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Phase Transitions, Critical Phenomena, and Instabilities

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Summary. Transformations among many of the diverse states of matter arise from microscopic interactions involving very many (approximately 10^{23}) constituent particles and result in dramatic changes in macroscopic properties. The values of some physical parameters vanish, while others approach infinity. These changes and their evolution are strikingly similar in systems as apparently different as liquids, magnets, superconductors, ferroelectrics, and liquid crystals, which suggests that there is an underlying unity to phase transition phenomena. The basis and extent of this unity are reviewed for many-body systems in equilibrium, and analogies with instability phenomena in systems far from equilibrium (such as lasers, fluid flows, and avalanche electronic devices) are pointed out.

There are intimate relations among the physical properties of materials and the states of matter that comprise the materials. We are all familiar with the drastic differences in properties, for example, between the liquid and solid states of water. Although they are less familiar to most people than the liquid-solid transition, many other types of state changes, or phase transitions, result in physical property changes that are no less spectacular. Properties such as magnetization, viscosity, and electrical conductivity are observed to change by orders of magnitude in materials as they enter magnetic, superfluid, or metallic states, respectively. What causes such dramatic changes and how can they be understood?

In some cases (such as the liquid-solid transition) the changes are abrupt, resulting from the free energy of a new phase falling below that of the old phase as some external parameter such as temperature is varied. Such transitions are discontinuous and are said to be first-order because of the discontinuous behavior in the first derivatives of various thermodynamic functions. In other cases (such as the onset of magnetism, superfluidity, or phase separation in a fluid mixture) the new phase grows continuously and homogeneously from the old, so that many of the physical properties exhibit singular behavior in the vicinity of the transition. Such transitions are said to be second-order or continuous, and this article is devoted exclusively to them. The diverging compressibility of a fluid, susceptibility of a magnet, dielectric constant of a ferroelectric all represent singular behavior and arise from the cooperative participation of astronomical numbers ($\sim 10^{23}$) of microscopic particles in altering the materials' macroscopic properties. The singular behaviors of such properties are not merely qualitatively similar for quite different physical systems (liquids, magnets, ferroelectrics, superconductors), they are often quantitatively identical. How to understand and relate these similarities in systems whose microscopic constituents are as different as, for example, helium atoms and liquid-crystal molecules has been a challenge to science for many decades.

Thanks to the vigorous efforts of theorists and experimentalists over the past 15 years, we are now in a position to understand these diverse phenomena from a unified viewpoint and even to make quantitative predictions for the behavior of yet untested systems. This article describes some of the theoretical concepts and experimental findings that have led to our present unified view of phase transitions and critical phenomena in equilibrium systems. It also indicates some possible avenues for extension of this view to strongly driven systems far from equilibrium. The study of phase transitions and critical phenomena presents the scientific challenge of relating singular macroscopic properties to interactions among very large numbers ($\sim 10^{23}$) of microscopic particles, but it is also of technological importance in relation to the possible control and engineering of properties of materials that might rest on a proper understanding of their microscopic origins. For example, greatly enhanced performance of spinodally decomposed alloys, high-temperature superconductors, acousto-optic modulators, magnetic ferrites, and so on are now understood to arise from the phenomena that are responsible for phase transitions in these materials.

This article necessarily treats many of the sophisticated and subtle concepts associated with the modern theory of critical phenomena in a rather superficial manner. A number of excellent critical reviews (*1*-*6*) of various scientific aspects of this field are available to those interested in exploring in more depth the concepts touched on here. Further, the activity in these fields over the past decade has been so vigorous and the contributors so numerous that exhaustive citation is impossible in an article of this length. Instead, selected examples are presented to illustrate the major ideas and advances. This selection is, of course, subjective and carries an implicit apology to the many fine researchers

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whose work is not explicitly discussed.

I will begin with the classical mean field theory of phase transitions, which serves to define many of the fundamental terms (order parameter, correlation function, critical exponent, and so on) and to provide a framework for discussing the more subtle effects (due to fluctuations) central to our present understanding. I will then discuss some experimentally observed departures from the predictions of mean field theory, and modern developments such as the scaling and renormalization group theories, which epitomize the present level of our understanding in this field. Finally, I will mention the appearance of order and the role of fluctuations in systems driven far from equilibrium, such as lasers, hydrodynamic instabilities, and electronic devices. Such systems present many attractive analogies with continuous equilibrium phase transitions, which excites the hope that some of the powerful techniques so successful in the latter field might fruitfully be brought to bear on the former.

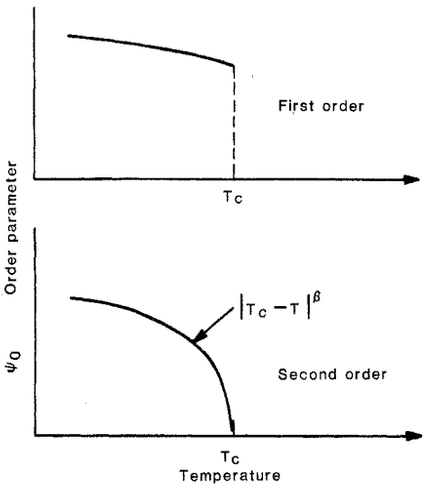


Fig. 1. Schematic showing the behavior of the order parameter, ψ_0, near the critical temperature, T_c, in first- and second-order phase transitions.

