

Scaling Analysis of Thermodynamic Properties in the Critical Region of Fluids

This paper [1] was an outgrowth of the renewed interest, beginning in the early 1960s, in the problem of how to describe the critical point, the limit point of phase transitions. This interest came about in part from new abilities to make light scattering and neutron scattering measurements and in part from theoretical work that pointed toward universal property behavior at and near critical points. The universal behavior was thought to be independent of the substance and of the type of phase transition. A 1965 conference held at NBS [2] brought this work into focus and set the stage for the developments that followed. The conference stimulated much new research, including important contributions from Anneke Sengers and Mel Green of NBS.

The prospect of a unifying principle, universality of critical point behavior, excited the interest of many scientists. The “classical theory” of the critical point makes the strong assumption that the free energy of the fluid is an analytic function of the density and temperature at the critical point. (Fluid terminology will be used here, keeping in mind that the concepts are equally applicable to other critical points, such as the Curie point of a ferromagnet or the Néel point of an antiferromagnet, with the appropriate change of variable names. For a fluid, the critical point is characterized by a particular value of the density, ρ_c , and of the temperature, T_c . At the critical point, the density of the liquid phase becomes equal to the density of the coexisting vapor phase.) This means that the thermodynamics of the fluid in the critical region can be expressed in terms of a Taylor’s series expansion of the free energy about the critical point in terms of the difference of the temperature and density from the critical temperature and critical density. The classical theory makes predictions that were known (if not always remembered) to be in conflict with experimental results. Soon after the conference it was shown that near the critical point, thermodynamic properties, such as the equation of state, could be described usefully in a scaled form [3,4]. The scaling theory includes the classical theory as a special case, but does not require the free energy to be analytic at the critical point. The units to use are appropriate combinations of the critical temperature, critical density, and critical pressure for a fluid and the analogous variables for magnetic systems. The scaling form has the additional feature that symmetries can

be expressed simply in terms of the scaled, reduced variables.

A very important task involved the critical evaluation of existing data on many different fluids and magnetic systems. This was needed to determine how the universal behavior is reflected in the thermodynamics of the critical point. It is one thing to postulate a form for the equation of state and the chemical potential in terms of scaled variables, and quite another thing to demonstrate that the form is useful over a significant range of the variables. That demonstration is the contribution of this paper [1] and of subsequent companion papers [5,6].

The paper contains an extensive discussion of how thermodynamic properties of a fluid close to the critical point are to be formulated in a proper manner and, at the same time, in a way that permits comparison with experiments. It would be inappropriate to go through the arguments in detail, so only a bare outline will be presented here.

First, the reader is introduced to some power law descriptions of thermodynamic anomalies in the critical region. An example is the coexistence curve, $\Delta\rho = B(-t)^\beta$, where $\Delta\rho = (\rho - \rho_c)/\rho_c$ and $t = (T - T_c)/T_c$. Other power laws describe the critical isotherm, the isothermal compressibility, and the specific heat at constant volume. (The classical theory predicts $\beta = 1/2$, while the experimental value is on the order of 0.32.) Next, a scaled form for the equation of state, as described by Widom and by Griffiths [3,4], is discussed. Thermodynamics is properly formulated in terms of the Helmholtz free energy as a function of the temperature and the volume. The equation of state is then a partial derivative of the free energy, often in terms of the pressure as the volume derivative of the free energy. The chemical potential is seen from the data to reflect the symmetry properties of the critical point better than does the pressure, so the equation of state is described in terms of the chemical potential as the density derivative of the free energy per unit volume.

The form for the coexistence curve suggests the introduction of a scaling variable, $x = t/\Delta\rho^{1/\beta}$, that reflects the properties of the critical region. The next stage of the paper involves casting these ideas into a scaling function, $h(x)$, that allows them to be tested using experimental data.

With these tools in hand, the existing thermodynamic property data for Ar, Xe, CO₂, ⁴He, and water are examined carefully. The scaling formulation is shown to work quite well for the existing data, but the scaling hypothesis is far from being fully verified. An example of the type of fit to experiment is shown in Fig. 1 where data for carbon dioxide are matched to the form for $h(x)$.

A problem identified in the paper was that the range of density and temperature around the critical point over which scaling is applicable could not be decided on the basis of existing data, which stimulated a number of new experiments.

Although not part of this paper, some very interesting comments on how this work evolved are found in a later paper on the problem [7]. Some of the human side of research is revealed in that reference.

