Critical-point universality and fluids

Near a critical point the behavior of widely diverse systems simplifies to one of a few universal patterns—but fluids for years resisted being fit into the slot that theory had prepared for them.

Anneke Levelt Sengers, Robert Hocken and Jan V. Sengers

The similarity of critical behavior in dissimilar systems has long fascinated scientists. When Pierre Curie, in 1895, measured the magnetic equation of state of nickel, he was struck by how much the curves he obtained by plotting magnetization against temperature looked like the density–temperature isobars of carbon dioxide near the critical point. In 1907 Pierre Weiss fashioned his mean-field theory describing the equation of state of nickel after Van der Waals's equation for fluids.

These old theories are not quantitatively correct; we now have much more refined models, and a highly successful new theoretical method, called the "renormalization-group" approach. Yet the basic idea about the sameness of critical behavior in unlike systems remains very much alive. It has been the moving force behind recent international meetings, at which experimentalists and theorists, physicists and chemists, experts in fluid and solid state physics all found a common ground in the topic of critical behavior.

The curious fact is that fluids, the first systems in which critical points were found, 150 years ago, have stubbornly refused to fit into the slot that modern theory of critical behavior had prepared for them. Only very recently have we learned how fluids do fit in. Some of this progress has resulted from optical experiments performed with the 20-microdegree thermostat shown in figure 1. As our story about critical-point universality in fluids unfolds, the reasons why fluids have been so long in yielding will, we hope, become clear.

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Physical systems with critical points

Many physical systems have phase transitions terminating in a critical point: Below a characteristic critical temperature, fluids separate into liquid and vapor; certain liquid mixtures, into two phases of different composition. Ferromagnets spontaneously develop a magnetization; ferroelectrics, a polarization. Liquid helium becomes superfluid, and many metals become superconducting. Antiferromagnets, certain ammonium salts and binary alloys develop an ordered phase. This ubiquity of critical-point phase transitions is indeed impressive. Even more impressive is the fact that such richness and variety of physical behavior can be understood and classified from a common point of view. A book by Eugene Stanley[1] gives a general review of the subject; the Domb–Green series[2] contains up-to-date detailed reviews.

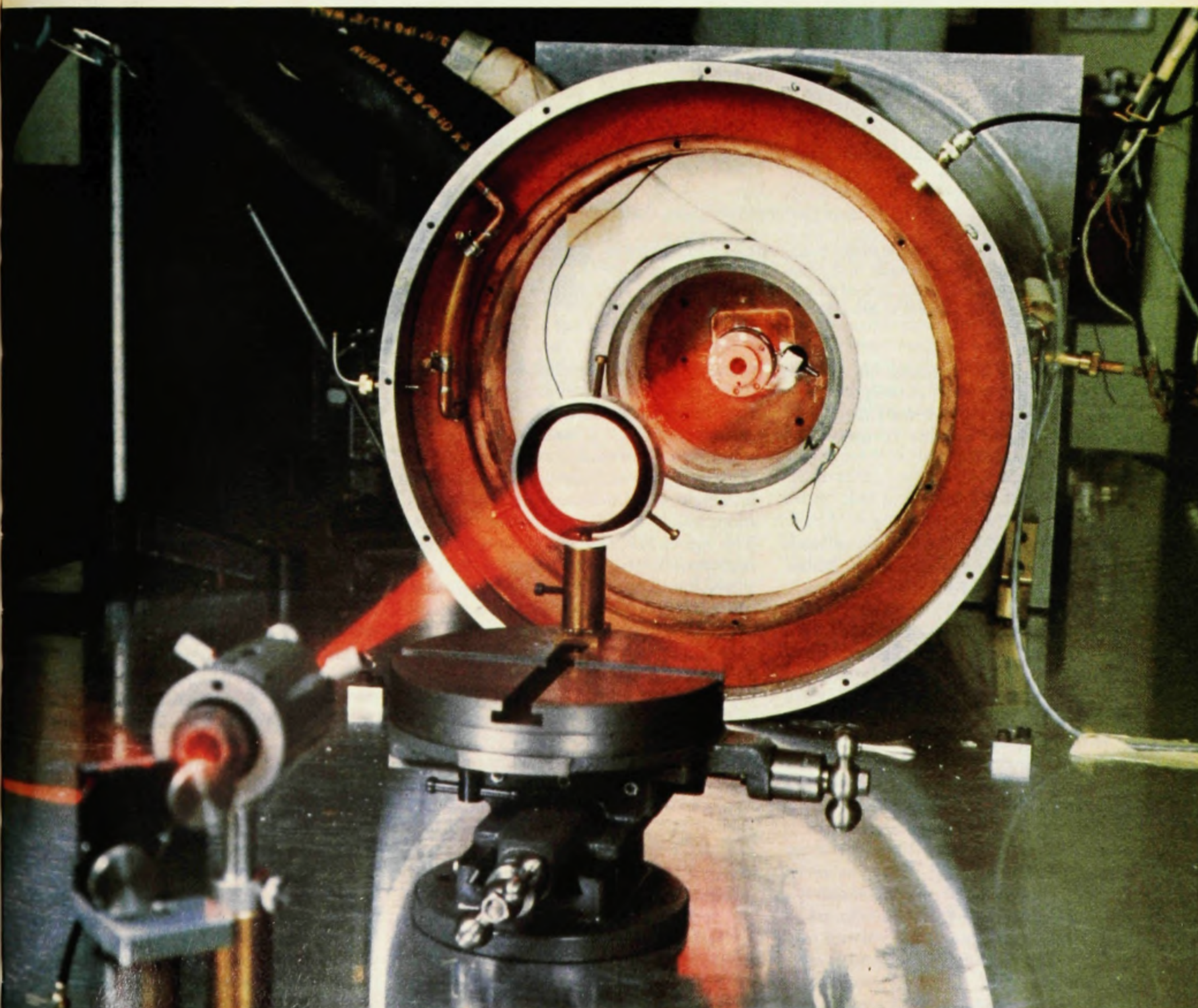
The phase below the critical point is an ordered phase; it can be characterized by an *order parameter* that goes to zero at the critical point. In all cases, a *response function* of the order parameter (specifying the response of the system to an external stress) diverges at the critical point, indicating that the system has reached a limit of stability. In fluids, the order parameter is the density difference from critical, $\rho - \rho_c$; its response function, the derivative of density with respect to pressure, is proportional to the isothermal compressibility K_T.