Mean Field Theory

All phase transitions considered here represent the development of long-range order in some physical property (*7*). This property may be utilized as a quantitative measure of the development of the new phase and is called the order parameter, denoted here as ψ_0. In a ferromagnet ψ_0 represents the magnetization. In a liquid crystal it might denote the optical birefringence. The order parameter is, by definition, zero on one side of the transition and nonzero on the other side. If the order parameter increases continuously from zero in the new phase, the transition is said to be continuous or second-order; if discontinuously, it is said to be discontinuous or first-order (Fig. 1). The appearance of order can be viewed as the breaking of a symmetry. For example, a structural phase transition between a nonpiezoelectric and a ferroelectric state in a crystal represents the breaking of inversion symmetry. In group theoretical language, the ordered (or lower symmetry) phase is then viewed as a subgroup of the parent (or higher symmetry) phase, with the reduced set of symmetry operations being represented by the order parameter. In general, the order parameter need not be a simple, one-component scalar quantity; it may be quite complicated depending on the complexity of the two phases that it connects. The complexity of the order parameter is related to the number of components, n, needed to specify it completely.

To examine the development of order, consider a large collection, N_0, of microscopic objects, each describable by a dynamic variable $\psi_i(\mathbf{r}_i, t)$, which may represent a local spin variable, an array of atomic displacements, and so on. If we choose ψ_i correctly, the macroscopic order parameter $\langle\psi\rangle$ can be expressed as

$$\langle\psi\rangle = \frac{1}{N_0}\left\langle \sum_i \psi_i(\mathbf{r}_i, t)\right\rangle \qquad (1)$$

where $\langle\rangle$ represents an average over a statistical ensemble. For example, in a ferromagnet ψ_i represents the direction in space of an elemental magnetic or spin vector. The condition $\langle\psi\rangle \neq 0$ expresses the fact that there is some net alignment of these spins even in the absence of an external field, in the ordered phase. Physically, this must come about through some interactions among the elemental spins, which somehow develop a cooperativity such that long-range order results. Otherwise there could be no finite average value for ψ on a macroscopic scale. The simplest description of this cooperativity is known as mean field theory. It assumes that the behavior of a given ψ_i can be calculated from its response to the local field generated by the average spin configuration of its neighbors—that is, by the mean field that they generate. In this view, deviations from this average (fluctuations) are ignored. It then follows that the energy difference between the ordered and disordered phases is expressible solely in terms of $\langle\psi\rangle \equiv \psi_0$. The mean field (or Landau) expansion for this free energy, A, may be written (*1-3*)

$$A = a\psi_0^2 + b\psi_0^4 + c\psi_0^6 + \cdots \qquad (2)$$

where a, b, c, . . . are analytic functions of $T - T_c$ (the temperature and critical temperature, respectively) and we have considered a case where symmetry forbids odd powers.

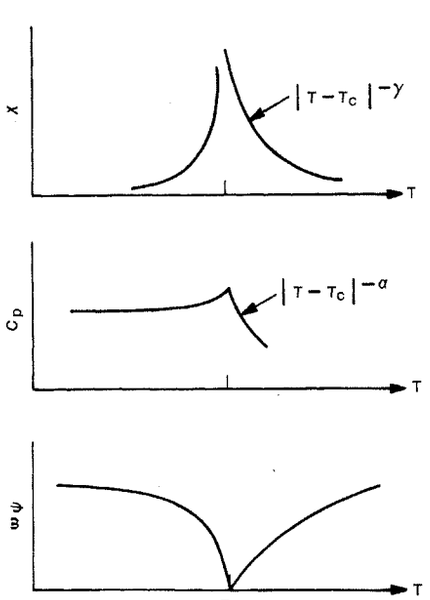


Fig. 2. Behavior of the static susceptibility, χ, the specific heat, C_p, and the soft-mode frequency, ω_ψ, near T_c for a second-order or continuous phase transition.

It is rigorously true that for an equilibrium system, A can be expressed in terms of $\langle\psi^p\rangle$'s. Mean field theory amounts to the assumption that $\langle\psi\rangle^p = \langle\psi^p\rangle$. From the above form for A—since it is a thermodynamic quantity—a variety of important and directly measurable physical properties may be calculated. For example, the value of ψ_0 is simply obtained by differentiating A and applying stability criteria (*6*). The equation $\partial A/\partial\psi_0 = 0 = (2a + 4b\psi_0^2)\psi_0$ admits of two solutions: $\psi_0 = 0$ and $\psi_0^2 = -a/2b$. Thus where $a = a'\tau$ [with $\tau \equiv (T - T_c)/T_c$], one sees immediately that when T_c is approached from below, ψ_0 vanishes as a power law in the reduced temperature, τ. That is, $\psi_o = C|\tau|^\beta$. The quantity β is the critical exponent for the order parameter; its value in mean field theory is 1/2. For many types of transitions it is subject to direct experimental tests (for instance, by measuring macroscopic magnetization, polarization, birefringence, or density). Only in special circumstances—now largely understood—is the mean field value of β actually observed. The same may be said for other important physical quantities that exhibit singular behavior as $|\tau| \to 0$. Perhaps the two most familiar of these are the static susceptibility χ (with critical exponent, γ)

and the specific heat C_p (with critical exponent, α) (Fig. 2).

