A Nonparametric Equation of State for Critical Fluids

V.G. Martynets,[C,S] P.P. Bezverkhy, and E.V. Matizen
Institute of inorganic chemistry of Russian Academy of Science (Siberian Branch), Russia
mart@che.nsk.su

Compared to the parametric equations of type [1], we propose a new nonparametric equation of state based on pure scaling. This equation describes the singular parts of the equilibrium and thermodynamic properties of systems (pressure, magnetic moment, entropy, thermal capacity, etc.) near the second kind of phase transitions (critical points of liquids and ferromagnetics). The method for deriving the nonparametric equation in terms of a rigorous theory is presented in [2]. The new equation directly takes into account the existence of some curve in which the thermal capacity at constant volume diverges in the labile region of PVT space. The equation contains only three fitting constants. The experimental adequacy of the equation is demonstrated by approximating both the PVT data for He^4, H_2O, and C_2H_4, with a mean-square error of 0.2 to 0.5 % over the ranges of critical densities $-0.25 < (\rho - \rho_c)/\rho_c < 0.4$, temperatures $–0.024 < \tau < 0.037$, and the C_v data for He^4 with an error of 4 % over the range of temperatures $–0.12 < \tau < 0.14$ and densities $- 0.1 < \Delta\rho < 0.16$. The approximation was performed by the method of square functional minimization over the entire array of corresponding data. First, we determined three fitting constants from the PVT data. Then, using these constants, we calculated a single part of the thermal capacity in order to approximate a regular part used for direct comparison with the experimental data.

[1] P. Schofield, *Phys. Rev. Lett.* **22**, 606 (1969).
[2] P.P. Bezverkhy, V.G. Martynets, and E.V. Matizen, *ZhETF* **126**, 1146 (2004).