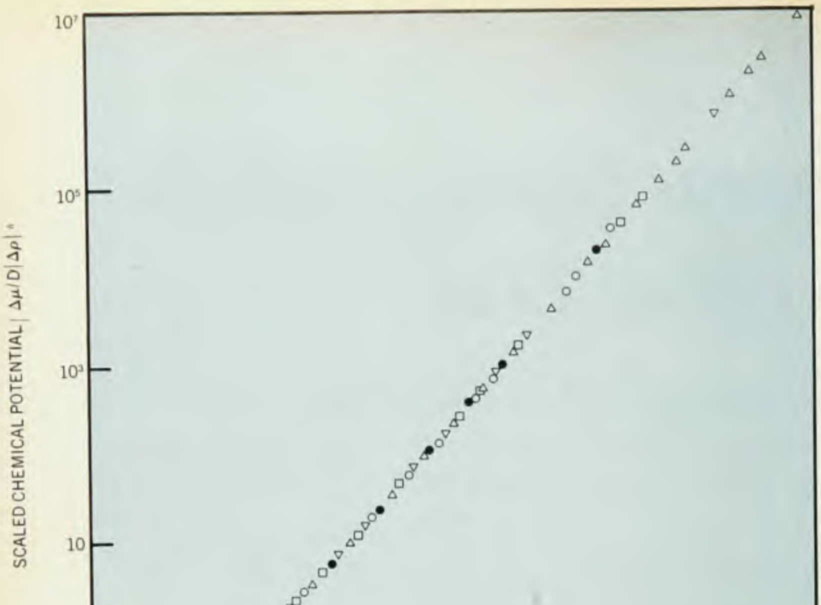
When the response function diverges, large-scale fluctuations of the order parameter can occur at low cost in free energy. These manifest themselves in an anomalous critical scattering of light. This "critical opalescence," which gives near-critical fluids their typical milky appearance, is perhaps the most striking harbinger of the critical state. A way of describing this phenomenon is by means of the *correlation function* $G(r)$, which measures the extent to which local particle densities a distance r apart are correlated. Ordinarily the range of $G(r)$, the *correlation length* ξ, is approximately the range of interaction between two particles. In the vicinity of a critical point, however, large-scale fluctuations are present. That is, the correlation length ξ now greatly exceeds the range of pair interaction and, in fact, diverges at the critical point. The Fourier transform of $G(r)$, the *structure factor* $S(k)$, governs the scattering power of the medium. At the critical point $S(k)$ diverges for small wavenumber k, reflecting the weak decrease of $G(r)$ at large r.

Due to the presence of these fluctuations, many static and dynamic properties show striking or subtle anomalies in their behavior. Because the fluctuations extend over regions containing very many particles, the details of the particle interaction are irrelevant, and a great deal of similarity is found in the critical behavior of diverse systems. This similarity, which will be explained more precisely below, is known as *universality*.

The anomalous behavior of physical properties near the critical state is described by simple rules, some of which were already formulated by Johannes Van der Waals in 1892. The approach of a property to its critical value may be

Seven-layered thermostat, capable of 20-mK stability in its core. Light traversing the fluid in an optical cell there forms, because of the fluid's density gradient, a diffraction pattern, which yields its equation of state. The resulting critical exponents are near those of the Ising model. Figure 1





A single curve from five different fluids, produced by scaling chemical-potential and temperature data, illustrates the universality of fluid behavior near the critical point. The fluids are helium 3 (O), helium 4 (●), xenon (□), carbon dioxide (∇) and water (Δ). On the coexistence boundary $x = -x_0$; the quantities D and x_0 are system-dependent. Figure 2

written simply as a power law with a characteristic *critical exponent*. For example, the power law for the specific heat at constant volume is, above the critical temperature,

$$C_V = A^+ \, |\Delta T|^{-\alpha}$$

where $\Delta T = (T - T_c)/T_c$.

In table 1 we give examples of such power laws and of the critical anomalies they describe for three different systems, pure fluids near their critical points, binary liquids near their consolute points and ferromagnets near their Curie points.

Model systems with critical points

In attempting to understand critical behavior, theorists have invented numerous models that have critical-point phase transitions. The earliest, the Van der Waals (mean-field) model, correctly represents systems with weak, long-range forces—in which fluctuations can be ignored. This model has a critical point in all dimensions and its critical exponents are integers or simple fractions independent of dimension. These mean-field exponents differ, however, from those found in real systems with short-range forces, as Jules Verschaffelt noted for fluids in 1900.

Wilhelm Lenz and Ernest Ising in 1926 constructed the first statistical model for a lattice system with short-range forces. The "Ising model," as it is now called, is an array of up and down spins. It was soon followed by many other models. The Ising, XY and Heisenberg models represent lattice systems with, respectively, one-, two- and three-component magnetic spins. None of these models predicts a phase transition in one dimension but all do in three.

Exact or approximate values of critical exponents are known for all these models in three dimensions. The averages of the two most recent estimates[3] for the critical exponents of the models mentioned are listed in table 2. Critical-exponent values in model systems depend on the range of the forces (long or short), the dimensionality d and the number of spin components n but are independent of many other properties of the model, such as the lattice structure and the number of values the spin can assume. This confirms the notion that such details of the interaction are irrelevant to critical behavior.

Theory predicts that each of the examples listed in the tables defines a *universality class*, a collection of models and experimental systems that all have the same critical exponents. Tsung Dao Lee and Chen Nin Yang showed in 1952 that the ferromagnetic Ising model was isomorphic with a model of the gas–liquid transition, the so-called "lattice gas." The expectation is therefore that fluids belong to the universality class of the Ising model, with $d = 3$ and $n = 1$.