The static susceptibility (6) is defined as

$$\left.\frac{\partial^2 A}{\partial \psi^2}\right|_{\psi=\psi_0} \equiv \chi^{-1}$$

$$\chi^{-1} =$$

$$2a + 12b\psi_0^2 \begin{cases} = 2a = 2a'\tau & \tau > 0 \\ = -4a = 4a'|\tau| & \tau < 0 \end{cases} \quad (3)$$

Thus in mean field theory $\chi \sim \tau^{-1} \sim \tau^{-\gamma}$, so that χ diverges on approach to T_c from either side with the same critical exponent, $\gamma = 1$. Note that the amplitude of the divergence differs by a factor of 2 on either side.

In a more general context, it is useful to define a space- and time-dependent correlation function $C(\mathbf{r}, t)$ of the order parameter

$$C(\mathbf{r}, t) \equiv \langle \psi(\mathbf{r} - r', t - t')\psi(\mathbf{r}', t') \rangle \quad (4)$$

whose Fourier transform is closely related to the dynamic susceptibility (6) $\chi(\mathbf{q}, \omega)$. Equation 4 expresses the likelihood that if the microscopic order parameter ψ has a given value at some point in space $\mathbf{r}'$ and time t', it will have a value at some other point $(\mathbf{r}' - \mathbf{r})$ and time $(t' - t)$. Of particular importance is the equal-time correlation function $C(\mathbf{r}, 0)$, which expresses the spatial extent of correlations in the order parameter. For small distances, r, the precise form taken by $C(\mathbf{r})$ will depend on the microscopic interactions mentioned earlier, but usually (8) $C(\mathbf{r})$ will decay exponentially at large distances

$$C(\mathbf{r}, 0) \sim C_0 e^{-r/\xi} \quad (5)$$

The characteristic decay distance, ξ, is called the correlation length and is another of the important singular quantities. Simple arguments show that in mean field theory, the correlation length diverges with a critical exponent, ν, which has the value 1/2

$$\xi = \xi_0 \tau^{-\nu} = \xi_0 \tau^{-1/2} \quad (6)$$

The most direct experimental probes (6) of ξ, and more generally of $C(\mathbf{r}, t)$, are scattering experiments.

Within mean field theory the specific heat, C_p, is discontinuous but not divergent at T_c, corresponding to the value of $\alpha = 0$ for its critical exponent. It may also be expressed in terms of the equal-time autocorrelation function for the energy density, which involves higher powers of ψ than does Eq. 4. The corresponding general space- and time-dependent correlation functions have not been calculated in as much detail as $C(\mathbf{r}, 0)$, although some experiments (light scattering, ultrasonic attenuation) measure certain aspects of them.

Although mean field theory contains most of the concepts (order parameter, correlation length, critical exponents) required for a unifying discussion of phase transitions, it falls severely short in that it neglects correlated fluctuations in the order parameter and, of course, their considerable influence on critical behavior. It is particularly striking that in the absence of fluctuation effects, all continuous phase transitions would have precisely the same singular behavior; that is, the same critical exponents, $\alpha = 0$, $\gamma = 1$, $\beta = 1/2$, and $\nu = 1/2$, are predicted for all transitions.

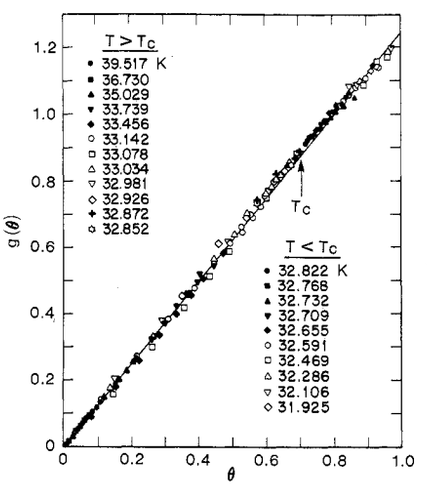


Fig. 3. Comparison of experimental measurements (points) of the reduced magnetization, $g(\theta)$, with predictions from the magnetic equation of state (solid line) expressed in terms of statically scaled variables. The parameter θ locates points in the temperature-magnetic field plane along thermodynamic paths of constant specific heat [modified from (9)].

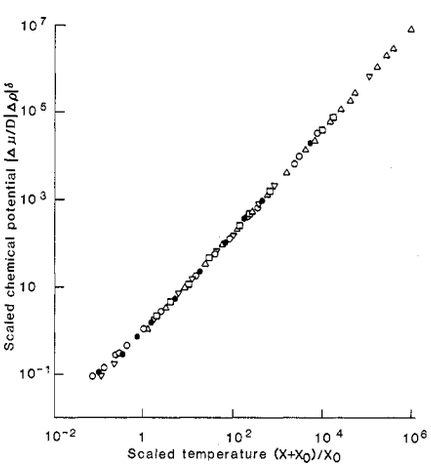


Fig. 4. Behavior of scaled chemical potential versus scaled temperature for five different fluids near their liquid-vapor critical points: (○) helium-3, (●) helium-4, (□) xenon, (▽) carbon dioxide, and (△) water [modified from (10)].

