Definition, Measurement, and Interpretation of Near-Critical Gas-Liquid Heat Capacities

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At phase boundaries on the Gibbs density surface, when the number of phases (P) changes, heat capacity C_p (T) diverges when the rigidity $(\mathrm{d}p/\mathrm{d}\rho)T = 0$. In isochoric processes, higher-order breaks in $C_v(T)$ occur. Internal energy isochores show weak discontinuity in $(\mathrm{d}U/\mathrm{d}T)v$ over a range of densities at T_c, but no logarithmic divergence of the slope. Transitions with divergence at one side of a phase bound have been collectively termed "lambda transitions". We re-interpret the science of variously re-defined experimental heat capacities. We show that observation of lambda-like singularity in near-critical measurements, cannot be identified with divergence of C_v , or with universal scaling for gas-liquid equilibria, but relates to C_p divergence via orthobaric coexistence heat capacities. A heat capacity measured in a fixed volume adiabatic cell is defined by the lever rule for two-phase coexistence and designated Cλ . Measurement of Cλ for SF6 has been the subject of a microgravity experiment aboard the NASA Space Shuttle [1] that appeared to confirm earlier reports of a divergence of C_v [2] and hence support a concept of universality for critical phenomena [3]. We will show that is not thermodynamically feasible. When space shuttle experimental data are plotted alongside $(\mathrm{d}U/\mathrm{d}T)$v parameterized as a simple quadratic for $T < T_c$ and linear for $T > T_c$, the equations for $U(T)$, at the same density as the μg experiment, differentiate to give C_v. In contrast to space shuttle SF6 heat capactity [4] data, there is no divergence of C_v at T_c. We apply these findings to re-examine the concept of universality [5] and in particular its relevance to near-critical and supercritical gas-liquid phase transitions in model and real fluids.

References:

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