Scaling: the empirical approach

The first successful attempt to bring order into the bewildering variety of critical exponents and power laws can perhaps be best described as enlightened empiricism. Benjamin Widom noticed in 1965 that all known power laws can be derived from one assumption: that the critical part f of the free energy is a *homogeneous function* of its two independent variables x and y such that

$$f(\lambda^p x, \lambda^q y) = \lambda^d f(x,y)$$

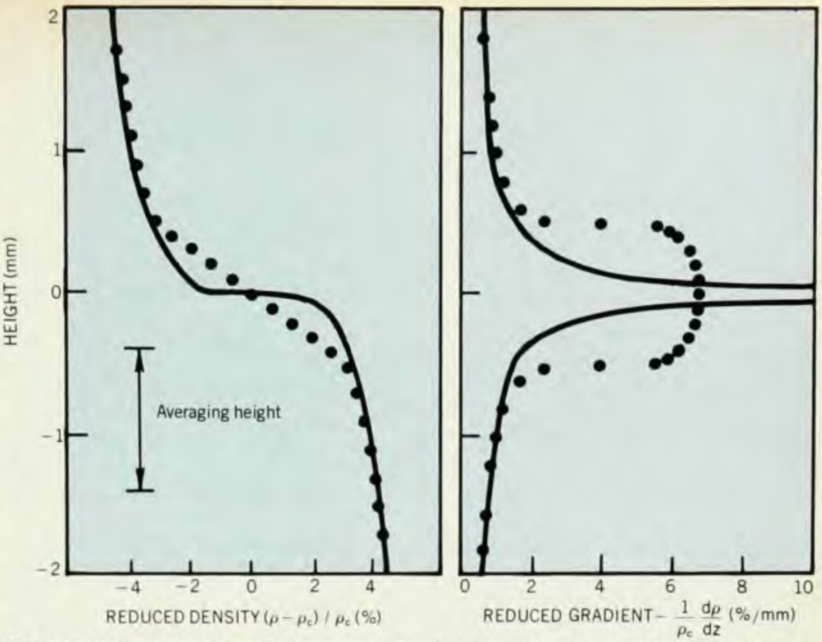
Here p and q are two critical exponents, d is the dimensionality and λ is an arbitrary constant. In the magnetic case, for example, x is proportional to the magnetic field H and y to the temperature difference from critical, $T - T_c$. All critical exponents defined in table 1 now become combinations of p, q and d. All amplitude factors in the many power laws depend only on the two scale factors relating x and y to the physical variables, once p, q and the form of f are given.

The homogeneity assumption is quite restrictive: It implies that once the anomalous free energy f is known on one contour in the x–y plane around the critical point, then it is known everywhere. Therefore one independent variable can be eliminated, by a process called *scaling*. How scaling works was first shown for fluid data in 1967 by Melville Green, Matilde Vicentini-Missoni and one of us, Levelt Sengers.[4] The process is illustrated in figure 2, which is an updated version[5] of the original scaling plot. It is a graph of the scaled chemical potential, $|\Delta\mu|/|\Delta\rho|^{\delta}$, divided by one of the free, fluid-dependent amplitudes D, plotted as a function of the scaled temperature, $x = \Delta T/|\Delta\rho|^{1/\beta}$, divided by the other free amplitude, x_0. Shown are equation-of-state data over a range within 5% in temperature and 30% in density of the critical point, for five fluids, including noble gases, quantum fluids and a highly polar fluid, water. The critical-point scaling function produced illustrates the power of the homogeneity assumption; it also demonstrates critical-point universality by representing large amounts of data for quite diverse fluids with only two critical exponents.

There is, however, a problem. To achieve scaling in this range, the following choices had to be made for the two free exponents: $\beta = 0.35$, $\delta = 4.5$. Although these choices were quite representative of exponent values reported for fluids since 1900, they were different from those of the known model systems listed in table 2. In particular, they differed substantially from those of the three-dimensional Ising model, thought to be in the same universality class. This was the situation up to a few years ago: Scaling worked well, yet the odd values of the fluid critical exponents could not be reconciled with theoretical expectations.

The physical basis for the homogeneity property of the free energy in the critical region was unknown when Widom postulated the scaling property in 1965. In 1966, however, Leo Kadanoff showed that homogeneity follows from applying what is now called the *universality principle* to the Ising model under changes of scale.[6] Since the free-energy anomaly is caused by the presence of large-scale fluctuations, Kadanoff reasoned, it should be possible to describe a spin system such as the Ising model on a scale somewhat coarser than a lattice spacing without affecting the character of the critical anomalies.

The result of averaging on a scale of L lattice spacings is a system of block spins that interact with the field and with each other in a way that depends on the value of L. The block system is at a new effective distance from its critical point; however, because small-scale averaging should not affect critical behavior, the new system is equivalent to the old. A relationship is thus obtained between the anomalous free energies of what is effectively the same system at different distances from its critical point. This relationship turns out to be identical with the homogeneity assumption of Widom.



The density of a near-critical fluid, compressed by its own weight, varies with height (solid curve, left); the density gradient peaks sharply at the level where density is critical (right). A practical limitation to the determination of these profiles is the finite size of the probe; if a probe 1 mm high is used to make the measurements, it will record averages (full circles) that differ considerably from the local property. (From reference 15) Figure 3

The renormalization-group approach

Kadanoff's idea of studying the effect of scale transformations on near-critical Hamiltonians inspired the development of a new and powerful theory, the renormalization-group approach. This new theory (or method, intuition or faith, depending on one's point of view) originated in quantum field theory; it remained largely formal until Kenneth Wilson applied it in 1971 to systems with large-scale fluctuations, that is, to critical systems.[7] The new approach studies the transformation under repeated changes of scale of $\mathcal{H}/k_BT$, where $\mathcal{H}$ is the Hamiltonian of the system. In the remainder of this article the term "Hamiltonian" will be used to refer to the quantity $\mathcal{H}/k_BT$.