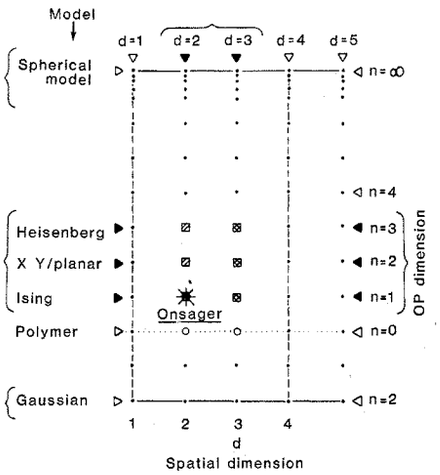
Indeed, for many decades this was generally believed to be the case (6), even to the extent that experiments on the liquid-vapor coexistence curve near the critical point of a fluid were considered to be in error when they produced values of β closer to 1/3 than to 1/2. "Error" in this sense need not impugn the ability of the experimenter involved; it might be taken to mean that the system has not been probed sufficiently close to T_c, so that the asymptotic behavior predicted by theory for vanishing τ might lie undiscovered. This emphasizes that critical exponents are meant to describe the behavior of the leading singularity, and such a description is asymptotically valid only at sufficiently small τ. Just how small this is—or what the extent of the asymptotic region is—has no general answer even today, although renormalization group theory makes predictions in some specific cases.

Failures of Mean Field Theory

Detailed accounts of experimental observations in conflict with mean field theory, beginning in the 1950's, have been published (6). Suffice it to say here that a variety of increasingly precise measurements in magnets, superfluids, liquid mixtures, and so on of order parameters, susceptibilities, correlation lengths, and specific heats have yielded values for critical exponents that differ significantly from those predicted by mean field theory.

Despite these differences, there are several types of phase transitions (in physical systems as different as a fluid and a magnet) for which the same critical exponent values have been found. Thus the absolute universality predicted by mean field theory is in reality replaced by a more limited kind of universal critical behavior. Systems that exhibit the same critical behavior are said to belong to the same universality class.

From a theoretical point of view, a system's universality class (2) is defined through the Hamiltonian function that describes it, most especially through the Hamiltonian's symmetry properties (that is, the power and combinations of ψ^p terms; the dimensionality of space, d; and the number, n, of components of ψ). According to this universality hypothesis, terms added to the Hamiltonian (or parameters adjusted in an experiment) that do not alter its symmetry should not change the critical behavior (although they may shift T_c). For example, the critical exponents describing the superfluid transi-



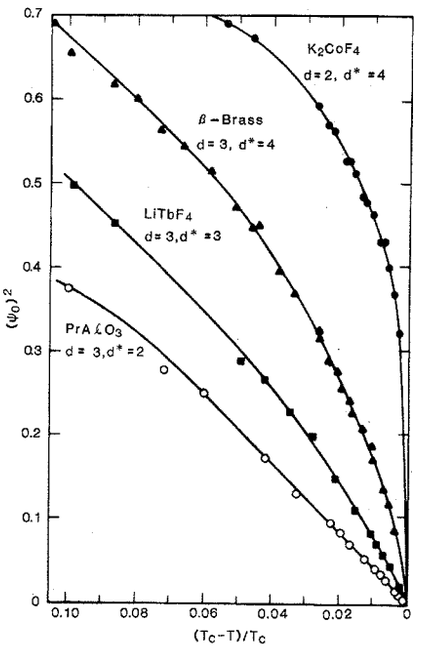


Fig. 5 (left). Diagram of the (d,n) plane. Specific systems of interest are identified as points or squares, including the two-dimensional ($d = 2$) Ising ($n = 1$) model, which was solved exactly by Onsager [modified from (*2*)]. Fig. 6 (right). Squared order parameter as determined by neutron scattering for transitions of differing spatial dimensionality, d, and marginal dimensionality, d^*. For $d > d^*$ a straight line—indicative of mean field behavior—is expected and observed for $(1 - T/T_c) \to 0$. As d^* becomes larger relative to d, the increasing departure from mean field theory is evident [modified from (*8*)].

tion in liquid helium are expected to be unaffected by variations in the pressure.

Predating the universality hypothesis, which relates critical behaviors for different physical systems, a separate hypotheses called scaling was introduced which permits determination of the values of some critical exponents given a knowledge of other critical exponents for the same system (*1-4*). For example, the scaling prediction $\alpha + 2\beta + \gamma = 2$ is satisfied within mean field theory, but it has been verified as well in systems where the individual critical exponents differ substantially from their mean field values. The scaling relations among critical exponents follow from the hypothesis that the free energy and correlation function are homogeneous functions of thermodynamic variables that can be scaled in terms of a single characteristic length (the correlation length, ξ). Scaling relations should be valid regardless of the universality class to which the system belongs. Considerable experimental effort has been devoted to testing scaling and homogeneity properties. Examples of particular beauty are depicted in Fig. 3 for the ferromagnetic transition in $CrBr_3$ (*9*) and in Fig. 4 for the critical points of several fluids (*10*).

Experiments on static singular behaviors near ordinary critical points have repeatedly confirmed the scaling and universality hypotheses. Considerably more complex behaviors are currently under consideration in the more exotic situations broadly referred to as multicritical phenomena. These occur at points of intersection of two or more paths of singularities in the thermodynamic plane, and they continue to provide formidable challenges to theorists and experimenters alike; however, they are beyond the scope of this article (*2, 4, 5*).

