description of liquid-state equilibria, and glasses. The RCP limiting density, with well-characterized structure, can be produced by both irreversible and reversible processes which establish a thermodynamic status. Alongside recent findings that the Mayer cluster integral expansion cannot represent dense fluid equations-of-state beyond low-density percolation transitions, this means RCP belongs to the same thermodynamic phase as the equilibrium liquid. MD calculation of the limiting critical parameters of cohesive spheres, and also existing literature data for liquid-vapor coexistence in the square-well model fluid reaffirm this conclusion. Since, for any liquid-system Hamiltonian, the thermodynamic state functions are continuous in all the derivatives with respect to state variables, within the phase bounds, it follows that all real liquids must also have a well-defined thermodynamic amorphous ground state (AGS) at temperatures approaching absolute zero. The AGS density (ρ_a) is obtainable for any liquid from equilibrium liquid-vapor coexistence densities, as $\rho_a = 2\rho_m$ where ρ_m is the limiting $T \rightarrow 0$ mean-density constant in the law of rectilinear diameters (LRD). LRD has been known for 100 years, but the constant ρ_m has not been identified as an amorphous ground state. We further report relevant discoveries for the square-well model liquid. The limiting critical-point density of "cohesive spheres", well-width $\lambda \rightarrow 1$, is coincident upon the square-well percolation transition for available volume (ρ_{pa}). Consequently, the liquid-vapor coexistence shows a remarkable simple symmetry. Within the margins of numerical uncertainty, as $\lambda \rightarrow 1$, the amorphous ground state density ρ_{RCP} corresponds to packing fraction 0.6366 ± 0.0005 (Buffon's constant $2/\pi$); the RCP ground-state residual entropy per sphere $\Delta S(0) \sim k_B$ (Boltzmann constant); at the critical point the percolation transition density, the critical point density, and the LRD constant density are ALL equal, i.e. at $T=T_c$, $\rho_{pa} = \rho_c = \rho_m = \rho_{RCP}/2$, whereupon the LRD slope α = zero, and the critical kinetic energy $(3/2)\, k_B T_c \sim \varepsilon$ (square-well depth). Moreover, for all square-well fluids we observe that $\rho_a = \rho_{RCP}$ and the LRD mean density $\rho_m = \rho_{RCP}/2$.