The two-parameter Ising-model Hamiltonian is considered as a member of a much wider class of Hamiltonians in a multidimensional parameter space. These parameters change under a scale transformation; when the scale is changed repeatedly these Hamiltonians will jump along well-defined paths in parameter space. Critical Hamiltonians will move along a "critical line"; because the correlation length is infinite it will remain so under any finite change of scale. Noncritical Hamiltonians will move away from this critical line, because the correlation length shrinks by L each time the length scale is increased by this factor. The critical Hamiltonian is expected to stop changing after small-scale details are averaged out; a fixed point of the transformation will have been reached. From the properties of the transformation near such a fixed point, formulated in differential form, Wilson was able to derive the homogeneity relation.

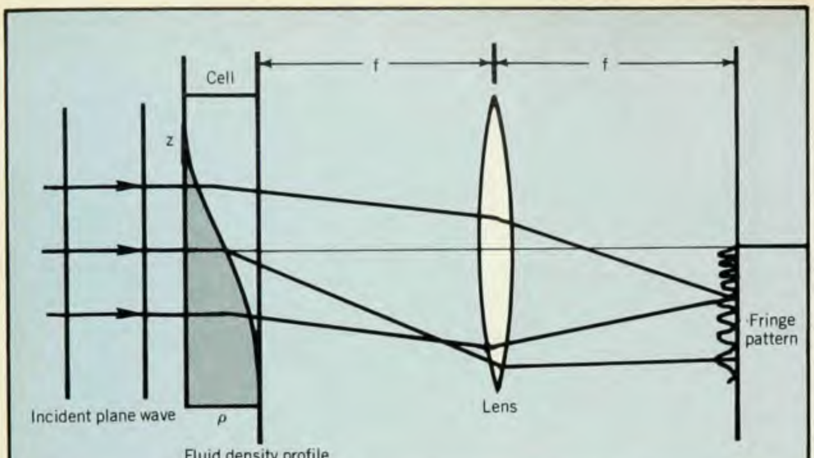
The renormalization-group picture of universality is that all systems with critical Hamiltonians that move to the same fixed point under repeated change of scale belong in the same universality class, and that they have the same critical exponents and the same scaling functions. For systems with short-range forces, the universality class is solely determined by the system's dimensionality d and the number of spin components n.

Those Hamiltonian parameters or fields with a difference from their critical value that *grows* under renormalization are called *relevant*: They move the system away from criticality. Hamiltonians converging to the Ising fixed point have only two relevant fields, namely H/k_BT and $1/k_BT$, where H is the magnetic field. Because of the lattice-gas analogy, the same is expected for fluids, where the relevant fields are combinations of the chemical potential and temperature differences from critical.

There may be fields initially present in the Hamiltonian that *shrink* under changes of scale. These fields have disappeared from the Hamiltonian by the time the fixed point is reached, and are therefore called *irrelevant* fields. J. Hubbard and Peter Schofield showed in 1972 that the lack of symmetry of a real fluid (as distinct from a lattice gas) does not affect the leading anomalies and is therefore irrelevant. Franz Wegner showed that irrelevant fields are of importance because they determine the *corrections* to scaling when the system is not asymptotically close to critical.[8]

In the space of Hamiltonian parameters there may be several fixed points. Depending on the initial state, a critical trajectory may first seem to approach one fixed point but ultimately reaches another; this phenomenon is called *crossover*.[9] An example is a Heisenberg interaction with slight anisotropy added. David Jasnow and Michael Wortis showed that such a system behaves as a Heisenberg model far from the critical point, but "crosses over" to Ising behavior close by.

Wilson's work did not end with this appealing picture of critical-point universality. As a second major achievement, he devised a way of actually calculating approximate values of the critical exponents from the renormalization-group equations. Following his lead, a variety of sophisticated computational methods have been developed in the last few years, resulting in accurate values of the critical exponents as well as the form of the scaling functions, the structure of corrections to scaling and nature of crossover functions. Volume 6 of reference 2 gives an impressive overview of the capabilities of the new methods.



Formation of a Fraunhofer pattern. A parallel beam of light is bent through various angles by the refractive-index gradient of the near-critical fluid in the cell on the left; the density profile of the fluid is shown. An interference pattern is generated in the other focal plane of the lens. The thermostat depicted in figure 1 keeps the cell at constant temperature. The equation of state near the critical point can be deduced from the interference pattern as a function of temperature, shown in the photograph of figure 5. Figure 4

Renormalization-group calculations have been performed for models of spins in a lattice. Often, however, the Hamiltonian is modified so as to treat spin as a continuous variable; this is the way the exponent values listed in table 2 were obtained. Precise estimates of the critical exponents for the three-dimensional Ising model were available prior to the development of the new approach. They had been obtained by analyzing the coefficients of series expansions of the partition function, an art in which the British school of Cyril Domb, Michael Fisher and others has long excelled.[10] These series-expansion coefficients however differ slightly but significantly from the values we have listed for the $d = 3$, $n = 1$ class. Moreover, the series-expansion exponents do not accurately obey two-exponent scaling, as it is built into Wilson's approach. Whether this discrepancy reflects failure of the renormalization-group approach, exceptional behavior of the Ising model or overly optimistic assessment of the precision of the various calculations is still being debated. Our own preference for these values arises solely from the practical observation that fluid data fit into the universality picture more readily with the renormalization-group exponents for $d = 3$, $n = 1$, Ising-like systems than with the exponents from Ising-model series expansions.