Renormalization Group Approach

Scaling and universality represent progress beyond mean field theory, but they are really hypotheses rather than proper theories, and in themselves they provide no general method for predicting or calculating the values of critical exponents. A number of theoretical techniques (high temperature series, Pade approximants, and so on) have been devised over the years to calculate approximately the exponents for particular models (*6*) and a very few exactly soluble models (such as the two-dimensional Ising model) have been found for phase transitions. Nevertheless, until Wilson introduced the renormalization group viewpoint, the theoretical state of affairs in phase transitions and critical phenomena remained less than satisfactory. To gain a reasonable appreciation of this viewpoint, one should consult reviews (*2, 5, 11*) and books (*3, 4*) on the subject. In this article I can only mention some of its more transparent qualitative features. One important feature is the recognition of the so-called marginal dimensionality, d^*. Generally, a phase transition system is characterized by the dimensionality of space, d (which, of course, need not be three for mathematical models), and the number of components, n, of the order parameter. In the space spanned by n and d several familiar and sometimes exactly soluble models occupy points of particular significance. For mathematical convenience one may regard both n and d as continuous variables and examine the effects of this variation on critical behavior (Fig. 5).

Recall that a major theoretical challenge is the proper treatment of fluctuations. The stronger the fluctuations, the less well does the mean field describe the behavior of the system as a whole. The relative importance of fluctuations can be estimated by a method due to Ginzburg (*12*). For mean field theory to remain valid below T_c, the fluctuations $\delta\psi$ in ψ must remain small compared to its mean value ψ_0

$$(\delta\psi)^2_{\Omega_\xi} << (\psi_0^2)_{\Omega_\xi}$$

Fluctuations are correlated only over distances of order ξ, so it is proper to take the above averages over a correlation volume Ω_ξ (which, of course, diverges as $\tau \to 0$). It is straightforward to show that the Ginzburg criterion can be rewritten (*8*)

$$\tau^{-\gamma} << \tau^{2\beta - \nu d} \qquad (7)$$

where we have used the fact that $\Omega_\xi = \xi^d$. This requires for arbitrarily small τ that $(\gamma + 2\beta) \leq \nu d$, or equivalently that $d \geq (\gamma + 2\beta)/\nu$. In mean field theory $(\gamma + 2\beta)/\nu = 4$. Therefore the neglect of fluctuations in mean field theory is self-consistent only for $d > 4$. When $d = 4$ we have marginal dimensionality, $d^* = d$, wherein mean field theory almost works and only weak (usually logarithmic) corrections are expected and observed. For $d < d^*$ we expect scaling relations to be valid. In some situations (*8*), such as in strongly anisotropic systems, Ω_ξ grows as ξ^{d+m} rather than as ξ^d. The condition $m > 0$ means that the correlation volume grows more rapidly than ξ^d. Consequently, the fluctuation effects are averaged over a greater volume and are suppressed, so that mean field theory becomes a better approximation. A nonzero m means that d in Eq. 7 is replaced by $d + m$ and has the effect of pushing d^* below 4 and into the region of real physical systems. The appropriate value of m for a system depends on the form and range of its microscopic interactions (*8*). For interactions of short range, $m = 0$, so that $d^* = 4$. Thus a two-dimensional ($d = 2$) Ising system, like K_2CoF_4, where $d^* - d$ is large, should have strong fluctuations and a marked non-mean field behavior. A three-dimensional Ising system has $d^* = 4 > d = 3$ and exhibits a less

strong but still significant departure from mean field theory. A dipolar uniaxial system can be shown to have $m = 1$, so that $d^* = 3$. Consequently, a three-dimensional uniaxial crystal has $d^* = d = 3$ and only logarithmic departures from mean field theory are expected. Observations bear out expectations for $LiTbF_4$ quantitatively (*13*). For still other systems $m = 2$ so that $d^* = 2$. Several structural phase transitions in three-dimensional crystals fall into this class. Whenever $d > d^*$, mean field theory is expected to be valid. Figure 6 shows a striking experimental confirmation of these ideas (*8*).

The recognition of marginal dimensionality, above which mean field theory is valid, was incorporated by K. Wilson and others into a formalism treating d as a continuous variable and $\epsilon \equiv 4 - d$ as an expansion parameter. As a result, values of critical exponents could be calculated to various orders in ϵ for a number of systems. Typical results (*2*) are:

$$\gamma = 1 + \frac{n+2}{2(n+8)}\epsilon + \mathbf{O}(\epsilon^2)$$

$$\alpha = \frac{4-n}{2(n+8)}\epsilon + \frac{(n+2)^2(n+28)}{4(n+8)^3}\epsilon^2 + \mathbf{O}(\epsilon^3)$$

$$\beta = \frac{1}{2} - \frac{3}{2(n+8)}\epsilon + \mathbf{O}(\epsilon^2)$$

For a three-dimensional system, setting $\epsilon = 1$ at the end of the perturbation procedure may seem mathematically foolhardy, but it produces quite reasonable agreement with experiments. For example, calculations (*14*) of the critical exponents γ, η, and ν for the three-dimensional Ising model are in excellent agreement with experiments on binary liquid mixtures (*15*).

