The Van der Waals Ten Commandments Resulted in Four Empirically-Based Molecular Parameters for the VDW 1873 Equation of State

Connor Albrecht [S], Neeraj Kumar and Akanni S. Lawal [C]
Reservoir and Petrophysical Research Laboratory, Texas Tech University, Lubbock, TX, U.S.A.
akannislawal@aol.com

As yet, fluids have refused to be boxed into the two-parameter cubic equation of state that Van der Waals (VDW) prepared for them. But, the VDW 1873 theory specified four properties for determining the P, v, T relation of a substance, including the fluid gas-liquid critical point, which is in accord with the four critical constraint criteria used to specify those properties for the VDW theory of cubic equations of state and that also is in agreement with the four parameters stipulated by the theory of cubic polynomial equations of state. Since the VDW theory has acknowledged molecular size and molecular attraction into the 1873 equation, the possibility of including two inspired parameters into the VDW 1873 theory can be inferred from the 1910 Nobel Prize Lecture in which VDW categorically rejected non-molecular based and non-physically meaningful empirical parameters into the 1873 theory, which we have justified by the judiciously constructed VDW Ten commandments for the designers of cubic equations-of-state. By relating the empirical parameters (a, ß) of the Lawal-Lake-Silberberg (LLS) equation to the microscopic force-parameters derived from the statistical mechanics energy potential functions and performing perturbation and other sensitivity analysis; the sensitivity of the derivatives of the structural parameters (Pc, Zc, Tc) and the sensitivity of the derivatives of second, third and fourth virial coefficients with respect to a show non-linear trend with a-parameter and thus, a replicates structure of pure substances in the configuration of the LLS equation. Similar analysis of the derivatives of the critical volume (Vc) and Boyle temperature (TB) with respect to ß show non-linear trend with ß-parameter and thus ß reflects shapes of pure substances in the configuration of the LLS equation. The empirically-based molecular parameters (a, ß) bring the VDW 1873 equation in conformity to the stipulated shapes of the potential energy and length scale of the statistical mechanical potential functions and reconcile the VDW theory with liquid-phase properties and gas-liquid critical point.