Universality in magnets and superfluids

Although Jens Als-Nielsen and his coworkers in 1967 reported Ising-like critical exponents in beta brass near its order–disorder transition,[11] attempts at verifying universality in magnetic systems have led to many complications.[12] The range of most interest, temperatures within 0.01% of critical, is usually excluded because of such disturbing effects as impurities and lattice strains. Furthermore, magnetic substances are seldom true representatives of one universality class because the interactions usually have anisotropy and some long-range character, which lead to crossover behavior from one universality class to another. A major accomplishment of renormalization-group theory is its ability to specify which properties of the Hamiltonian determine critical behavior and how the crossover phenomenon occurs, thus bringing order into a large variety of complex phenomena. For a full treatment, see the reviews by Fisher[13] and by Amnon Aharony.[9]

In view of the complexity of magnetic systems, perhaps other systems should be considered for tests of universality. Advocates of the renormalization-group theory have not hesitated to claim applicability to fluid systems. Superfluid helium, they say, should belong to the universality class of the XY model, with $n = 2$ (see table 2).

Liquid helium near the superfluid transition has been the subject of extensive and precise studies by Guenter Ahlers at Bell Labs. Two critical exponents are experimentally accessible, namely α and ν. In a recent review Ahlers[14] quotes $\alpha = -0.02 \pm 0.02$, $\nu = 0.67 \pm 0.01$, values that nicely span those expected for this universality class. The universality hypothesis also implies that critical exponents and amplitude ratios should be independent of the pressure at which the transition is studied along the lambda line. Initially, this did not appear to be the case. A careful reanalysis of the data, incorporating corrections to scaling as predicted by the theory, enabled Ahlers to remove most of the original discrepancies. Although some fine points are still being debated, the superfluid-helium story reads like a success story for renormalization-group theory and for Ahlers.

Fluids

Let us now turn to less esoteric substances and ask about verification of universality in common pure fluids and fluid mixtures. Theory assigns to fluids the Ising-model universality class with $d = 3$ and $n = 1$. We have seen that application of the scaling concepts to fluid data in the range within 5% of the critical temperature has led to exponent values that differ systematically and significantly from the Ising values. The question is whether this difference is real, or whether it may be due to insufficiently close approach to the critical state.

At a first glance fluids would seem to be ideal candidates for comparison with theory. They are not subject to strains and dislocations, as solids are; they can be studied at convenient temperatures, and even an impure fluid, a fluid mixture, is a member of the same universality class. Indeed, the pioneering calorimetric studies of Alexander Voronel in the USSR in the early 1960's, in which an Ising-like divergence of C_V was discovered in argon, nitrogen and oxygen, brought fluids, long neglected, back into the limelight. Voronel's work was corroborated by Michael Moldover's C_V studies in helium and,

Table 1. Power laws and critical exponents

Property	Fluid	Binary liquid	Magnet	Power law
Specific heat	C_V	C_{Px}	C_H	$= A^{\pm}\lvert\Delta T\rvert^{-\alpha}$
Order parameter s	$\rho - \rho_c$	$\phi - \phi_c$	M	$= B\lvert\Delta T\rvert^{\beta}$
Response function	$\rho^2 K_T$	χ_T	χ_T	$= \Gamma^{\pm}\lvert\Delta T\rvert^{-\gamma}$
Critical isotherm	$\lvert\mu - \mu_c\rvert$	$\lvert\mu_2 - \mu_1\rvert$	$\lvert H\rvert$	$= D\lvert s\rvert^{\delta}$
Correlation length	ξ	ξ	ξ	$= \xi_0^{\pm}\lvert\Delta T\rvert^{-\nu}$
Critical correlation function	$G(r)$	$G(r)$	$G(r)$	$= r^{-(d-2+\eta)}$

The reduced temperature, ΔT, is $(T - T_c)/T_c$; the μ's are chemical potentials, ρ is the density, ϕ the concentration or volume fraction, H the magnetic field and M the magnetization. The superscript + indicates the supercritical, − the subcritical, temperature range.

later, by the refined measurements of C_V in CO_2 and xenon by Michael Buckingham and his co-workers in Australia.

Unfortunately fluids present an experimental problem all their own. As a pure fluid is brought near its critical point, its compressibility diverges and therefore it becomes compressed under its own weight in the Earth's gravitational field, as first predicted by Louis-Georges Gouy in 1892. Thus in any finite-size sample, substantial density gradients exist for temperatures within 0.01% from the critical. These density profiles limit the validity or interpretation of thermodynamic measurements near a critical point and especially of weak anomalies such as that of C_V, as was analyzed by Hartland Schmidt, and by Pierre Hohenberg and Martin Barmatz. There are two effects to be considered, one fundamental, the second merely a practical limitation that can, at least in part, be overcome:

The fundamental effect can only be removed in the absence of gravity. We have seen that as the critical state is approached, the correlation length for density fluctuations diverges. Because of the presence of the density gradient, however, the critical state, in a gravitational field, can only exist in an infinitesimally thin layer where the density is critical: In any earthbound experiment the correlation length in pure fluids will not become much larger than 10^{-3} mm. Sufficiently close to the critical state, the local properties of the fluid will begin to vary appreciably over heights of the order of one correlation length; they can no longer be identified with those of a hypothetical homogeneous system in the thermodynamic limit. Present-day experimentation is on the verge of entering this fascinating regime.

The second effect is much more prosaic. All known "probes" examine a finite sample volume. When that volume contains a distribution of thermodynamic states, some average fluid property is measured. This is illustrated in figure 3, where the reduced density $(\rho - \rho_c)/\rho_c$ and the density gradient are plotted as functions of height for a typical fluid, xenon, at its critical point. Also shown are the values of these properties averaged over a 1-mm height.