This calculational method is only one of the significant contributions of the Wilson theory. Another is certainly the generalization in viewpoint to consider not merely one Hamiltonian for a given system, but a whole Hamiltonian space in which one moves about by applying well-prescribed mathematical transformations. If executed in real-space variables, these transformations can be viewed as summing over larger and larger volumes, so as to retain the essential interactions responsible for ordering while rescaling space at each step in a consistent way. Whether carried out in real space or in some other convenient mathematical framework, the generation of a new Hamiltonian from the old by application of a transformation operator $\tilde{R}$ can be schematically written

$$RH = H'$$

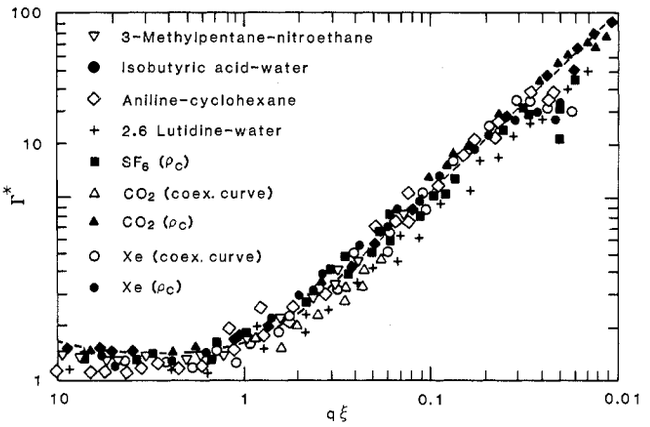


Fig. 7. Behavior of scaled critical frequency, Γ^*, for several fluids and fluid mixtures versus $q\xi$, where q is the scattering wave vector and ξ the correlation length. The dashed curve nearly covered by data points represents theory [modified from (*18*)].

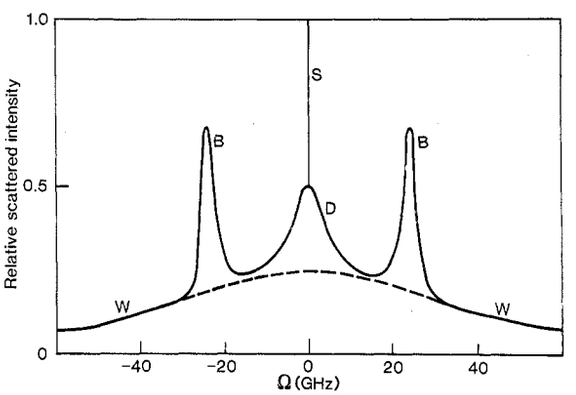


Fig. 8. Schematic of the light-scattering spectrum near T_c observed in lead germanate, showing the soft-mode (W) and acoustic phonon (B) features coupled with the dynamic central peak (D) and a singular impurity-induced central peak (S) [modified from (*22*)].

Successive applications of the renormalization group operator R can be thought of as generating "flows" in this space of Hamiltonians. Hamiltonians (or points) that may appear initially quite different will converge on the same fixed point, provided their initial differences can be expressed solely in terms of so-called irrelevant variables. A fixed-point Hamiltonian has the property (*2, 4*)

$$\tilde{R}H^* = H^*$$

The resulting eigenproblem generates eigenvalues that turn out to be the critical exponents. While full renormalization group procedure is overwhelming to most of us, we may appreciate its power and beauty to some degree without actually having to indulge in it. Specifically, the renormalization group provides a mathematical mechanism and a physical foundation for both scaling and universality. And, of course, it provides a means of calculating scaling functions as well as critical exponents. It must be regarded as one of the major theoretical advances in contemporary condensed-matter physics.

Dynamical Aspects

Thus far I have considered only the static aspects of critical phenomena—those describing equilibrium situations and expressible in terms of equal-time correlation functions. Considerably more challenging are the dynamics of phase transitions (*5*). Most generally, dynamics require the calculation of space- and time-dependent correlations on the theoretical side and time-dependent or nonequilibrium measurements on the experimental side. Although critical dynamics may be explored by macroscopic measurements of transport coefficients (*16*) (such as thermal conductivity or viscosity), more complete dynamic information is available from direct measurements of the time dependences of fluctuations in the order parameter and related quantities by inelastic scattering experiments (*17*). On approach to T_c the characteristic frequency of the fluctuations in ψ decreases, a manifestation of the increasing susceptibility which the system exhibits toward distorting into the new phase. This decrease is called critical slowing down.

The dynamic equivalent (*5*) of the static mean field theory is the so-called van Hove or conventional theory of critical slowing down. It asserts that no singular behavior develops in any transport or kinetic coefficient, so that the slowing down may be expressed solely in terms of static critical exponents (most especially through the static susceptibility). Since the characteristic time for order parameter (*5*) relaxation is a ratio of a

static susceptibility and a transport or kinetic coefficient, the observation of singular behavior in a transport coefficient signals a failure of the conventional theory.

Experimental observations of singular thermal conductivity in the superfluid transition and anomalous Rayleigh scattering line widths (*18*) in fluids and mixtures near their critical points, for example, have confirmed the breakdown of conventional theory. Theoretical refinements began by considering interactions of the slow order parameter mode with other possible slow modes of the system. These so-called mode coupling theories (*19*) of dynamic critical behavior represented approximate calculations, which were often in quite good agreement with experiment (Fig. 7). A more general approach, called dynamic scaling (*5*), builds on the idea of a rescalable frequency, similar to the rescalable length in static scaling. While successful in many regards, dynamic scaling was nevertheless phenomenology, and it has recently been incorporated into dynamic generalizations of the renormalization group approach.

