Critical Phenomena: Experiments Show Theory on Right Track

The impressive edifice of theoretical physics owes its success largely to the fortunate circumstance that much of what is inherently a nonlinear world can be effectively modeled by linear theories. An important exception is the study of critical phenomena, such as occur in the equilibrium between a liquid and a gas at the critical point. These phenomena are due to such strongly nonlinear interactions between atoms that, until the last few years, no adequate theory existed to describe behavior near a critical point. But the spectacular success of a new approach, called renormalization group theory, has allowed scientists to greatly expand the range of critical phenomena which can be investigated (*Science*, 13 July 1973, p. 147). Three sets of experiments completed in the last year, of the many that have been carried out, show especially well that theorists are indeed on the right track.

Such verification is important because the use of this new theoretical approach to represent behavior near a critical point marks one of the first successful large-scale attempts to understand strongly nonlinear phenomena in physics. And its success brings the conquest of nonlinear problems in other fields much closer because the renormalization concept, which in fact predates its application to critical phenomena, is quite general. Kenneth Wilson of Cornell University, who pioneered the development of the present renormalization group theory, is now applying his ideas to certain problems in field theories of elementary particles, for example.

Most scientists first encountered critical phenomena in an undergraduate thermodynamics course when they learned that above a certain temperature, the critical point, a pure fluid can exist in only one phase, regardless of the pressure applied to it. At lower temperatures, a liquid and a gas phase can coexist, but, as the two-phase mixture is heated, the densities of the gas and the liquid converge until they become identical at the critical point. After a comment or two regarding the theory of van der Waals, who provided the first mathematical account of critical behavior in fluids in the 1870's, the subject was usually dismissed.

Critical phenomena are much more common than is often realized, and they include far more than critical points in fluids. Among the many examples are the Curie point, which is the temperature above which a ferromagnet loses its magnetization; the superconducting transition temperature above which superconductivity is destroyed; and the order-disorder temperature above which the ordered arrangement of metal atoms in some alloys disappears. These are just a few of the many examples of critical phenomena; it is little wonder that physicists are excited by the prospect that a single theory can encompass such a variety of disciplines and phenomena.

The Universality Hypothesis

The unifying character of the renormalization group theory goes even further in saying that not only can a wide variety of phenomena be encompassed in one theory, but behavior near a critical point is the same within broad classes of substances of widely varying character known as universality classes. When a substance is close enough to the critical point, it makes no difference whether one is looking at a fluid or a magnet. This apparent slap in the face of common sense is a central assertion of the theory and is called universality. The universality concept actually predated renormalization group theory and was developed by, among others, Benjamin Widom of Cornell and Leo Kadanoff of Brown University. The role of the renormalization group was to construct a firm theoretical foundation for what was previously a hypothesis.

A particular statement of the universality principle is that fluids should belong to the same universality class as one of the most frequently encountered models for critical phenomena in crystalline solids—the three-dimensional lattice gas, or Ising lattice as it is called. In this model, all atoms of the substance sit on the sites of a lattice. Although the discrepancy between the behavior predicted by theory, which is calculated from the lattice model, and that observed in experiments on fluids has narrowed over the years as both improved, a recent summary of many such experiments done previously that was compiled by Anneke Levelt-Sengers of the National Bureau of Standards (NBS) and Jan Sengers of the University of Maryland showed that the difference has remained large enough to constitute a serious obstacle to acceptance of the universality principle as applied to fluids. Meanwhile, theorists have tried and failed to explain how fluids and lattice models could be in separate universality classes.

Now, experiments by Robert Hocken and Michael Moldover of NBS, by Sengers and his colleagues at Maryland, and by Sandra Greer at NBS have closed the gap between theory and experiment to the point where the experimenters think that fluids do indeed belong to the same universality class as the lattice model. What the investigators showed in their experiments was that previous measurements were not taken closely enough to the critical temperature to reveal the theoretically predicted behavior. The term critical behavior usually means the variation of some property of the substance with temperature near the critical point. True critical behavior only occurs asymptotically close to the critical point. Away from the critical point, behavior changes, and the results of most experiments in the past have reflected this.

Hocken and Moldover measured quantities called critical exponents. A number of thermodynamic properties of a substance have a temperature dependence near the critical temperature of the form $|1 - T/T_c|^n$, where T_c is the critical temperature and n is the critical exponent. Each property has its own exponent. One statement of universality is that the set of these critical exponents is the same for all substances in the same universality class.