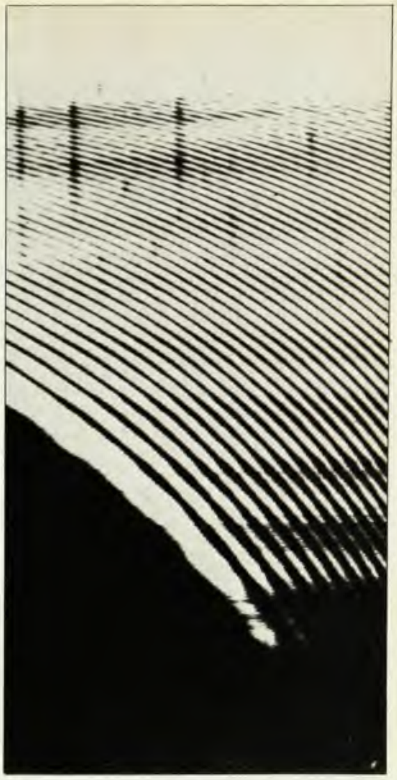
The large differences between the local and the averaged properties make it easy to understand why conventional experiments must fail to yield the correct divergences when these gradients are present. Since density gradients begin to develop at about 0.01% from the critical temperature in most fluids (about 0.03 deg C from critical in CO_2 and Xe), the approach to the critical point in fluids by conventional experiments is as limited as in magnets. To overcome this difficulty, there are basically three options:

- The most demanding experiments, those involving weak anomalies, could be carried out in space in the absence of gravity. Indeed, the feasibility of critical-region experimentation in the coming NASA spacelab is currently under study.[15]
- One might search for fluid systems other than pure fluids, in which the gravity effect is less.
- Finally, one might obtain information about near-critical behavior by a detailed study of the density profile itself.

The last route has been followed by a number of experimenters, beginning with Gustav Teichner in 1904. The most successful technique has been that developed by Lee Wilcox and David Balzarini at Columbia University, and later refined by W. Tyler Estler, one of us, Hocken, and Thomas Charlton, working with Wilcox at Stony Brook.[16] This technique uses the Fraunhofer diffraction pattern produced when light traverses a fluid in which density gradients exist.

Figure 4 explains the origin of this interesting pattern. If a thin slab of fluid is illuminated by a plane wave, light rays crossing the fluid are bent downward by an amount proportional to the density gradient. Furthermore, these rays are phase-shifted by an amount proportional to their optical path in the fluid, which is related to the local density through the Lorentz–Lorenz relation. To a good approximation the fluid-density profiles are antisymmetric with respect to the inflection point, while the density gradient is symmetric, as figure 3 shows. Therefore, rays entering at equal distances above and below this plane of symmetry bend through the same angle, but experience a differential phase shift proportional to the density difference between the two levels.

These rays, after passing a lens, interfere in its focal plane to produce the striking pattern shown as a function of temperature in figure 5. This picture was obtained on a film traversing in the focal plane while the sample's temperature was swept linearly. Even though it took several days to produce this picture, the sample was never fully at equilibrium and figure 5 should therefore be seen only as an illustration of the method. The region at left in the picture represents supercritical states; the critical temperature occurs at the point where the first bright wide fringe appears to head down towards minus infinity. This fringe is formed by rays that have traversed the sample very close to the maximum of the gradient, and therefore the deflection of this first fringe diverges as the compressibility, namely as $|\Delta T|^{-\gamma}$.



An interference pattern formed by the apparatus of figure 4. To obtain the photo, the temperature was swept slowly (several days) through the critical region while the film was transported in the focal plane. At the critical temperature the fringes dip down the farthest; supercritical temperatures are on the left. The photograph was made by W. T. Estler. Figure 5

When such a pattern is produced at fixed temperature, only a thin vertical slice of figure 5 is seen. From the pattern, the profile of density as a function of height can be deduced. Because the

Table 2. Critical exponents in four theoretical models

Property	Exponent	Van der Waals (any dimensionality)	Three-dimensional models Ising (n = 1)	XY (n = 2)	Heisenberg (n = 3)
Specific heat	α	0	0.110	−0.007	−0.115
Order parameter	β	0.5	0.325	0.346	0.365
Response function	γ	1	1.240	1.316	1.387
Critical isotherm	δ	3	4.82	4.80	4.80
Correlation length	ν	0.5	0.630	0.669	0.705
Critical correlation function	η	0	0.03	0.03	0.03

height is directly proportional to the chemical potential μ, the density–height relation at various temperatures is equivalent to an equation of state. To put it differently, the hydrostatic pressure caused by the fluid's own weight varies with height, so that the profiles can be thought of as a relation between the density of the fluid and its pressure, again an equation of state.

In a series of experiments carried out over the past few years, one of us, Hocken, with Moldover at the National Bureau of Standards,[17] used Wilcox's technique to measure the equation of state of several fluids in the range within 0.01% from the critical temperature, which is inaccessible to conventional techniques. The main improvements over the previous work were in the temperature control and measurement system and in the design of special cells. Figure 1 shows the cell and the thermostat before it was closed. The thermostat was made of seven layers of controlled and passive symmetric shells. This thermostat reproduced the core temperatures with a standard deviation of 20 microdegrees over the length of a run, which was sometimes several months.

Even this method is limited by the averaging effects mentioned earlier. Although the cell was only 3 mm thick, very close to the critical point the rays bend so much that they sample the fluid over a range of heights; the only parts of the fringe pattern that are unaffected are those caused by rays passing near the top and the bottom of the cell, where the gradients are smaller. Nevertheless, a whole new range of temperatures, from a few hundredths of a degree to 20 microdegrees from critical, had been covered entirely or in part, and the results obtained were quite different from the picture that had emerged from data analysis in the conventional regime. For all fluids studied, the coexistence-curve exponent β was considerably lower than that which had been obtained in ranges further from critical, while the compressibility exponent γ was higher. Because of the controversial nature of these results, possible sources of error were investigated thoroughly. Numerical ray tracing was done on model profiles, to ensure that no optical effect had been misunderstood. An experiment was done on a deliberately contaminated sample; no effect of the impurity on the critical exponent values was found.