Both dynamic scaling and the renormalization group have shown that dynamic universality classes require, in addition to the specification of n and d, a specification of the conservation laws and Poisson bracket relations among the order parameter and the conserved densities (*5*). Thus dynamic critical exponents cannot, in general, be calculated from static critical exponents.

Modern dynamic theories have been successful for some systems—particularly fluids and fluid mixtures. But the situation is less satisfactory for other cases such as structural phase transitions. Let us now examine briefly some examples of the experimental information obtained in both areas.

Inelastic scattering experiments (with photons or neutrons) are nearly ideally suited to the study of fluctuation dynamics because they provide a direct measure of the space- and time-dependent correlation functions of central interest (*17*). The scattered spectrum, $S(\mathbf{q}, \omega)$, is just proportional to the number of particles scattered within a given energy or frequency interval for fixed momentum transfer, $\hbar\mathbf{q}$ ($\hbar$ is Planck's constant divided by 2π). In many cases it may be expressed as

$$S(\mathbf{q}, \omega) = \text{constant} \times \text{Im}\, \chi(\mathbf{q}, \omega)$$

where Im $\chi(\mathbf{q}, \omega)$ is the imaginary part of the Fourier transform of the space- and time-dependent susceptibility referred to after Eq. 4. Thus the critical behavior in

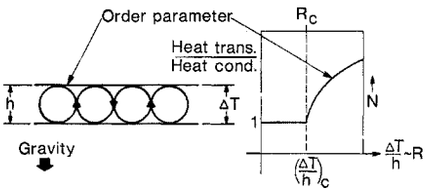


Fig. 9. The simplest hydrodynamic instability is the onset of convection. At the left is a schematic end-on view of a fluid layer subjected to an adverse temperature gradient, and the flow pattern achieved above R_c. The graph at the right shows the normalized vertical heat transport, N, as a function of normalized imposed gradient, R, illustrating the onset of convective flow for $R > R_c$.

order parameter fluctuations will be dramatically manifested in the spectrum.

For example, critical slowing down can be directly measured from the characteristic frequency of $S(\mathbf{q}, \omega)$ as T approaches T_c. In the simplest, quasiharmonic situations (*20*) $S(\mathbf{q}, \omega)$ can be written in a Lorentzian form

$$S(\mathbf{q}, \omega) = \text{constant} \times \frac{2\Gamma_q \omega}{(\omega_q^2 - \omega^2)^2 + 4\omega^2\Gamma_q^2}$$

In the simplest undamped ($\Gamma_q = 0$) cases, this can be described by a power law behavior in $\omega_q \approx \tau^z$ and corresponds to the simple "soft-mode" picture which has been so useful for sorting out ferroelectric and other structural phase transitions. However, in general, the spectral

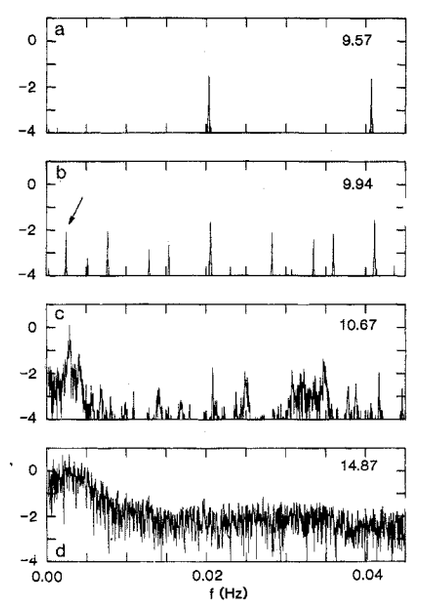


Fig. 10. Power spectral densities of top plate temperature fluctuations in a fluid layer well above convective onset. Note the logarithmic scales of the vertical axes. The sharp frequency in (a) corresponds to time-periodic flow, which first becomes more complex but remains periodic (b) and then develops time aperiodicity or turbulence as R is increased between 9 and $15R_c$ [courtesy of G. Ahlers (unpublished data)].

shape of $S(\mathbf{q}, \omega)$ does not return this simplicity very close to T_c, where mode coupling effects are dominant.

For fluids and critical mixtures the theoretical predictions of critical slowing down are impressively borne out by experiment (*15*) (Fig. 7). For structural phase transitions, on the other hand, where the slow mode is an optic or acoustic phonon, the spectra are usually much more complicated. Phonon interactions, anharmonicities, and even crystalline defects have been invoked to account for these complications (*21*). No simple or general explanation has proved satisfactory, and scattering experiments have identified several different mechanisms operative in different situations (*20*). Thus far, singular central peaks prototypical of the breakdown in quasiharmonic behavior have been experimentally identified from the following mechanisms: (i) entropy fluctuations, (ii) phonon density fluctuations, (iii) intrinsic annealable defects, and (iv) extrinsic nonannealable defects. Particularly illustrative are light (*20, 22*) and neutron scattering (*23*) results for the displacive ferroelectric transition in lead germanate. It belongs to the uniaxial dipolar static universality class whose marginal dimensionality is $d^* = 3$. The initial neutron studies (*23*) revealed an unresolved singular central peak. Higher resolution experiments with light scattering (*22*) showed that the central peak in lead germanate is composed of two singular components, one static and one dynamic (Fig. 8). The static peak diverges strongly near T_c with a power law dependence and has been ascribed to static symmetry-breaking defects. The intensity divergence in the dynamic peak is much weaker than that in the static peak and is consistent with the logarithmic behavior predicted for a $d^* = 3$ system from renormalization group theory. The dynamic peak is intrinsic in origin, arising from nonlinear interactions of the soft mode with both acoustic phonons and multiphonon processes. The latter should represent a fairly common mechanism for several types of structural transitions. Firm theoretical predictions remain to be developed. Similarly, while the static central peak probably arises from defects, intriguing questions regarding the influence of defects (*24*) on critical dynamics remain to be fully explored.