The NBS researchers used an optical interferometric technique to extract information about the density and compressibility of xenon, sulfur hexafluoride, and carbon dioxide in their experiment (Fig. 1). Exceptional care in maintaining temperature stability enabled the researchers to make measurements at values of $|1 - T/T_c|$ much smaller than 1.5×10^{-5}; this value is about an order of magnitude smaller than that achieved before. They estimated the stability of their system to be $\pm 20 \times 10^{-6}$ °K for periods of several days.

At Maryland, Sengers, Ren-Fang Chang, and Herschel Burstyn used a light scattering technique to monitor critical behavior in the binary liquid consisting of 3-methylpentane and nitroethane. In a binary liquid, two immiscible liquid phases merge into one at the critical, or consolute, point.

The quantity probed by light scattering is called the correlation length. In a binary liquid, molecules of the same species tend to attract primarily one another, but above the consolute point, the thermal energy is sufficient to disrupt the attractive forces, and the molecules tend to be randomly dispersed—that is, there

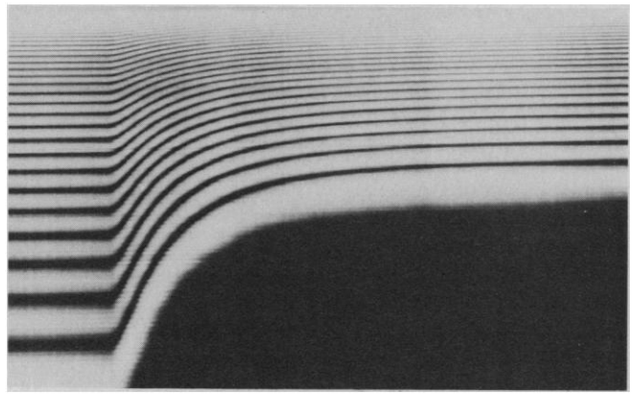

Fig. 1. Interference pattern produced by shining laser light through a cell containing a pure fluid near its critical temperature. The interference fringes provide information about the density of the fluid. The change in the pattern from left to right represents the effect over a 24-hour period of changing the temperature. The abrupt change near the left edge marks a jump in the temperature from T_c + 0.002°K to T_c + 0.004°K, where T_c is the critical temperature. The gradual change thereafter indicates that it takes several hours for the sample to come to thermal equilibrium. The visually apparent change in the fringe pattern after a 0.002°K change in temperature is indicative of a large signal to noise ratio which permits precise determination of critical behavior. [Source: Michael Moldover, National Bureau of Standards]

is one liquid phase. Closer to the consolute point, the attractive forces are strong enough to cause, momentarily at least, small clusters of like molecules—that is, the molecules assume an ordered arrangement in the cluster. Such ordering is characteristic of all critical phenomena, but the physical parameter that becomes ordered is different for each kind of substance. The correlation length characterizes the cluster size.

Just above the consolute point, the cluster size grows rapidly; when it becomes equal to the size of the container holding the fluid, the two phases separate. It is in the details of how the correlation length diverges that the nonlinear aspects of critical phenomena become important. The size of the clusters can be determined by examining the intensity of the laser light that scatters from the clusters when it passes through the fluid. Critical exponents for both the correlation length and the fluid compressibility were obtained in this way.

In an independent experiment at NBS, Greer studied the critical behavior of the binary liquid isobutyric acid–water by measuring the buoyant force on a float in the cell containing the two liquid phases below the critical temperature. The buoyant force is a direct measure of fluid density. As the critical temperature is approached, the density difference between the two liquids decreases with the same critical exponent as characterizes the pure fluid.

Taken together, the sets of critical exponents from these three experiments agree closely with renormalization group calculations by George Baker of the Los Alamos Scientific Laboratory and his colleagues. These exponents therefore provide considerable substance to the claim that fluids are in the same universality class as the lattice gas model. But, as Horst Meyer of Duke University, who has studied the critical behavior of both normal and superfluid helium, points out, there is one discouraging implication. It may be that true critical behavior can only be observed so close to the critical temperature that it is experimentally inaccessible in many substances.