The critical exponent values obtained for Xe, CO_2, SF_6 and impure SF_6 were in the range 0.321 to 0.328 for β, 1.23 to 1.28 for γ. These values span those for the $d = 3$, $n = 1$ Ising-like universality class, as obtained by field-theoretical methods, very nicely, as table 2 shows. The universal amplitude ratios are also very close to those characteristic of that universality class. These new experimental results are therefore in conformity with the principle of universality, which says that the critical behavior of fluids is the same as that of Ising-like magnetic systems. In fluids, however, the range of asymptotic behavior is apparently quite small; the earlier odd values of fluid critical exponents had been obtained in ranges where corrections to scaling are not negligible. In fact, such a decrease in β on close approach to the critical point had been observed previously.[16,18,19]

Magnetic buoy levitated in a fluid. The buoy, about 1 cm high, is used to make an accurate measurement of the fluid density. Figure 6

Liquid mixtures

Further confirmation has come from recent experiments in binary liquids. The consolute point, at which two liquids become miscible in all proportions, is another critical point; it is in the same universality class as the gas–liquid critical point. Here too theory claims the exponents should be those of the Ising model. In 1974 Balzarini had measured the exponent β for a mixture of cyclohexane and aniline by an optical technique related to Wilcox's method, and he found[19] $\beta = 0.328$. He published this result without interpretation; it was not consistent with the Ising value from series expansions $\beta = 0.3125$, the only value known at the time. Balzarini's results were at the low end of a whole spectrum of values available in the literature.[20] To clarify the situation Sandra Greer of the National Bureau of Standards undertook, in 1975, a precise direct determination of the coexisting densities of a binary liquid.[21] In earlier work she had shown that significant gravity-induced density gradients may also develop in binary liquid mixtures. However, by selecting a mixture of isobutyric acid and water, components closely matched in density, she was able to show that no noticeable density gradients developed during the time of the experiment. (Many of us regretted this decision because the overpowering smell of rancid tennis shoes was not conducive to scientific thought.)

The apparatus used for the experiment was a magnetic densimeter built by Greer with the assistance of Moldover and Hocken. Instruments of this type, first developed by Jesse Beams at the University of Virginia, measure density by using a solenoid to levitate a magnetic buoy in the liquid being studied. The current required to levitate the buoy is a measure of the buoyant force, and thus, as known since the days of Archimedes, of its mass density. For the coexistence-curve measurements, the buoy was levitated in each of the coexisting phases. Figure 6 shows the buoy used by Greer levitated in a liquid mixture; it is about 1 cm high.

By obtaining a sensitivity of 20 ppm with this apparatus, Greer produced the most precise binary coexistence curve to date. Choosing the volume fraction, the ratio of the volume of one component to that of the mixture, as the order parameter, Greer found $\beta = 0.328$ for this mixture, confirming Balzarini's result. Thus, she concluded, binary liquids may be placed in the same universality class as pure fluids and Ising-like systems, if the renormalization-group values for the exponent β are accepted. Subsequently, Donald Jacobs and associates found similar results for methanol–cyclohexane.

Another interesting point that emerged from Greer's work concerns the range of asymptotic behavior. For the system isobutyric acid–water she found Ising-like values for β in a range several degrees from critical, where pure fluids already deviate appreciably from Ising-like behavior. She then analyzed coexistence curve data in the system, of carbon disulfide and nitromethane, studied by E. S. Raja Gopal and his co-workers. Since these data extend over 60 deg C from critical, it was possible to study how corrections to scaling set in. Greer showed that even in this large range, the data were well represented by an Ising-like scaling term, if corrections to scaling, as predicted by Wegner for this universality class[7] are included.

Critical opalescence

That the intensity of scattered light is a source of information about fluctuations in near-critical fluids was known to Heike Kamerlingh Onnes and Willem Keesom

says Ed Kluth, outspoken Managing Director of Ortec-Brookdeal.

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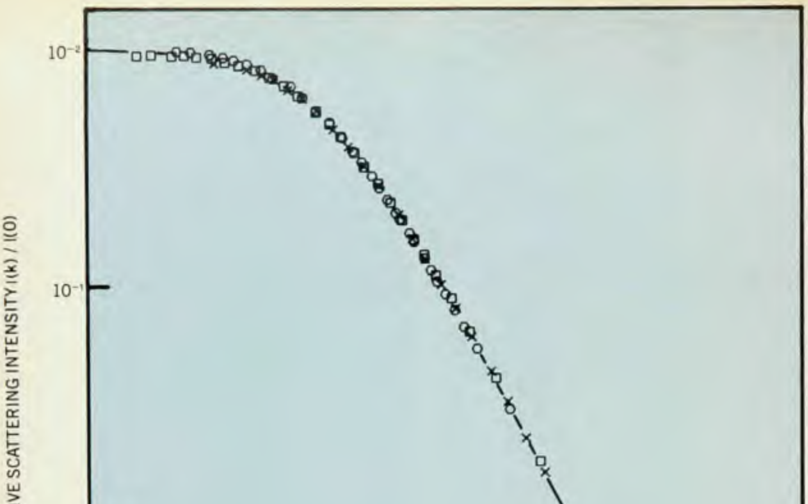

Light-scattering intensities $I(k)$ in a binary liquid taken at three different scattering angles (different values of wavenumber k) and at various temperatures above critical collapse onto a single curve when the ratio $I(k)/I(0)$ is plotted as a function of $k\xi$, where ξ is the correlation length. The angles are 40° (squares), 60° (hexagons) and 90° (crosses). Figure 7

in Leiden, who performed a scattering experiment near the critical point of ethylene in 1908, even before the classical papers of Albert Einstein and Marian Smoluchowski had appeared in the literature. A theory for critical scattering was then developed by Leonard Ornstein and Frits Zernike. They concluded that long-range fluctuations cause an anisotropy in the intensity of scattered light; this angular dependence is a measure of the magnitude of the correlation length ξ. Moreover, according to Einstein, the scattering intensity in the limit of zero angle, $I(0)$, is proportional to the compressibility K_T. Hence light (as well as x-ray and neutron) scattering can enable us to determine two critical exponents, ν and γ (see table 1).

In the period between the two world wars, light-scattering studies near the critical point of fluids were performed by a number of investigators, mainly under the influence of Peter Debye and his school. The method, however, remained qualitative until the advent of the laser and the development of refined electronic detection techniques. Since 1965 light scattering has made important contributions to our knowledge of the critical state of fluids and fluid mixtures. In a 1972 review, Benjamin Chu[22] concluded that the more reliable data give the exponent values $\gamma = 1.23 \pm 0.02$ and $\nu = 0.63 \pm 0.02$. These values agreed with the series-expansion estimates for the Ising model within combined error.