As far as critical dynamics are concerned, the major remaining challenges revolve about the difficulty for the experimentalist in measuring the universal or intrinsic dynamics in nonideal solid-state systems and for the theorist in calcu-

lating the nonuniversal and extrinsic complications in the same systems. Fluids, fluid mixtures, and superfluids have shown theory and experiment to agree (*18, 25*). More work remains for solid-state dynamics.

Instabilities in Systems Far from Equilibrium

Within the past few years an attack has been mounted on another class of problems involving fluctuations and instabilities. It was inspired partly by analogies between phase transitions in equilibrium systems and instabilities in systems far from equilibrium (*26-28*) such as lasers at threshold, fluid flows, and electronic devices.

For illustrative purposes I will consider only the simplest hydrodynamic instability—the Rayleigh-Benard problem of the onset of convection in a horizontal fluid layer subjected to a vertical temperature gradient (Fig. 9). The dimensionless heat flow, normalized by the thermal conductivity, is expressed by the Nusselt number, N, and the dimensionless temperature gradient is expressed by the Rayleigh number, $R \equiv g\beta h^3 \Delta T/K\nu$, where g is the gravitational acceleration, h the layer thickness, ΔT the temperature difference, K the thermal diffusivity, ν the kinematic viscosity, and β the thermal expansion coefficient. Figure 9 shows a typical plot of N versus R for such a fluid layer. For $R < R_c$, $N = 1$, and the heat flow is by conduction alone. At R_c convective flow sets in and N increases continuously, reminiscent of the behavior for the order parameter in a continuous phase transition. The physical origin of the finite threshold, R_c, for convection lies in the competition between the driving force provided by the thermal expansion coefficient and imposed temperature gradient and the dissipative force provided by thermal conductivity and viscosity. Thus R_c is analogous to T_c, with $R < R_c$ corresponding to $T > T_c$. Also, $N - 1$ is analogous to ψ_0. One may even identify the soft mode for the convective instability from a stability analysis of the hydrodynamic equations (*29*) for a fluid layer under an imposed temperature gradient. The particular Fourier component of the velocity field that becomes unstable corresponds to the flow pattern sketched in Fig. 9. This velocity field eigenvector results in the development of spatial structure above R_c that is influenced by the fluid boundary conditions. Experiments (*26, 30*) have even measured the mode softening on approach to R_c.

Other instabilities (for example, laser thresholds) may be viewed in this way as well, with appropriate identification of the physical quantities involved. A particularly important question which has received considerable theoretical attention is the proper description and role of "fluctuations" in such threshold phenomena. The simplest analyses of threshold onsets correspond, in phase transition language, to the mean field approximation. Indeed, the $N(R)$ slope observed near R_c corresponds to $\beta = 1/2$. More sophisticated mathematical treatments (*26*) suggest that departures from mean field theory will become important only extremely close to threshold [for the Rayleigh-Benard problem $(R - R_c)/R_c \leq 10^{-7}$]. Hence the region analogous to the critical regime in phase transitions is expected to be experimentally inaccessible (more by virtue of boundary condition effects which would round the transition than of insufficient temperature control) for transitions between one nonequilibrium steady state and another.

While additional careful experiments should be done on such transitions, it appears that the most fruitful and challenging area for study of fluctuations in nonequilibrium systems will center not on the transitions between steady states (such as the onset of convection) but rather on the transition from steady or time periodic to chaotic or randomly time-dependent behavior. The latter area involves such fundamental questions as the evolution of turbulence, the interactions of strong fluctuations, and the origins of irreversibility. Early experimental measurements (*30*) of the power spectra in the Rayleigh-Benard problem well above R_c have already revealed an unexpected richness in the nonlinear behavior leading to the evolution of turbulence. Figure 10 shows a sequence of such power spectra for $R \sim 10R_c$ in the vicinity of turbulent onset. Below $R/R_c < 7.4$ the flow is completely steady. Above $R/R_c = 7.4$ the flow becomes periodic with a single characteristic frequency, which appears together with its harmonic in Fig. 10a. Beyond $R/R_c = 9.9$ a second incommensurate frequency appears, so that Fig. 10b can be fully indexed as $mf_1 \pm nf_2$, where m and n are integers. As R increases further the lowest frequency (arrow) decreases and nearly reaches zero at $R/R_c = 10.6$. At higher R the power spectra are broad, indicative of aperiodic or turbulent flow (Fig. 10d).

This example, while dramatic, illustrates but one of many different paths to turbulence that have been observed in the Rayleigh-Benard system under different boundary conditions. At present we lack any unifying principles for even classifying these differences. Nevertheless, there is reason to hope that by virtue of (i) increased theoretical understanding of mode coupling and strong fluctuation phenomena and (ii) application of precise and sophisticated experimental techniques, the kind of systematic understanding of equilibrium transitions that emerged in the 1970's may emerge for nonequilibrium systems in the 1980's.

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