If so, what researchers need is a theory for describing behavior slightly away from the critical point. In fact, Franz Wegner of the University of Heidelberg has used renormalization group theory to derive "corrections" to the critical exponents in the form of a mathematical series. The farther one is from the critical point, the more terms one needs in the series. Greer herself used two terms of the series in analyzing her binary liquid experiment. At about the same time as Wegner's research, Dennis Greywall and Guenter Ahlers of Bell Laboratories also experimentally obtained correction terms from their experiments on superfluid helium-4. Although helium-4 is in a universality class different from normal fluids, it has been an exceptionally fruitful subject for detailed comparison of experiment with theory because it has properties permitting relatively easy experiments with high precision.

Marginal Dimensionality

At first sight, it might seem strange that a lattice model could describe a fluid, which has nothing particularly lattice-like about it. The origin of universality can be traced to the notion that things taking place on a distance scale smaller than the cluster size do not have much influence on critical behavior. Thus, researchers argue, characteristic distances such as the size of a unit cell in a crystalline material, and the strength of short-range interactions, such as some interatomic forces, are no longer relevant to critical behavior. Near a critical point, the only microscopic aspects of a substance that remain important are those relating to its symmetry.

The symmetry properties of a substance also determine a characteristic called the marginal dimensionality, which is especially important in the theory of critical phenomena because it marks the spatial dimensionality of a system for which nonlinear effects become important. Theoreticians, who have no trouble constructing hypothetical substances of any desired spatial dimensionality, have long known that, for these hypothetical substances, a linear theory called mean-field theory correctly describes critical behavior, provided that the dimensionality of the system is high enough. But when the dimensionality is less than or equal to the marginal dimensionality, renormalization group theory is needed to give the correct description. For example, the marginal dimensionality of substances with the symmetry of the lattice gas model or real fluids is four, whereas the actual spatial dimensionality is three, and renormalization group theory is required.

When the actual spatial dimensionality is less than the marginal dimensionality, even renormalization group theory is only approximately correct in the sense that computational difficulties prevent obtaining exact numerical results. Theorists have shown, however, that, for any system in which the spatial and marginal dimensionalities coincided, the exact result of the renormalization group theory would be calculable. As Bertrand Halperin, a theorist at Harvard University, points out, the most precise comparison of renormalization group theory and experiment is therefore obtainable in those substances in which the marginal dimensionality is the same as the actual spatial dimensionality.

Three recent experiments by Ahlers and his associates at Bell Laboratories, by Jens Als-Nielsen of the Massachusetts Institute of Technology (MIT), and by J. David Litster of MIT and his coworkers on the ferromagnet $LiTbF_4$ have confirmed previous theoretical treatments of critical behavior when the marginal dimensionality coincided with the spatial dimensionality. The $LiTbF_4$ Ising magnet provides one of the rare instances in which this situation occurs. The magnetic interactions in this material are highly anisotropic. The anisotropy has the effect of lowering the marginal dimensionality to three.

Ahlers and his associates measured the variation of the specific heat of $LiTbF_4$ with temperature near its Curie point and the ratio of the specific heats above and below the Curie point. Als-Nielsen used the technique of neutron

scattering to obtain the correlation length and magnetic susceptibility of the same material. Neutron scattering in magnetic solids is analogous to optical scattering in fluids, and the magnetic susceptibility is equivalent to the fluid compressibility. Als-Nielsen determined both the dependence on temperature of the correlation length and the ratio of the susceptibilities above and below the Curie point. Litster, John Griffin (now at the University of Pennsylvania), and Arthur Linz of MIT relied on optical scattering to determine the spontaneous magnetization of $LiTbF_4$ with temperature near the Curie point. Because $LiTbF_4$ is an Ising magnet, the magnetization is large only parallel to one particular crystallographic axis of the magnet. The magnetized crystal consists of domains, some with magnetization in one direction along this axis and some with magnetization in the opposite. The onset of this structure is what gives rise to optical scattering when a laser irradiates the material.

In each case, the investigators found the predicted temperature dependences and ratios. The former consisted of a mean-field theory critical exponent and a logarithmic modifying term. The specific form of these terms had been conjectured by A. I. Larkin and D. E. Khmel'nitzkii of the Institute of Theoretical Physics in Moscow even before the emergence of renormalization group theory. Recently, Amnon Aharony of Tel-Aviv University used renormalization group theory to arrive at the same terms for the anisotropic Ising magnet.

Random Systems

Among those who have devised methods for using the renormalization group when such exact results are not possible are Wilson and Michael Fischer of Cornell, Dorus Niemeyer and Hans van Leeuwen of the Delft University of Technology, Eberhard Riedel of the University of Washington, Wegner, and Kadanoff. These researchers concerned themselves with nonrandom substances. Nonrandom means, in the case of a crystalline substance, that all the atoms are on their proper lattice sites and that no impurities or imperfections are present. Interest is now shifting to critical phenomena in random solids.