This result might have put to rest any doubts about the validity of the universality hypothesis for fluid scattering data. However, the quest for more refined exponent values, questions about the critical scattering function, the introduction of neutron-scattering studies in fluids and subtle inconsistencies between renormalization-group and series-expansion results for the Ising model all conspired to keep a number of scientists engaged in lively controversies for several years after Chu's review.

In 1960 Green conjectured that the decay of the correlation function at the critical point might differ from the $1/r^{d-2}$ behavior predicted by the classical Ornstein–Zernike theory. Fisher then introduced a correction exponent, η, such that, at the critical point, $G(r) \propto 1/r^{d-2+\eta}$. The value of η is quite small in three-dimensional models, typically 0.03. Because η is a direct measure of the breakdown of the classical theory for the critical correlation function, a great deal of experimental effort has been devoted in pursuit of this little exponent. Initially use was made of the Fisher relation, $(2-\eta)\nu = \gamma$, which permits deduction of the value of η once values of γ and ν are known. In view of the small value of η, however, obtaining it from ν and γ through the Fisher relation can obviously not give very accurate results—a different strategy was needed. A closer look at the scattering function is necessary to understand the strategy developed.

Universality of the scattering function

In scattering experiments the intensity I is measured as a function of the wavenumber k of the fluctuation. The intensity $I(k)$ is proportional to the structure factor. The structure factor is a function of k and of two thermodynamic variables, such as temperature and either density (for a pure fluid) or concentration (for a binary liquid). Near the critical point it is expected to be a homogeneous function of its variables. Thus if the scattered intensity is measured at the critical density or composition as a function of k and $(T - T_c)$, the intensity ratio $I(k)/I(0)$ should become a function of the single variable $k|\Delta T|^{-\nu}$ or $k\xi$.

An example of such scaling of the structure factor is shown in figure 7. The light-scattering intensities plotted, obtained by Ren Fang Chang and his colleagues for a binary liquid at various temperatures and scattering angles, all scale onto a single curve. This is the scattering scaling function $g(k\xi)$, which, theory tells us, should be identical for all systems in this universality class. At small k the scaling function approaches the Ornstein–Zernike form $1/(1 + k^2\xi^2)$, but at large $k\xi$ it is expected to behave as $1/(k\xi)^{2-\eta}$, slightly different from the Ornstein–Zernike prediction $1/(k\xi)^2$. Therefore scattering behavior has to be studied at large values of $k\xi$ to deduce reliable values for η.

This region is entered by making either k or ξ large. Given the small values of k accessible in light scattering, the data must be taken very close to the critical point so that ξ is sufficiently large. Most fluids, however, are then so strongly opalescent that light is scattered more than once, distorting the value of η. Much larger k values are accessible with x-ray and neutron scattering. In fact, neutron-scattering studies, particularly those conducted at the Brookhaven Laboratories, have been an important source of information on the critical behavior of solids. A. Tucciarone and his co-workers reported $\eta = 0.055 \pm 0.010$ for the antiferromagnet $RbMnF_3$, believed to be a representative of the $n = 3$ universality class. For fluids, however, the studies of Bernard Mozer and his colleagues on neutron scattering in helium and neon yielded surprisingly high values for η. For the true asymptotic form of the structure factor to be visible, not only should $k\xi$ be large but k should be small enough that the short-range structure of the fluid is not seen. It is not certain that this latter condition was met in the x-ray and neutron studies conducted in fluids so far.

It therefore became desirable to return to the longer wavelengths accessible in light scattering. In pure fluids, light scattering intensities at large $k\xi$ (that is, at large ξ) can not be obtained reliably because of the multiple-scattering problem. In binary liquids, however, multiple scattering can be greatly reduced by selecting a mixture in which the refractive indices of the two components are matched. Therefore, Chang, Herschel Burstyn and one of us, Jan Sengers,[23] following a suggestion of Donald McIntyre, selected a mixture of 3-methylpentane and nitroethane, which has a very low cross section for light scattering. It was necessary to increase the precision of the intensity measurements and to stabilize the intensity of the laser beam. The intensity of the scattered light was monitored continuously relative to the incident light intensity by one and the same automated photocounting detection system. A reference beam of roughly the same intensity as that of the scattered light was generated from the incident light with a beam splitter and a reflector; its intensity was further reduced with a diffuser cavity. The intensities of the scattered light and the reference beam were registered at alternating 100-sec intervals during prolonged periods. The group was thus able to obtain intensity data with a precision of 0.25% at $k\xi$ values up to 26. Their exponent values agree within combined error with those currently predicted by renormalization-group methods for Ising-like systems, given in table 2. The scattering function obtained in this experiment and shown in figure 7 agrees with that formulated by Alan Bray for the three-dimensional Ising model. Thus, this recent experiment has removed another obstacle to putting the fluids in the Ising-like universality class.

Outlook

The question of whether universality has been "rigorously" proven theoretically or "definitively" established experimentally is the subject of many debates among scientists. Nevertheless, the fact that careful experimentation in continuous systems such as pure fluids and fluid mixtures has revealed critical behavior in close agreement with that predicted by a theory developed for spin systems on lattices yields significant support for the principle of universality.

The renormalization-group method recently has been extended to the treatment of dynamical critical phenomena.[24] With respect to the critical behavior of dynamical properties, systems can again be grouped into universality classes. However, the dynamical universality classes are somewhat more restricted, because they also depend on the conservation laws.

Critical behavior is only one example of the development of long-range fluctuations due to incipient instability. Other examples are the onset of hydrodynamic instability such as in the transition from laminar to turbulent flow; the breakdown of hydrodynamics in two-dimensional fluids. The applicability of renormalization-group methods to all these phenomena is under active study.

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