Dielectric Constant of Fluids and Fluid Mixtures at Criticality: Scaling Formulation and Experimental Testing

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The current scaling description of the dielectric constant e of fluids and fluid mixtures at criticality [1], henceforth to be referred to as SBMG, dates to 1980. Subsequent experimental studies as well as newly developed conceptual issues make this topic worthy to be revisited. According to SBMG, e exhibits a $\Delta T^{1-\alpha}$ [with $\Delta T \equiv (T-T_c)/T_c$ and $\alpha \approx 0.110$] singularity when the vapor-liquid critical point of pure fluids is approached along the critical isochore in the one phase-region. The same is expected for a binary liquid-liquid mixture along the critical isopleth (at constant pressure). For the two-phase region, SBMG predicts that the coexistence-curve diameter $e_d(T)$, i.e., the mid points of the phase boundary in the e-T plane, shows for both cases a $-\Delta T^{1-\alpha}$ singularity. These predictions find support from experimental data in the one-phase region; however, results for liquid-liquid phase transitions [2] clearly point towards the existence of a $-\Delta T^{2\beta}$ (with $\beta \approx 0.326$) contribution in $e_d(T)$. Here we show that such a $-\Delta T^{2\beta}$ singularity can be accommodated into scaling theory by revising SBMG in terms of complete scaling [3]. Specifically, it is found that pressure mixing into the ordering field is required in both cases; for single fluids the $-\Delta T^{2\beta}$ term has the same roots as the Yang-Yang anomaly, while for liquid-liquid phase transitions its origin is different since pressure acts as a nonordering field. Furthermore, by analyzing available dielectric-constant data for fluids and fluid mixtures, we find that theory and experiment are completely consistent.

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