Since van der Waals renowned two-term equation for Andrews experimental CO2 p-V isotherms, incorporating his “continuity of gas and liquid” hypothesis, cubic equations for thermodynamic fluid property data banks require ever-increasing numbers of terms and fitted parameters as the experimental measurements have increased in intensity and accuracy [1]. Functional forms that accommodate the hypothesis of “continuity of gas and liquid” along critical and supercritical isotherms may become inadequate in the vicinity of the critical temperature ($T_c$) and pressure ($p_c$), and the supercritical density mid-range between gas- and liquid-like states. A mesophase, within percolation loci that bound gas and liquid states by discontinuities in 3rd derivatives of Gibbs energy, has been identified [2]. State functionals of the mesophase density are linear combinations. Both gas- and liquid-state pressures can be represented by 3- or 4-term virial expansions. Gas states require only known virial coefficients, and physical constants belonging to the fluid, i.e. Boyle temperature ($T_B$), $T_c$, $p_c$ and coexisting densities of gas ($\rho_cG$) and liquid ($\rho_cL$) at $T_c$. A notable finding is that for isotherms below $T_B$, the contribution of 4th-virial term is near-zero within experimental uncertainty. Use can be made of a symmetry between gas and liquid in the state-function rigidity ($\frac{dp}{d\rho}T$) [2] to specify lower-order liquid-state coefficients. Selected isotherms were previously reported for exemplary fluids, CO2, argon, water and SF6, with focus on the critical region [3]. Here, we report equations-of-state for argon, over the whole equilibrium fluid range, and compare with the Tegeler-Span-Wagner equation for experimental data via the NIST fluid thermophysical property database [4].

References: