This Week's Citation Classic

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Widom B. Equation of state in the neighborhood of the critical point.
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Near the critical point the equation of state takes on a homogeneity of form. The indices that determine the shapes of the coexistence curve and critical isotherm and the rates of divergence of the compressibility and constant-volume specific heat are all related. [The *SCI®* indicates that this paper has been cited in over 390 publications since 1965.]

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"From the time of my postdoctoral work with O.K. Rice at the University of North Carolina in 1952-1954, I had been interested in the deviations from classical, van der Waalsian behavior at critical points. Rice had impressed upon me the apparent universality of such deviations, as seen, for example, in the shapes of liquid-vapor coexistence curves near critical points, which Guggenheim had analyzed in his great paper on the law of corresponding states,[1] or as seen in the shapes of the analogous temperature-composition coexistence curves of two-component liquid mixtures near consolute points. In the van der Waals theory coexistence curves are parabolic near critical points but in reality they are more nearly cubic. There are similar deviations in the shapes of critical isotherms, which are cubic in classical theories but of nearly the fifth degree in reality. Later I came to realize (largely from the work of Fisher—that with Essam,[2] for example) that similar deviations from the predictions of the classical equations of state are found in the rate of divergence of the compressibility and in the behavior of the constant-volume specific heat—the latter being finite at the critical point classically, but in reality diverging.

"Between 1962 and 1964 I tried several times to construct an equation of state that would incorporate such deviations from classical behavior. Early in 1965, while I was on leave in Guggenheim's department at the University of Reading, I calculated the constant-volume specific heat implied by one of the many nonclassical equations of state I had considered at Cornell University (all of them unsatisfactory for one reason or another), and found to my amazement that it diverged logarithmically at the critical point, just as that of the two-dimensional Ising model. The essential feature of the equation of state that led to that result turned out to be a certain homogeneity of form (called scaling in the later literature), and by insisting on that alone, but on none of the other details of the trial equation of state, I was able to get rid of all of its unsatisfactory features while retaining those that were responsible for its success in reproducing the known nonclassical behavior. On returning to Cornell early that summer I wrote it all up (with a companion paper[3] on the relation of surface tension to density fluctuations and their nonclassical behavior near critical points) and submitted it for publication.

"The paper's success was due no doubt to its timeliness: 1965 saw an explosion of interest in phase transitions and critical points among chemists, physicists, and engineers. Ideas equivalent to these were being developed independently by others and were published not long after; all became part of the general lore now known as scaling. A half dozen years later they were incorporated in the modern renormalization-group theory,[4] a great intellectual achievement. It has been exciting to see this classical, nineteenth-century subject take so dramatic a turn."

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1. **Guggenheim E A.** The principle of corresponding states. *J. Chem. Phys.* **13**:253-61, 1945.
2. **Essam J W & Fisher M E.** Padé approximant studies of the lattice gas and Ising ferromagnet below the critical point. *J. Chem. Phys.* **38**:802-12, 1963.
3. **Widom B.** Surface tension and molecular correlations near the critical point. *J. Chem. Phys.* **43**:3892-7, 1965.
4. **Pfeuty P & Toulouse G.** *Introduction to the renormalization group and to critical phenomena.* London: Wiley, 1977. 190 p.