An Accurate Equation of State Based on the Virial Theorem in the Statistical Mechanics of the Square-well Potential

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We present an equation of state (EOS) based on the statistical mechanical formulation of multiple square-well (n-SW) potentials that can mimic behavior of structured molecules (e.g., hydrocarbons). By adding a temperature-dependent parameter, D/Tb^2, we can model polar effects (thus for ketones, alcohols, and amines). This equation differs from earlier equations of state in form, being not in polynomials or in the van der Waals format—such as the Peng-Robinson or the Redlich-Kwong EOS. The n-SWEOS repulsive term includes the hard-sphere effects (from Carnahan-Starling and Nezbeda equations); and the second virial term B(T) is accurately predicted. The higher density effects are built alongside the second virial term as its multiplicative factor, so as to effectively damp the precipitously negative B(T) at low temperatures—a deleterious trend that plagues many EOS formulations*. Thus our formulation is more advanced than the Kreglewiski equation. We tested against more than 60 industrial gases up to 10 MPa and wide temperature ranges with average deviation of 1% in density and vapor pressure predictions. The n-SWEOS has 8 parameters, two of which can be related to the critical temperature T_c and critical volume. Thus the n-SWEOS can also be generalized with little effort to other components not tested in this work. In most comparisons, this EOS performs better than the Peng-Robinson and Mohanty-Davis equations in density prediction and vapor pressure prediction.

*The advantage of the multiplicative factor is that it can bring down the negativity value of B(T) quickly, rather than compensating by adding the third virial C(T), and fourth virial D(T),…and so forth to achieve adjustment. [Note: the product: B(T)*x can become very small in absolute value when x is small, say -125*0.02= -2.5; while by addition, B(T)+x, x has to be of similar magnitude as B(T) -125+122.5 = -2}.