The reasons for interest in random solids are many. For one thing, solid state physicists have been devoting more and more time in recent years to the study of liquid metals, amorphous metallic glasses, and amorphous semiconductors, partly because they think that crystalline solids are a well-mined area. After a long gestation period, for example, research on certain types of amorphous semiconductors may soon be paying off in the form of electronic devices ranging from computer memories to solar cells. In addition, all real solids are somewhat random to the degree that they are subject to strains, can be inhomogeneous, and contain impurities, all of which seem to affect critical behavior to some extent. In this respect, randomness has always been a part of the problem.

The chief reason for the interest, however, is simply that the renormalization group is permitting quantitative calculations of critical behavior in random solids to be done that once were prohibitively difficult. At present, most of the investigations have been by theorists rather than by experimenters, and the theory predicts a variety of effects. In one instance where comparison can be made, a random distribution of two magnetic atoms in a crystal lattice, an experiment by Robert Birgeneau and Als-Nielsen of MIT and Gen Shirane of the Brookhaven National Laboratory seems to confirm calculations by theorists.

At first glance, randomness might be expected to have no effect on critical behavior. The atoms in a fluid, for example, are in constant motion and there is no long-range order in their positions. Yet a fluid has a sharply defined critical temperature. Theorists distinguish, however, between two types of randomness. In the first type, exemplified by the fluid, the substance remains homogeneous and thermal equilibrium is maintained throughout. With respect to critical behavior, such a substance is not random.

In contrast, the atoms in a crystalline material with a random distribution of impurities over the lattice sites cannot diffuse fast enough through the lattice to assume a thermal equilibrium configuration. Among others, A. Brooks Harris and Tom Lubensky of the University of Pennsylvania, and Geoffrey Grinstein of the University of Illinois and Alan Luther of Harvard have used renormalization group theory to calculate the effect of this type of randomness on critical phenomena in magnetic materials. Contrary to arguments advanced by earlier investigators, according to these theorists, randomness does not "smear out" critical behavior over a wide temperature range. Depending on the properties of the magnet, a sharp phase transition continues to take place, but with either the same critical exponents as a pure magnet or with new exponents.

The researchers found that the most important parameter determining the behavior observed is the number of components in the atomic magnetic moments, which are vector quantities. Depending on the orientations that the moments take with respect to the crystal lattice, the number of components may be one, two, or three. If there is only one, the case corresponds to the Ising model. When the number of components is less than a special number, new critical exponents are expected; when the number of components is greater than this number, the exponents characteristic of pure magnets are predicted.

The special number of components is thought to be either one or two for three-dimensional magnets, according to Lubensky. Although all physical substances would seem to be necessarily three-dimensional, there are many instances where for all practical purposes a magnet is one- or two-dimensional. For example, the interactions in magnets leading to critical behavior may be strong only between atoms lying in certain planes of the crystal lattice but weak between atoms lying in neighboring planes. According to recent calculations by Matsuo Suzuki of the University of Tokyo and Urey Krey of the University of Regensburg, a two-dimensional Ising magnet should have critical exponents characteristic of pure substances, modified by the seemingly ubiquitous logarithmic corrections.

This is precisely the type of magnetic system studied by Birgeneau, Als-Nielsen, and Shirane, who used neutron scattering techniques to study critical behavior in three two-dimensional antiferromagnets: K_2NiF_4, K_2MnF_4, and $Rb_2Mn_{.5}Ni_{.5}F_4$. In antiferromagnets, neighboring atomic magnetic moments are aligned antiparallel rather than parallel as in a ferromagnet. The third compound is the disordered one in the sense that the magnetic nickel and manganese atoms are randomly dispersed. The investigators found the same critical exponents for the correlation length and the magnetic susceptibility in all three materials, despite the fact that, for an equal number of manganese and nickel atoms, the effect of randomness should have been at its largest. The result was interpreted as indicating that the small logarithmic corrections expected can probably be observed only at temperatures much closer to the critical temperature than the researchers were able to reach.

The diversity of the research in critical phenomena is such that finding a common theme other than the broadening effect that the advent of the renormalization group method has had on the range of investigation is not possible. Experiments such as those reported here seem to confirm the theory's validity, and there is every indication of continued success.—ARTHUR L. ROBINSON