A large amount of research has been performed to extend the analysis started in this paper. The task of identifying the domain where scaling is applicable has gone through several phases. The renormalization group approach to critical phenomena has been central to these developments [8]. One result is the formulation

of “practical” free energy surfaces for industrially important fluids that are consistent with the new understanding of the critical region of the fluid [9]. Another result is the development of a “cross-over” theory that connects the scaling formulation with the rest of the thermodynamic space in a continuous way. Finally, a very large amount of experimental work has been carried out with the result that many of the questions left unanswered by this paper now have clear answers.

There are numerous industrial processes where supercritical fluids play a significant role. Only two will be mentioned here.

Supercritical fluids are utilized as solvents in supercritical extraction processes. The density of a supercritical fluid can be varied over a wide range of values by small changes in the pressure. This means that solutes extracted at high fluid densities can be extracted from the solvent simply by lowering the pressure.

Supercritical water is a medium where oxidation reactions can proceed at relatively low temperatures. This is an attractive alternative for hazardous waste destruction, since incineration produces undesirable by-products as a result of the high flame temperatures.

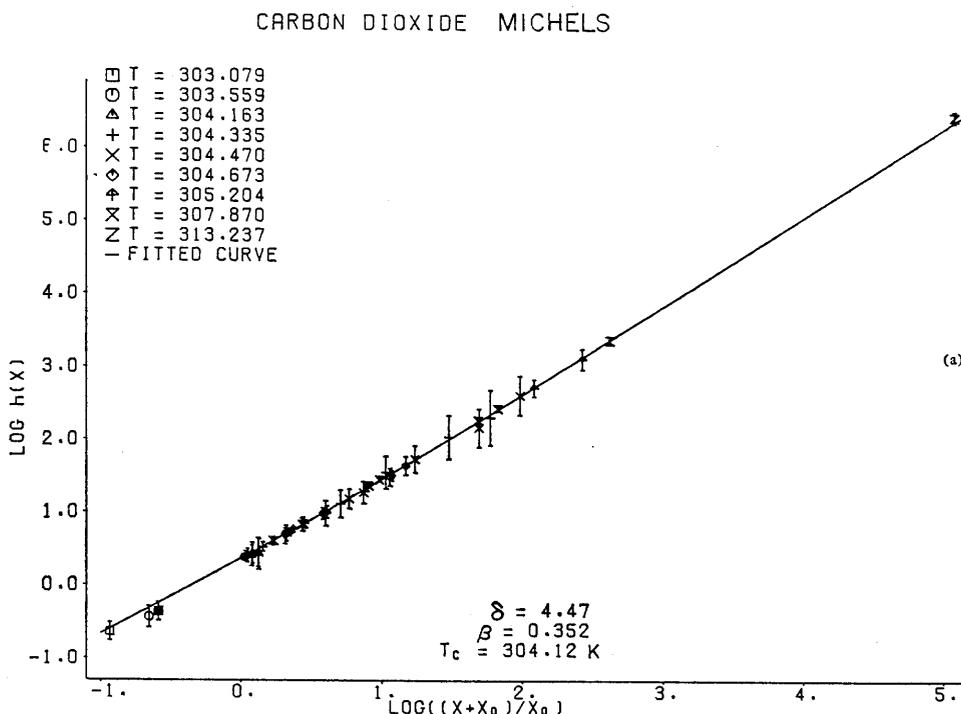


Fig. 1. This plot illustrates the accuracy of the scaling representation for carbon dioxide in the critical region. The scaling variable, x , has the value $-x_0$ on the liquid vapor coexistence curve. The solid line is fit to a particular form for $h(x)$ while the points are determined directly from the experimental data.

J. M. H. (Anneke) Levelt Sengers joined NBS in 1963 as a member of the Equation of State Section. A partial list of honors includes NIST Senior Fellow, Member of the National Academy of Engineering, and Member of the National Academy of Sciences. Her work on critical phenomena has taken many forms. In addition to the careful analytical work described here, she has performed many crucial experiments. She has worked extensively on the formulation of practical equations of state for water and steam [10]. In addition, she has examined the history of the development of the ideas underlying the scaling approach and has written some interesting and informative historical pieces [11,12].

M. S. Green joined NBS in 1954 and became the first Chief of the Statistical Physics Section in 1960. He was intensely interested in critical phenomena and organized the very successful conference that was held at NBS in 1965 [2]. In 1968 he left NBS to join the Physics Department of Temple University in Philadelphia. He maintained contact with NBS until his death in 1979. An excellent tribute to Mel by H. J. Raveché is found in the M. S. Green memorial volume [13].

M. Vicentini-Missoni was a guest worker at NBS while on leave from the University of Rome.

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